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# Kinetic theory for condensation of multicomponent vapor under dynamic conditions

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**Abstract**

The kinetics of the multicomponent condensation under dynamic external conditions is described analytically. The multidimensional problem is reduced to the one-dimensional case. Concrete expressions for all main characteristics of the process are obtained with the help of an iteration procedure. As a result an analytical theory for the whole process of transformation of a metastable multicomponent mixture of vapors into a state of liquid disperse phase is completely constructed.

## 1. Introduction

The present paper is devoted to multicomponent condensation kinetics in the most natural situation when the variation of external conditions has a rather smooth character.

The theory presented here is based on the classical theory of nucleation. The basic concepts of the classical theory of nucleation are founded by Volmer [1], Becker and Doering [2], Zeldovitch [3], Frenkel [4], Kramers [5]. Some reconsiderations were made by Lothe and Pound [6]. The modern state of the nucleation theory can be characterized by the contributions of Reiss [7], Reiss, Katz and Cohen [8], Feder, Russel, Lothe and Pound [9], Hung, Katz and Krasnopoler [10], Reiss, Tabazadeh and Talbot [11] and others.

The creation of stationary nucleation theory allows to study kinetic problems of nucleation. Among the first publications devoted to this topic one must stress the publications by Wakeshima [12] and by Raiser [13]. The theory of the

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homogeneous decay of the metastable phase was founded by Grinin, Kuni and Kabanov [14]. The theory of homogeneous condensation in the dynamical conditions was examined in [15,16]. The theory of heterogeneous condensation was investigated in [17,18].

Binary condensation was investigated by Reiss in [19] and by Stauffer in [20]. The rate of binary nucleation was obtained in [19] and was corrected in [20]. The stationary theory of binary condensation with the help of Lorentz transformation was investigated in [21].

All above cited publications form the base for the theory of the decay of metastable mixture presented here. This publication is based on ideas proposed in [22–24].

Some concrete model has to be accepted in order to give an opportunity to present concrete calculations. This model includes the following positions:

- The system is homogeneous in space.
- The regime of substance exchange between an embryo and environment is free molecular one.
- Thermal effects are neglected.

All these assumptions can be overcome by modification of the theory and are not observed here due to the lack of volume of the publication.

Coalescence is not considered here. Asymptotical expansions are constructed in [25,26].

We shall choose the system of unit volume and measure all energy-like values in thermal units.

## 2. Embryo free energy

In capillarity approximation we can write the following expression:

$$F(\{\nu_b\}) = a\left(\sum_{b=1}^{n} v_{\ell\, b}\, \nu_b\right)^{2/3} - \sum_{a=1}^{n} b_a \nu_a \,, \tag{1}$$

for the free energy $F$ of an embryo containing $\nu_a$ molecules of component $a$. The value of $F$ is taken in units $k_B T$ ($k_B$ is the Boltzmann constant, $T$ is the absolute temperature). The value $v_{\ell\, b}$ is the partial molecular volume of component $b$ in the liquid phase. The value of $a$ is defined from

$$a\left(\sum_{b} v_{\ell\, b}\, \nu_b\right)^{2/3} = \gamma S \,, \tag{2}$$

where $\gamma$ is the surface tension measured in units of $k_B T$, $S$ is the surface area.

In the liquid solution we have for $b$,

$$b_a = \ln\left(\frac{n_a}{n_{aa}}\right) - \ln\left[\left(\frac{\nu_a}{\Sigma_b \nu_b}\right) f_a\right], \tag{3}$$

where $f_a$ are the coefficients of activity. These coefficients are regarded here and below as functions of $\nu_a / \Sigma_b \nu_b$. When $f_a = 1$ the solution is an ideal one. Here $n_a$ is the molecule number density of the vapor of component $a$, $n_{aa}$ is molecule number density of the pure vapor of component $a$ saturated over the plane liquid phase.

One must note that the analytical structure of expression (1) will be essential in justification of further approximations. We suppose also that coefficients $f_i$ are rather smooth functions of their arguments.

## 3. Flows and velocities

Let us introduce the following values:

$$\mu_a = \frac{\nu_a}{\Sigma_b \nu_b}. \tag{4}$$

We have the following expressions for flows of the vapor molecules on the droplets:

$$W_a^+(\{\nu_a\}) \sim v_{\mathrm{t}\,a} S n_a, \tag{5}$$

where $\nu_{\mathrm{t}\,a}$ are thermal velocities and condensation coefficients $\alpha_i$ are put to unity for simplicity. In any case we can put them into effective values of thermal velocities. We can rewrite the formulas as follows:

$$W_a^+(\{\nu_a\}) = \frac{n_a}{n_{aa}} \frac{(\Sigma_b \nu_b v_{\ell\, b})^{2/3}}{\tau_a}, \tag{6}$$

where

$$\tau_a \sim (n_{aa} v_{\mathrm{t}\,a})^{-1} \tag{7}$$

is some characteristic time. For fraction $W_a^+ / W_b^+$ we obtain

$$\frac{W_a^+}{W_b^+} = \frac{v_{\mathrm{t}\,a} n_a}{\nu_{\mathrm{t}\,b} n_b}, \tag{8}$$

which does not depend on droplets size.

Now let us define inverse flows. The equilibrium distribution must satisfy the following equation:

$$W_a^+ n^e(\{\nu_i\}) = W_a^-(\nu_a + 1, \{\nu_b\}_{b\neq a})\, n^e(\nu_a + 1, \{\nu_b\}_{b\neq a}) \,. \tag{9}$$

As far as

$$n^e(\{\nu_a\}) = N \exp[-F(\{\nu_a\})] \,, \tag{10}$$

where in the last equation $N$ is the normalizing factor, we have for $W_a^-$ the following expression:

$$W_a^-(\nu_a + 1, \{\nu_b\}_{b\neq a}) = W_a^+ \exp[-F(\{\nu_a\}) + F(\nu_a + 1, \{\nu_b\}_{b\neq a})] \,. \tag{11}$$

In order to justify the substitution of finite differences by the derivatives we calculate the free energy derivatives for super-critical embryos:

$$\begin{aligned} \frac{\partial F}{\partial \nu_a} &= \frac{2a(\Sigma_b\, \nu_{\ell\, b}\, \nu_b)^{-1/3} \nu_{\ell\, a}}{3} - \ln\left(\frac{n_a}{n_{aa}}\right) + \ln(\mu_a)\, f_a(\mu_a) \\ &\rightarrow -\ln\left(\frac{n_a}{n_{aa}}\right) + \ln(\mu_a)\, f_a(\mu_a) \,, \end{aligned} \tag{12}$$

$$\frac{\partial^2 F}{\partial \nu_a^2} \rightarrow \frac{\nu_b}{\nu_a(\Sigma_b\, \nu_b)} \rightarrow 0 \,. \tag{13}$$

To obtain (12), (13) we must take into account the Gibbs–Duhem equation, which realization in this particular case is the following one:

$$\sum_a \mu_a \frac{\partial b_a}{\partial \mu_i} + \frac{S}{\Sigma_b\, \nu_b} \frac{\partial \gamma}{\partial \mu_i} = 0 \,. \tag{14}$$

We must get this equation in the limiting case of supercritical embryo corresponding to the limit in (12). So we have

$$\sum_a \mu_a \frac{\partial b_a}{\partial \mu_i} = 0 \,. \tag{15}$$

This equation helps to expel the crossing terms in derivatives of $\partial F / \partial \nu_i$. So we have for inverse flow

$$W_a^- = W_a^+ \frac{n_{aa} \mu_a}{n_a} f_a(\mu_a) \,. \tag{16}$$

For velocity of $\nu_a$ changing we have

$$\frac{\mathrm{d}\nu_a}{\mathrm{d}t} = \frac{(\Sigma_b \nu_b v_{\ell\, b})^{2/3}}{\tau_a} \left( \frac{n_a}{n_{aa}} - \mu_a f_a(\mu_0) \right) . \tag{17}$$

## 4. Supersaturation and ideal supersaturation

In order to characterize the power of metastability in the system we shall introduce supersaturations by

$$\zeta_a = \frac{n_a}{n_{aa}} . \tag{18}$$

So the laws of growth can be rewritten in the following form:

$$\frac{\mathrm{d}\nu_i}{\mathrm{d}t} = (\zeta_i - \mu_i f_i) \frac{(\Sigma_b \nu_b v_{\ell\, b})^{2/3}}{\tau_i} . \tag{19}$$

To extract the external influence we introduce the values of ideal supersaturations as supersaturations which can be formed in conditions when there are no vapor consumption by droplets. We shall mark them as $\Phi_a$. The role of these values is stressed by the fact that they are controlled by external conditions. Moreover one can see that all essential external influences upon the system are going through the variations of the ideal supersaturations. So we have

$$\Phi_a = \frac{n_{\mathrm{tot}\, a}}{n_{aa}} . \tag{20}$$

Here $n_{\mathrm{tot}\, a}$ is the total molecule number density of component $a$.

Traditionally the smooth character of ideal supersaturation variation is ensured [16–18] by power approximation of ideal supersaturation in time. When this approximation is adopted for one component it is necessary to justify this approximation for another components.

In the case of isochoric cooling due to the well known thermodynamic formula, we have

$$n_{aa}(T) = n_{aa}(T_0) \exp\left( \beta_a \frac{T - T_0}{T_0} \right) , \tag{21}$$

$$n_{bb}(T) = n_{bb}(T_0) \exp\left( \beta_b \frac{T - T_0}{T_0} \right) , \tag{22}$$

where $\beta_a$ and $\beta_b$ are partial molecules heats of condensation. Hence, we come to the following equations:

$$\Phi_a(T) = \Phi_a(T_0) \exp\left(-\beta_a \frac{T - T_0}{T_0}\right) . \tag{23}$$

$$\Phi_b(T) = \Phi_b(T_0) \exp\left(-\beta_b \frac{T - T_0}{T_0}\right) . \tag{24}$$

When $\Phi_a$ is given by the power approximation

$$\Phi_a(t) = \Phi_a(t_0) \left(\frac{t - t_0}{t_\infty}\right)^{m_a} \tag{25}$$

with parameters $t_\infty$ and $m_a$, the variation of the temperature occurs according to

$$\frac{T - T_0}{T_0} = -\frac{m_a}{\beta_a} \ln\left(\frac{t - t_0}{t_\infty}\right) . \tag{26}$$

So, we have for $\Phi_b$ the following expression:

$$\Phi_b(t) = \Phi_b(t_0) \left(\frac{t - t_0}{t_\infty}\right)^{\beta_b m_a / \beta_a} . \tag{27}$$

It is also power approximation with parameters $t_\infty$ and $m_b = m_a \beta_b / \beta_a$.

In the case of isothermal compression we have

$$\Phi_a(t) = \Phi_a(t_0) \frac{V(t_0)}{V(t)} , \tag{28}$$

where $V$ is the volume and

$$\frac{\Phi_a(t)}{\Phi_b(t)} = \frac{\Phi_a(t_0)}{\Phi_b(t_0)} . \tag{29}$$

Hence, it follows that power approximation of one component ensures the power approximation for another component with the same parameters.

In the case of adiabatic cooling the temperature and volume are connected by the equation

$$T(t)\, V^{\gamma - 1}(t) = T(t_0)\, V^{\gamma - 1}(t_0) , \tag{30}$$

where

$$\gamma = \frac{\sum_a n_{aa} \Phi_a c_{p\,a} + n_g c_{p\,g}}{\sum_a n_{aa} \Phi_a c_{v\,a} + n_g c_{v\,g}} \tag{31}$$

where $n_g$ is the passive gas molecule density, $c_{p\,a}$, $c_{p\,g}$, $c_{v\,a}$, $c_{v\,g}$ are heat capacities of component $a$ and passive gas under the constant pressure and constant volume respectively. So we have

$$\Phi_a(T) = \Phi_a \left(\frac{T}{T_0}\right)^{1/(\gamma-1)} \exp\left(-\beta_a \frac{T - T_0}{T_0}\right), \tag{32}$$

$$\Phi_b(T) = \Phi_b \left(\frac{T}{T_0}\right)^{1/(\gamma-1)} \exp\left(-\beta_b \frac{T - T_0}{T_0}\right). \tag{33}$$

Due to $\beta_a \gg 1$, $\beta_b \gg 1$ for the majority of substances in ordinary thermodynamical conditions the relative deviation of the temperature is small and we have the following approximative result:

$$\left(\frac{T}{T_0}\right)^{1/(\gamma-1)} \approx \exp\left(\frac{T - T_0}{(\gamma - 1)T_0}\right) \tag{34}$$

and this case is reduced to the case of isochoric cooling with renormalisation of values

$$\beta_a^+ = \beta_a - \frac{1}{\gamma - 1}, \qquad \beta_b^+ = \beta_b - \frac{1}{\gamma - 1}. \tag{35}$$

The variation of the external conditions leads to the metastability in the vapor mixture. But at the beginning of the process of condensation the power of metastability is rather low, the activational barrier of nucleation is very high and practically in the system there is no droplets of the new phase. We shall call this period 'the period of preparation'.

The action of external conditions leads to an increasing of the power of metastability. So, embryos of the new phase begin to appear in the system. Certainly, they begin to accumulate the molecules from the vapor. This accumulation is effectively compensated by the action of external conditions. At some moment the power of metastability attains a maximum value. Near this moment the majority of the supercritical embryos are born. We shall use for this period the abbreviation PIFD ('the period of intensive formation of droplets').

Later the intensity of accumulation of the vapor phase by droplets increases and the external conditions cannot compensate for the exhaustion of the vapor. So the power of metastability falls and the rate of nucleation vanishes. Now we have a system with a fixed given number of droplets. We shall speak about the evolution of such systems as about ‘the further evolution’. This evolution will be investigated up to the beginning of the process of coalescence.

Let us stress that this picture is too general and a very approximative one. All necessary details, proofs and estimates will be given below.

## 5. Stationary intensity of embryo formation

In order to obtain the intensity of formation of the droplets we shall note the following facts:

- Under the conditions of validity of the capillarity approximation for the critical embryo, the main role in vapor consumption is played by supercritical embryos, i.e. by droplets.
- Under the same conditions as the current ones the state of near-critical embryos can be regarded as quasi stationary one.

These facts can be proved analytically.

For stationary rate of nucleation we have

$$J_s(\{\zeta_a\}) = Z\Big(\sum_a \Psi_a \exp(-\Delta_a F_c)\Big)\,, \tag{36}$$

where

$$\Psi_a = \frac{n_{aa}}{n_{aa} + n_{bb}}\,, \tag{37}$$

$$\Delta_a F_c = F(\{\nu_{b\,c}\}) + \ln(n_a v_{\ell\,a})\,, \tag{38}$$

and index “c” here and below marks the values at the saddle point. The value of $Z$ is the factor of Zeldovitch [3,20] and it is a rather smooth function of supersaturations. All other terms in (36) are initiated by the equilibrium distribution in the region of small sizes of the embryos. With probability $\Psi_a$ the critical embryo is formed on the $a$ component molecule and for formation of the critical embryo it is necessary to spend the work $\Delta_a F$.

The near-critical region is extracted by the condition

$$|F(\{\nu_i\}) - F_c| \leqslant 1\,. \tag{39}$$

The time of relaxation in the near-critical region can be estimated from the above. Let us transmit by linear transformation to the set of $\nu_{*\,i}$ which reduces the square form of the free energy to the sum of squares. Thanks to the fact that the set $\{\Sigma_j \nu_j v_{\ell\,j},\ \{\mu_i\}_{i=1}^{i=n-1}\}$ diagnolizes the square form of the free energy, it is easy to do. Every $\nu_{*i}$ has the same scale as $\nu_i$ has. Then we have

$$t_{\mathrm{rel}} = \frac{(\operatorname{diam} \nu_c)^2}{W_c}, \tag{40}$$

where

$$\operatorname{diam} \nu_c = \left[2 \Big/ \left(\sum_j \frac{\partial^2 F}{\partial \nu_{*j}^2 {}_t}\right)\right]^{1/2}, \tag{41}$$

$$\operatorname{diam} \nu_c \sim \operatorname{perim} \nu_c, \quad \operatorname{perim} \nu_c = \sum_j \left[2 \Big/ \left(\frac{\partial^2 F}{\partial \nu_{*j}^2}\right)\right]^{1/2}, \quad W_c = \min(W_{i\,c}^{+}), \tag{42}$$

and derivatives are taken at the saddle point of the free energy. One can obtain this estimate by sequential considering the diffusion over the first and over the second variable. Long tails of the near-critical region along the diagonals of a rectangular with coordinates

$$\nu_{*ic} \pm \left[2 \Big/ \left(\frac{\partial^2 F}{\partial \nu_{*i}^2}\right)\right]^{1/2}$$

are omitted.

## 6. Concentration of the solution in droplets

Now let us define the concentration of droplets at this period. The dynamic equations for $\mu_i$ can be written in the following manner:

$$\frac{d\mu_i}{dt} = \frac{(\Sigma_b \nu_b v_{\ell b})^{2/3}}{\Sigma_j \nu_j} \left( \frac{\zeta_i - \mu_i f_i(\mu_i)}{\tau_i} - \mu_i \sum_j \frac{\zeta_j - \mu_j f_j(\mu_j)}{\tau_j} \right). \tag{43}$$

The first term of the last equation is not expressed through $\mu_i$ because we work now in the set of variables $\{\mu_i\}$, $(\Sigma_b \nu_b v_{\ell b})^{2/3} / \Sigma_j \nu_j$. The stationary solutions are obtained from

$$\frac{\zeta_i - \mu_i f_i(\mu_i)}{\tau_i} = \mu_i \sum_j \frac{\zeta_j - \mu_j f_j(\mu_j)}{\tau_j}. \tag{44}$$

The values of $\mu_i$ are not independent but satisfy the obvious restriction

$$\sum_i \mu_i = 1 . \tag{45}$$

So we have to use the Lagrange method. Let us measure time $t$ here in units of $(\Sigma_b \nu_b v_{\ell\, b})^{2/3}/\Sigma_j \nu_j$. We obtain the potential $U$ from

$$\frac{\mathrm{d}\mu_i}{\mathrm{d}t} = -\frac{\partial U}{\partial \mu_i} . \tag{46}$$

The function $U$ exists due to the homogeneous character of restriction (45). The equation of conditional extremum for $U$ will be the following one:

$$\frac{\partial U}{\partial \mu_i} - \alpha \frac{\partial}{\partial \mu_i}\Big(\sum_j \mu_j - 1\Big) = 0 , \tag{47}$$

with arbitrary $\alpha$. This equation leads to

$$\alpha + \frac{\zeta_i - \mu_i f_i(\mu_i)}{\tau_i} = \mu_i \sum_j \frac{\zeta_j - \mu_j f_j(\mu_j)}{\tau_j} . \tag{48}$$

The value of $\alpha$ must be chosen according to (45). Let us introduce

$$\delta_i = \frac{\zeta_i - \mu_i f_i(\mu_i)}{\tau_i} \tag{49}$$

and

$$\Delta = \sum_j \delta_j . \tag{50}$$

From (48) we see that

$$\frac{\alpha}{\mu_i} + \frac{\zeta_i - \mu_i f_i(\mu_i)}{\mu_i \tau_i} = \Delta \tag{51}$$

is invariant for every $i$. In the approximation of the ideal solution eq. (48) can be rewritten as

$$\alpha + \delta_i = (\zeta_i - \delta_i \tau_i)\Delta \tag{52}$$

and gives an expression for $\delta_i$ through $\Delta$. Substitution of this expression into (50) leads to

$$\Delta = \sum_i \frac{\zeta_i \Delta - \alpha}{1 + \tau_i \Delta} . \tag{53}$$

Condition (45) also must be expressed through $\Delta$:

$$\sum_i \frac{\zeta_i + \alpha \tau_i}{1 + \tau_i \Delta} = 1 . \tag{54}$$

Equations (53) and (54) coincide when $\alpha = 0$. So $\alpha = 0$ ensures an extremum and the condition on $\Delta$ is reduced to

$$1 = \sum_i \frac{\zeta_i}{1 + \tau_i \Delta} . \tag{55}$$

Due to $\zeta > 0$, $\tau_i > 0$, the uniqueness of $\Delta$ is obvious. The last equation is an ordinary algebraic equation of power $n$. As far as in solution ordinary there are no more than four or five components for which this equation can be easily solved analytically. This equation can be also solved by an iteration procedure. For a rather intensive process of condensation it is necessary to have at least one supersaturation many times greater than unity. This value(-es) can be regarded as the leading parameter in the iterational procedure.

Considerating the limiting case one can prove that this extremum is stable. On the base of $\Delta$, concentrations can be reconstructed with the help of (51). Only there we shall use condition $\mu_i > 0$. The characteristic time of the relaxation can be found from

$$t_{\mathrm{rel}} = \max_i \left\{ \frac{\mathrm{d}}{\mathrm{d}t} \left( \frac{\mathrm{d}\mu_i}{\mathrm{d}t} \right) \right\} , \tag{56}$$

where the derivative must be taken at the stationary value of the concentration. Here we must put all values to some characteristic values at PIFD. They must be taken from further consideration or by simple estimates. Under the conditions of applicability of the capillarity approximation for the description of the critical embryo the following inequality:

$$t_{\mathrm{rel}} \ll \Delta t , \tag{57}$$

is valid where $\Delta$ marks the variation of the magnitudes during PIFD. After obtaining the value of $\Delta t$ we can prove this inequality analytically by simple substitution.

## 7. Stationary rate approximation

Let us denote some moment which belongs to PIFD as $t_*$ and mark all values at this moment by index "*". For the height of the activation barrier we have the following approximation:

$$F_{\mathrm{c}}(\{\zeta_a\}) = F_{\mathrm{c}}(\{\Phi_{a\,*}\}) + \sum_i \frac{\mathrm{d}F_{\mathrm{c}}}{\mathrm{d}\zeta_i}\bigg|_{\zeta_i=\Phi_{i\,*}} (\zeta_i - \Phi_{i\,*})\,. \tag{58}$$

Let us calculate the derivatives in this approximation,

$$\frac{\mathrm{d}F_{\mathrm{c}}}{\mathrm{d}b_a} = \frac{\partial F}{\partial b_a}\bigg|_{\mathrm{c}} + \sum_b \frac{\partial F}{\partial \nu_b}\bigg|_{\mathrm{c}} \frac{\partial \nu_b}{\partial b_a} + \sum_{b\neq a} \frac{\partial F}{\partial b_b}\bigg|_{\mathrm{c}} \frac{\partial b_b}{\partial b_a}\,. \tag{59}$$

The last term on the r.h.s. of the last equation is important as far as

$$b_i = 2av_{\ell\,i} \cdot \tfrac{1}{3}\nu_+^{-1/3} \tag{60}$$

at the saddle point. Here

$$\nu_+ = \sum_b v_{\ell\,b}\,\nu_b \tag{61}$$

and, hence,

$$b_a = b_b \frac{v_{\ell\,a}}{v_{\ell\,b}} \tag{62}$$

at the saddle point. So we come to the equation

$$\frac{\mathrm{d}F_{\mathrm{c}}}{\mathrm{d}b_i} = -\frac{\nu_{+\,\mathrm{c}}}{v_{\ell\,i}}\,. \tag{63}$$

We can obtain this equation also by differentiating the explicit result

$$F_{\mathrm{c}} = \tfrac{1}{3}a\nu_{+\,\mathrm{c}}^{2/3}\,. \tag{64}$$

Let us introduce

$$\Gamma_i = -\zeta_i \frac{\mathrm{d}F_{\mathrm{c}}}{\mathrm{d}\zeta_i} = \frac{\nu_{+\,\mathrm{c}}}{v_{\ell\,i}}\,. \tag{65}$$

In the capillarity approximation these values are rather great in comparison with unity. So the relative variations of $\zeta_a$ at PIFD are less than $\Gamma_a^{-1}$. Moreover we can obtain that during PIFD it follows that

$$\frac{\zeta_i - \Phi_{i*}}{\Phi_{i*}} \leq \Gamma_{i*}^{-1} . \tag{66}$$

It can be proved that during PIFD there is no full compensation in formation of the droplets by increasing the supersaturation of one component and by decreasing the supersaturation of another component.

On the base of obtained expansions the following approximation:

$$J_s(\{\zeta_a\}) = J_s(\{\Phi_{a*}\}) \exp\Bigl(\sum_i \Gamma_{i*} \frac{\zeta_i - \Phi_{i*}}{\Phi_{i*}}\Bigr) \tag{67}$$

can be constructed.

## 8. Period of the intensive formation of droplets

Due to (67) at this period we have approximately

$$\zeta_a = \Phi_{a*} \tag{68}$$

in all functional dependencies except (67). We shall regard $\mu_a$ as $\mu_a(\{\Phi_{b*}\})$. So, the following correspondence can be obtained:

$$\nu_a = \frac{\mu_a}{\mu_b} \nu_b , \tag{69}$$

$$\frac{\mathrm{d}\nu_a}{\mathrm{d}t} = \frac{\mu_a}{\mu_b} \frac{\mathrm{d}\nu_b}{\mathrm{d}t} . \tag{70}$$

For the velocity of growth we have

$$\frac{\mathrm{d}\nu_a}{\mathrm{d}t} = \nu_a^{2/3} \Bigl[\Bigl(\sum_b \frac{\mu_b}{\mu_a} v_{\ell\, b}\Bigr)^{2/3} (\zeta_a - \mu_a f_a)\Bigr] \Big/ \tau_a . \tag{71}$$

We shall use the variables

$$\rho_a = \nu_a^{1/3} . \tag{72}$$

Their velocity does not depend upon the values of these variables,

$$\frac{\mathrm{d}\rho_a}{\mathrm{d}t}=\Big(\sum_b \mu_b v_{\ell\, b}\Big)^{2/3}\mu_a^{-2/3}(\zeta_a-\mu_a f_a)/3\tau_a=\lambda_a\,. \tag{73}$$

Let us introduce $z_a$ as the coordinates on axis $\rho_a$ of the embryo formed at $t=t_*$. Then

$$z_a=\int_{t_*}^{t}\frac{\mathrm{d}\rho_a}{\mathrm{d}t}\,\mathrm{d}t=\lambda_a(t-t_*)\,. \tag{74}$$

Instead of the distribution functions over $\{\nu_a\}, t$ we shall use the distribution functions over $\{\rho_a\}, t$. We shall mark them by the letter $\varsigma$. We can also consider instead of the full distribution function $\varsigma(\{\rho_a\},t)$ the brief distributions $\varsigma_a(\rho_a,t)$. We shall normalize them on the total embryos number in unit volume. Zeldovitch equation can be rewritten as

$$\frac{\partial\varsigma_i}{\partial t}=-\frac{\partial\varsigma_i}{\partial\rho_i}\frac{\mathrm{d}\rho_i}{\mathrm{d}t} \tag{75}$$

with the well known solution

$$\varsigma_i(\rho_i,t)=\varsigma_i(x_i)\,,\qquad x_i=z_i-\rho_i\,. \tag{76}$$

To obtain the form of functions $\varsigma_a(x_a)$ one must use the boundary condition in the region of rather small sizes. Namely, we must use the boundary condition at the bound of the near-critical and supercritical region. One can prove that in a macroscopic (thermodynamical) description of the critical embryo the quasi-stationary approach is valid. So have

$$\varsigma_i(\rho_i,t)|_{\rho_i=0}=J_{\mathrm{s}}\Big(\frac{\mathrm{d}\rho_i}{\mathrm{d}t}\Big)^{-1}=\frac{J_{\mathrm{s}}}{\lambda_i}=\varsigma_{\mathrm{s}\,i}\,. \tag{77}$$

The solutions of the Zeldovitch equation have the form

$$\varsigma_i(x_i)=\varsigma_{\mathrm{s}\,i}(\{\zeta_a(x_i)\})\,. \tag{78}$$

Due to

$$\mu_b^{1/3}x_a=\mu_a^{1/3}x_b\,,\qquad \mu_a^{1/3}\varsigma_a(x_a)=\mu_b^{1/3}\varsigma_b(x_b)\,, \tag{79}$$

we can consider in the set (75) only one equation.

## 9. Balance equation

To obtain $\zeta_a$, $\varsigma_a$, the dependence on time and on $x_i$, it is necessary to consider the balance equations for the substances. Let us denote the number of $a$ component molecules in all supercritical embryos as $n_{aa}$. Then for $g_a$ we have the following equations:

$$g_a = \int_{-\infty}^{z_a} (z_a - x_a)^3 \frac{\varsigma_a(x_a)}{n_{aa}} \, dx_a \,. \tag{80}$$

We have a simple connection between $g_a$ and $g_b$ ,

$$g_b = g_a \frac{n_{aa}\mu_b}{\mu_a n_{bb}} \,. \tag{81}$$

Balance equations are written in the following way:

$$\Phi_i = \zeta_i + g_i \,. \tag{82}$$

Let us linearize the ideal supersaturations as functions of $x_a$:

$$\Phi_a = \Phi_{a\,*} + k_a x_a \,. \tag{83}$$

After obtaining the explicit formulas one can easily check the validity of these linearizations.

On the basis of the approximation for the rate of nucleation one can obtain the approximation for the stationary distribution function:

$$\varsigma_{s\,a}(\{\zeta_a\}) = \varsigma_{s\,a}(\{\Phi_{a\,*}\}) \exp\Bigl(\sum_i \Gamma_{i\,*} \frac{\zeta_i - \Phi_{i\,*}}{\Phi_{i\,*}}\Bigr) \,. \tag{84}$$

Taking into account the balance equations and expressions with linearizations we obtain

$$\varsigma_{s\,a}(\{\zeta_a(x_a)\}) = \varsigma_{s\,a}(\{\Phi_{a\,*}\}) \exp[k x_a - q g_a(x_a)] \,, \tag{85}$$

where

$$k = \sum_b \frac{\Gamma_{b\,*} k_b \mu_b^{1/3}}{\Phi_{b\,*} \mu_a^{1/3}} \,, \tag{86}$$

$$q=\sum_b \frac{\Gamma_{b*} n_{aa}\mu_b}{\mu_a n_{bb}\Phi_{b*}} . \tag{87}$$

Then from this expression we can find the closed equation for $g_a(z_a)$:

$$g_a(z_a)=\frac{J_s(\Phi_{a*}, \Phi_{b*})}{\lambda_a n_{aa}} \int_{-\infty}^{z_a} (z_a - x_a)^3 \exp(kx_a - qg_a)\, \mathrm{d}x_a . \tag{88}$$

The structure of this equation coincides with the one component case and the methods from [15–18] can be applied. It is not necessary to analyze it here. As result we obtain the explicit formulas for all characteristics of PIFD and can directly check all assumptions made above.

The crucial point in the description of this period is the solution of the equation for the parameters of the spectrum. We can write this equation as follows:

$$J_s(\Phi_a, \Phi_b)\, q = k^4 n_{aa}\lambda_a \times \text{const.} \tag{89}$$

The value of const depends on the manner of choice of $t_*$. When $t_*$ is chosen as the moment when the droplet formation is at maximal intensity or the moment when half of the total number of droplets is formed then the calculations can be made with the help of the procedure described in [17,18]. So we can get all necessary information about the considered period. The equation of the parameters of PIFD is an ordinary equation. We can easily solve it with great effectiveness by iterations considering

$$\exp[-F_c(\{\Phi_{a*}\})]$$

as the unknown part. In the reconstruction of $t_*$ and $\Phi_{a*}$ on the base of the already known value of $F_c$ we can construct internal iterations in the manner of heterogeneous condensation kinetics [27,28]. In further constructions we shall use the approximation of the ideal solution. The generalization is obvious.

Let us stress that the given description is based on the thermodynamical capillarity approximation. Although the capillarity approximation cannot be observed directly in the final formulas, it must be taken into account in justifications of approximations (67), (73), (84). These justifications are based on the analytical structure of the expression for the free energy in the capillarity approximation. Certainly, it is possible to include here the microscopical corrections to the free energy.

## 10. Further evolution

Let us stress that soon after the end of PIFD the size spectrum is monodispersious in $\mu_i$. So we can write evolution equations as follows:

$$\frac{\mathrm{d}\nu_i}{\mathrm{d}t} = \frac{S}{\tau_i}\left[\zeta_i - \frac{\nu_i}{\Sigma_b \nu_b} f_i\left(\frac{\nu_i}{\Sigma_b \nu_b}\right)\right], \tag{90}$$

where $S = (\Sigma_b v_{\ell\, b}\, \nu_b)^{2/3}$. For arbitrary components of the embryos with given $S$ the increasing of $\nu_a$ initiates the decrease of $\mathrm{d}\nu_a/\mathrm{d}t$ and the increase of $\mathrm{d}\nu_b/\mathrm{d}t$ for another component. Analogously, the increasing of $\nu_b$ initiates the decrease of $\mathrm{d}\nu_b/\mathrm{d}t$ and the increase of $\mathrm{d}\nu_a/\mathrm{d}t$. Hence, the size spectrum remains monodisperse in $\mu_i$. From the last equation it follows that

$$\frac{\mathrm{d}S^{1/2}}{\mathrm{d}t} = \sum_a \frac{\zeta_a - \mu_a f_a(\mu_a)}{3\tau_a} v_{\ell\, a} \tag{91}$$

and the velocity of the $S^{1/2}$ growth depends only upon $\mu_a$. So it is constant for all embryos. As soon as after the final PIFD the spectrum is monodisperse, it remains monodisperse in the further evolution unit coalescence.

In the monodisperse (in $S^{1/2}$ and $\mu_a$) approximation the system of kinetics equations can be rewritten in the following form:

$$\frac{\mathrm{d}\nu_i}{\mathrm{d}t} = \frac{1}{\tau_i}\left(\sum_b \nu_b v_{\ell\, b}\right)^{2/3}\left(\Phi_i - N\frac{\nu_i}{n_{ii}} - \mu_i f_i(\mu_i)\right), \tag{92}$$

where $N$ is the total number of droplets.

We shall describe the further evolution on the example of the isothermal evolution with a homogeneous source of vapors. The situations considered above can be in some sense reduced to this one. If $m_a \leqslant 3$ for all components, the period of essential formation cannot be reproduced, during further evolution, more than a number of components. We shall investigate this situation. Even in this situation the second peak of droplet formation can appear. This is obvious from comparison with the situation when we have a vapor mixture of substances which cannot be mixed in the liquid phase. So we must utilize the methods developed in the description of the simultaneous action of heterogeneous and homogeneous formation in the dynamical conditions [29]. This forms a separate publication. Here we shall analyze the solutions for the last kinetic equations with given $N$.

To investigate these equations we can apply some methods of investigation similar to the situation of the decay of the binary mixture [30]. So only new methods will be discussed here. We shall leave out the activity coefficients for simplicity. These coefficients must be introduced in every place where concentration appears. The evolution equation leads to the following equation for $S$:

$$\frac{\mathrm{d}S^{1/2}}{\mathrm{d}t}=\sum_a\left(\Phi_a-\frac{N\nu_a}{n_{aa}}-\frac{\nu_a}{\Sigma_b\,\nu_b}\right)v_{\ell\,a}/3\tau_a\,. \tag{93}$$

In initial approximation we consider $S$ to satisfy the following equation:

$$\frac{\mathrm{d}S^{1/2}}{\mathrm{d}t}=\sum_a\,[\Phi_a-\mu_a(\{\Phi_a\})]v_{\ell\,a}/3\tau_a\,, \tag{94}$$

which can be easily integrated. On the base of $S$ as function of time we can obtain $\nu_a$ as functions of time from the first order linear differential equation

$$\frac{\mathrm{d}\beta_a}{\mathrm{d}t}=\frac{S}{\tau_a}\left(\Phi_a-N\frac{\nu_a}{n_{aa}}-\mu_a(\{\Phi_a\})\right). \tag{95}$$

Actually we are now at the first step of the iterational procedure, which can be continued in an obvious manner. The values of $S(t)$, $\nu_a(t)$, $\nu_b(t)$ obtained at the previous step are the initial values in the iteration procedure:

$$\frac{\mathrm{d}S^{1/2}_{(i+1)}}{\mathrm{d}t}=\sum_a\frac{v_{\ell\,a}}{3\tau_a}\left(\Phi_a-\frac{N\nu_{a\,(i)}}{n_{aa}}-\frac{\nu_{a\,(i)}}{\Sigma_b\,\nu_{b\,(i)}}\right), \tag{96}$$

$$\frac{\mathrm{d}\nu_{a\,(i+1)}}{\mathrm{d}t}=\frac{S_{(i+1)}}{\tau_a}\left(\Phi_a-N\frac{\nu_{a\,(i+1)}}{n_{aa}}-\frac{\nu_{a\,(i)}}{\Sigma_b\,\nu_{b\,(i)}}\right). \tag{97}$$

In order to investigate the final period one can take as initial approximations the new values of $\nu_{a\,\mathrm{lim}}$. These values can be attained when all supersaturated substance is in the droplets. We can define these values from the equations

$$\Phi_a=N\frac{\nu_{a\,\mathrm{lim}}}{n_{aa}}+\frac{\nu_{a\,\mathrm{lim}}}{\Sigma_b\,\nu_{b\,\mathrm{lim}}}\,. \tag{98}$$

Then we can calculate $S$ in initial approximation,

$$S_{\mathrm{lim}}=\left(\sum_b\nu_{b\,\mathrm{lim}}\,v_{\ell\,b}\right)^{2/3}. \tag{99}$$

Several intermediate approximate procedures must be taken into account also. At some periods of evolution when $\Phi_a\gg 1$ we can neglect $\nu_a/\Sigma_b\,\nu_b$. Let us stress that for the possibility of rather rapid condensation it is necessary that

$$\Phi_a \gg 1 \tag{100}$$

for some component $a$ (we choose components in such a way). So we can substitute

$$\frac{\nu_a}{\Sigma_b \nu_b} \to \frac{\nu_{a\,\mathrm{lim}}}{\nu_{a\,\mathrm{lim}} + \Sigma_{b \neq a} \nu_b} \tag{101}$$

and utilize this substitution in the whole evolution process.

We must also stress the possibility of investigation of the final period on the basis of the initial approximation

$$\nu_b = \nu_{b\,\mathrm{lim}} \,. \tag{102}$$

The next approximation is obtained by

$$\frac{\mathrm{d}\nu_{a\,(i)}}{\mathrm{d}t} = \frac{S_{(i)}}{\tau_a} \left( \Phi_a - N \frac{\nu_{a\,(i+1)}}{n_{aa}} - \frac{\nu_{a\,(i)}}{\Sigma_b \nu_{b\,(i)}} \right), \tag{103}$$

$$S_{(i)} = \left( \sum_a v_{\ell\, a}\, \nu_{a\,(i)} \right)^{2/3} . \tag{104}$$

The combination of the last iteration procedure for one component and the previous iterational procedure for another component is also very effective in intermediate situations.

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# Kinetics of heterogeneous condensation under dynamic conditions

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An analytical kinetic condensation theory for arbitrary power in the law of supercritical growth of embryos is constructed. Exhausting of the heterogeneous centers is taken into account. A system of balance equations is formulated based on a quasistationary approach. Properties of the solution for the essential period of the droplet formation are obtained using an iteration procedure. The universal solution method gives practically precise expressions for all coefficients in the brief description of the evolution process.

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## I. INTRODUCTION

Condensation of supersaturated vapor into droplets can be regarded as a model of first-order phase transitions where some alternative methods of description are implemented. We introduce some ideas to describe phase transitions in this situation. Usually some heterogeneous centers become centers of supercritical embryos during condensation, which indicates the occurrence of the process of heterogeneous condensation. Heterogeneous condensation is described by nonlinear equations since droplets consume metastable substances and free heterogeneous centers decrease at the same time.

Kinetic theory of first-order phase transition appears naturally from the classical theory of nucleation, which describes formation of embryos of the new phase. This theory was developed first by Volmer [1], Becker and Doering [2], Zeldovitch [3] and Frenkel [4] and modified later by Lothe and Pound [5], Reiss, Cohen and Katz [6], Reiss [7] and Fisher [8].

Wakeshima [9] started to investigate the kinetic problem of the metastable phase decay. Homogeneous decay of the metastable phase was studied by Kuni, Grinin, and Kabanov [10]. The theory of homogeneous condensation under dynamical conditions was considered in [11,12]. A corresponding iteration procedure for homogeneous condensation was proposed by Kuni [12]. Heterogeneous condensation under dynamic conditions was investigated in [13]. The method of the universal solution was introduced in [14] and was studied in detail in [15,16]. All the theories mentioned above are valid only until the beginning of coalescence (Ostwald ripening). The coalescence process, which is not observed here, was investigated first by Slyozov and Lifshitz [17,18].

The process of phase transition is caused by the variation in time of the external conditions. The most natural external conditions have a rather smooth continuous form—the variation of the external thermodynamic parameters occurs during the whole period of the phase transformation. Such external conditions will be called dynamical. The main goal of the present paper is to give an analytical description of the phase transition under dynamic external conditions. This description will be based on the methods suggested in [19] and is valid when the critical embryo contains a large number of molecules. This means that the capillarity approximation for the free energy can be used.

The following assumptions will be used in this paper:

(i) The system is homogeneous in space (it means that the elementary hydrodynamical element can be considered).

(ii) All heterogeneous centers are of the same nature.

(iii) The total number of the heterogeneous centers in the whole system is fixed.

(iv) The regime of the substance exchange between an embryo and environment is free molecular.

(v) No thermal effects are observed.

We want to mention that the method presented here is rather general and can be applied to some other complicated physical phenomena.

## II. EXTERNAL SUPERSATURATION

All values of magnitudes will belong to the unit volume of the considered system in the further considerations. All the energylike values, such as free energy $F$ of the formation of the embryo, will be measured in thermal units $k_b T$, where $k_b$ is the Boltzman constant and $T$ is the temperature of the system. Let us denote the total number of the condensing molecules by $n_{\text{tot}}$ and the total number of the heterogeneous centers by $\eta_{\text{tot}}$. Values of $\eta_{\text{tot}}$ and $n_{\text{tot}}$ are certain functions of time, which are supposed to be known. The temperature is defined by the external conditions, so the number of molecules of the saturated vapor is also known at every moment. The approximate but rather precise connection is given by the thermodynamic equation

$$n_\infty(T)=n_\infty(T_*)\exp\left[\beta\frac{T-T_*}{T_*}\right],$$
$$\frac{T}{T_*}\approx\left[\frac{n_{\infty *}}{n_\infty}\right]^{1/\beta}, \tag{1}$$

where $\beta$ is the condensation heat per one molecule and the index $*$ marks the values at some moment $t_*$ of time.

Since approximations like (1) are based on values at a particular time $t_*$, the choice of $t_*$ leads to an estimated error of the theory. In order to minimize this error the time $t_*$ has to be chosen as the time when the number of already condensated droplets is equal to the number of droplets which will be formed later.

The power of the initial phase metastability can be described by the supersaturation

$$\zeta=\frac{n}{n_\infty} , \tag{2}$$

where $n$ is the number of molecules in the vapor. Let us introduce the magnitude similar to the supersaturation but independent from the vapor consumption. Ideal supersaturation is given by

$$\Phi=\frac{n_{\text{tot}}}{n_\infty} , \tag{3}$$

where $n_{\text{tot}}$ is the total number of the molecules of the substance. This value can be considered as the supersaturation which can be attained in the system where no vapor consumption by the droplets occurs. Meanwhile, the value of the supersaturation can be decreased by binding part of molecules with the heterogeneous centers in the process of solvatation. So the value of ideal supersaturation must be substituted by the value of external supersaturation

$$\Omega=\frac{1}{n_\infty}(n_{\text{tot}}-\eta_{\text{tot}}\nu_e|_{\zeta=\Omega}) , \tag{4}$$

where $\nu_e$ is the number of molecules in the equilibrium embryo. Equation (4) gives the self-consistent definition of $\Omega$. Due to the weak dependence of $\nu_e$ on $\Omega$ this equation can be easily solved by standard iterations. The first iteration

$$\Omega=\frac{1}{n_\infty}(n_{\text{tot}}-n_{\text{tot}}\nu_e|_{\zeta=\Phi}) \tag{5}$$

is sufficient for the majority of cases. The behavior of $\Omega$ resembles the behavior of $\Phi$. We shall assume that it changes smoothly in time.

## III. EQUATIONS OF THE CONDENSATION KINETICS

Let us extract the characteristic of the supercritical embryo which has $\nu$ molecules and grows in time with a regular velocity independent from the embryo size. A rather wide class of the supercritical embryo growth laws is covered by the power functions $d\nu/dt \sim \nu^{1-\alpha}\varphi(\zeta(t))$ where $\varphi$ is a known function. Then the variable

$$\rho=\nu^{\alpha} \tag{6}$$

grows with the regular velocity independent from the size of the supercritical embryo.

The iterational procedure suggested in [19] provides rather precise results for $\alpha \ll 1$. The procedure suggested here can be applied for arbitrary $\alpha \le 1$. When $\alpha=1$ the system of condensation equations can be solved analytically. We assume that $1-\alpha$ is not too small in comparison with unity.

We shall use two assumptions which will be justified later. The first one establishes that the leading role in vapor consumption belongs to the supercritical embryos, i.e., to the droplets. So the characteristic size $\rho_1$ of the embryos at the middle of the period of essential formation of new droplets (PEFD) strongly exceeds the size $\rho_c$ of the critical embryo:

$$\rho_1 \gg \rho_c . \tag{7}$$

Hence we can consider only regular growth and set the initial size of embryos entering the supercritical region equal to zero. In the regular growth approximation the Volmer-Zeldovitch-Frenkel equation for the distribution function $p(\rho,t)$ is reduced to the equation

$$\frac{\partial}{\partial t}p(\rho,t)=-\frac{\partial}{\partial t}\left[p(\rho,t)\frac{d\rho}{dt}\right] . \tag{8}$$

In the region of the positive arguments the solution has to be multiplied by the characteristic function of the positive half-axis $\Theta\{\Theta(\rho \ge 0)=1,\Theta(\rho<0)=0\}$. As a result, the distribution $p(\rho,t)$ of the droplets over the $\rho$ axis is given by the expression

$$p(\rho,t)=\frac{n_{\infty *}V_*}{n_\infty V}\Theta(z-x)f(x) , \tag{9}$$

where $f$ is some function of the argument

$$x=z-\rho \tag{10}$$

and $z$ is the coordinate on the $\rho$ axis of the droplet which appeared at $t=t_*$. Thus the function $z$ can be obtained as the solution of the equation

$$\frac{dz}{dt}=\frac{d\rho}{dt}\equiv\varphi(\zeta(t)) , \tag{11}$$

$$z|_{t=t_*}=0 . \tag{12}$$

The form of the function $f(x)$ in (9) is determined from the boundary conditions. This function is called the size spectrum.

The second assumption is necessary to obtain the boundary conditions. We assume that the state of the near-critical embryos during the PEFD is close to the quasistationary one. This distribution is described by the stationary distribution function $f_s(\zeta)\eta/n_\infty$, where explicit dependence on $\eta$ is extracted. The stationary classical theory gives the following formula for the stationary distribution:

$$f_s \sim \frac{K\exp(-\Delta F)}{\Delta\nu_e\Delta\nu_c\varphi(t)} , \tag{13}$$

where $\Delta F$ is the height of the activation free energy, $K$ is the kinetic factor obtained from the gas kinetic theory and Folmer-Frenkel theory, $\Delta\nu_e$ is the normalizing factor of the equilibrium distribution

$$\Delta\nu_e \approx \sum_{\nu=1}^{(\nu_c+\nu_e)/2}\exp[-F(\nu)+F(\nu_e)] , \tag{14}$$

$\Delta\nu_c$ is the half-width of the near-critical region

$$\Delta\nu_c \approx \left|2\Big/\frac{d^2F(\nu)}{d\nu^2}\right|^{1/2}, \tag{15}$$

and $\nu_c$ is the number of molecules in the critical embryo.

The second assumption must be valid during the period of the essential formation of droplets. Let $t_\zeta$ be the characteristic time of the variation of the stationary state in the near-critical region and let $t_s$ be the time of relaxation to the stationary state in the near-critical region. Then the required assumption can be written as

$$t_\zeta \gg t_s \ . \tag{16}$$

These assumptions will be valid in all situations except the case when almost all heterogeneous centers are exhausted at the end of the essential formation period. In this case the result of the PEFD is obvious: the number of droplets coincides with the total number of the heterogeneous centers, the form of the spectrum is unessential during the period of essential formation, and the spectrum is monodispersive when the supersaturation starts to fall.

We obtain the following expression for the function $f(x)$ using $f_s(\zeta)\eta/n_\infty$ as the boundary condition for the distribution $p(\rho,t)$ when $\rho=0$:

$$f(x)=f_s(\zeta)|_{\zeta=\zeta(x)}\frac{\eta(x)}{n_\infty} \ . \tag{17}$$

In order to determine the form of the functions $\zeta(x)$ and $\eta(x)$ the balance equations must be taken into account:

$$\Omega=\zeta+g \ , \quad g(z)=\frac{n_{\infty *}V_*}{n_\infty V}\int_{-\infty}^{z}dx(z-x)^{1/\alpha}f(x) \ , \tag{18}$$

$$\eta_{\text{tot}}=\eta+N \ , \quad N(z)=\frac{n_{\infty *}V_*}{V}\int_{-\infty}^{z}dx\, f(x) \ . \tag{19}$$

The first equation is the balance equation for the condensing substance. The second is the balance equation for the heterogeneous centers. These balance equations together with explicit expressions (13) and (17) for $f(x)$ form a closed system.

## IV. SOME APPROXIMATIONS

Several approximations will be used in order to simplify the balance equations. We introduce parameter $\Gamma$:

$$\Gamma=-\Omega_*\frac{d\Delta F(\zeta)}{d\zeta}\bigg|_{\zeta=\Omega_*} \ . \tag{20}$$

Due to the equation

$$\Gamma=\nu_c(\Omega_*)-\nu_e(\Omega_*) \tag{21}$$

this parameter satisfies the strong inequality

$$\Gamma\gg 1 \ . \tag{22}$$

Due to (22) the following inequality is valid in the neighborhood of $\Omega_*$ for the majority of external conditions:

$$\Gamma\left[\frac{d\Omega}{dx}\right]^2\gg\Omega\frac{d^2\Omega}{dx^2} \ . \tag{23}$$

This inequality describes the class of dynamic external conditions completely. Actually all natural external conditions belong to this class. Inequality (23) allows us to write a linear approximation for $\Omega(x)$ at the essential formation period.

Due to (13) and (17) the function $f(x)$ is a sharp function of the supersaturation $\zeta$ and argument $x$. The exponential dependence in (13) and (17) is much stronger then the power dependence $(z-x)^{1/\alpha}$ and the subintegral functions in (18) and (19) are well localized on the $x$ axis. Thus the PEFD can be extracted on the basis of the behavior of the subintegral function in (18) and (19). The following inequalities are valid during this period:

$$\frac{\Omega-\Omega_*}{\Omega_*}\le\Gamma^{-1} \ , \quad \frac{\zeta-\Omega_*}{\Omega_*}\le\Gamma^{-1} \ . \tag{24}$$

These inequalities will appear in further considerations automatically. Equation (24) leads to

$$V\approx V_* \ , \quad n_\infty\approx n_{\infty *} \tag{25}$$

during the PEFD. Due to (13), (17), and (24), the approximation

$$f(x)=f_s\exp\left[\Gamma\frac{\zeta(x)-\Omega_*}{\Omega_*}\right]\frac{\eta(x)}{n_\infty} \ , \quad f_s\equiv f_s(\Omega_*) \tag{26}$$

is valid during the PEFD. To justify (26) the following estimates have to be taken into account:

$$\frac{d\nu_c}{d\zeta}\sim\frac{d\nu_{c\,\text{hom}}}{d\zeta} \ , \quad \frac{d\nu_c}{d\zeta}-\frac{d\nu_e}{d\zeta}\sim\frac{d\nu_c}{d\zeta} \ , \quad \nu_c-\nu_e\sim\nu_c \ , \tag{27}$$

where $\nu_{c\,\text{hom}}$ is the number of molecules in the critical homogeneous embryo. Then we come to the strong inequality

$$\left|\frac{d\Delta F(\zeta)}{d\zeta}\right|^2\gg\left|\frac{d^2\Delta F(\zeta)}{d\zeta^2}\right| \ . \tag{28}$$

According to (28) we can linearize $\Delta F$ as a function of $\zeta$. We suppose that the sharpest dependence on the supersaturation is given by $\exp(-\Delta F)$. This assumption puts, however, very weak restrictions on $\varphi(t)$. Certainly, it is necessary to check (28) directly for every concrete model of heterogeneous centers.

Another parameter will be defined by the expression

$$c=\frac{\Gamma}{\Omega_*}\frac{d\Omega(x)}{dx}\bigg|_{x=0} \ . \tag{29}$$

This parameter is important for the linearization of the function $\Omega(x)$ during the PEFD. Linearization leads to the equation

$$\Omega(x)=\Omega_*+\frac{\Omega_* cx}{\Gamma} \ . \tag{30}$$

This linearization is based on the strong inequality

$$\left[\frac{d\Omega}{dx}\right]^2 \gg \delta_1\Omega \frac{d^2\Omega}{dx^2} , \tag{31}$$

where $\delta_1\Omega$ is the variation of $\Omega$ during the PEFD. Taking into account (24) we see that Eq. (31) follows from (23). Equation (23) leads to the following form of (18):

$$g(z)=f_s \int_{-\infty}^{z} dx (z-x)^{1/\alpha} \exp\left[cx-\Gamma\frac{g(x)}{\Omega_*}\right]\frac{\eta(x)}{n_{\infty*}} . \tag{32}$$

The balance equation for the heterogeneous center leads to the form

$$f(x)=-\frac{d\eta(x)}{n_{\infty*}dx} . \tag{33}$$

This differential equation can be easily solved:

$$\eta(z)=\eta(-\infty)\exp\left[-f_s\int_{-\infty}^{z} dx \exp\left[cx-\Gamma\frac{g(x)}{\Omega_*}\right]\right] . \tag{34}$$

The argument $-\infty$ marks values of the magnitudes at the very beginning of the PEFD and the argument $\infty$ corresponds to the end of the PEFD.

The total number of the droplets is introduced by the equality

$$N(x)=\eta(-\infty)-\eta(x) . \tag{35}$$

The following integral representation for $N(z)$ can be derived:

$$N(z)=\int_{-\infty}^{z} f(x)dx\, n_{\infty*} . \tag{36}$$

## V. ITERATION PROCEDURE

Some properties of the solution of the system of balance equations ar important to justify further constructions. We are going to determine these properties using an iteration procedure. Let us denote the operator on the right-hand side (rhs) of (32) by $G(g(x),\eta(x))$ and operator on the rhs of (34) by $H(g(x))$. The iterations will be constructed in accordance to the following rule:

$$g_{a(i+1)}=G(g_{a(i)},\eta_{a(i)}) , \quad \eta_{a(i+1)}=H(g_{a(i)}) . \tag{37}$$

If the initial approximation is chosen as $g_{ax(0)}=0, \eta_{a(0)}=\eta(-\infty)$, then the iteration procedure gives upper and lower bounds for the solution. These bounds converge to the exact solution. The main property of the operators $g$ and $h$ is the "monotonous" character of these operators. Namely, if

$$g_p(x)\geq g_q(x)$$

for all values of the arguments then

$$H(g_p(x))\geq H(g_q(x)) \tag{38}$$

for all values of $x$. If

$$g_p(x)\geq g_q(x) , \quad \eta_q\leq\eta_p$$

for all values of the arguments then

$$G(g_p(x),\eta_p(x))\leq G(g_q(x),\eta_q(x)) . \tag{39}$$

From (38) and (39) and the obvious inequalities

$$\begin{aligned} &g_{a(0)}\leq g , \quad g_{a(2)}\geq g_{a(0)}=0 , \\ &\eta\leq\eta_{a(0)} , \quad \eta_{a(2)}\leq\eta_{a(0)}=\eta(-\infty) , \end{aligned} \tag{40}$$

the following chains of inequalities can be constructed:

$$\begin{aligned} &g_{a(0)}\leq g_{a(2)}\leq \cdots \leq g_{a(2i)}\leq \cdots \leq g \\ &\quad \leq \cdots \leq g_{a(2i+1)}\leq \cdots \leq g_{a(3)}\leq g_{a(1)} , \end{aligned} \tag{41}$$

$$\begin{aligned} &\eta_{a(0)}\geq \eta_{a(2)}\geq \cdots \geq \eta_{a(2i)}\geq \cdots \geq \eta \\ &\quad \geq \cdots \geq \eta_{a(2i+1)}\geq \cdots \geq \eta_{a(3)}\geq \eta_{a(1)} . \end{aligned} \tag{42}$$

It follows from (41) and (42) that iterations $\{g_{a(2i)}\}$ and $\{\eta_{a(2i+1)}\}$ are growing monotonically, being restricted from below. A similar fact is valid for $\{g_{a(2i+1)}\}$ and $\{\eta_{a(2i)}\}$. So odd iterations and even iterations converge. A solution of the system exists if the limits of the odd and even iterations coincide. The limits of odd and even iterations are solutions of the iterated system (32) and (34). If the initial system has a solution then this solution is a solution of the iterated system also and the limits of the odd and even iterations coincide. We have proved the uniqueness of the solution of the system. The existence of the solution has to be proved also.

New iterations $g_{b(i)}$ (reduced iterations) will be constructed in accordance with the rule

$$g_{b(i+1)}=G(g_{b(i)},H(g_i)) . \tag{43}$$

For the initial approximation we take $g_{b(0)}=0$. These iterations slightly differ from the initial iterations $g_{a(i)}$ and $\eta_{a(i)}$. Iterations $g_{a(2i)}$ and $g_{a(2i+1)}$ estimate iterations $g_{b(i)}$:

$$g_{a(2i+1)}\geq g_{b(2i+1)} , \quad g_{a(2i)}\leq g_{b(2i)} . \tag{44}$$

Equation (43) can be rewritten in the form

$$g_{b(i+1)}=\int_{-\infty}^{z} (z-x)^{1/\alpha} L(g_{b(i)}(x))dx , \tag{45}$$

where we have extracted the function

$$\begin{aligned} L(g_i(z))=f_s\frac{\eta(-\infty)}{n_{\infty*}}&\exp\left[\frac{cx-\Gamma g_i(z)}{\Omega_*}\right] \\ &\times\exp\left[-f_s\int_{-\infty}^{z}\exp\left[\frac{cx-\Gamma g_i}{\Omega_i}\right]dx\right] . \end{aligned} \tag{46}$$

The next iteration (both initial and reduced) is formed on the basis of the previous iteration with an argument less than $z$. So the second iteration of type "$a$" gives an estimate from above for the region of the essential values of $z$, i.e., the estimate from above for the end of the PEFD. These iterations give also approximations for the droplet number and size spectrum:

$$N_{(i)}(z)=\eta(-\infty)-\eta_{(i)}(z) , \tag{47}$$

$$f_{(i)}=-\frac{d\eta_{(i)}}{n_{\infty*}dz} . \tag{48}$$

The second approximation gives

$$f_{a(2)}(x)=\frac{\eta(-\infty)}{n_{\infty *}}f_s\exp\left[cx-hf_s\frac{\exp(cx)}{c}-\frac{1-\exp\left[-hf_s\frac{\exp(cx)}{c}\right]}{h}\right], \tag{49}$$

$$\eta_{a(2)}=\eta(-\infty)\exp\left[-\frac{1-\exp\left[-hf_s\frac{\exp(cz)}{c}\right]}{h}\right], \tag{50}$$

$$N_{a(2)}=\eta(-\infty)\left[1-\exp\left[-\frac{1-\exp\left[-hf_s\frac{\exp(cx)}{c}\right]}{h}\right]\right], \tag{51}$$

where

$$h=\frac{\gamma\left[\frac{1}{\alpha}\right]\Gamma\eta(-\infty)}{\Omega_* n_{\infty *}c^3}, \qquad \gamma\left[\frac{1}{\alpha}\right]=\int_0^\infty y^{1/\alpha}\exp(-y)dy . \tag{52}$$

The chain of inequalities for $N_{a(i)}$ is valid:

$$N_{a(2)}\le N_{a(4)}\le\cdots\le N_{a(2i)}\le\cdots\le N \le\cdots N_{a(2i+1)}\le\cdots\le N_{a(3)}\le N_{a(1)} . \tag{53}$$

It follows from (49) that the upper bound for the PEFD in variable $z$ can be well defined. This bound will be denoted by "$b$". Analysis of $g(x)$ and $\eta(x)$ asymptoticly leads to the existence of the absolutely unessential region of big negative values of $z$ due to (1) inequalities

$$g(x)\ge 0 , \quad \eta(x)\ge\eta_{a(2)} , \quad \frac{d\eta}{dx}\le 0 , \quad \frac{dg}{dx}\ge 0 ;$$

(2) the explicit form of $f(x)$:

$$f(x)=f_s\frac{\eta(-\infty)}{n_{\infty *}}\exp\left[\frac{cx-\Gamma g(x)}{\Omega_*}\right] ; \tag{54}$$

and (3) the explicit form of subintegral functions in expressions for $g$ and $\eta$.

We shall mark the upper boundary of this region by "$-a$." Substitution of the lower limit of integration by $-a$ is unessential.

Let us consider $L$ as a functional of two arguments

$$L(y)=L\left[y,\psi=f_s\int_{-a}^{z}\exp\left[\frac{cx-\Gamma g}{\Omega_*}\right]\right] . \tag{55}$$

Then

$$L(y_1)-L(y_2)\le\max_{-a\le x\le b}\left|\frac{\partial L}{\partial y}\right|(y_1-y_2) + \max_{-a\le x\le b}\left|\frac{\partial L}{\partial\psi}\right|(\psi_2-\psi_2) . \tag{56}$$

Introducing

$$\|y\|=\max_{-a\le x\le b}y , \tag{57}$$

we obtain the inequality

$$L(y_1)-L(y_2)\le l_1+l_2 , \tag{58}$$

where

$$l_1=\max_{-a\le x\le b}\left|\frac{\partial L}{\partial y}\right|\|y_1-y_2\| , \tag{59}$$

$$l_2=\max_{-a\le x\le b}\left|\frac{\partial L}{\partial\psi}\right|\|y_1-y_2\| \times\max_{-a\le x\le b}\left|\frac{d\exp\left[cx-\frac{\Gamma g}{\Omega_*}\right]}{dg}\right|f_s(b+a) . \tag{60}$$

This inequality can be rewritten as

$$L(y_1)-L(y_2)\le\max_{-a\le x\le b}\left|\frac{\partial L}{\partial y}\right|\omega , \tag{61}$$

where

$$\omega=1+(b+a)\max_{-a\le x\le b}\left|\frac{\partial L}{\partial\psi}\right|\frac{n_\infty}{\eta(-\infty)}\|y_1-y_2\| . \tag{62}$$

The final estimate is

$$L(y_1)-L(y_2)\le\beta\|y_1-y_2\| , \tag{63}$$

where $\beta$ is a certain constant.

We have the following expression and inequalities for the iterations:

$$g_{b(i+1)}-g_{b(i)}=\int_{-a}^{z}dx(z-x)^{1/\alpha}[L(g_{b(i)})-L(g_{b(i-1)})] , \tag{64}$$

$$g_{b(i+1)}-g_{b(i)}\le\int_{-a}^{z}dx(z-x)^{1/\alpha}\|g_{b(i)}-g_{b(i-1)}\|\beta , \tag{65}$$

$$g_{b(i+1)}-g_{b(i)}\le(z+a)(a+b)^{1/\alpha}\beta\|g_{b(i)}-g_{b(i-1)}\| . \tag{66}$$

Recurrent procedure leads to

$$\|g_{b(i)} - g_{b(i+1)}\| \le \frac{(z+a)^i}{i!}\text{const} . \tag{67}$$

Summation of the rhs of (67) over all $i$ gives the function const $\exp(z+a)$. So this sequence is fundamental. All terms of the rhs of (57) are positive. So the sequence of iterations is a fundamental sequence, and also the sequence of iterations is converging. The limit of iteration defines the solution of the system of balance equations. We have proved the existence of the solution. Odd and even iterations are converging to one and the same limit. The solution of balance equation system is unique.

Inequalities (41) and (42) allow one to estimate the errors of $g_{a(i)}$ and $\eta_{a(i)}$ and due to (44) the error of $g_{b(i)}$. The measure of the sufficient precision has to be defined in accordance with the accuracy of modern experiments. The most important characteristic of the process is the total number of droplets. So we shall measure the accuracy of our theory in the relative error in the total number of droplets:

$$\Delta_i = \frac{\|f_i - f\|_{L_1}}{\|f\|L_1} \equiv \frac{\int_{-\infty}^{\infty} f_i - f\,dx}{\int_{-\infty}^{\infty} f\,dx} . \tag{68}$$

Due to (53) we can obtain the following estimate for the error of the initial iterations:

$$\Delta_{a(2i)} \le \frac{|N_{a(2i+1)}(\infty) - N_{a(2i)}(\infty)|}{N_{a(2i)}(\infty)} . \tag{69}$$

One the basis of (69) we can see that the initial iterations are converging rather fast. The second iteration gives the relative error less than 0.16. It can be shown by comparison of (51) with the expression

$$N_{a(3)} = \eta(-\infty)[1 - \exp(-Y/h)] , \tag{70}$$

where

$$Y = \int_{-\infty}^{\infty} d\xi \exp\left[\xi - \tfrac{1}{6}\int_{-\infty}^{\xi} (\xi-\sigma)^{1/\alpha} \exp\left[\sigma - \frac{h+1}{h}\exp(\sigma)\right] d\sigma\right] . \tag{71}$$

Unfortunately, an analytical expression for $g_{a(2)}$ can not be obtained. Hence an analytical expressions for the further iterations can not be presented either. So the real problem is to obtain a more precise approximation.

First of all, we can use the second initial iteration for analytical estimates for the duration of the PEFD in order to justify (24). We require that the relative number of droplets formed outside the PEFD is equal to $\delta$:

$$|N(0) - N(\pm\Delta_{\pm}x)| = |N(0) - N(\pm\infty)|(1-\delta) , \tag{72}$$

where the parameter $\delta$ has a rather small value. We denote by $\delta_{\pm}x$ the right and left characteristic sizes of the PEFD in $x$ scale. Then we have for $\delta_{\pm}x$ in the second approximation in iteration procedure $a$ almost precise expressions:

$$\Delta_{\pm}x = \frac{1}{c}\left|\ln\frac{\ln(1+h\ln\lambda_0)}{\ln(1+h\ln\lambda_{\pm})}\right| , \tag{73}$$

where

$$\lambda_0 = \frac{1}{2}\left[1 + \exp\left[-\frac{1}{h}\right]\right] , \tag{74}$$

$$\lambda_- = 1 - \frac{\delta}{2}\left[1 - \exp\left[-\frac{1}{h}\right]\right] , \tag{75}$$

$$\lambda_+ = \exp\left[-\frac{1}{h}\right] + \frac{\delta}{2}\left[1 - \exp\left[-\frac{1}{h}\right]\right] . \tag{76}$$

Thus the value of $\Delta_{\pm}x$ has the power of $c^{-1}$. Hence $\Delta\Omega$ has the power $\Omega_*/\Gamma$ and the first inequality (24) is justified. The second inequality follows immediately from the first and from (26). During the period of essential formation of the droplets the variations of $\zeta$, $\Omega$, and $\varphi$ are very small.

Inequalities (7) and (16) can be rewritten as

$$c^{-1} \gg \rho_c , \tag{77}$$

$$t_s \ll c^{-1}\varphi^{-1} . \tag{78}$$

## VI. UNIVERSAL SOLUTION

The leading idea for the further consideration is to reduce the description of the process thought the minimal set of variables. Let us extract those characteristics of the spectrum $f(x)$ which are sufficient for the condensation process.

The balance equation for the condensing substance can be presented in the form (18), which is valid not only during the PEFD but also during the whole evolution. So $g$ can be expressed through

$$\mu_i = \int_{-\infty}^{z} x^i f(x) dx . \tag{79}$$

When the essential formation period is over the balance equation for the heterogeneous centers is unessential and the evolution of the system is described only by the balance equation for the substance. The following expression for $g$ is valid due to the rapid vanishing of $f(x)$:

$$g = \frac{n_{\infty *}V_*}{n_\infty V}\int_{-\infty}^{\infty} f(x)(z-x)^{1/\alpha} dx . \tag{80}$$

Now the evolution is determined by the constant values of the full momentums of spectrum. Even when the law of droplet growth differs from the free-molecular one the leading term is proportional to the total number of embryos—the zero momentum of the spectrum

$$g(z) \approx \mu_0 z^{1/\alpha}\frac{n_{\infty *}V_*}{n_\infty V} . \tag{81}$$

The turning point in our consideration will be the analysis of the velocity of convergence of the iterations $g_{a(i)}$ and $\eta_{a(i)}$. Calculations by (51), (70), and (71) show that the error increases with the growth of the parameter $h$. Hence the situations $h \ll 1$ are well described. But the situations of the pseudohomogeneous condensation when $h \gg 1$ are described with a certain error. At the same time the final approximations for the internal iterational procedure are obtained directly without taking into account the exhausting of the free heterogeneous centers.

The balance equation for the heterogeneous centers disappears when $\eta \equiv \eta(-\infty)$ and the balance equation for the substance has the form of the homogeneous condensation. Hence it can be reduced to the universal form. This form can be obtained by analytical expression of the solution as a function of the parameter $f_s$ from the situation when $t_*$ is the moment of the supersaturation maximum. We introduce the function

$$\phi = \Gamma \frac{\Omega - \zeta}{\Omega_*} \tag{82}$$

and obtain the universal equation [14–16]

$$\phi(z) + \frac{1}{\alpha} z \int_{-\infty}^{0} (z-x)^{-1+1/\alpha} \exp[-\phi(x)]dx = \int_{-\infty}^{z} (z-x)^{1/\alpha} \exp[-\phi(x)]dx \tag{83}$$

in appropriately normalized variables. It follows from (83) that $\phi(x)$ is a universal function [15]. The approximation of the pseudohomogeneous universal solution is a base for the further iterations.

The change of the variables from $x,z$ to $cx,cz$ and from $g,\eta$ to $G = \Gamma_g/\Omega_*$, $\Theta = \eta/\eta(-\infty)$ leads to the equations

$$G = A \int_{-\infty}^{z} (z-x)^{1/\alpha} \Theta(x) \exp(x-G)dx \ , \tag{84}$$

$$\Theta = \exp\left[ -B \int_{-\infty}^{z} \exp(x-G)dx \right] , \tag{85}$$

where constants $A$ and $B$ are defined by

$$A = \frac{\Gamma f_s \eta(-\infty)}{c^{1+1/\alpha} \Omega_* n_{\infty *}} \ , \quad B = \frac{f_s}{c} \ . \tag{86}$$

Some choice of the basic point in the construction of approximations (linearization of the external supersaturation as a function of $x$ and linearization of the free energy as a function of the supersaturation) is essential only if the exhausting of vapor plays a leading role in the interruption of the embryo formation, i.e., $h \gg 1$. In the alternative situation $h \ll 1$ ("almost total exhausting of the heterogeneous centers") the result of the condensation is obvious—almost all heterogeneous centers are the centers of droplets. So the total number of droplets is equal to the total number of heterogeneous centers and the spectrum has a monodispersious form. If the parameters of the ideal supersaturation are fixed then the relative sizes of region $\Delta_g \Omega$ of $\Omega_*$ corresponding to all situations except $h \ll 1$ are rather small:

$$\frac{\Delta_g \Omega}{\Omega_*} \le \frac{\epsilon}{\Gamma} \ , \quad \epsilon \sim 3 \ . \tag{87}$$

The inequalities mentioned above are so strong that linearization remains valid in a region covering $\Delta_g \Omega$. So the choice of an arbitrary point in this interval as the base for the approximations leads to the applicability of linearization in every situation except $h \ll 1$. So the value of $\Omega$ at the moment when half of the imaginary droplets are formed can be used as a base point in the case of pseudohomogeneous formation. Then the coefficient

$$A_0 = \frac{1}{\alpha} \int_{-\infty}^{0} (z-x)^{-1+1/\alpha} \exp[-\phi(x)]dx$$

is determined as a constant. For example, $A_0 = 0.136$ in the case $\alpha = \frac{1}{3}$.

As far as the dependence in the evolution process is implemented through $\{\mu_i\}$ and $\int_{-\infty}^{z} \exp[x - G(x)]dx$, an ordinary evolutional (not the net one) calculation is required. Moreover, as far as the position of the base point is not essential we do not need the exact definition of $t_*$ but must keep in mind the values of $\mu_0(\infty)$ and $\mu_0(0)$. Instead of the precise value of the source intensity $(1/\alpha) \int_{-\infty}^{0} (z-x)^{-1+1/\alpha} \exp[-\phi(x)]dx$ we can take some appropriate number ($\sim \frac{1}{5}$ in the case $\alpha = \frac{1}{3}$). The result of calculation gives the total number of droplets. This number ($\sim \frac{1}{5}$ in the case $\alpha = \frac{1}{3}$) is connected with the accuracy of the procedure. It must be chosen to minimize the error introduced by the approximations.

This solution has maximum at some point $z_0$. The notation that this point must be the real maximum of supersaturation gives the algebraic equation on the parameters of the process similar to [13]. It must be solved by ordinary numerical methods or by the methods proposed in [20].

The concrete value of $A_0$ with the help of (86) allows one to justify (77) and (78) for all situations except $h \ll 1$. Let us take for $t_s$ the estimate analogous to Zeldovitch's for the homogeneous case [3]:

$$t_s \approx \frac{(\Delta \nu_c)^2}{W^+} \tag{88}$$

where $W^+$ is the direct flow on the critical embryo which can be estimated as

$$\frac{W^+}{\nu_c^{1-\alpha}} \sim \varphi \ .$$

The height of the activation barrier $\Delta F$ can be estimated by $F|_{\nu=\nu_c}$. According to Gibbs equation this value is proportional to the surface square

$$F \sim \rho_c^{(1/\alpha)[(\mathrm{dim}-1)/\mathrm{dim}]} \tag{89}$$

(dim is the dimension of space). Then we can justify (77) and (78).

In further considerations the initial approximation will be the solution for $h \gg 1$. It will be marked by the subscript $\infty$. In application of the initial iteration procedure the first and second approximations for $\eta$ will coincide as far as $g_{a(0)} = g_{a(1)} = g_\infty$. It is impossible to obtain an analytical formula for the second approximation for $g$ and for the third approximation for $\eta$. So we shall consider reduced iterations only. The first iteration takes into account the exhausting of the heterogeneous centers:

$$G_{(1)} = A_0 \int_{-\infty}^{z} dx (z-x)^{1/\alpha} \times \exp\left[-B \int_{-\infty}^{x} d\xi \exp[\xi - G_\infty(\xi)]\right] \times \exp[x - G_\infty(x)] , \tag{90}$$

where

$$G_\infty(x) \equiv G(x)|_{\Theta=1} .$$

For the normalized total number of droplets an explicit expression can be used:

$$N_{(2)}^{+}(\infty) \sim \int_{-\infty}^{\infty} f(x) dx \sim \int_{-\infty}^{\infty} \exp(x - G_{(1)}) dx . \tag{91}$$

As far as

$$N_{(1)}^{+}(z) = \int_{-\infty}^{z} d\xi \exp(\xi - G_\infty) \tag{92}$$

is a universal function, we can construct universal expansion at the first step. Decomposition of the exponential gives

$$N_{(2)}^{+}(\infty) = \int_{-\infty}^{\infty} dz \exp[z - A_0 Q_0(z)] \prod_{l=1}^{\infty} D_l , \tag{93}$$

where

$$D_j = \sum_{l=0}^{\infty} \left[\frac{(-1)^{j+1} B^j}{j!} Q_j A_0\right]^l \frac{1}{l!} , \tag{94}$$

$$Q_i = \int_{-\infty}^{z} dx (z-x)^{1/\alpha} \exp[x - G_\infty(x)] N_{(1)}^{i}(x) , \tag{95}$$

which leads to the representation

$$N_{(2)}^{+}(\infty) = \sum_i P_i B^i , \tag{96}$$

where $P_i$ are some constants. This expression can be linearized as a function of $B$ because the result will be substituted into the exponential formula for the number of the free heterogeneous centers:

$$N_{(2)}^{+}(\infty) = P_0 + P_1 B , \tag{97}$$

where

$$P_0 = \int_{-\infty}^{\infty} \exp[x - A_0 Q_0] dx , \tag{98}$$

$$P_1 = \int_{-\infty}^{\infty} \exp[x - A_0 Q_0] Q_1 dx \; A_0 . \tag{99}$$

Then the final expression is

$$N_{+}(\infty) = 1 - \exp[-B(P_0 + P_1 B)] . \tag{100}$$

In the case $\alpha = \frac{1}{3}$ the relative error of this expression is less than 0.003. The analogous results can be obtained for arbitrary $\alpha$. It means that further iterations are unessential. The expressions for the other times of the spectrum can be obtained by the same procedure.

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# Density profiles in the theory of condensation

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**Abstract**

The process of nucleation is described by an analytical theory which takes into account the influence of the profiles of density and the temperature around the droplets. The theory predicts all main characteristics of the process. The comparison with the already known results is given.

## 1. Introduction

Among numerous examples of the phase transitions of the first order the case of condensation of supersaturated vapor into a liquid phase is investigated most completely. Namely, the new methods in the description of the phase transition of the first order are introduced in this example. The classical theory of nucleation was formulated by Becker and Doering [1] and was completed by Zeldovitch and Frenkel [2] at the end of the forties. The formulation of the classical theory of nucleation did not solve all the problems in the description of the first order phase transition. The classical theory was reconsidered by Lothe and Pound [3] by some corrections. The role of such corrections is the matter of discussion during the last 30 years. The construction of realistic kinetic pictures of the phase transformation was started by Wakeshima [4] and Raiser [5]. These efforts were continued in the last years. As a result the kinetic theory of the homogeneous condensation after the instantaneous creation of the supersaturation was presented in [6]. Some kinetic problems of the phase transitions under the dynamic external conditions were investigated in [8] by means of the steepest descent method and in [7] with the help of a iteration procedure. A complete theory for the heterogeneous condensation under the same conditions is given in [9]. The theory for the multidimensional kinetics of the phase transformation is presented in [11].

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All the kinetic theories mentioned above use the free-molecular regime of the growth of the droplets. This implies the collective character of the vapor consumption by the droplets. So, the vapor in the system is regarded as being homogeneous in the volume.

Due to the consumption of the vapor by the super-critical embryos the density of the vapor around every super-critical embryos is smaller than the average density in the volume (at least than the density far from the droplet). The consumption of the vapor in the region near the droplet initiates the process of diffusion.

In many important cases the process of diffusion cannot completely compensate the consumption of the vapor. Thus, one can observe the profile of the density of the vapor around the droplet. Only in the case of the *"pure free molecular regime of the substance exchange"* this effect can be neglected.

The same picture can be observed in the distribution of temperature around the droplets. The extraction of the heat of the condensation leads to the increase of temperature around the droplet. The process of heat conductivity can compensate this extraction only partially. The mathematical structure of equations in this case resembles the case of the density profiles of substance. In order to present the most simple variant of the theory which is easy to understand on spot we shall take into account only the density profiles of the substance. The generalization is rather obvious. The situation of the decay of the metastable state of the vapor will be considered as the model for the external conditions. The generalization for the external conditions of the dynamic type [9] is also presented.

The aim of this publication based on [10] is to construct a theory of the condensation when the density profiles are taken into account.

Due to the lack of the volume only the sketch of such a theory will be presented. This publication has the following structure:

- In Section 2 the density profile of the single droplet will be considered.
- In Section 3 the boundary of the region of the nucleation will be extracted.
- In Section 4 some kinetic models of the global evolution of the phase transformation will be presented.
- In Section 5 the theory will be spread over all regimes of vapor consumption.

All results will be valid only when the critical embryo can be described with the help of the capillary approximation, i.e. when the critical embryo contains more than a few dozens of molecules. These conditions appear to be natural in the frames of thermodynamics. Such conditions will be called as the *capillary approximation conditions (CAC).* The inverse number of molecules in the critical embryo will be the small parameter of the theory.

## 2. Density profile of the single droplet

The construction of the theory implies some simplifications which are necessary to present some concrete mathematical model of the phenomenon. These simplifications are based on some rigorous statements which are presented below. The validity of CAC gives the restriction from above on the supersaturation in the system. Due to the vapor consumption by the droplets the supersaturation can only decrease. As the result we come to the following:

*Statement 0. If the CAC are valid at the beginning of the process they remain to be valid during the whole process of the nucleation.*

The next statement is not so evident as the previous one:

*Statement 1. In the CAC the leading role in the vapor consumption is played by the super-critical embryos, named later as "droplets".*

The most simple way to prove it is to note that the characteristic length of the spectrum in this case is greater than the characteristic length in the pure molecular case [9] where this statement is valid. Also one can directly check the validity of this fact in the final expressions for the length of the spectrum.

The process of condensation after the instantaneous creation of the external metastable conditions can be split into several characteristic periods. At the initial moment of time, the rate of nucleation, i.e. the rate of appearing of the super-critical embryos of the liquid phase, attains a maximum. Later this rate vanishes due to the vapor consumption.

*One can correctly define the moment when the rate of nucleation becomes inessential and extract the "period of intensive formation of the droplets" (PIFD).*

The rate of the embryos growth is approximately proportional to the density of the vapor in the system. The rate of nucleation, i.e. the rate of appearing of the super-critical droplets is a very sharp function of the vapor density. That's why it is possible to observe the vanishing of the rate of nucleation under some small relative variations in the density of the vapor (and in the rate of the droplets growth). Namely, this situation takes place in the nucleation. Also one can come to

*Statement 2. In CAC the growth of the super-critical embryos has no influence during PIFD on the rate of the growth of the neighboring droplets.*

Thus, we can describe the evolution of the single separated (isolated) droplet in the volume, which will be the matter of our consideration in this section. The derivation of the stationary rate of the nucleation implies that the density of the vapor is constant in time and the system is homogeneous in space. The next statement establishes the connection between the stationary rate of the nucleation and the real rate of the nucleation:

*Statement 3. In the CAC during the PIFD in the given spatial point in some moment of time the rate of the nucleation is approximately equal to the stationary rate of nucleation with some current values of the characteristics of the vapor considered as the constant ones.*

The last statement has at least two aspects: the variation of the density in time and the profiles of the density in space. In order to prove the last one an interpretation of the rate of the nucleation as some probability for the super-critical embryo to appear must be taken into account. Only in the rather small neighborhood of the droplet these conditions are essentially non-stationary ones. These regions do not play any essential role in the kinetics of the process of nucleation.

Later it will be shown that all the volume can be approximately split into two regions. In the first region (the "unexhausted region" - UR) the density of the vapor is practically unperturbed so that the current density corresponds to the practically ideal rate of nucleation. In the second region (the "exhausted region" - ER) the rate of nucleation is negligible in comparison with the rate in the first region. So according to Statement 1:

*In the CAC the leading role in the process of the growth of the ER belongs to the subregions around the super-critical embryos (not around the small embryos).*

The statements mentioned above allow us to construct the mathematical model of the process of condensation.

Denote the concentration of the molecules in the vapor as $n(r)$. The evolution in time $t$ of the density profile will satisfy the diffusion equation

$$\frac{\partial n}{\partial t} = D\Delta n, \tag{1}$$

where $D$ is the coefficient of diffusion. This coefficient is considered to be approximately constant. The density $n$ is now the function of the spatial argument $r$.

We shall use the diffusion regime of droplet growth because this situation, as it will be clear from the further considerations, is the worst one for some estimates in the given theory.

As far as the density of the vapor is now the function of the spatial coordinate, the value of the supersaturation

$$\zeta = \frac{n(r) - n_\infty}{n_\infty} \tag{2}$$

is also the function of the spatial coordinate. In (2) the value $n_\infty$ is the concentration of the molecules in the saturated vapor over the plane liquid.

The value of the ideal supersaturation introduced by

$$\Phi = \frac{n_{\text{tot}} - n_\infty}{n_\infty}, \tag{3}$$

where $n_{\text{tot}}$ is the total number of the molecules in the unit volume[1], is not the function of the spatial coordinate.

For the stationary rate of the nucleation in the Fokker-Planck approximation the following expression is valid [2]:

$$I_s(\zeta) \sim \sqrt{\frac{a}{\pi}}\frac{(\zeta+1)^2}{\tau}\exp(-F_c(\zeta))n_\infty, \tag{4}$$

where $a$ is the normalized surface tension, $\tau$ is the characteristic time between collisions of a fixed molecule of vapor with another molecule of vapor, $F_c$ is the free energy of

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[1] The process of diffusion is excluded from the consideration here. The value of $\Phi$ is the imaginary supersaturation in the system where the formation if the droplets is forbidden. So, $\Phi$ is described by the external conditions.

formation of the critical embryo. Some microscopical corrections to the free energy can be introduced in the manner of Lothe and Pound. In the CAC $F_c$ is given by

$$F_c = \frac{a}{3}\left(\frac{2a}{3\ln(\zeta+1)}\right)^2 . \tag{5}$$

In the CAC one can analytically prove that the following approximation for the stationary rate given by (4) as function of $\zeta$ is valid during PIFD[2]:

$$I_s(\zeta) = I_s(\Phi)\exp\left(\Gamma\frac{\zeta-\Phi}{\Phi}\right) . \tag{6}$$

Eq. (6) remains valid with the microscopical corrections taken into account. Here the value of $\Gamma$ is defined as

$$\Gamma = \frac{\Phi\nu_c}{\Phi+1} , \tag{7}$$

where $\nu_c$ is the number of the molecules inside the critical embryo,

$$\nu_c = \left(\frac{2a}{3\ln(\zeta+1)}\right)^3 . \tag{8}$$

In order to obtain $\zeta$ in the approximation (6) it is necessary to solve Eq. (1). Let us consider the single droplet. One can use the spherical symmetry of the system and put the droplet into the center. The variable $r$ will mark the distance from the center of the droplet. To solve Eq. (1) one can put the following natural boundary conditions:

$$n(r=\infty) = (\Phi+1)n_\infty , \tag{9}$$

$$n(r=r_k) = n^e \approx n_\infty , \tag{10}$$

where $r_k$ is the radius of the droplet and $n^e$ is the the concentration of the molecules in the vapor which is in equilibrium with the embryo of the given size.

The stationary solution of the equation of diffusion has a rather simple form,

$$n^s(r) = -\frac{\Phi n_\infty r_k}{r} + (\Phi+1)n_\infty . \tag{11}$$

On the base of the evident inequality,

$$(\Phi+1)n_\infty - n^s(r) \geq (\Phi+1)n_\infty - n(r) \geq 0 , \tag{12}$$

where $n(r)$ is the real concentration of the molecules in the vapor[3], it is seen that the supersaturation $\zeta(r)$ can be essentially deviated from $\Phi$ only when $r$ is near $r_k$.

---

[2] It is necessary to substitute (5) into (4), note that the most essential dependence on the supersaturation is concentrated in the argument of the exponent, calculate the first and the second derivatives of $F_c$ on $\zeta$, take into account that when $|-\zeta+\Phi| \gg \Phi/\Gamma$ the rate of the nucleation is negligible and the result is not essential. Then we compare the weight of the first and the second term in the Tailor's series and see that the second term is negligible (in the whole essential interval) which leads to (6).

[3] This inequality can be proved on the base of the Green's functions superposition if we note that the flow on the droplet in the nonstationary situation continuously grows in time.

Namely the ratio $\exp(1)r/r(k)$ defines the characteristic scale of the region of the essential perturbation of the supersaturation (not the essential perturbation of the rate of formation of the embryos).

When in the region $r \le r_k \exp(1)$ one can see the stationary density distribution, the stationary flow of the molecules on the droplet can be introduced according to

$$j^s = -4\pi r^2 D \frac{\partial n}{\partial r} . \tag{13}$$

The stationary approach in the calculation of (13) is valid in the CAC. The distribution (11) of the density gives the following expression for the flow:

$$j^s = -4\pi \Phi D r_k n_\infty . \tag{14}$$

In the region $r \le \exp(1) r_k$ due to (6),(7) and $\Gamma \gg 1$ the rate of the nucleation is negligibly small. The region where the vapor is only slightly exhausted is important for the nucleation.

One must establish the profile of the density in the region $r \le \exp(1) r_k$ in order to know $j^s$. Then the flow $j^s$ is already known on the base of (14). At the distances $r \gg r_k$ one can consider the droplet as the point source of the vapor consumption. So the density of vapor at $r \gg r_k$ can be obtained on the base of Green's function for the process of diffusion

$$G = \Theta(t) \frac{\exp(-r^2/4Dt)}{(4\pi D t)^{3/2}} . \tag{15}$$

For the intensity of the vapor consumption by the point source situated in the point $r = 0$ the following expression:

$$\frac{d\nu}{dt} = \lambda t^{1/2} \tag{16}$$

is valid[4]. Here $\nu$ is the number of the molecules in the droplet and the constant $\lambda$ is defined as

$$\lambda = (4\pi)^{3/2} \left( \frac{v_l}{2\pi} \right)^{1/2} (\Phi n_\infty D)^{3/2} , \tag{17}$$

where $v_l$ is the volume in the liquid phase per one molecule. For the total number of the molecules in the droplet the following expression:

$$\nu(t) = (4\pi)^{3/2} \left( \frac{3 v_l}{4\pi} \right)^{1/2} (\tfrac{2}{3} \Phi n_\infty D)^{3/2} t^{3/2} \tag{18}$$

---

[4] The analysis of the behavior of $n(r)$ on the base of the Green's functions superposition shows that in the region $r \le r_k \exp(1)$, i.e. in the region of the essential deviation of the supersaturation, one can observe $\Phi - \zeta_s \sim \Phi - \zeta$, where $\zeta_s$ is the supersaturation in the stationary approximation. So we can use (16). But as it will be seen in the further considerations the asymptotes where $r \gg r_k \exp(1)$ will be the most essential. To get these asymptotes we must use the nonstationary approach as far as $\Phi - \zeta_s \gg \Phi - \zeta$ for the tail of the density profile. Certainly, the approximation (16) can be treated as the zero approximation in the iteration procedure, and the first step is fulfilled in this paper.

is valid.

One can spread the rate[5] of the droplet growth (18) over all values of $\nu$ and come to

$$n(\infty) - n(r) = \int_0^t \frac{\lambda x^{1/2}}{8(D\pi(t-x))^{3/2}} \exp\left(-\frac{r^2}{4D(t-x)}\right) dx . \tag{19}$$

Assuming $n(\infty) = n_\infty(\Phi + 1)$ one can get the following equation:

$$\Phi - \zeta(r) = c_0 \Phi^{3/2} \left(\frac{v_l}{v_v}\right)^{1/2} f(\beta) , \tag{20}$$

where $v_v$ is the volume in the saturated vapor per one molecule.

It is necessary to stress that the rigorous demonstration for expression (4) can be given only in the free molecular regime of the vapor exchange. As far as according to Statement 2 the characteristic size of the droplets strongly exceeds during the PIFD the critical size there is no contradiction between the free-molecular regime for the near-critical embryos and the diffusion regime for characteristic droplets during the PIFD.

Note that the approximation (6) accumulates the analytical structure and is based mainly on the estimate

$$I_s \sim \exp(-F_c) .$$

This estimate is obviously based on the Boltzmann distribution, which is evidently valid. Only the value of $F_c$ may be slightly reconsidered according to the sense of $F_c$ as the minimal work of the formation of the critical fluctuation.

The function $f(\beta)$ has the form

$$f(\beta) = \int_\beta^\infty \left(\frac{1}{\beta^2} - \frac{1}{x^2}\right)^{1/2} \exp(-x^2) dx , \quad c_0 = \left(\frac{2}{\pi}\right)^{1/2} , \tag{21}$$

and the variable $\beta$ is defined as

$$\beta = \frac{r}{2\sqrt{Dt}} . \tag{22}$$

The universal profile is illustrated by Fig. 1.

In the case of the arbitrary Knudsen numbers the value of $\Phi - \zeta$ will decrease with the growth of $r$ sharper than in the case under consideration. This will lead to some more strong inequalities forming the base of the theory.

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[5] We use the law (16) for the super-critical embryos. According to Statement 2 we can consider only the embryos with the size which strongly exceeds the critical one and we can formally prolong the law (16) until $\nu = 0$. This approximation leads to the relatively small errors. Certainly, we have to use for the rate of the droplets formation the expression (4) which is obtained on the base of the fluctuations and of the precise law of the embryo evolution.

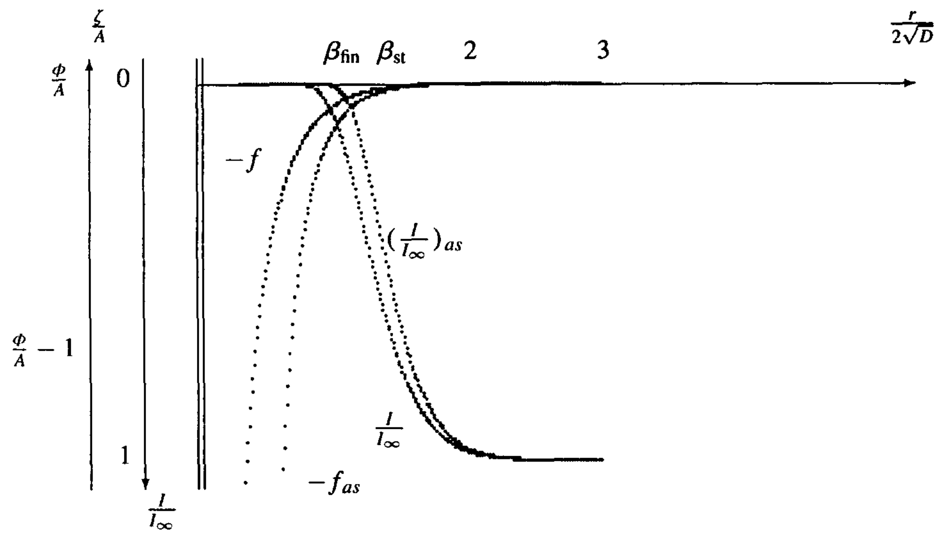

Fig. 1. The universal profile of the density $f(\beta)$, the relative intensity $I/I(\infty)$ and their asymptotic approximations. Here $A = c_0\Phi^{3/2}(v_l/v_v)^{1/2}$. In the calculation of relative intensity $I/I(\infty)$ and $\beta_{\rm st}$, $\beta_{\rm fin}$ the coefficient $k$ is put to 30.

## 3. Approximation for the rate of nucleation

The essential feature of Eqs. (20)-(22) is the fact that the profile of the supersaturation essentially depends only upon one variable $\beta$. Let us introduce the characteristic values of $\beta_{\rm st}$ and $\beta_{\rm fin}$ by equations

$$f(\beta_{\rm st}) = \frac{\Phi^{-1/2}(v_v/v_l)^{1/2}}{\Gamma c_0 \exp(1)}, \tag{23}$$

$$f(\beta_{\rm fin}) = \frac{\Phi^{-1/2}(v_v/v_l)^{1/2}}{\Gamma c_0} \equiv c_f. \tag{24}$$

In the region of $r$ corresponding to $\beta > \beta_{\rm st}$ the rate of the nucleation practically coincides with the unperturbed value $I_s(\Phi)$. This conclusion is based on (6), (20)-(22). For $r$ corresponding to $\beta < \beta_{\rm fin}$, the intensity of the droplet formation is negligibly small. The values $r_{\rm fin}$ and $r_{\rm st}$ are defined as the distances where $\beta$ attains the values $\beta_{\rm fin}$ and $\beta_{\rm st}$ correspondingly.

Consider the supersaturation in some spatial point $r_0$. For

$$t \le t_{\rm st} = \frac{r_0^2}{4\beta_{\rm st}^2 D} \tag{25}$$

one cannot observe any essential deviation of the rate of the droplets formation from the ideal value and for

$$t \ge t_{\rm fin} = \frac{r_0^2}{4\beta_{\rm fin}^2 D} \tag{26}$$

the rate of the droplets formation becomes negligibly small.

Eqs. (23),(24) lead as far as $\Gamma \gg 1$ to

$$f(\beta_{\mathrm{st,fin}}) \ll 1 , \tag{27}$$

which can be attained only at

$$\beta_{\mathrm{st,fin}} \gg 1 . \tag{28}$$

For $\beta$ corresponding to the last inequality the asymptotic behavior

$$f(\beta) \sim \frac{\exp(-\beta^2)}{\beta^3} \tag{29}$$

can be observed. It shows that the relative deviation $\beta_{\mathrm{fin}}$ from $\beta_{\mathrm{st}}$ is very small[6]. So the value of the parameter

$$\delta = \frac{t_{\mathrm{fin}} - t_{\mathrm{st}}}{t_{\mathrm{fin}} + t_{\mathrm{st}}} \tag{30}$$

is also small. The intensity of the droplets formation in the relative time scale remains practically constant and then rather fast turns to be negligible. Note that in (23),(24) another small parameter $(v_l/v_v)^{1/2}$ exists. So (27),(28) appear to be a matter of discussion. It seems that practically in all situations $\delta$ is really small, but rigorous proof is absent. Despite this we shall formally follow (27)-(29) and later the generalization will be given. The small value of $\delta$ together with the smooth behavior of $I_s(\zeta)/I_s(\Phi)$ as the function of $\zeta$ for $|\zeta - \Phi| \leq \Phi/2\Gamma$ allows to use the value of $\beta_{\mathrm{eff}}$ as some characteristic value defined in the following manner: at the distances corresponding to $\beta > \beta_{\mathrm{eff}}$ the rate of the droplet formation is considered as an unperturbed one and at the distances corresponding to $\beta < \beta_{\mathrm{eff}}$ the rate of the droplets formation is negligibly small.

Let us define the variation in the whole rate of nucleation connected with the formation of one droplet of given size. It is convenient to introduce the parameter

$$k = \frac{\Gamma(\Phi - \zeta)}{f(\beta)\Phi} = \Gamma c_0 \Phi^{1/2} \left(\frac{v_l}{v_v}\right)^{1/2} . \tag{31}$$

The deviation from the maximum intensity is given by the following expression:

$$\Delta I_s = I_s \int_0^\infty \left(1 - \exp\left(\frac{-\Gamma(\Phi - \zeta(r))}{\Phi}\right)\right) 4\pi r^2 dr , \tag{32}$$

which can be reduced to

$$\Delta I_s = I_s 4\pi (2D^{1/2}t^{1/2})^3 \int_0^\infty (1 - \exp(-kf(\beta))\beta^2 d\beta . \tag{33}$$

---

[6] As is seen from Fig. 1 the values $\beta_{\mathrm{st}}$, $\beta_{\mathrm{fin}}$ are not so big in reality. So, the asymptote (29) is not so close to $f(\beta)$. But the final conclusion that the relative deviation $\beta_{\mathrm{st}}$ from $\beta_{\mathrm{fin}}$ is very small remains valid. Only this conclusion will be essential in the further consideration.

We are going to introduce the following function $\Delta I^0$ via some expression:

$$\Delta I^0 = 4\pi(2D^{1/2}t^{1/2})^3 \int_0^{\beta} x^2 dx . \tag{34}$$

The value of $\beta_{\text{eff}}$ (and correspondingly $r_{\text{eff}}$) is defined from the following equation:

$$\Delta I^0(\beta_{\text{eff}}) = \Delta I_s . \tag{35}$$

Inside the volume

$$V_{\text{eff}} = \tfrac{4}{3}\pi r_{\text{eff}}^3 \tag{36}$$

there is practically no nucleation. Outside this volume the rate of nucleation is not perturbed by the droplet situated in $r = 0$. It is essential that the value $\beta_{\text{eff}}$ remains constant during the PIFD,

$$\beta_{\text{eff}} = \text{const.} = 3 \int_0^{\infty} [1 - \exp(-kf(\beta))]\beta^2 d\beta , \tag{37}$$

and can be easily found from (35). The value of $k$ as it is clear from the r.h.s. of (31) is not a function of $r$, $\beta$ and $t$. On the base of $\beta_{\text{eff}}$ one can find the value of

$$r_{\text{eff}} = 2\beta_{\text{eff}} D^{1/2} t^{1/2} , \tag{38}$$

which is the evident function of time. The volume $V_{\text{eff}}$ grows in time as

$$V_{\text{eff}} = \tfrac{32}{3}\pi \beta_{\text{eff}}^3 D^{3/2} t^{3/2} \equiv c_v t^{3/2} . \tag{39}$$

## 4. Kinetics of the nucleation process

Until the current moment only the single droplet was considered. This droplet was formed at $t = 0$. Now the interaction between the droplets will be taken into account. Certainly, all already formed droplets interact through the exhausting of the vapor. The direct interaction between some already formed droplets is rather weak according to Statement 2. But one must take into account the interaction through the interruption of formation of the droplets. Note that

*The relative deviation of the supersaturation by the small value of $\Gamma^{-1}$ leads to the interruption of the droplets formation.*

To deviate the rate of growth another droplet must be formed too close to the droplet under consideration. It can be done only at the same moment as the given droplet is formed. It can be shown that the probability of such coincidence is too small.

As far as we have seen that essential deviation of the supersaturation (not the rate of growth) occurs in the region $r < r_k \exp(1)$ it means that the distance between droplets must have the order $2r_k \exp(1)$ So, the time distance between the moments of formation of these droplets must be shorter than

$$\Delta t_{\text{int}} \sim \left[\frac{r_k}{\beta_{\text{eff}} D^{1/2}}\right]^2 .$$

But this interval[7] is negligible in comparison with the characteristic time of the process of droplet formation which can be found from the results of this section.

So, relatively fast every droplet forms the ER with such a size to guarantee that the rate of growth will be unperturbed by the other droplets. Hence, the majority of the droplets are formed at such distances that their rate of growth is unperturbed.

In this section three models will be presented. The second one seems to be the most accurate, but the all of them are necessary in order to see the inclusion of this picture into already investigated situations [6].

### 4.1. Model without overlapping

The total volume $W_{\text{eff}}$ where the rate of the droplets formation is negligibly small can be approximately written in the following form:

$$W_{\text{eff}} \sim \int_0^t c_v(t-t')^{3/2} P(t')dt' , \tag{40}$$

where $P(t')$ is the probability of the formation of the droplet in the moment $t'$. For the value of $P(t')$ the following expression can be presented:

$$P(t') = I_s(\Phi)(1 - W_{\text{eff}}) . \tag{41}$$

Expression (41) closes (40). In (40),(41) the overlapping of the ER is not taken into account.

The system (40),(41) can be reduced to the Volterra equation. The kernel is rather trivial and this equation can be easily solved (in Laplace representation it is extremely simple).

This model, however, has some disadvantages. The main disadvantage is that the overlapping of the ER is not taken into account at all. We shall overcome this disadvantage in the next model.

### 4.2. Model of the chaotic overlapping of the ER

Let us introduce an equation for the evolution of the value $W_{\text{free}}$, i.e. the volume in which the rate of the nucleation is practically ideal (unperturbed). Approximately this evolution can be described by the following equation:

$$-\frac{dW_{\text{free}}}{dt} = \frac{d\sum V_{\text{eff}}}{dt} W_{\text{free}} , \tag{42}$$

---

[7] Certainly, for $r \sim r_k$ the model of the superposition of the Green functions which leads to the above estimate is not suitable. But as far as we need the estimate from above for the interval, we can use instead $r \sim r_k \exp(1)$ some value of $r$ corresponding to $r_k \ll r \ll N^{-1/3}$, where $N$ is the total number of droplets that appeared during the process. For such value of $r$ all conclusions remain valid.

where the sum is taken over all existing droplets. The term $W_{\text{free}}$ in the r.h.s. of (42) can be considered as some probability that the new ER is going to occupy the free (unperturbed) region. Taking into account the evident relation

$$\frac{d\sum V_{\text{eff}}}{dt} = \sum \frac{dV_{\text{eff}}}{dt}, \tag{43}$$

we have the following expression:

$$\frac{d\sum V_{\text{eff}}}{dt} = \frac{3}{2}\int_0^t c_v (t-t')^{1/2} P(t') dt', \tag{44}$$

where

$$P(t') = I_s(\Phi)(1 - W_{\text{eff}}) = I_s(\Phi) W_{\text{free}}(t'). \tag{45}$$

Then one can come to

$$-\frac{dW_{\text{free}}}{dt} = \frac{3}{2}\int_0^t c_v (t-t')^{1/2} W_{\text{free}}(t') I_s(\Phi) dt' W_{\text{free}}(t). \tag{46}$$

After an integration of (46) we have

$$-\ln W_{\text{free}} = \int_0^t I_s(\Phi) c_v (t-t')^{3/2} W_{\text{free}}(t') dt' + \text{const}. \tag{47}$$

Due to the initial conditions the constant of the integration *const.* is equal to zero. In terms of function $F = -\ln W_{\text{free}}$ one can reduce (47) to

$$F(t) = \int_0^t I_s(\Phi)(t-t')^{3/2} c_v \exp(-F(t')) dt'. \tag{48}$$

Eq. (48) coincides in the mathematical structure with the free-molecular case and was investigated in [12].

### 4.3. Model with the formation of the droplets inside the ER

Eq. (42) in the last section states the chaotic overlapping of the ER. Certainly, this fact is rather approximate. Here we shall try to analyze the role of the overlapping of the ER. In order to see this role let us formulate the following model.

Imagine that the ER are initiated also by the droplets imaginary formed in the ER of the other droplets. This statement is not certainly valid but it allows to formulate the model corresponding to the first iteration in the iteration procedure and, thus, to clarify the physical sense of the first iteration.

The ER of the "new" droplet "imaginary formed" in the ER of the "old" droplet can appear outside the ER of the "old" droplet. Namely, this fact leads to the error of the last supposition and to the error in the value of the volume free for the formation of the droplets. But nevertheless let us accept this model for a moment.

So, instead of (45) one can use

$$P(t') = I_s(\Phi) . \tag{49}$$

Then instead of (46) one has

$$-\frac{\partial W_{\text{free}}}{\partial t} = \frac{3}{2} \int_0^t c_v (t-t')^{1/2} I_s(\Phi) dt' W_{\text{free}}(t) \tag{50}$$

and after an integration

$$-\ln W_{\text{free}} = \int_0^t I_s(\Phi) c_v (t-t')^{3/2} dt' + \text{const.} \tag{51}$$

The value of const. is equal to zero due to the initial conditions.

The role of the model under the consideration appears from the last expression. It is an expression for the first iteration in the iteration solution for the second model. Such a solution can be given analogously to [12,9]. So, now the physical sense of the first iteration is clear.

Also one can show that the results of the second and the third models are very close[8]. As the result one can see that some concrete manner of the overlapping of the ER is not very important. This note will be used in the next section.

## 5. Collective character of the vapor consumption

The next problem to discuss is to consider the generalization of the theory for the arbitrary regime of the droplet growth. One can extract the following regimes of the droplets growth.

- The pure diffusion regime of growth.

  This regime is extracted by the condition

  $$\frac{r_k}{R_{\text{free}}} \gg 1 , \tag{52}$$

  where $R_{\text{free}}$ is the average length of free motion of the molecule in the vapor and for simplicity the coefficient of the condensation $\alpha$ here and later is put to be equal to unity. This case was considered above.
- The regime of intermediate Knudsen numbers.

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[8] In [12] the calculations were stopped at the first iteration and it was shown that the first iteration forms the base of expressions which are near the exact solution.

This regime is extracted by the condition

$$\frac{r_k}{R_{\text{free}}} \sim 1 . \tag{53}$$

This situation can be described by the simple resubstitution of the intensity in (16) by another intensity obtained from the macroscopic law of droplet growth which is a well-known one. Intensity of the droplets growth can be approximated by the dependence of the power type.

Now we are going to investigate the regime of the free-molecular growth. This regime is extracted by condition

$$\frac{r_k}{R_{\text{free}}} \ll 1 . \tag{54}$$

We shall extract two subregimes

- The subregime of the pure free-molecular growth.

This regime is extracted in the following manner. The macroscopic law of droplets growth gives the intensity of the vapor consumption. So one can put the stationary diffusion problem with the given intensity and solve it. In the situation

$$\zeta(\infty) - \zeta(R_{\text{free}}) \ll \frac{\zeta(\infty)}{\Gamma(\zeta(\infty))} ,$$

one can speak about the pure free-molecular growth. Namely in this case the consumption of the vapor has the collective character and was investigated in [6].

- The subregime of the intermediate free-molecular growth.

This regime is extracted by the same procedure as the previous case but with condition

$$\zeta(\infty) - \zeta(R_{\text{free}}) \geq \frac{\zeta(\infty)}{\Gamma(\zeta(\infty))} .$$

Certainly, restriction (54) must also be observed. Here the evolution is rather complicate because one must take into account the collective consumption of the vapor and also the profiles of the density.

The answer is nevertheless an extremely simple one: Eq. (48) coincides in the mathematical structure with the balance equation in [12] and this fact states that the second model describes also this case (with renormalizations). In [12] one can find the iteration method of the solution of the balance equation and notice the following interesting fact:

*The solution of the third model is the first iteration in the iteration solution of the second model.*

Meanwhile it is known [12] that the first iteration as the base for the final result leads to the practically precise solution. The relative error in the number of droplets calculated on the base of the first iteration[9] is less than 0.01. It means that the

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[9] It can be shown on the base of the monotonous properties of the functional which corresponds to the number of the molecules in the droplets (see [12,9]).

solution of the second model is practically the solution of the third model and the physical effects of the overlapping lead to rather small errors during the PIFD. Thus, one can use the second or the third model and describe with the help of such models all situations. Certainly, the macroscopic laws of the droplets growth must be chosen in the appropriate way.

The same situation takes place with inequalities (27),(28). Now it is clear that in principle (27),(28) are not necessary. If they are not valid then the situation resembles in the mathematical construction the subregime of the intermediate free-molecular growth and can be solved analogously.

The approximate coincidence of the results from the second and the third models has one more important consequence. Let us clarify what is the reason of such coincidence. The total volume of the ER grows so rapidly that the droplets formed at the beginning of the process (when the probability of the overlapping of the ER was rather small) are the dominating consumers of the vapor. Their ER play the leading role in the ensemble of the ER of all droplets during the whole PIFD. So, the problem of overlapping is not so important as it seems from the first point of view. This notice is important in the problem of justification of the models. All of them contain rather approximate suppositions that the chaotic appearing of droplets leads to the chaotic overlapping of the ER. This approximation is suitable due to the relatively small role of the interference effects of the overlapping at the beginning of the the PIFD and due to the leading role of the droplets that appeared at the beginning of the PIFD in evolution during the PIFD.

In the dynamic external conditions [7,9] the theory can be constructed by the formal generalization of the presented procedure.

In Section 1 Statement 0 is not valid now. Now one must require the validity of the CAC near the maximum of $\zeta$. This requirement remains also natural in the frames of thermodynamics because the majority of droplets appears when the supersaturation is near the maximum. This conclusion is based on the following statement.

*Statement 4. For*

$$\frac{d^2\Phi}{dt^2} \leq 0$$

*it follows that*

$$\frac{d^2\zeta}{dt^2} < 0$$

*during the PIFD.*

Note that the possibility of the definition of the boundaries of the PIFD is based on the last inequality together with Statement 3 and Eq. (4).

The function $\Phi$ introduced by (3) becomes the function of time. The following statement can be proved:

*The relative variation of $\Phi$ during the PIFD is very small. The influence of the variation of $\Phi$ upon $\beta_{st}$ and $\beta_{fin}$ is negligible. The relative duration of the PIFD is rather short.*

The last statement gives the base for approximation (6). According to (6) and to Statement 4 one can see that the relative variation of $\Phi$ has the order of $\Gamma^{-1}$,

$$\frac{\Delta\Phi}{\Phi} \leq \Gamma^{-1}. \tag{55}$$

Due to the last statement[10] the function $\Phi$ as a function of time can be linearized in all practically important situations,

$$\Phi(t) = \Phi_* + ct. \tag{56}$$

Here index $*$ marks the values at some characteristic moment during the PIFD, $c$ is the parameter of the linearization. This moment can be chosen in some different manners. For example, it can be the moment when $\zeta$ attains the maximum [8] (in the situation of the decay this moment was chosen at $t = 0$). Then according to (6),

$$I_s(\zeta) = I_s(\Phi_*) \exp\left(\frac{\Gamma}{\Phi_*}ct\right) \exp\left(\Gamma\frac{\zeta - \Phi_*}{\Phi_*}\right). \tag{57}$$

The value of $\Phi_*$ is constant in time and in space.

According to (55) all equations concerning the consideration of the single droplet remain valid. Certainly, the r.h.s. of (23),(24) are the functions of time now, but this dependence is very weak. The perturbation of $\beta_{\mathrm{st}}$ and $\beta_{\mathrm{fin}}$ during the PIFD is negligible. The results of Section 3 can be accepted.

In the description of the kinetics of the nucleation one must put in the r.h.s. of (41) $I_s(\Phi)$ as

$$I_s(\Phi(t')) = I_s(\Phi_*) \exp\left(\frac{\Gamma}{\Phi_*}ct'\right). \tag{58}$$

The same improvements must be done in (45)-(51). The lower limit of the integration in (40),(44), (46)-(48), (50), (51) must be put to $-\infty$. Then Eq. (48) becomes analogous to the equation from [7] corresponding to the balance of the substance. The last equation can be solved by iterations. Eq. (51) corresponds to the first iteration. The relative error of the first iteration for the second model (corresponding to the third model) is small. Note that in order to consider the transformation to the collective character of vapor consumption this error must be calculated in the free-molecular regime of vapor consumption [7] where it is less than 0.15 (in the arbitrary regime it is less than 0.25).

The process of the heterogeneous condensation is analyzed in the same mathematical manner as in [9] with some improvements going from this consideration.

The effects of the extraction of the heat of the condensation can be taken into account by the simple renormalization[11].

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[10] This statement is justified on the base of the iteration procedure.

[11] In the pure free-molecular regime the renormalization is given in [7]. Here the process also allows the renormalization which is a little bit more complicated.

## 6. Discussion

The consideration of the density profiles in the kinetics of condensation leads to the more deep understanding of the evolution of the system during the first order phase transition. But the final formulas of the presented approach give us also the opportunity to compare the quantitative results of this approach with some already known ones. For example we shall choose the situation of the decay.

Earlier the process of the condensation with the arbitrary Knudsen numbers was described in [13,14] with the help of the mean field theory. Namely, the profile of the density is assumed to be homogeneous and the value of the density independent from the space point is given by the solution of the balance equation. The homogeneous profile of the density was introduced without any demonstration. Here we have seen that it is valid only in the case of the pure free-molecular regime of the vapor molecules exchange.

To clarify the difference between the final results of the two theories let us introduce the following new artificial model ("intermediate theory"). Imagine that instead of the real profile of the vapor density we have the profile corresponding to the density $n_\infty(\Phi + 1 - \Phi/\Gamma)$ in the ER and to $n_\infty(\Phi + 1)$ outside the ER. The boundary of the ER is chosen to ensure the same given lack of the molecules of the vapor caused by the vapor consumption by the droplets. This model is rather close to the model [13,14]. The difference is only due to the double overlapping of the ER and due to the nonlinear behavior of $\exp((\zeta - \Phi)\Gamma/\Phi)$ as the function of $\zeta$ for $\zeta$ going from $\Phi$ to $\Phi(1 - 1/\Gamma)$. As far as this non-linearity is not so essential this theory approximately coincides with [13,14], but allows the clear comparison with the new theory.

To construct the density profile in the intermediate theory one has to spread the lack of the density with the relatively small difference between $n_\infty(\Phi+1)$ and $n_\infty(\Phi+1-\Phi/\Gamma)$. Note that this difference is defined by the rate of the droplets growth and does not depend on the type of the theory for the separate droplet. The size of the ER strongly exceeds the size of the ER in our theory (see Fig. 2). Under the diffusion regime one can get for the ratio $(V_{\mathrm{eff}})_{\mathrm{intermediate}}/(V_{\mathrm{eff}})_{\mathrm{profile}}$, i.e. for the ratio of the volumes given by the "intermediate" and "new" theories:

$$\frac{(V_{\mathrm{eff}})_{\mathrm{intermediate}}}{(V_{\mathrm{eff}})_{\mathrm{profile}}} = \frac{\pi^{1/2}}{4} \frac{k}{\beta_{\mathrm{eff}}^3},$$

with the big parameter $\Gamma$ and the relatively small magnitude of the value $(v_l/v_v)^{1/2}$ inside parameter $k$.

So, the rate of the exhausting of the free volume in the intermediate theory strongly exceeds this rate in our theory. As a result, the total number of droplets in our theory strongly exceeds the number of droplets in the intermediate theory and in the mean-field theory.

When the regime of the vapor exchange is going to approach the pure free-molecular one, the discrepancy between these theories turns to be not so essential. The supersat-

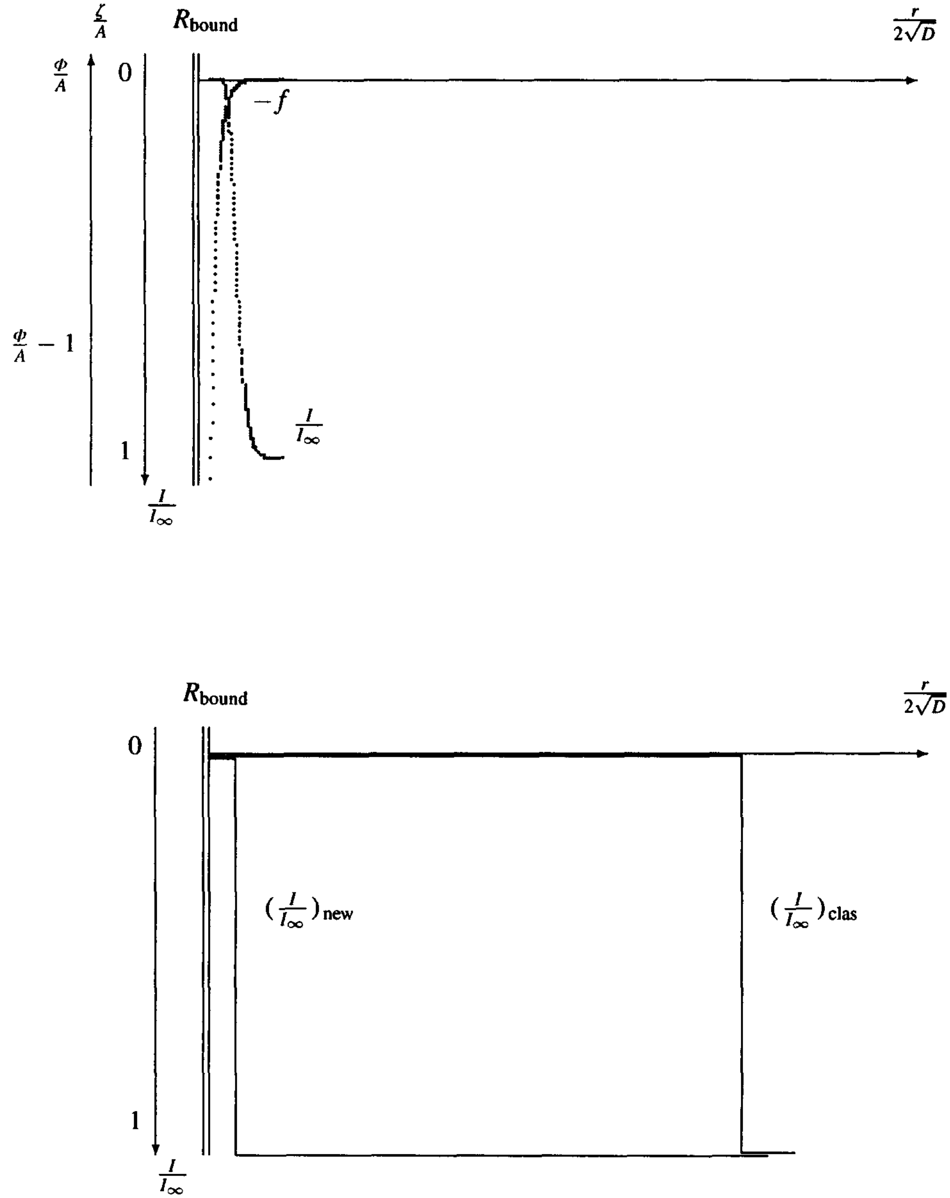

Fig. 2. The density profile and the sizes of the ER for the different models in the situation of some arbitrary regime of the vapor exchange with intermediate Knudsen numbers. In the upper axis the function similar to $f$ and the relative intensity $I/I_\infty$ are drawn. The value of $R_{\text{bound}}$ is defined as $\max\{r_k, R_{\text{free}}\}$. In the lower axis the model profiles for relative intensity in the "intermediate" ("clas") and our ("new") theories are shown. They have here absolutely different orders of the magnitudes. The absence of units on the $r/2\sqrt{D}$ axis shows the qualitative character of this picture.

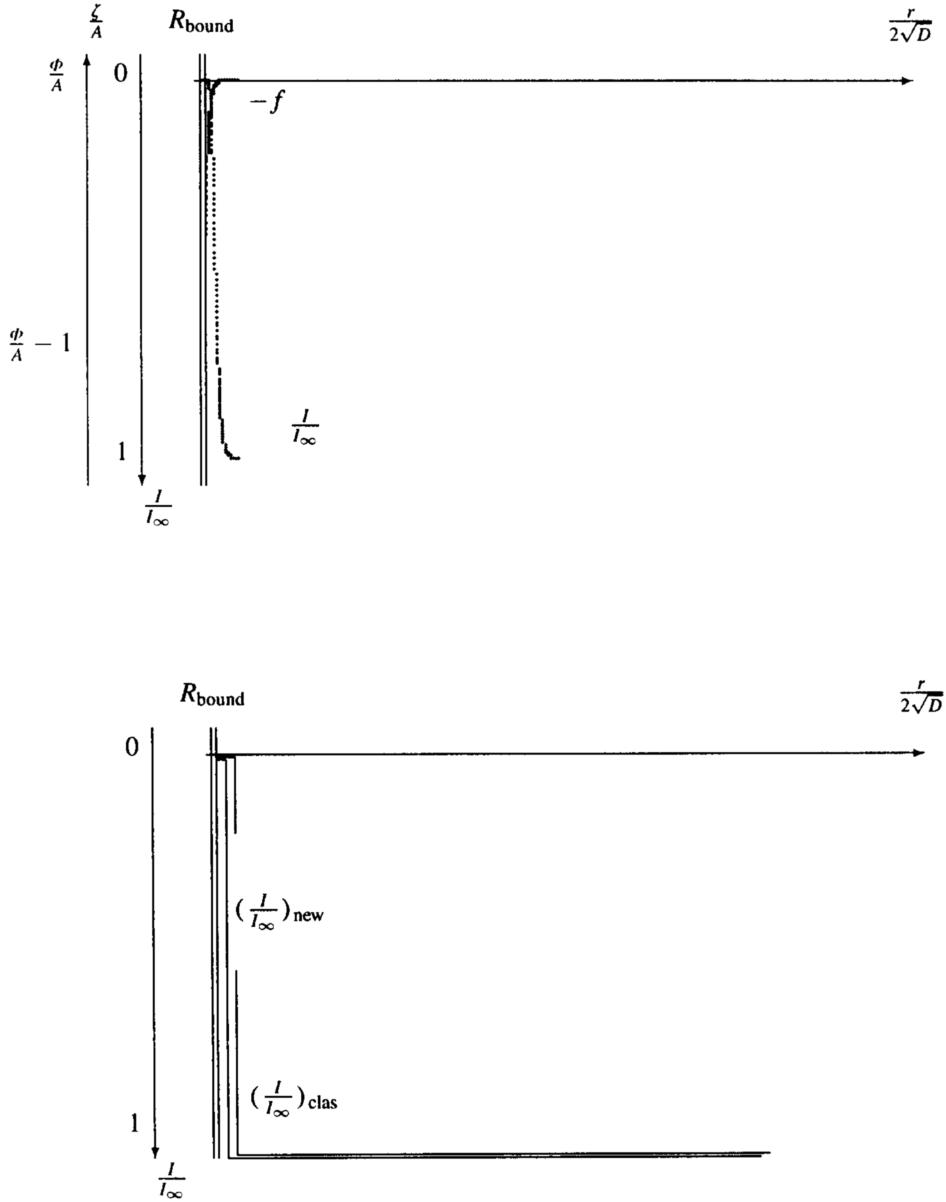

Fig. 3. The density profile and the sizes of the ER for different models in the situation of the free-molecular regime of the vapor exchange. In the upper axis the function similar to $f$ and the relative intensity $I/I_\infty$ are drawn. The value of $R_{\text{bound}}$ is defined as $\max\{r_k, R_{\text{free}}\} = R_{\text{free}}$. In the lower axis the model profiles for relative intensity in the "intermediate" ("clas") and our ("new") theories are shown. They have here one and the same order of the magnitudes. The absence of units on the $r/2\sqrt{D}$ axis shows the qualitative character of this picture. The curves are drawn so close to axis to compare them with Fig. 2.

uration falls at the distance $R_{\text{bound}}$ (see Fig. 3) only to some value relatively close to $\Phi$ and non-linearity in $\exp((\zeta - \Phi)\Gamma/\Phi)$ does not lead to the error in the order of magnitudes.

In the linear problem we can rearrange the profile in any possible manner so that the total lack of the substance be kept constant. The results of the new theory are going to approach the results of the old mean field theory. So, the inclusion of this theory into the theory for the free-molecular regime of the droplets growth [9] is observed.

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# Multicomponent nonisothermal nucleation

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**Abstract**

The theory for the multicomponent nonisothermal nucleation is constructed. It is shown that the Fokker–Plank description is not suitable and a new more advanced description is formulated. The differential kinetic equation for this process is derived and solved by the Chapman–Enskog procedure. The relaxation stage is described without any special limitations on the power of thermal effects. The further evolution is investigated with the help of a new way to cut off the tails of decompositions which appeared in the Chapman–Enskog procedure. As a result all main characteristics for the nucleation process are established analytically. The comparison with experimantal results and already presented theories is given. ⓒ 2000 Published by Elsevier Science B.V. All rights reserved.

The first-order phase transition usually occurs in the systems with many different components. During the process of nucleation, i.e., formation of droplets, the heat of condensation is extracted and changes the rate of nucleation. Theoretical description of this process should take into account these two features. Hence developement of the nonisothermal theory for the multicomponent nucleation is of great importance.

The adequate theoretical description of the nucleation stage was given for many different situations starting from the pure isothermal nucleation of one-component substance. Even in this case described by the so-called classical theory of nucleation no coincidence between theoretical predictions and experimental results occurs. Nevertheless, this disagreement cannot be the reason to reject all further modifications of the theory to grasp the effects of the heat extraction and to extend the theory for the multicomponent case.

The first theory where the thermal effects were taken into account rather adequately was presented by Kantrowitz [1]. In this publication embryos of given size were characterized by the unique average temperature. Only the so-called “weak thermal effects”

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were considered there. But an essential decrease of the nucleation rate occurs under the "strong thermal effects" considered by Kuni [2].

Certainly, there exists the distribution of the embryos of given size over the temperature. Feder et al. [3] took this phenomenon into account for the weak thermal effects. The energy distribution of embryos under the strong thermal effects was studied by Kuni and Grinin [4].

The standard way to construct kinetic equation is to use the Fokker–Planck approximation. Then kinetic equation can be solved using the approaches developed by Langer [5] and by Kuni et al. [6] respectively, for the stationary, nonstationary cases.

The methods described in Ref. [5] allow to study various problems. Namely the binary nucleation was studied by Lazaridis and Drossinos [7] under the Fokker–Planck approximation.

Concerning the mentioned publication [7] one has to note that due to a rather large quantity of the molecular heat extracted in the elementary act of a molecule condensation the restriction by the Fokker–Planck approximation is not sufficient. Then kinetic equation contains high derivatives and one has to use the Chapman–Enskog procedure to solve it.

Until now the most advanced approach for the nonisothermal nucleation is the application of the Chapman–Enskog procedure which was suggested by Kuni and Grinin for the case of one-component nucleation [4]. In Ref. [8] this approach was generalized to include the binary nucleation. Unfortunately, it was not done in a rigorous way. Therefore, the subject of current publication is a natural development of the theoretical methods described.

Particularly, this publication is aimed at presenting the nonisothermal theory of nucleation in the multicomponent mixture and to correct some of the errors which appeared in Ref. [8]. We shall present self-consistent theory which gives the analytical expression for the nucleation rate. To make our presentation more consistent we omit some standard details (for example, the solution of kinetic equation in the Fokker–Planck approximation).

In this publication we are going to use all standard definitions of the classical nucleation theory. The unit volume will be considered. All quantities with the energy dimension will be measured in the units of an elementary thermal energy $k_b T$ ($k_b$ is the Boltzmann constant and $T$ is the temperature), and all quantities with the heat capacity dimension — in the $k_b$ units.

## 1. Substance exchange

Here, we shall derive kinetic equation from the balance equation for the distribution $n$ over the embryo sizes. This balance equation can be written in the following form:

$$\frac{\partial n}{\partial t} = V + G ,$$

where $V$ is the operator associated with the substance exchange between the embryo and the environment (one also has to take into account here the energy exchange[1] due to the extraction of the condensation heat) and $G$ is the operator associated with the energy exchange with the help of the passive gas molecules due to the difference of the temperature $T$ of the embryo from the temperature $T_0$ of the environment (the effects of the heat extraction are already included into $V$).

The function $n$ is the number of embryos of given size in a unit volume. Later, we shall specify variables of the embryos state description.

At first, we shall study kinetic equation without thermal relaxation by a passive gas, i.e., in the form

$$\frac{\partial n}{\partial t} = V \tag{1}$$

and then we shall study thermal relaxation, i.e., operator $G$.

We shall suppose that there exists a vapor mixture with $i_0$ condensating components. All these components can be found both in the vapor and in the embryo (contrary to the passive gases which can be found only in the vapor phase). The distribution $n(\{v_i\}, t)$ of embryos is the function of $i_0$ variables of the number of molecules $v_i$ of the $i$th component (substance) inside the embryo and also the function of time $t$.

The process of the absorption of a molecule of the $j$th component occurs with intensity $W_j^+ \alpha_{j\text{cond}}$ where $W_j^+$ is the intensity of collision of the given embryo with an arbitrary molecule of the $j$th component and $\alpha_{j\text{cond}}$ is the condensation coefficient for the $j$th component. The most natural is to suppose that the length of the free motion in the gas media strongly exceeds the linear size of the embryo (the so-called free molecular regime of the substance exchange). Then the value $W_j^+$ can be easily found by the gas kinetic theory

$$W_j^+ \sim S n_j \, ,$$

where $S$ is the surface square of the embryo and $n_j$ is the molecular number density of the $j$th component.[2] Due to the small relative size of the near-critical region[3] we can see that $W_j^+$ remains practically constant in the near-critical region.[4]

Any reliable information about the condensation coefficient $\alpha_{j\text{cond}}$ is absent (in the literature one can find rather different estimates). But we believe that $\alpha_{j\text{cond}}$ is a rather

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[1] The condensated vapor also plays the role of a passive gas.

[2] One has also to note that in the near-critical region all embryos are in quasiequilibrium with the surrounding vapor. This quasiequilibrium also leads to small inhomogeneities in the vapor phase. These inhomogeneities would lead to the diffusion flows on the embryo. That is why one can approximately say that the vapor around the near-critical embryo is unperturbed and calculate the flow by the previous formula.

[3] One can use the standard classical nucleation theory for this estimate.

[4] Rigorously speaking, one has to take into account the functional dependence of $W_j^+$. Then one has to apply also to $W_j^+$ the Taylor decompositions analogous to those made later. All formulae will be more complicative but the detailed analysis shows the validity of the $W_j^+$ approximation by a constant.

smooth function of the embryo state and can be regarded in the near-critical region as some constant value.[5]

The process of absorption of the molecule leads to the variation of the number of the molecules inside the embryo

$$\{\nu_i\} \to \{\nu_{i\neq j}, \nu_j + 1\}$$

and also to the extraction of the condensation heat $\beta_j$ (measured in the natural thermal units) and this effect is going to increase the temperature of the embryo $T$ by the value

$$T \to T + \frac{\beta_j}{\sum_i c_i \nu_i} ,$$

where $c_i$ are molecular specific heats[6] in liquid phase (taken in units of $k_b$), the sum is taken over all components. The value $W_j^+$ depends only on the state of a vapor–gas mixture. Contrary to $W_j^+$ the intensity of the ejection of the molecule of the $j$th component $W_j^-$ strongly depends on the temperature of the embryo. The embryo has to be characterized by the temperature $T$ of the embryo[7] or some function of the temperature. Instead of $T$ one can introduce the value of additional energy $E$ according to

$$E = \left(\frac{T}{T_0} - 1\right) \sum c_i \nu_i ,$$

where $T_0$ is the temperature of the media. The evident advantage of $E$ is that the equilibrium value coincides with the zero point. Now, we shall normalize $E$ in order to have no coefficient in the square form of the equilibrium distribution[8] $n^e$ along additional energy near $E = 0$:

$$n^e \sim \exp(-\mu^2) .$$

To find $\mu$ we shall start with the Clapeyron–Clausius formula for the molecular number density $n_{\infty\, j}$ of the saturated vapor over a plane surface of liquid

$$n_{\infty\, j}(T) = n_{\infty\, j}(T_0) \exp\left(\beta_j \frac{T - T_0}{T_0}\right) .$$

As long as[9] the planar surface

$$W_j^-(n_{\infty\, j}) = W_j^+(n_{\infty\, j}) \sim n_{\infty\, j} ,$$

---

[5] This follows also from the model where $\alpha_{j\mathrm{cond}}$ appears as the probability to overcome the energy barrier near the surface of the liquid phase.

[6] They are close to those defined under the constant pressure.

[7] We suppose that the temperature relaxation inside occurs very rapidly. It can be justified by estimates analogous to Ref. [4].

[8] We shall omit the normalizing factor $\pi^{-1/2}$ of the equilibrium distribution. It can be easily reconstructed anywhere.

[9] Here we suppose that the surface tension does not depend on the embryos temperature. Details of this approximation can be found in [9].

one can come to[10]

$$\frac{W_j^-(T)}{W_j^-(T_0)} = \frac{n_{\infty\ j}(T)}{n_{\infty\ j}(T_0)} = \exp\left(\beta_j \frac{T-T_0}{T_0}\right) . \tag{2}$$

One the other hand,

$$W_j^-(E) n^e(E) = W_j^+ n^e(E-\beta_j)$$

and

$$W_j^-(E=0) n^e(E=0) = W_j^+ n^e(-\beta_j)$$

which leads to

$$W_j^-(E) = \frac{n^e(E-\beta_j)}{n^e(E)} W_j^-(E=0) \frac{n^e(E=0)}{n^e(-\beta_j)} = W_j^-(E=0) \exp\left(E\beta_j \frac{\partial^2 F}{\partial E^2}\right) , \tag{3}$$

where $F$ is the free energy of the embryos formation and it is taken into account that the equilibrium distribution $n^e \sim \exp(-F)$.

Eqs. (2) and (3) will coincide when

$$\frac{\partial^2 F}{\partial E^2} = \left(\sum_i c_i v_i\right)^{-1} .$$

Then[11]

$$\mu = \frac{E}{(2\sum_i c_i v_i)^{1/2}} .$$

One can write kinetic equation (1) in variables $\{v_i\}$, $\mu$ in the following form:

$$\frac{\partial n(\{v_i\},\mu,t)}{\partial t} = \sum_j W_j^+ n(\{v_{i\neq j}, v_j-1\}, \mu-\tau_j) - \sum_j W_j^- n(\{v_{i\neq j}, v_j\}, \mu) - \sum_j W_j^+ n(\{v_{i\neq j}, v_j\}, \mu) + \sum_j W_j^- n(\{v_{i\neq j}, v_j+1\}, \mu+\tau_j) ,$$

where

$$\tau_j = \frac{\beta_j}{(2\sum_i c_i v_i)^{1/2}} .$$

---

[10] More carefully, one has to go at first from the critical embryo to the planar surface, then use the mentioned relation for the planar surface and finally return to the critical embryo.

[11] More carefully, it can be done in terms of the finite differences.

One can present the following split of the last equation:

$$\frac{\partial n(\{v_i\},\mu,t)}{\partial t}=\sum_j\left[J_j(\{v_{i\neq j},v_j-1\},\mu-\tau_j)-J_j(\{v_{i\neq j},v_j\},\mu)\right],$$

where the flow $J_j$ is defined by

$$J_j(\{v_i\},\mu)=W_j^+n(\{v_{i\neq j},v_j\},\mu)-W_j^-n(\{v_{i\neq j},v_j+1\},\mu+\tau_j)\,.$$

Now we have to substitute the finite differences by derivatives.

One has to mention that the elementary steps 1 along $v_i$ are small in comparison with the characteristic scale corresponding to the essential variation of exponent of the free energy. This allows to substitute the finite difference along $v_i$ only by the first derivative.[12]

An elementary step $\tau_j$ along $\mu$ corresponds to essential violation of exponent of the free energy. So, one has to substitute the finite difference by the whole Tailor decomposition. As a result we have

$$\frac{\partial n(\{v_i\},\mu,t)}{\partial t}=\sum_j\sum_{l=1}^{\infty}\frac{(-\tau_j)^l}{l!}\frac{\partial^l}{\partial\mu^l}J_j(\{v_{i\neq j},v_j-1\},\mu)$$
$$-\sum_j\left(\frac{\partial}{\partial v_j}-\frac{1}{2}\frac{\partial^2}{\partial v_j^2}\right)J_j(\{v_{i\neq j},v_j\},\mu)\,.$$

We have to note that the possibility to substitute $J_j(\{v_{i\neq j},v_j-1\},\mu)-J_j(\{v_{i\neq j},v_j\},\mu)$ by $-(\partial/\partial v_j)J_j(\{v_{i\neq j},v_j\},\mu)$ can be made when we consider the situation near the quasistationary one. Then in one-dimensional projection on $v_j$ we shall get the small value for $J_j(\{v_{i\neq j},v_j-1\},\mu)-J_j(\{v_{i\neq j},v_j\},\mu)$ which allows to substitute it only by the first derivative.[13]

The flow $J_j$ can be expressed with the help of a function

$$f(\{v_i\},\mu)=\frac{n(\{v_i\},\mu)}{n^e(\{v_i\},\mu)}$$

as

$$J_j(\{v_{i\neq j},v_j\},\mu)=W_j^+n^e(\{v_i\},\mu)[f(\{v_{i\neq j},v_j\},\mu)-f(\{v_{i\neq j},v_j+1\},\mu+\tau_j)]\,.$$

The analogous substitution of the finite differences by the whole Taylor decomposition gives

$$J_j(\{v_{i\neq j},v_j\},\mu)=W_j^+n^e(\{v_i\},\mu)\left[\left(-\frac{\partial}{\partial v_j}-\frac{1}{2}\frac{\partial^2}{\partial v_j^2}\right)f(\{v_{i\neq j},v_j+1\},\mu)\right.$$
$$\left.-\sum_{m=1}^{\infty}\frac{\tau_j^m}{m!}\frac{\partial^m}{\partial\mu^m}f(\{v_{i\neq j},v_j+1\}\,,\mu)\right]\,.$$

---

[12] This produces certain restrictions and this effect will limit later the Chapman–Enskog expansion.

[13] We decompose until the second derivative to ensure at least the same power as in the one-dimensional case.

To be close to the standard form of one-component nonisothermal theory [4] we shall use instead of function $f$ the following function:

$$P(\{v_{i\neq j}, v_j\}, \mu) = \frac{n(\{v_{i\neq j}, v_j\}, \mu)}{\exp(-\mu^2)} .$$

The free energy $F$ of the embryos formation can be split as

$$F(\{v\}, \mu) = F(\{v\}, \mu = 0) + \mu^2$$

which gives

$$f(\{v\}, \mu) = P(\{v\}, \mu)\exp(F(\{v\}, \mu = 0)) .$$

One can present an expression for $J_j$ in terms of function $P$ as

$$\begin{aligned} J_j(\{v_{i\neq j}, v_j\}, \mu) = W_j^+ n^e(\{v_i\}, \mu) \Bigg[ & \left( -\frac{\partial}{\partial v_j} - \frac{1}{2}\frac{\partial^2}{\partial v_j^2} \right) \exp(F(\{v\}, \mu = 0)) \\ & \times P(\{v_{i\neq j}, v_j\}, \mu) - \exp(F(\{v_{i\, i\neq j}, v_j + 1\}, \mu = 0)) \\ & \times \sum_{m=1}^{\infty} \frac{\tau_j^m}{m!} \frac{\partial^m}{\partial \mu^m} P(\{v_{i\neq j}, v_j + 1\}, \mu) \Bigg] \end{aligned}$$

or

$$\begin{aligned} J_j(\{v_{i\neq j}, v_j\}, \mu) = W_j^+ n^e(\{v_i\}, \mu) \Bigg[ & \left( -\frac{\partial}{\partial v_j} - \frac{1}{2}\frac{\partial^2}{\partial v_j^2} \right) \exp(F(\{v\}, \mu = 0)) \\ & \times P(\{v_{i\neq j}, v_j\}, \mu) - \left( 1 + \frac{\partial F}{\partial v_j} + \frac{1}{2}\frac{\partial^2 F}{\partial v_j^2} + \frac{1}{2}\left(\frac{\partial F}{\partial v_j}\right)^2 \right) \\ & \times \exp(F(\{v_{i\, i\neq j}, v_j\}, \mu = 0)) \sum_{m=1}^{\infty} \frac{\tau_j^m}{m!} \frac{\partial^m}{\partial \mu^m} P(\{v_{i\neq j}, v_j + 1\}, \mu) \Bigg] . \end{aligned}$$

Having introduced an operator[14]

$$L_j = L_j^0 + \Delta L_j ,$$

where

$$L_j^0 = -W_j^+ \left[ \frac{\partial F}{\partial v_j} + \frac{\partial}{\partial v_j} \right] ,$$

$$\Delta L_j = -W_j^+ \left[ \frac{1}{2} \left( \frac{\partial F}{\partial v_j} + \frac{\partial}{\partial v_j} \right)^2 \right] ,$$

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[14] We fulfil decompositions until the order appeared in the isothermal theory.

one can present the last expression for $J_j$ as[15]

$$J_j(\{v_{i\neq j}, v_j\}, \mu) = \exp(-\mu^2) L_j P(\{v_{i\neq j}, v_j\}, \mu)$$
$$- \left(1 + \frac{\partial F}{\partial v_j} + \frac{1}{2}\frac{\partial^2 F}{\partial v_j^2} + \frac{1}{2}\left(\frac{\partial F}{\partial v_j}\right)^2\right) \exp(-\mu^2) W_j^+$$
$$\times \sum_{m=1}^{\infty} \frac{\tau_j^m}{m!}\frac{\partial^m}{\partial \mu^m} P(\{v_{i\neq j}, v_j + 1\}, \mu).$$

According to the smooth dependence along $v_j$ one can go from the argument $v_j \pm 1$ of function[16] $P$ to the argument $v_j$ with the help of the first terms in the Tailor decomposition.

Then as long as

$$\left.\left(1 + \frac{\partial F}{\partial v_j} + \frac{1}{2}\frac{\partial^2 F}{\partial v_j^2} + \frac{1}{2}\left(\frac{\partial F}{\partial v_j}\right)^2\right)\right|_{v\to v+1} = \left(1 + \frac{\partial F}{\partial v_j} - \frac{1}{2}\frac{\partial^2 F}{\partial v_j^2} + \frac{1}{2}\left(\frac{\partial F}{\partial v_j}\right)^2\right),$$

the kinetic equation can be presented as

$$\exp(-\mu^2)\frac{\partial P(\{v_i\}, \mu), t}{\partial t}$$
$$= \sum_j \sum_{l=1}^{\infty} \frac{(-\tau_j)^l}{l!}\frac{\partial^l}{\partial \mu^l}\left[\exp(-\mu^2) L_j|_{v_j-1}\left(1 - \frac{\partial}{\partial v_j} - \frac{1}{2}\frac{\partial^2}{\partial v_j^2}\right) P(\{v_i\}, \mu)\right.$$
$$\left. - \left(1 + \frac{\partial F}{\partial v_j} - \frac{1}{2}\frac{\partial^2 F}{\partial v_j^2} + \frac{1}{2}\left(\frac{\partial F}{\partial v_j}\right)^2\right) \exp(-\mu^2) W_j^+ \sum_{m=1}^{\infty} \frac{\tau_j^m}{m!}\frac{\partial^m}{\partial \mu^m} P(\{v_i\}, \mu)\right]$$
$$- \sum_j \left(\frac{\partial}{\partial v_j} - \frac{1}{2}\frac{\partial^2}{\partial v_j^2}\right)\left[\exp(-\mu^2) L_j|_{v_j} P(\{v_i\}, \mu)\right.$$
$$- \left(1 + \frac{\partial F}{\partial v_j} + \frac{1}{2}\frac{\partial^2 F}{\partial v_j^2}\right)\left(1 + \frac{\partial}{\partial v_j} + \frac{1}{2}\frac{\partial^2}{\partial v_j^2}\right) \exp(-\mu^2) W_j^+$$
$$\left. \times \sum_{m=1}^{\infty} \frac{\tau_j^m}{m!}\frac{\partial^m}{\partial \mu^m} P(\{v_i\}, \mu)\right].$$

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[15] We shall forget about $\Delta L_j$ and use instead of $L_j$ operator $L_j^0$. We shall also neglect the difference between $L_j|_{v_j-1}$ and $L_j|_{v_j}$. The reason is that we shall get the nucleation rate in the main order. From the comparison with the isothermal case as the limit one it is clear that it will contain operator $L_j$ only one time and take it in the main order. But still we have to calculate several first approximations and have to control the appearance of $L_j$. If operator $L_j$ appears more than one time then one has to take into account the mentioned differences. But fortunately $L_j$ will appear only once.

[16] Later, it will be seen that $\partial/\partial v_j$ produces some small parameter as far as the action of $\partial F/\partial v_j$. We write this equation in the first two orders of this parameter. This corresponds to the order essential in the isothermal version of the theory.

We shall neglect $-\frac{1}{2}\partial^2/\partial v_j^2$ in comparison with $\partial/\partial v_j$ in the last part of the kinetic equation. When $-\frac{1}{2}\partial^2/\partial v_j^2$ is applied after $L_j$ then the order of the small parameter will be too high. When $-\frac{1}{2}\partial^2/\partial v_j^2$ is applied to the second part of $J_j$ then it will act on the same level with $\partial F/\partial v_j$. We shall control the appearance of $\partial F/\partial v_j$ in the final result. If it appears in the final result then we cannot neglect the action of $-\frac{1}{2}\partial^2/\partial v_j^2$. Fortunately, $\partial F/\partial v_j$ is absent in the final formulae.

The action of $\partial/\partial\mu$ on $\exp(-\mu^2)\psi$ where $\psi$ is the arbitrary function is obviously given by

$$\frac{\partial^l}{\partial\mu^l}\exp(-\mu^2)\psi = \exp(-\mu^2)\left(\frac{\partial}{\partial\mu} - 2\mu\right)^l \psi \, .$$

Certainly one cannot take $2\mu$ away from $\partial/\partial\mu$ and has to consider $(\partial/\partial\mu - 2\mu)^l$ as sequential action of operators in brackets. This turns kinetic equation to

$$\begin{aligned}\frac{\partial P(\{v_i\},\mu)}{\partial t} = &\sum_j \sum_{l=1}^{\infty} \frac{(-\tau_j)^l}{l!}\left(\frac{\partial}{\partial\mu} - 2\mu\right)^l \\ &\times\left[L_j\left(1 - \frac{\partial}{\partial v_j}\right)P(\{v_i\},\mu) - W_j^+\left(1 + \frac{\partial F}{\partial v_j} - \frac{1}{2}\frac{\partial^2 F}{\partial v_j^2} + \frac{1}{2}\left(\frac{\partial F}{\partial v_j}\right)^2\right)\right. \\ &\left.\times\sum_{m=1}^{\infty}\frac{\tau_j^m}{m!}\frac{\partial^m}{\partial\mu^m}P(\{v_i\},\mu)\right] - \sum_j \frac{\partial}{\partial v_j}\left[L_j P(\{v_i\},\mu)\right. \\ &\left. - W_j^+\left(1 + \frac{\partial F}{\partial v_j} + \frac{\partial}{\partial v_j}\right)\sum_{m=1}^{\infty}\frac{\tau_j^m}{m!}\frac{\partial^m}{\partial\mu^m}P(\{v_i\},\mu)\right] \, .\end{aligned}$$

We decompose the finite differences along $v_j$ until the second derivatives (or the second order of the small parameter) because in the classical theory of isothermal one-component nucleation two derivatives have to be taken into account (an account of the first derivative could not lead to the suitable rate of nucleation).

One can easily note that operators

$$S_{1j} = 1 - \frac{\partial}{\partial v_j} \, ,$$

$$S_{2j} = 1 + \frac{\partial F}{\partial v_j} - \frac{1}{2}\frac{\partial^2 F}{\partial v_j^2} + \frac{1}{2}\left(\frac{\partial F}{\partial v_j}\right)^2 \, ,$$

$$S_{3j} = 1 + \frac{\partial F}{\partial v_j} + \frac{\partial}{\partial v_j}$$

are absent[17] in Ref. [8]. Really, in the first two steps of the Chapman–Enskog procedure described later these terms will not be essential. But it occurs only in frames

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[17] Also, the difference between $L_j$ and $L_j^0$ and the substitution of $\partial/\partial v_j - \frac{1}{2}\partial^2/\partial v_j^2$ instead of $\partial/\partial v_j$ into the last term of kinetic equation have to be taken into account.

of the Chapman–Enskog procedure and cannot be seen directly from kinetic equation. We shall call $S_{1j}, S_{2j}, S_{3j}$ as the shift operators.

Now, we shall turn to the thermal relaxation by the passive gas in order to include it in the presented equation.

## 2. Thermal relaxation

The physical reason to consider the interaction of the embryo with the passive gas is rather simple. Really, due to heat extraction the temperature of the embryo is higher than the temperature of the environment and the embryo heats the molecules of the passive gas. Certainly, the temperature of the embryo falls and this effect reduces the ejection rate. This has to be taken into account and the consideration of the interaction with the passive gas is important.

An obvious restriction only by the regular term in the presence of the big quantities of the passive gas will lead to the thin spectrum in the energy scale of the $\delta$-function form. Certainly, this does not coincide with the equilibrium distribution. Thus, one has to use at least the Fokker–Planck approximation. The physical reason is rather obvious — molecules of a passive gas have different velocities and equilibrium distribution in energies. This has to be taken into account and leads at least to the Fokker–Planck approximation. As far as the variation of the energy in the elementary act of interaction with a passive gas molecule is small in comparison with the characteristic width of the equilibrium distribution one can restrict this description by the Fokker–Planck approximation.

In Fokker–Planck approximation the kinetic equation can be written as

$$\frac{\partial n}{\partial t} = B\frac{\partial}{\partial \mu} n^e \frac{\partial}{\partial \mu} f \, ,$$

where $B$ is kinetic coefficient.[18] It can be determined by consideration of the limit situation where the last equation transforms into an equation only with the regular term

$$\frac{\partial n}{\partial t} = B\frac{\partial}{\partial \mu}\left[2\mu + \frac{\partial}{\partial \mu}\right] n \to B\frac{\partial}{\partial \mu} 2\mu n \, .$$

This form has to be reproduced by the standard analysis. We begin with the balance equation

$$\frac{\partial n}{\partial t} = W^{+} n(\mu + \delta\mu) - W^{+} n(\mu) \to W^{+}\delta\mu \frac{\partial n}{\partial \mu} \, ,$$

where $W^{+}$ is the rate of collisions of the given embryo with the molecules of the passive gas, the regular variation $\delta\mu$ is given by

$$\delta\mu = \frac{c_g}{\sum c_j v_j}\mu$$

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[18] It is supposed to be a smooth function of $\mu$.

and $c_g$ is the molecule heat capacity of the passive gas. This leads to

$$B = W^{+} \frac{c_g}{2\sum c_j v_j} .$$

Now the kinetic equation can be written in the following form:

$$\frac{\partial n}{\partial t} = W^{+} \frac{c_g}{2\sum c_j v_j} \frac{\partial}{\partial \mu} n^e \frac{\partial}{\partial \mu} f .$$

One has to put the coefficient of thermal accommodation $\alpha_{\mathrm{acc}}$ into $W^{+}$ in order to take into account the fact that thermal accommodation occurs with some probability.

The generalization of the previous equation on the mixture of passive gases leads to

$$\frac{\partial n}{\partial t} = \sum_{i'} W_{i'}^{+} \alpha_{\mathrm{acc}\ i'} \frac{c_{g\ i'}}{2\sum c_j v_j} \frac{\partial}{\partial \mu} n^e \frac{\partial}{\partial \mu} f ,$$

where indexes with prime denote different passive gases.

One has to take into account the fact that the condensating substances also take part in the cooling. With the probability $(1 - \alpha_c)\alpha_{\mathrm{acc}}$ the act of cooling takes place. The molecules accumulated by embryos also have to be taken into account. As a result one can get[19]

$$\begin{aligned}\frac{\partial n}{\partial t} &= \sum_{i'} W_{i'}^{+} \alpha_{\mathrm{acc}\ i'} \frac{c_{g\ i'}}{2\sum c_j v_j} \frac{\partial}{\partial \mu} n^e \frac{\partial}{\partial \mu} f \\ &+ \sum_{i} W_{i}^{+} (1 - \alpha_{c\ i}) \alpha_{\mathrm{acc}\ i} \frac{c_i}{2\sum c_j v_j} \frac{\partial}{\partial \mu} n^e \frac{\partial}{\partial \mu} f \\ &+ \sum_{i} W_{i}^{+} \alpha_{c\ i} \frac{c_i}{2\sum c_j v_j} \frac{\partial}{\partial \mu} n^e \frac{\partial}{\partial \mu} f .\end{aligned}$$

It is quite obvious that now to get the general kinetic equation we have to add the part associated with the condensating substance. So, it is necessary to formulate the part under consideration in terms of function $P$. Here one has to fulfill the same actions and get

$$\begin{aligned}\frac{\partial P}{\partial t} &= \sum_{i'} W_{i'}^{+} \alpha_{\mathrm{acc}\ i'} \frac{c_{g\ i'}}{2\sum c_j v_j} \left( \frac{\partial}{\partial \mu} - 2\mu \right) \frac{\partial}{\partial \mu} P \\ &+ \sum_{i} W_{i}^{+} (1 - \alpha_{c\ i}) \alpha_{\mathrm{acc}\ i} \frac{c_i}{2\sum c_j v_j} \left( \frac{\partial}{\partial \mu} - 2\mu \right) \frac{\partial}{\partial \mu} P \\ &+ \sum_{i} W_{i}^{+} \alpha_{c\ i} \frac{c_i}{2\sum c_j v_j} \left( \frac{\partial}{\partial \mu} - 2\mu \right) \frac{\partial}{\partial \mu} P .\end{aligned}$$

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[19] The difference between the heat capacity in the vapor and liquid phases can be effectively included into $\alpha_{\mathrm{acc}\ i}$.

As a result, for the general kinetic equation one can get

$$\frac{\partial P(\{\nu_i\},\mu)}{\partial t} = \sum_j \sum_{l=1}^{\infty} \frac{(-\tau_j)^l}{l!} \left(\frac{\partial}{\partial\mu} - 2\mu\right)^l \times \left[ L_j S_{1j} P(\{\nu_i\},\mu) - S_{2j} W_j^+ \sum_{m=1}^{\infty} \frac{\tau_j^m}{m!} \frac{\partial^m}{\partial\mu^m} P(\{\nu_i\},\mu) \right]$$
$$- \sum_j \frac{\partial}{\partial\nu_j} \left[ L_j P(\{\nu_i\},\mu) - S_{3j} W_j^+ \sum_{m=1}^{\infty} \frac{\tau_j^m}{m!} \frac{\partial^m}{\partial\mu^m} P(\{\nu_i\},\mu) \right]$$
$$+ \sum_{j'} W_{j'}^+ \alpha_{\mathrm{acc}\ j'} \frac{c_{g\ j'}}{2\sum_j c_j \nu_j} \left(\frac{\partial}{\partial\mu} - 2\mu\right) \frac{\partial}{\partial\mu} P(\{\nu_i\},\mu)$$
$$+ \sum_{i'} W_{i'}^+ (1 - \alpha_{c\ i'}) \alpha_{\mathrm{acc}\ i'} \frac{c_{i'}}{2\sum_j c_j \nu_j} \left(\frac{\partial}{\partial\mu} - 2\mu\right) \frac{\partial}{\partial\mu} P(\{\nu_i\},\mu)$$
$$+ \sum_{i'} W_{i'}^+ \alpha_{c\ i'} \frac{c_{i'}}{2\sum_j c_j \nu_j} \left(\frac{\partial}{\partial\mu} - 2\mu\right) \frac{\partial}{\partial\mu} P(\{\nu_i\},\mu)\,. \qquad (4)$$

Here indexes $i'$ and $j$ mark the different components of the condensating substances and index $j'$ marks the different components of the passive substances.

One can easily note that the number of components of the condensating mixture does not act on the properties of passive gases. This is in contradiction with results presented in Ref. [8] where the action of the passive gas is referred to the action of every component of condensating substance and then the direct summation over the condensation components is carried out. So, according to Ref. [8] one can speak about the separate cooling of different components (in kinetic sense, the droplet is being cooled as a whole object). Here we speak about the common cooling of different components (in kinetic sense). The physical essence is another here. We believe in our version of the thermal effects account.

## 3. Estimates of operators

Now we shall give the method to solve the last equation. The general scheme is well known. At first, the extraction of the main operator with the well-known eigenfunctions has to be presented. This main operator has to ensure the relaxation to the stationary state and this effect allows to consider the relaxation period. Such a structure allows to apply the Chapman–Enskog procedure.

An attempt to investigate the situation of the binary nonisothermal nucleation was made in Ref. [8] but the initial kinetic equation was wrong. Contrary to Ref. [8] we shall use the correct kinetic equation. Here this equation is already generalized for the multicomponent case.

Besides the new object of investigation the approach presented here has also some new principal features.

One has to recall the specific feature of the relaxation stage description given in the mentioned papers. When the main operator has only the formal priority then a standard consideration of the relaxation stage requires a small value of some specific parameter. This leads to the serious restriction of the approach used earlier. In the situations of intensive droplets formation this parameter is not too small and the relaxation does not take place. Then the initial condition for the Chapman–Enskog procedure is violated. This does not formally allow one to apply this procedure.

We shall use another split on the r.h.s. of kinetic equation into the main operator and the additional one. As a result, we come to procedure with two sets of the main and additional operators. But still in such situation it will be possible to generalize the Chapman–Enskog procedure and come to the final formulae. It will be possible to get the relaxation to the stationary state without the restriction used in Ref. [8]. One has to mention that the cited papers could not overcome the main nontrivial feature of the nonisothermal condensation – the main operator extracted in these papers has only formal priority based on the presence of factorials in denominators in the Taylor decomposition terms. So, one has to fulfill at least many steps in the Chapman–Enskog procedure. Here, we shall present a method to take into account the tails of these series and to come to the compact final results.

Now, it is worth mentioning the inclusion of the present analysis into the general scheme.

One can note some specific features of the thermal effects in comparison with the general situation of the non-Fokker–Planck evolution considered in Ref. [10]. Namely, these features allow us to go further in comparison with Ref. [10] and to get the compact final formulae.

These features are as follows:

- The temperature of the embryo can have an arbitrary value.
- Non-Fokker–Planck evolution occurs only along the temperature of the embryo.
- Non-Fokker–Planck evolution occurs under a constant value of $\beta_j$.

The third feature is rather important. Really, as long as we have the Clapeyron–Clausius relation we can reconstruct $W^-(T)$. Then on the base of $W^+$ (it is given by the simple gas kinetics formula) and $W^-$ one can get the equilibrium distribution. The knowledge of the equilibrium distribution gives on the base of the Boltzmann formula the form of the free energy $F$ of the embryo formation (the constant shift which appeared from the normalizing factor of the equilibrium distribution is not important). These constructions result in a rather simple form of the free energy. In the arbitrary situation (see Ref. [10]) the form of the free energy can be complicated and this causes the additional difficulties.

The mentioned simple form of the free energy corresponds to the simplicity of transition from the function $n$ to the function $P$ defined by

$$n = \exp(-\mu^2)P .$$

Certainly $\exp(-\mu^2)$ represents here the equilibrium distribution and $\mu^2$ appears due to the square character of the free energy. This leads to the $P$ relaxation to a constant. To conserve such relaxation in the general more complicated situation one has to choose in the argument of exponent instead of $\mu^2$ another more complicated function which reflects the more complicated behavior of the free energy. As a result, the eigenfunctions of the "main" operator will be unknown.

In the general situation instead of $\mu$ in the combinations $-2\mu + \partial/\partial\mu$ in the kinetic equation appear high powers of $\mu$. This blocks the presented approach to get solution.

We are going to act in frames of the macroscopic description of the free embryo. This leads to the big parameters

$$v_{ic} \gg 1$$

for all components which are marked by the index $i$. The index $c$ corresponds to the critical embryo.

The last inequality allows as it is shown in Ref. [10] to state that

- The Fokker–Planck approximation is valid to describe the evolution along $v_i$.
- The square approximation for the free energy along $v_i$ in the near-critical region is valid.

In Ref. [10] all specific situations appear only when the derivative of the free energy along the concentration of the solution inside the embryo provides another large parameter. Certainly, the large values of this derivative are rather ordinary in nature but one cannot consider them as the large parameter going to infinity.

Really, the derivative along $v_i$ has a large value in comparison with the derivative along the steepens descent line [10]. This appears as the base for the hierarchy in the near-critical region [10]. But the value of this large parameter is not sufficient to compensate the influence of the large parameter $v_i$ (as long as all $v_i$ have one and the same power we shall drop the index $i$ in the estimates). Namely, the half-width $\Delta v$ along $v$ has the order $v_c^{1/2}$, the half-width along the steepest descent line has the order $v_c^{2/3}$. But as long as $\Delta v$ is greater than 1 (it is not so great as in the one-component theory but it is still great) we can see that the differential form of the kinetic equation is valid.

The last result can be directly seen from the explicit expression for the free energy of the embryos formation as the function of $\{v_i\}$. In the capillary approximation this expression can be written as

$$F \sim -\sum_j b_j v_j + a\left(\sum_j \upsilon_j v_j\right)^{2/3} .$$

Here $\upsilon_j$ are the molecule volumes in the liquid phase, $b_j$ are the excesses of the chemical potentials, $a$ is the renormalized surface tension. The surface of tension is put so as to contain precisely the volume of the embryo. All $\upsilon_j$ are supposed to have one and the same order, all $v_c$ are also supposed to have one and the same order.

One can easily note that the half-width $\Delta v \sim v^{1/2}$ in the multicomponent theory differs from the same value in the one-component theory $\Delta v \sim v^{2/3}$. The reason is the interaction between components. This phenomenon is not in contradiction with the general theory because the steepest descent line does not coincide with any $v_i$ and the half-width along the steepest descent line coincides with the half-width along $v$ in the one-component theory. But it shows that the direct differentiation of $F$ along $v_i$ without the influence of the other components being taken into account cannot lead to a really small parameter. An account of the mentioned interaction is rather difficult and it is more convenient to go to variables

$$\xi_i \sim v_i / \sum_j v_j$$

and

$$\kappa \sim a^{3/2} \sum_j v_j v_j \, .$$

Then the direction along $\kappa$ coincides with the steepest descent line and due to the Gibbs–Duhem equation an account of the interaction is attained automatically.

In the set $\{\xi_i\}, \kappa$ the form of the free energy is given by

$$F \sim B\kappa - \kappa^{2/3} \, ,$$

where $B$ is some function of $\{\xi_i\}$. The characteristic scale of $\kappa$ can be put so as to coincide with the scale of $v_i$.

To justify the validity of the square approximation one has to get the second and the third derivatives of the free energy. It is more convenient to use the last form of $F$. Then

$$\frac{\partial^2 F}{\partial \xi_i \partial \xi_j} \sim \frac{\mathrm{d}^2 B}{\mathrm{d}\xi_i \, \mathrm{d}\xi_j} \kappa$$

and the half-width along $\xi_i$ is given by[20]

$$\Delta \xi_i \sim \kappa^{-1/2} (B''(\{\xi_j\}))^{-1/2} \, .$$

As long as

$$\frac{\partial^3 F}{\partial \xi_i \partial \xi_j \partial \xi_k} \sim \frac{\mathrm{d}^3 B}{\mathrm{d}\xi_i \, \mathrm{d}\xi_j \, \mathrm{d}\xi_k} \kappa \, ,$$

the benefit $T_3$ of the third term in the Taylor decomposition is given by

$$T_3 \sim \frac{\partial^3 F}{\partial \xi_i^3} (\Delta \xi_i)^3 \sim \frac{B'''(\{\xi_j\})}{(B''(\{\xi_j\}))^{3/2}} \kappa^{-1/2} \, .$$

As long as the function $B$ and its derivatives do not contain any large parameter one can easily see that the action of the third term is small. That is why the square approximation for the behavior of $F$ along $\xi_i$ is valid. The behavior of $F$ along $\kappa$ is similar to the one-component case. The square approximation along $\kappa$ is, thus, valid. As a result, the square approximation for $F$ in the near-critical region can be used.

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[20] Prime marks a derivative over $\xi_j$.

These results explain why the Fokker–Planck approximation is adopted for the description of the evolution along $v_i$. For the evolution along temperature the Fokker–Planck approximation is not sufficient. The reason is the existence of another large parameter. This parameter is $\beta_i$.

Let us explain why[21] $\beta$ can be regarded as the large parameter of the theory. When the temperature decreases from the value of the second-order phase transition the value of $v_v$ of the molecule volume in the vapor phase grows and the value $v_l$ falls. So, far from the point of the second-order phase transition[22] one can come to

$$v_v \gg v_l \, .$$

The heat extracted in the phase transition can be presented as the difference of entropies in two phases multiplied by temperature. Then one can use the standard representation of the entropy as the logarithm of the states number. The number of states[23] can be very approximately estimated as the volume occupied by the system.[24] Then the last strong inequality leads to a large value of $\beta$.

In reality, one cannot go very far from the second-order phase transition temperature because the new phase transition (crystallization) occurs. Nevertheless, one has to say that $\beta$ is the large parameter of the theory.

Now we come to the direct solution of the kinetic equation. We can rearrange it in the following form:

$$\frac{\partial P(\{v_i\},\mu)}{\partial t} = [D_1 + D_2 + D_3 + D_4]P(\{v_i\},\mu)\, , \tag{5}$$

$$D_4 = -\sum_j \frac{\partial}{\partial v_j} L_j \, ,$$

$$D_2 = -\sum_j \sum_{l=1}^{\infty} \frac{(-\tau_j)^l}{l!} \left( \frac{\partial}{\partial \mu} - 2\mu \right)^l W_j^+ S_{2j} \sum_{m=1\ (m\neq l)}^{\infty} \frac{\tau_j^m}{m!} \frac{\partial^m}{\partial \mu^m} \, ,$$

$$D_3 = \sum_j \sum_{l=1}^{\infty} \frac{(-\tau_j)^l}{l!} \left( \frac{\partial}{\partial \mu} - 2\mu \right)^l L_j S_{1j} + \sum_j \frac{\partial}{\partial v_j} S_{3j} W_j^+ \sum_{m=1}^{\infty} \frac{\tau_j^m}{m!} \frac{\partial^m}{\partial \mu^m} \, ,$$

$$D_1 = \sum_{j'} W_{j'}^+ \alpha_{\mathrm{acc}\ j'} \frac{c_{g\ j'}}{2\sum_j c_j v_j} \left( \frac{\partial}{\partial \mu} - 2\mu \right) \frac{\partial}{\partial \mu}$$

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[21] The lower index will be omitted.

[22] Namely, only in this situation some actual assumptions of the classical theory of nucleation are valid, for example the uncompressibility of liquid phase.

[23] One can use quasiclassical approach.

[24] We can use very approximately the model of ideal gas.

$$+\sum_{i'} W_{i'}^{+}(1-\alpha_{c\ i'})\alpha_{\mathrm{acc}\ i'}\frac{c_{i'}}{2\sum_j c_j v_j}\left(\frac{\partial}{\partial\mu}-2\mu\right)\frac{\partial}{\partial\mu}$$
$$+\sum_{i'} W_{i'}^{+}\alpha_{c\ i'}\frac{c_{i'}}{2\sum_j c_j v_j}\left(\frac{\partial}{\partial\mu}-2\mu\right)\frac{\partial}{\partial\mu}$$
$$-\sum_j\sum_{l=1}^{\infty}\frac{(-\tau_j)^l}{l!}\left(\frac{\partial}{\partial\mu}-2\mu\right)^l W_j^{+}S_{2j}\frac{\tau_j^l}{l!}\frac{\partial^l}{\partial\mu^l}\,. \tag{6}$$

Now we shall estimate the actions of operators $D_1$, $D_2$, $D_3$, $D_4$. One can easily take into account the fact that the differentiation along $v_i$ can be estimated as

$$\frac{\partial}{\partial v_i}P \sim \frac{P}{\Delta v_i}$$

and this estimate produces the small parameter $1/\Delta v_i$. One has to take also into account that as already noted the value $\Delta v_i$ differs from the analogous value in the one-component case and this effect can lead to the error made in Ref. [8]. The values $\Delta v_i$ do not estimate the size of the near-critical region. (The standard definition of the near-critical region is given by the inequality $|F-F_c|\leqslant 1$. The infinite tails can be cut off to reduce the form of the near-critical region to a rectangular one.) To estimate the size of the near-critical region one can take derivatives of the free energy along $\kappa$, $\xi_i$. As a result, we come to the following convention: we use the notation $1/\Delta v_i$ but keep in mind that the real small parameter will be $1/\Delta\kappa$. Moreover, one cannot estimate the size of the near-critical region by $\Delta v_i$ as was done in Ref. [8] but must use the half-widths along $\kappa$ and $\xi_i$.

The value of the derivative $\partial F/\partial v_i$ also contains the small parameter $1/\Delta v_i$. So, the action of $L_i$ can be estimated as

$$L_i P \sim \frac{P}{\Delta v_i}\,.$$

The differentiation along $\mu$ does not produce any small parameter. The characteristic value of $\mu$ is 1.

Now we can calculate the powers of operators $D_1$–$D_4$. As a result, we see that

- Operator $D_4$ is the smallest one. It has the order $1/(\Delta v_i)^2$.
- Operator $D_3$ is small. It has the order $1/\Delta v_i$.
- Operators $D_1$ and $D_2$ have one and the same order 1. Here operator $D_1$ has the formal priority because $D_2$ has no terms without factorials in the denominators.

The main problem of the further analysis is that the main operator $D_1 + D_2$ ensures relaxation to the state which gives zero flow of the embryos from the precritical to the postcritical region. So, this state leads to the zero value of the nucleation rate. To overcome this difficulty one can use the Chapman–Enskog procedure.

## 4. Chapman–Enskog procedure

At first, we recall the standard version of the Chapman–Enskog procedure and then we shall present the generalization to our situation and fulfill calculations.

Consider the equation

$$\frac{\partial P}{\partial t} = -(A + B)P , \tag{7}$$

where operators $A$ and $B$ have the following properties:

- A self-adjoint operator $A$ depends on variable $x$, operator $B$ depends on $x$ and $y$. Both operators do not depend on time $t$.
- The operator $B$ is supposed to be small in comparison with $A$. Later, we shall rescale time so as to have $\|A\| \sim 1$, $\|B\| \ll 1$. The value $\|B\|$ will be the small parameter of the theory.
- The eigenvalues and eigenfunctions of $B$ are unknown. The eigenfunctions $A_i$ and eigenvalues $a_i$ of operator $A$ are supposed to be known. They have the following properties:

  $$a_0 = 0 ,$$

  $$a_i > \delta > 0, \quad i \neq 0$$

  with some positive small $\delta$. The eigenfunctions are supposed to be normalized.

One can introduce symbol $O(\|B\|)$ which means that the given expression has the order of $\|B\|$ or less.

Initial conditions for (7) are supposed to be known. Then one can directly describe the evolution during the first moments of time. Here one can neglect $B$. One has only to solve the equation

$$\frac{\partial P}{\partial t} = -AP . \tag{8}$$

Due to the known eigenfunctions of $A$ this solution is quite obvious

$$P = \sum_{m=0}^{\infty} \exp(-a_m t) p_m A_m , \tag{9}$$

where

$$p_m = (P|_{t=0}, A_m) \tag{10}$$

will be called the mode amplitudes ($A_m$ will be modes) and the symbol ( , ) denotes the scalar product. Here $p_m$ are initial mode amplitudes.

The final relaxation according to (9) is obvious

$$P \to p_0 A_0 . \tag{11}$$

The characteristic time of relaxation is

$$t_{\mathrm{rel}} = 1/a_1 , \tag{12}$$

where $a_1$ is the smallest eigenvalue of $A$ (except the zero value).

Now $A(p_0A_0)=0$ and operator $A$ exhausts its power. One has to consider the action[25] of $B$.

The deviation of $P$ from $p_0A_0$ can be caused only by the action of operator $B$. So, in some sense it is small. Then we shall seek the solution in the following form:

$$P = p_0A_0 + \varDelta \, . \tag{13}$$

For correction term $\varDelta$ in accordance with the perturbation theory one can consider the representation

$$\varDelta = \sum_{i}^{\infty} \delta^{(i)} \, , \tag{14}$$

where every term $\delta^{(i)}$ has the order $\|B\|^i$:

$$\delta^{(i)} \sim O(\|B\|^i) \, .$$

Now, we are going to consider the time dependence of the amplitudes $p_m$. One can note that the action of $A$ leads to the vanishing of $p_m$ for $m \neq 0$. The unique source to fill the given mode is to take into account the action of operator $B$ which is small but still can provide the transition from one mode to another. But $B$ does not depend on time. So, the intensities of transitions between modes do not depend on time also. Thus, the unique source of time dependence is the time dependence of the zero mode $p_0$. Later, this dependence will be spread by $B$ to all other modes.

As a result, we state that the time dependence of an arbitrary mode amplitude is going through the time dependence of $p_0$:

$$p_m(t) = p_m(p_0(t)) \, , \tag{15}$$

$$\frac{\partial p_m}{\partial t} = \frac{\partial p_m}{\partial p_0}\frac{\partial p_0}{\partial t} \, . \tag{16}$$

Certainly, the time dependence of $p_0$ is not fixed and cannot be obtained immediately. One has to recalculate it at every step of approximation.[26] The value $\delta^{(i)}$ depends on time $t$ through $p_0(t)$ in the $i$th approximation. At every new[27] $\delta^{(i)}$ one has new $p_m^{(i)}$ and new $p_0^{(i)}$. So, one has a new time dependence.

The substitution of expansion

$$P = p_0A_0 + \sum_{i=1}^{\infty} \delta^{(i)} \tag{17}$$

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[25] The physical reason to consider the further stages of evolution is that in the nucleation problem $A_0 \sim$ *const.* and the final state of relaxation does not provide any benefit to the value of the nucleation rate (it lies in the evident correspondence with the formula $J \sim \exp(F_c)/\Delta\nu$ of the one-dimensional theory where stands the large parameter $\Delta\nu$).

[26] It is also possible to leave this dependence as some formal parameter and to calculate it when the "final" approximation (i.e., the approximation with the necessary precision) is obtained.

[27] The lower index denotes modes, the upper one denotes the number of approximations.

into (7) gives

$$\frac{\partial p_0}{\partial t}A_0+\sum_{i=1}^{\infty}\frac{\partial\delta^{(i)}}{\partial t}=-(A+B)\left(p_0A_0+\sum_{i=1}^{\infty}\delta^{(i)}\right)\,. \tag{18}$$

Note that the $i$th term has order $i$, but the value with the order $i$ will have benefits from all terms with $j\geqslant i$.

The r.h.s. and l.h.s. of the last equation are some functions and we suppose that they can be decomposed into series over the small parameter $\|B\|$. We shall denote the term which has the order $\|B\|^i$ by the superscript $\langle i\rangle$. Then one can write for the r.h.s. of the previous equation

$$\left((A+B)\left(p_0A_0+\sum_{i=1}^{\infty}\delta^{(i)}\right)\right)^{\langle i\rangle}=A\delta^{(i)}+B\delta^{(i-1)},\quad i>1\,. \tag{19}$$

The consideration of the l.h.s. is more complicated. At first we have to see the expression for $\partial p_0/\partial t$. Having projected Eq. (7) on $A_0$ one can see that

$$\frac{\partial p_0}{\partial t}=-(A_0,BP)\,. \tag{20}$$

Hence, one can come to the estimate

$$\frac{\partial p_0}{\partial t}\sim O(\|B\|)\,.$$

One can rewrite the last relation using decomposition (17)

$$\frac{\partial p_0}{\partial t}=-\left(A_0,B\left(p_0A_0+\sum_{i=1}^{\infty}\delta^{(i)}\right)\right)\,. \tag{21}$$

Now it is evident that $\partial p_0/\partial t$ contains all powers of the small parameter and it has the order $O(\|B\|)$. Now it is worth determining the $j$th term in decomposition over parameter $\|B\|$. It is quite easy to do for $\partial p_0/\partial t$. Namely,

$$\left(\frac{\partial p_0}{\partial t}\right)^{\langle i\rangle}=-(A_0,B\delta^{(i-1)})\,. \tag{22}$$

Then one can fulfill the same transformations for $\partial\delta^{(i)}/\partial t$. One can present the following estimate:

$$\frac{\partial\delta^{(i)}}{\partial t}=\frac{\partial\delta^{(i)}}{\partial p_0}\frac{\partial p_0}{\partial t}\sim O(\|B\|^i)O(\|B\|)\sim O(\|B\|^{i+1})\,. \tag{23}$$

So, one can reduce the infinite sum to the finite sum

$$\left(\sum_{j=1}^{\infty}\frac{\partial\delta^{(j)}}{\partial t}\right)^{\langle i\rangle}\to\left(\sum_{j=1}^{i-1}\frac{\partial\delta^{(j)}}{\partial t}\right)^{\langle i\rangle}\,. \tag{24}$$

The next transformations are evident

$$\left(\sum_{j=1}^{i-1}\frac{\partial\delta^{(j)}}{\partial t}\right)^{\langle i\rangle}=\left(\sum_{j=1}^{i-1}\frac{\partial\delta^{(j)}}{\partial p_0}\frac{\partial p_0}{\partial t}\right)^{\langle i\rangle}$$

$$= \sum_{j=1}^{i-1} \frac{\partial \delta^{(j)}}{\partial p_0} \left( \frac{\partial p_0}{\partial t} \right)^{\langle i-j \rangle}$$

$$= - \sum_{j=1}^{i-1} \frac{\partial \delta^{(j)}}{\partial p_0} (A_0, B\delta^{(i-j-1)}) , \tag{25}$$

where

$$\delta^{(0)} = p_0 A_0 .$$

Now we can substitute all results into the initial equation and get

$$- (A_0, B\delta^{(i-1)}) A_0 - \sum_{j=1}^{i-1} \frac{\partial \delta^{(j)}}{\partial p_0} (A_0, B\delta^{(i-j-1)}) = -A\delta^{(i)} - B\delta^{(i-1)} . \tag{26}$$

As long as the eigenfunctions of $A$ are known one can use the last relation to get $\delta^{(i)}$.

## 5. Relaxation

Consider now our situation. Certainly, one can choose operator $D_1$ as the main one. An operator

$$D_0 = \left( \frac{\partial}{\partial \mu} - 2\mu \right) \frac{\partial}{\partial \mu}$$

has the known set of eigenfunctions which are the Hermite polynomials $H_j$ ($j = 0, 1, 2, 3, 4, \ldots$). The scalar product is defined as

$$(\Psi, \Phi) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \mathrm{d}x \exp(-x^2) \Phi(x) \Psi(x)$$

which leads to

$$(H_j, H_i) = \delta_{ij} 2^i i!$$

The eigenvalues of $D_0$ are

$$\lambda_i = -2i, \quad i = 0, 1, 2, \ldots .$$

One has to mention two important relations

$$\left( \frac{\partial}{\partial \mu} - 2\mu \right) H_i = -H_{i+1} ,$$

$$\frac{\partial}{\partial \mu} H_j = 2j H_{j-1} .$$

The first one gives the way to construct the set of Hermite polynomials. Both these equations allow to introduce in Ref. [10] the representation of modes. We shall call the operators on the r.h.s. of the two previous equations as the transition operators. The first one is the mode increase operator. The second one is the mode decrease operator. Then one can consider the operators of multiplication on $\mu$ and the differentiation over $\mu$ as the superposition of transition operators. Any additional operator appears from the non-Fokker–Planck behavior and from the higher terms in the free energy decomposition into the Taylor decomposition. Non-Fokker–Planck terms give high derivatives. Free energy can be well approximated in the near-critical region by polynomial and leads to additional multiplications on $\mu$. So, the additional term can be regarded as the superposition of the mode increase operators and mode decrease operators. This procedure resembles the formalism of the secondary quantization. It is described in Ref. [10]. Below we shall use another approach.

It is clear that $D_1$ can be represented as

$$D_1 = \sum_{l=1}^{\infty} d_l^{(1)} \left( \frac{\partial}{\partial \mu} - 2\mu \right)^l \frac{\partial^l}{\partial \mu^l}$$

with coefficients

$$d_l^{(1)} = -\sum_j \frac{(-\tau_j)^l}{l!} S_{2j} W_j^+ \frac{\tau_j^l}{l!}, \quad l = 2, 3, 4, \dots ,$$

$$d_1^{(1)} = \sum_{j'} W_{j'}^+ \alpha_{\mathrm{acc}\ j'} \frac{c_{g\ j'}}{2\sum_j c_j v_j} + \sum_{i'} W_{i'}^+ (1 - \alpha_{c\ i'}) \alpha_{\mathrm{acc}\ i'} \frac{c_{i'}}{2\sum_j c_j v_j}$$
$$+ \sum_{i'} W_{i'}^+ \alpha_{c\ i'} \frac{c_{i'}}{2\sum_j c_j v_j} - \sum_j (-\tau_j^2) W_j^+ S_{2j} .$$

Then the eigenfunctions of $D_1$ will be the Hermite polynomials[28] and the eigenvalues are given by

$$\lambda_j = \sum_{l=1}^{j} d_l^{(1)} (-2)^l \frac{j!}{(j-l)!} \quad \lambda_0 = 0 .$$

One can take $D_1$ as the main operator in the Chapman–Enskog procedure. The approximate form of kinetic equation will be the following one:

$$\frac{\partial P}{\partial t} = D_1 P .$$

But already in the investigation of the stationary distribution establishing one will see that the formal priority of $D_1$ in comparison with $D_2$ is not sufficient to ensure the relaxation to the stationary state.

Operator $D_2$ will be small in comparison with $D_1$ in terms of some small parameter (not in the formal sense described above) only when $\tau_j$ for all $j$ are small parameters. Then the main terms in operator $D_2$ will be the terms with the smallest sum of indexes $l + m$.

The required condition of the smallness of $D_2$ formulated in terms of the relaxation times will be

$$p_{\mathrm{rel}} \equiv \frac{|-\sum_j \tau_j^3 W_j^+|}{|\lambda_1|} \ll 1 .$$

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[28] In the main order $S_{2j}$ goes to 1.

Analogous parameter has been required[29] to be small in Ref. [8]. Then the solution at the relaxation stage can be written as the decomposition into the relaxation modes

$$P = \sum_{l=0}^{\infty} p_l^{(0)} \exp(-\lambda_l t) H_l \,,$$

where

$$p_l^{(0)} = (2^l l!)^{-1} (H_l, P(t=0))$$

are initial amplitudes. This decomposition ensures the relaxation to the stationary state $p_0^{(0)} H_0$:

$$P \to p_0^{(0)} H_0 \equiv P_{\mathrm{rel}} \,.$$

The time of relaxation $t_{\mathrm{rel}}$ is given by

$$t_{\mathrm{rel}\ D_1} \sim |\lambda_1| \,.$$

According to Ref. [8] restriction $p_{\mathrm{rel}} \ll 1$ practically excludes the nucleation under the strong thermal effects. So, the situation considered in Ref. [8] is rather poor.

Now we shall introduce another split of operators.

One can note that the final state $P_{\mathrm{rel}}$ corresponds to the equilibrium distribution over $\mu$. So, it is the eigenfunction of the operator $D_1 + D_2$ with the zero eigenvalue

$$(D_1 + D_2) P_{\mathrm{rel}} = 0 \,.$$

This can be easily proven when we return to the form of the finite differences and reconstruct $D_1$ and $D_2$.

Certainly, it is difficult to determine all eigenfunctions and eigenvalues of $D_1 + D_2$. We need not know all relaxation modes but only the final one. It is $P_{\mathrm{rel}}$. Also, we have to estimate the time of relaxation. One can prove that the relaxation time $t_{\mathrm{rel}\ D_1+D_2}$ for the equation

$$\frac{\partial P}{\partial t} = (D_1 + D_2) P$$

is less than or equal to the previous relaxation time $t_{\mathrm{rel}\ D_1}$

$$t_{\mathrm{rel}\ D_1+D_2} \leqslant t_{\mathrm{rel}\ D_1} \,.$$

Operator $D_2$ "helps" the relaxation to $P_{\mathrm{rel}}$. The way to prove the last estimate is to consider the blocks along the $\mu$-axis and estimate the action of $D_2$ between blocks.

As long as $D_3$, $D_4$ have a small parameter in comparison with $D_1$, no special condition is required. Now, we can consider $D_1 + D_2$ as the main operator at the relaxation stage. The smallness of $p_{\mathrm{rel}}$ is not required now.

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[29] With an account of the mentioned error.

## 6. Correction terms

When $P$ is close to $P_{\mathrm{rel}}$ which is the eigenfunction with the zero eigenvalue then the operator $D_1$ or $D_1 + D_2$ cannot be considered as the main one. One has to use the Chapman–Enskog asymptotic decomposition. But to fulfill this decomposition one has to know all eigenfunctions of the main operator. So we cannot use $D_1 + D_2$ as the main operator now.

One can easily note that to start the Chapman–Enskog procedure one has to know only $P_{\mathrm{rel}}$. So, there are no problems with the redefinition of the main operator after the relaxation period.

We shall redefine the main operator after the end of the relaxation stage. Now the main operator will be $D_1$. One can see that "correction operator" $D_2 + D_3 + D_4$ has a complicated structure. Operators $D_3$ and $D_4$ have small parameters. Operator $D_2$ is small only in the formal sense. So, the natural modification of the Chapman–Enskog procedure is to consider two Chapman–Enskog procedures. One can include the whole internal Chapman–Enskog procedure into every step of the external Chapman–Enskog procedure. The initial procedure has the aim to "invert" the action of operator $D_2$ and the external procedure will "invert" the action of $D_3 + D_4$.

Every new approximation will contain the small parameter $1/\Delta\kappa \sim \kappa^{2/3}$ (or at least $\Delta\kappa/\kappa \sim \kappa^{-1/3}$) in the order of the number of external approximations. This order decreases the order of flow calculated in the initial (zero) approximation. But one has to stop the external procedure until the resulting order is greater than $\kappa^0 = 1$ because the continuous description along $v_i$ will be violated in this order. One has to note that the evolution along $v_i$ is principally different in comparison with evolution along $\mu$. The domain along $v_i$ is concentrated only at the integer values (the value of $\mu$ is real). This difference leads to the specific lattice corrections described in Ref. [10]. These corrections have very complicated structure, an account cannot be fulfilled explicitly in the analytic way. As a result, we have to restrict ourselves by the first correction and adopt that the account of the first correction in the external procedure is already sufficient. The further corrections have the orders of the lattice corrections. So, they cannot be considered separately without the lattice correction analysis. But in the internal procedure we have to calculate all approximations.

Also, one has to note here the requirement to have no operators $S_{1j}$, $S_{2j}$, $S_{3j}$ in the final results. Really, the presence of these operators corresponds to the elementary shift taken into account. This is in contradiction with the absence of the lattice domain along $v_i$ in our approximation.

The matter under discussion is the rate of nucleation and to determine this rate we need only the embryos flows averaged over $\mu$. This operation corresponds to projection on $H_0 \sim const.$

Now we can focus on establishing equations for $\partial p_0/\partial t$. The last dependence is extremely important because in the Chapman–Enskog procedure all dependence of approximations on time is going through dependence of $p_0$ on time. To get $\partial p_0/\partial t$ one has to project kinetic equation

$$\frac{\partial P}{\partial t} = [D_1 + D_2 + D_3 + D_4]P$$

on $H_0$, i.e., to fulfill the integration $\int_{-\infty}^{\infty} \exp(-\mu^2)\dots \mathrm{d}\mu$. The l.h.s. gives $\partial p_0/\partial t$. Then

$$\frac{\partial p_0}{\partial t} = (H_0, [D_1 + D_2 + D_3 + D_4]P)\,.$$

The r.h.s. will lead to a more complicated expression. One can consider

$$(H_0, D_1 P) = \left( H_0, D_1 \sum_i p_i H_i \right) = \left( H_0, \sum_i \lambda_i p_i H_i \right) = \lambda_0 p_0 = 0$$

as long as $\lambda_0 = 0$. One can also consider

$$(H_0, D_2 P) = \left( H_0, D_2 \sum_{i=0}^{\infty} p_i H_i \right)\,.$$

From an explicit form of $D_2$ one can see that the last elementary operator in action of $D_2$ will be the mode increase operator $(\partial/\partial\mu - 2\mu)$. So, if we present $D_2 \sum_{i=0}^{\infty} p_i H_i$ as

$$D_2 \sum_{i=0}^{\infty} p_i H_i = \sum_{i=0}^{\infty} q_i H_i$$

then $q_0 = 0$. There is no projection on the zero mode. Then

$$\left( H_0, \sum_{i=1}^{\infty} q_i H_i \right) = 0$$

for arbitrary $q_i$. Then

$$(H_0, D_2 P) = 0\,.$$

Consider $(H_0, D_3 P)$. Operator $D_3$ can be split into two parts $D_{3a}$ and $D_{3b}$ defined as

$$D_{3a} = \sum_j \sum_{l=1}^{\infty} \frac{(-\tau_j)^l}{l!} \left( \frac{\partial}{\partial\mu} - 2\mu \right)^l L_j S_{1j}\,,$$

$$D_{3b} = \sum_j \frac{\partial}{\partial v_j} W_j^+ S_{3j} \sum_{m=1}^{\infty} \frac{\tau_j^m}{m!} \frac{\partial^m}{\partial\mu^m}\,,$$

$$D_3 = D_{3a} + D_{3b}\,.$$

Then

$$(H_0, D_{3a} P) = 0$$

and the reasons are the same as for $D_2$. The action of $D_{3b}$ can be presented as

$$(H_0, D_{3b} P) = \sum_j \frac{\partial}{\partial v_j} S_{3j} \left( H_0, W_j^+ \sum_{m=1}^{\infty} \frac{\tau_j^m}{m!} \frac{\partial^m}{\partial\mu^m} P \right)\,.$$

The last operator $D_4$ gives

$$(H_0, D_4 P) = -\sum_j \frac{\partial}{\partial v_j}(H_0, L_j P) \, .$$

As a result, one can get

$$\frac{\partial p_0}{\partial t} = -\sum_j \frac{\partial}{\partial v_j}\left(H_0, \left[L_j - W_j^+ S_{3j} \sum_{m=1}^{\infty} \frac{\tau_j^m}{m!} \frac{\partial^m}{\partial \mu^m}\right] P\right) \, .$$

The values on the r.h.s. of the last equation can be interpreted as the flows $J_j$ along the $v_j$ axis

$$J_j = \left(H_0, \left[L_j - W_j^+ S_{3j} \sum_{m=1}^{\infty} \frac{\tau_j^m}{m!} \frac{\partial^m}{\partial \mu^m}\right] P\right)$$

which transfers the last equation in the standard form

$$\frac{\partial p_0}{\partial t} = -\sum_j \frac{\partial}{\partial v_j} J_j \, . \tag{27}$$

## 7. Calculations

Now we can turn to direct calculations. The distribution $P$ can be presented in the following form:

$$P = p_0 H_0 + \sum_{l=0}^{\infty} p_l(p_0) H_l \, ,$$

$$p_l(p_0) = \sum_{m=1}^{\infty} p_l^{(m)}(p_0) \, ,$$

where the lower index indicates the number of modes and the upper index in brackets indicates the number of approximations. As already stated, we can fulfill in the external procedure only one step and it is not necessary to mark it. The upper index, thus, corresponds to the internal approximations.

Now, we can rewrite expression for $J_j$ in terms of announced decomposition. Then

$$J_j = \left(H_0, \left[L_j - W_j^+ S_{3j} \sum_{m=1}^{\infty} \frac{\tau_j^m}{m!} \frac{\partial^m}{\partial \mu^m}\right] \left[p_0 H_0 + \sum_{l=0}^{\infty} p_l(p_0) H_l\right]\right) \, .$$

Now we consider various terms of the last expression. Namely,

$$(H_0, L_j P) = L_j p_0 \, .$$

Then we can consider

$$\left(H_0, W_j^+ S_{3j} \sum_{m=1}^{\infty} \frac{\tau_j^m}{m!} \frac{\partial^m}{\partial \mu^m} \left[p_0 H_0 + \sum_{l=0}^{\infty} p_l(p_0) H_l\right]\right) \, .$$

The term $p_0 H_0$ does not lead to any influence because in $\sum_{m=1}^{\infty}(\tau_j^m/m!)\partial^m/\partial\mu^m$ there is at least one operator of the mode decrease. Then

$$\left(H_0, W_j^+ S_{3j} \sum_{m=1}^{\infty} \frac{\tau_j^m}{m!} \frac{\partial^m}{\partial\mu^m}\left[p_0 H_0 + \sum_{l=0}^{\infty} p_l(p_0) H_l\right]\right)$$

$$= \left(H_0, W_j^+ S_{3j} \sum_{m=1}^{\infty} \frac{\tau_j^m}{m!} \frac{\partial^m}{\partial\mu^m} \sum_{l=0}^{\infty} p_l(p_0) H_l\right)$$

$$= \left(H_0, W_j^+ S_{3j} \sum_{i=1}^{\infty}\sum_{m=1}^{\infty} \frac{\tau_j^m}{m!} \frac{\partial}{\partial\mu^m} p_i(p_0) H_i\right) = W_j^+ S_{3j} \sum_{m=1}^{\infty} \tau_j^m p_m(p_0) 2^m \, .$$

The resulting expression for $J_j$ will be the following:

$$J_j = L_j p_0 - W_j^+ S_{3j} \sum_{m=1}^{\infty} \tau_j^m p_m(p_0) 2^m \, .$$

In the main order we can omit $S_{3j}$. Certainly, the correction term in $S_{3j}$ has an order greater than that of $L_j$ but all non-zero modes can appear only from the zero one by the action of the operator which contains $L_j$. So, we have to keep $L_j$ and take away $S_{3j}$ here. Then

$$J_j = L_j p_0 - W_j^+ \sum_{m=1}^{\infty} \tau_j^m p_m(p_0) 2^m \, .$$

Now we can calculate the set of corrections. The initial condition for the asymptotic expansion will be the result of the relaxation stage, i.e. $P_{\text{rel}}$. One can easily note that

$$D_1 P_{\text{rel}} = 0 \, ,$$
$$D_2 P_{\text{rel}} = 0 \, ,$$
$$D_{3b} P_{\text{rel}} = 0 \, ,$$

because the first elementary operator is the mode decrease operator. In $D_{3a}$ there are only mode increase operators and then

$$D_{3a} P_{\text{rel}} = \sum_j L_j S_{1j} \sum_{l=1}^{\infty} \frac{(-\tau_j)^l}{l!} \left(\frac{\partial}{\partial\mu} - 2\mu\right)^l p_0 H_0$$

$$= \sum_j L_j S_{1j} \sum_{l=1}^{\infty} \frac{(-\tau_j)^l}{l!} (-1)^l p_0 H_l = \sum_j L_j S_{1j} \sum_{l=1}^{\infty} \frac{(\tau_j)^l}{l!} p_0 H_l \, .$$

The last operator contains the small parameter in the first order. In the main order one can take $S_{1j}$ away.

Operator $D_4$ has at least the small parameter in power 2. So, it is small in comparison with $D_{3a}$ which has it in the first power. As long as operators $D_1$, $D_2$ have no action we have to take into account $D_3$ but we can neglect the action of $D_4$.

Now we shall consider $(H_0, [D_2 + D_3 + D_4]P_{\mathrm{rel}})H_0$. As long as $P_{\mathrm{rel}} \sim H_0$ we have $D_2P_{\mathrm{rel}} = 0$, $D_{3b}P_{\mathrm{rel}} = 0$, the value $D_{3a}P_{\mathrm{rel}}$ is orthogonal to $H_0$. The value $D_4P_{\mathrm{rel}}$ has small parameter in the second power. So, one can neglect here $(H_0, [D_2 + D_3 + D_4]P_{\mathrm{rel}})H_0$.

In the zero approximation

$$\left(\frac{\partial p_0}{\partial t}\right)^{(0)} = 0 \,.$$

As a result, in the main order we have[30]

$$p_l^{(1)} = \frac{1}{\lambda_l l!} \sum_j \tau_j^l L_j p_0 \,.$$

In the first approximation as long as $D_2P_{\mathrm{rel}} = 0$ there is no internal procedure. Now, we are going to calculate the second external approximation. The structure of first approximation is rather simple because the zero approximation is localized only at the zero mode. Now, the current approximation has all modes and operator $D_2$ will lead to a non-zero result. So, the operator $D_2$ will be the main one and one can neglect[31] $D_3$ and $D_4$. In $D_2$, thus, one can neglect $S_{2j}$. But as long as $D_2$ gives a non-zero result there will be the internal procedure.

The time derivative can be also neglected. Really, due to (21)

$$\left(\frac{\partial p_0}{\partial t}\right)^{(1)} \sim -(H_0, [D_2 + D_3 + D_4]H_0)$$

in the main order.

One can easily see that

$$(H_0, D_2H_0) = 0 \,,$$
$$(H_0, D_{3b}H_0) = 0 \,,$$

as long as the first operator in the action of $D_2$ and $D_{3b}$ is the derivative over $\mu$ which gives zero in application to $H_0 \sim$ *const.*

As long as $D_{3a}$ has the small parameter and $D_4$ is the smallest one the result $(\partial p_0/\partial t)^{(1)}$ is small. As long as we calculate in the main order of small parameter we can neglect $(\partial p_0/\partial t)^{(1)}$.

In all approximations from the second one we can use (27) and see due to the smallness of $\partial/\partial v_i$ the smallness of $(\partial p_0/\partial t)^{(i)}$, $i = 2, 3, 4, \ldots$.

We see that the Chapman–Enskog procedure is now reduced to the trivial equation (except the zero mode)

$$p^{(i+1)} = -D_1^{-1} D_2 p^{(i)}$$

with the evident initial approximation.[32] In the main order one can take $S_{2j}$ away from the operator $D_2$. This form can be obtained from the simple analysis without Chapman–Enskog formalism.

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[30] The first time $L_j$ is used.

[31] This is done for the first time.

[32] In $D_1$ and $D_2$ there is no $L_j$. So, $L_j$ is used only one time.

The internal procedure does not have the Chapman–Enskog specifics because the time derivatives have the small parameter and they are absent in the last equation.

Also, one can reformulate the Chapman–Enskog procedure in another manner: the main operator will be $D_1 + D_2$ and now we have to invert it by some standard iteration approach.

We can present the last equation in the following form:

$$p_k^{(i+1)} = \sum_{q=1}^{\infty} \Gamma_{kq} p_q^{(i)}$$

as the matrix representation of the linear operator $D_1^{-1} D_2$ in the basis $H_i$ (without the zero mode). All $\Gamma_{qq}$ can be put to zero.

One can note the following important features:

- Any operator acts until the current moment in the already fulfilled part of the external Chapman–Enskog procedure only one time.
- Every operator has its own specific structure and cannot be reproduced by the actions of other operators.

Both these features allow one to forget about $S_{1j}$, $S_{2j}$, $S_{3j}$. If any operator had been used more than one time then one would take these operators into account.

The absence of $S_{1j}$, $S_{2j}$, $S_{3j}$ is very important in the context of the lattice structure of the domain in the $\{v_i\}$ plane. Only the absence of these operators allows one to ignore this lattice structure.

## 8. Final expressions

Now we have to establish the expression for $\Gamma_{kq}$. As long as $D_2$ is the superposition of the mode decrease operators and mode increase operators it will transfer $H_i$ into superposition of $H_i$. The action of $D_1^{-1}$ on $H_j$ (except zero mode) is evident – it is multiplication $H_j$ on $\lambda_j^{-1}$.

How does $D_2$ transfer $H_q$ into $H_k$? At first, according to the definition of $D_2$ the mode decrease operators will act. The number $l$ of the mode decrease operators will be between $l_0$ and $q$. Parameter $l_0$ appeared from the evident requirement that we have to fall lower than the $k$th level. So, $l_0 = 1$ if $k > q$ and $l_0 = q - k + 1$ if $q > k$. The result of the action of the mode decrease operators will give the coefficient $2^l q!/(q-l)!$. Then to get $H_k$ one has to apply $k-(q-l)$ mode increase operators which will give the coefficient $(-1)^{k-(q-l)}$. As the result

$$\Gamma_{kq} = \frac{1}{\lambda_k} \sum_j W_j^+ \sum_{l=l_0}^{q} \frac{\tau_j^{k-q+l}}{(k-q+l)!} \frac{\tau_j^l}{l!} 2^l \frac{q!}{(q-l)!} .$$

Also, one can consider another representation of $\Gamma_{kq}$. At first, we fall from the $q$ level to the $l$ level and this action gives $(\tau_j^{q-l}/(q-l)!)(q!/l!)2^{q-l}$. Then we increase the mode from the $l$ level to the $k$ level and this action gives $\tau_j^{k-l}/(k-l)!$. The result will be

$$\Gamma_{kq} = \frac{1}{\lambda_k} \sum_j W_j^+ \sum_{l=0}^{\min\{q,k\}-1} \frac{\tau_j^{q-l}}{(q-l)!} \frac{q!}{l!} 2^{q-l} \frac{\tau_j^{k-l}}{(k-l)!} .$$

Note that $\Gamma_{kq}$ does not depend on the number of approximations. This will lead to some important consequences. The first one is the possibility to write equation between $p_k$:

$$p_k = \sum_{q=1}^{\infty} \Gamma_{kq} p_q + p_k^{(1)}$$

or

$$p_k = \sum_{q=1}^{\infty} \Gamma_{kq} p_q + \frac{1}{\lambda_k k!} \sum_j \tau_j^k L_j p_0 .$$

Due to the linearity of equations the decomposition of the initial approximation will be reproduced in all approximations. Namely, we shall present $p_l^{(1)}$ in the following form:

$$p_l^{(1)} = \sum_j p_{lj}^{(1)} ,$$

where

$$p_{lj}^{(1)} = \frac{1}{\lambda_l l!} \tau_j^l L_j p_0$$

and the second lower index indicates component in the initial approximation (later $\Gamma_{kq}$ will be a mixture of different components).

The linearity results in the possibility of decomposition

$$p_k^{(i)} = \sum_j p_{kj}^{(i)} .$$

Index $j$ has no correspondence here with the direct decomposition over components.

For $p_{kj}^{(i)}$ the recurrent expression

$$p_{kj}^{(i+1)} = \sum_{q=1}^{\infty} \Gamma_{kq} p_{qj}^{(i)}$$

is valid.

The total amplitude $p_k$ can be also decomposed as

$$p_k = \sum_j p_{kj} ,$$

where $p_{kj}$ are

$$p_{kj} = \sum_{i=1}^{\infty} p_{kj}^{(i)} .$$

For $p_{kj}$ one can write

$$p_{kj} = \sum_{q=1}^{\infty} \Gamma_{kq} p_{qj} + p_{kj}^{(1)} .$$

One can also move operators $L_j$ through $\hat{\Gamma} \equiv \{\Gamma_{kq}\}$. This gives the set of relations. For the first approximation one can write

$$p_l^{(1)} = \sum_j L_j a_{lj}^{(1)} p_0 ,$$

where

$$a_{lj}^{(1)} = \tau_j^l \frac{1}{\lambda_l l!} .$$

The recurrent relations for $a_{lj}^{(i)}$ will be

$$a_{kj}^{(i+1)} = \sum_{q=1}^{\infty} \Gamma_{kq} a_{qj}^{(i)} .$$

In terms of $a_{kj}^{(i)}$ the value $p_k^{(i)}$ can be easily expressed as

$$p_k^{(i)} = \sum_j a_{kj}^{(i)} L_j p_0 .$$

Having introduced

$$a_{kj} = \sum_{i=1}^{\infty} a_{qj}^{(i)} ,$$

one can get

$$a_{kj} = \sum_{q=1}^{\infty} \Gamma_{kq} a_{qj} + a_{kj}^{(1)} .$$

In terms of $a_{kj}$ the value $p_k$ can be easily expressed as

$$p_k = \sum_j a_{kj} L_j p_0 .$$

The given decompositions are rather attractive from the first point of view, but actually one cannot simplify the problem with the help of these decompositions.

The equation for $p_0$ will be the following one:

$$\frac{\partial p_0}{\partial t} = -\sum_j \frac{\partial}{\partial v_j} \sum_i \left( \delta_{ij} - W_j^+ S_{3j} \sum_{m=1}^{\infty} \tau_j^m 2^m a_{mi} \right) L_i p_0$$

and in the main order

$$\frac{\partial p_0}{\partial t} = -\sum_j \frac{\partial}{\partial v_j} \sum_i \left( \delta_{ij} - W_j^+ \sum_{m=1}^{\infty} \tau_j^m 2^m a_{mi} \right) L_i p_0 ,$$

where indexes $i$ and $j$ mark components. The last equation has the standard form investigated in Ref. [6]. The part of Ref. [8] concerning the solution of the last equation in the two-dimensional case is also acceptable as long as it reproduces [11] in detail.[33]

Now, we shall present another method to calculate correction terms in the Chapman–Enskog procedure.

One can easily note that recurrent equations for $p_l^{(i)}$ and for $p_{l\,j}^{(i)}$ will lead to

$$\lim_{i\to\infty} p_{l\,j}^{(i)} \to const._{l\,j}(\gamma_{\max})^i \,,$$

$$\lim_{i\to\infty} p_l^{(i)} \to const._l(\gamma_{\max})^i \,,$$

where $\gamma_{\max}$ is the eigenvalue of $\hat{\Gamma} \equiv \{\Gamma_{pq}\}$ with the maximal absolute value. We suppose that $|\gamma_{\max}| < 1$.

Then one can say that starting from some number $m_{\lim}$ the tails of sums $\sum_i p_{l\,j}^{(i)}$, $\sum_i p_l^{(i)}$ resemble the tail of geometric progressions. Then one can easily calculate these sums

$$\sum_{i=m_{\lim}}^{\infty} p_{l\,j}^{(i)} \sim \frac{p_{l\,j}^{(m_{\lim})}}{1-\gamma_{\max}}$$

and

$$\sum_{i=m_{\lim}}^{\infty} p_l^{(i)} \sim \frac{p_l^{(m_{\lim})}}{1-\gamma_{\max}} \,.$$

The first $m_{\lim}$ terms have to be calculated explicitly. The boundary $m_{\lim}$ which depends on $j, l$ can be found as the characteristic boundary when $\hat{\Gamma}^{i+1}/\hat{\Gamma}^{i}$ approaches some constant independent of $i$. This procedure gives also the value of $\gamma_{\max}$.

Certainly, the most interesting situation is the strong manifestation of the thermal effects. Here the thermal effects cannot be considered as some corrections but radically change the character of the process.

Really, the main dependence of the nucleation rate is accumulated in exponent of the free energy of the critical embryo. The giant renormalization due to the thermal effects means that the temperature of the critical embryo essentially differs from the temperature of the vapor–gas media. The relative difference of the temperature expressed in the units of $\beta$ (in estimates we can forget about different components) can attain several units. It means that the characteristic value $\mu_0$ of $\mu$ attains several units.

One can easily note that to reproduce the real solution (i.e., to attain the values of $\mu$ in several units) we have to take into account a great number of modes. Really, the Hermite polynomials $H_n$ are the polynomials of power $n$. The characteristic region of localization of the function $H_n(\mu)\exp(-\mu^2)$ is $[\sim -\sqrt{n}, \sim \sqrt{n}]$. So, to describe the situation correctly we have to take into account at least $\mu_0^2$ modes. This quantity equals the dimension of the matrix $\hat{\Gamma}$ which becomes also great. This produces numerical difficulties.

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[33] Except several misprints appeared in Ref. [8]. Also, the initial matrix (with dimension 2) is not diagonal but this fact does not produce any difficulties.

Consider the matrix $\hat{\Gamma}$. Due to factorials in the denominators the values of the elements with large indexes are going to zero. It takes place under the arbitrary $\tau_j$. The r.h.s. of the matrix equation, i.e., the known vector $p^{(1)} = \{p_i^{(0)}\}$ also has vanishing elements when $i \to \infty$. The structure of the matrix $\hat{\Gamma}$ is the following: the upper triangle matrix has the elements with large values due to the large coefficient which appeared from the action of the mode decrease. The lower triangle matrix is "smaller" than the upper one. Thus, the following method will be rather effective:[34] one can split matrix $\hat{\Gamma}$ into the upper triangle matrix (with big elements) and the lower triangle matrix (with moderate elements). Then at every step of the iteration procedure the upper triangle matrix will be inverted (it is easy to do). The zero mode (in fact it is the first line in the matrix equation) will be calculated explicitly.

So, we have

$$\hat{\Gamma} = \hat{\Gamma}_+ + \hat{\Gamma}_- ,$$

where

$$\hat{\Gamma}_{+\ ij} = 0 \quad i > j ,$$

$$\hat{\Gamma}_{+\ ij} = \hat{\Gamma}_{ij} \quad i < j$$

and

$$\hat{\Gamma}_{-\ ij} = 0 \quad i < j ,$$

$$\hat{\Gamma}_{-\ ij} = \hat{\Gamma}_{ij} \quad i > j .$$

Then the equation

$$p = \hat{\Gamma} p + p^{(1)}$$

can be rewritten as

$$p = \hat{\Gamma}_+ p + \hat{\Gamma}_- p + p^{(1)} .$$

Then an iteration procedure can be formulated as

$$p^{(i+1)} = \hat{\Gamma}_+ p^{(i+1)} + \hat{\Gamma}_- p^{(i)} + p^{(1)}$$

with initial condition $p^{(1)}$.

One can easily note that the iteration solutions of the matrix equation take us back to the initial formulation of the problem at the level of the recurrent relations. So, the presented approach to calculate the maximal eigenvalue gets now a solid ground. It is also effective because it allows to estimate the necessary number of modes taken into account directly (by the smallness of the higher mode at every step).

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[34] With a special account of the Chapman–Enskog specific features.

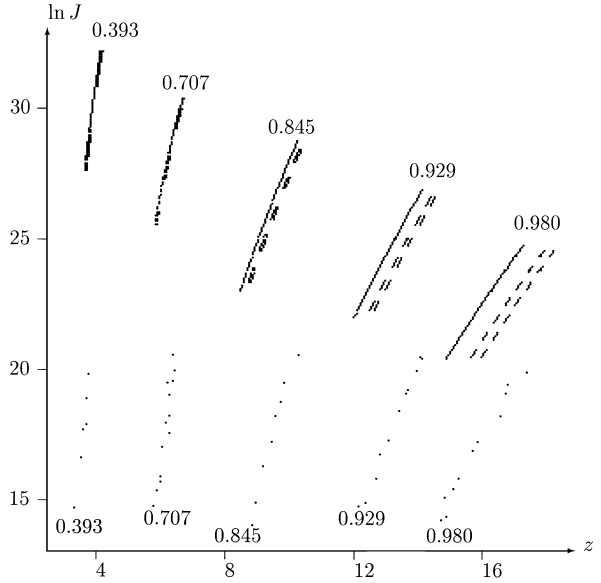

Fig. 1. Experimental and theoretical results for ethanol–hexaganol nucleation.

## 9. Numerical results and conclusions

To show the numerical effects of the error approach [8] we shall consider the same situation as was done in Ref. [8]. As long as it has not been declared in Ref. [8] as to which normalizing factor of the equilibrium distribution had been used to calculate the stationary rate of nucleation we have to use the isothermal rate of nucleation published in Ref. [8] (see Fig. 1 there) as some given data.[35] The detailed description of the experimental conditions and data can be found in Refs. [8,12].

The condensation of the ethanol (first component) – hexaganol (second component) is considered [8]. The nucleation rate logarithm over the mean activity $z=\sqrt{\zeta_1^2+\zeta_2^2}$ is drawn for the several values of the activity fraction $q=\zeta_1/(\zeta_1+\zeta_2)$. In Fig. 1, the points correspond to the results of Strey and Visanen [12]. The solid lines show the isothermal rates of nucleation. Two dashed lines present the nonisothermal nucleation rates for two different values of the passive gas (argon) accommodation coefficient $\alpha_{accg}$. The lower curve corresponds to $\alpha_{accg}=0.01$, the upper corresponds to $\alpha_{accg}=0.1$ (for all activity fractions).

The values of $q$ are written below the series of experimental points and above the theoretical curves. For small values of $q$ the isothermal and nonisothermal curves practically coincide, but this occurs only due to the large slope of the drawn dependencies. Moreover, one can analytically show that the difference in $J$ between isothermal and

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[35] The same qualitative picture will be with the arbitrary normalizing factor.

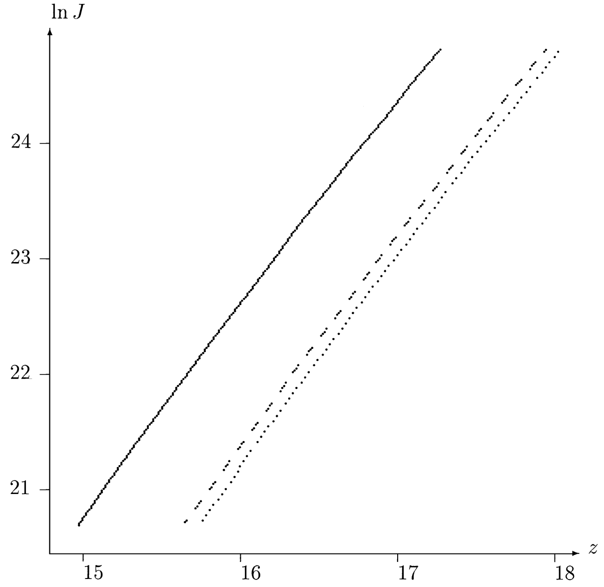

Fig. 2. Different theoretical predictions for $q = 0.980$.

nonisothermal approaches is growing with the growth of the nucleation rate and, thus, for small $q$ this difference is the greatest one.

We omit the comparison with the results of Lazaridiz and Drossinos [7] because their nucleation rates are higher than the classical isothermal results. This is in contradiction with the principle of stability. It is quite possible that Lazaridis and Drossinos used other input data as parameters of their theory.

Figs. 2 and 3 show the difference between the nucleation rates logarithms calculated by Djikaiev et al. [8] and by the formulae presented here. Our results are denoted by dotted lines, the results of Djikaiev et al. by dashed lines, the nonisothermal rates logarithms by solid lines. All curves are drawn for $\alpha_{accg}=0.1$. The greater the nucleation rate the greater the manifestation of the thermal effects and the greater is the difference between the nucleation rate logarithms calculated by Djikaiev et al. and our results. That is why we take two situations with the lowest theoretical nucleation rates which correspond to $q = 0.980$ (Fig. 2) and $q = 0.929$ (Fig. 3). Certainly, the difference for $\ln J$ is not too large, but the correct account of the passive gas cooling changes $J$ several times in comparison with results of Djikaiev et al. Our results are closer to the experimental data.

To show the qualitative difference we can assume that $\tau_j$, $W_j^+ n_{\infty\ j} \partial F/\partial \nu_j$ have equal values for all components. Then all components cannot be separated and we have the nonisothermal nucleation for one component but the passive gas is taken $i_0$ times into account in Ref. [8] ($i_0$ is the number of condensating components). Also, we can approximately assume that the main cooling of the embryo occurs due to the passive gas. Then taking into account the fact that the renormalization of the stationary rate

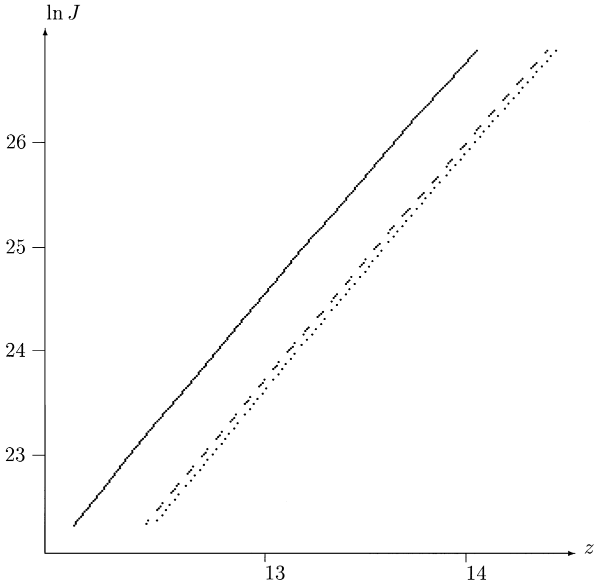

Fig. 3. Different theoretical predictions for $q = 0.929$.

is proportional now to the quantity of the passive gas [2] we can see that the error in $J$ attains $i_0$ times (two times in the binary condensation). This error is likely more significant than the difference between the Stauffer approach [13] and the steepest descent method [14].

All necessary limit transitions of the presented theory (to the one-component theory, to the nonisothermal theory) are observed and give the correct asymptotes to the already described situations.

To finish our description we can briefly recall the new facts presented here in comparison with other publications. Certainly, the most advanced version of the theory was presented by Djikaiev et al. [8], but even in comparison with this publication the new features are the following ones:

- The theory is now presented for the multicomponent case.
- The shift terms in kinetic equation are obtained. The sense of these terms is clarified, their negligible role is justified. It is shown that their negligible role can be shown only in frames of the initial steps of the Chapman–Enskog procedure. The connection of the vanishing of the shift terms and the possibility to forget about the lattice structure of the distribution domain is shown.
- The common cooling by the passive gas instead of the separate cooling is considered. This leads to an essential numerical difference in the nucleation rate.
- The relaxation in the absence of the specific parameter required in Ref. [8] is based. It allows to consider by the known Chapman–Enskog approach the situation of the strong thermal effects.

- The wrong parameter of decomposition presented in Ref. [8] is now corrected. This clarifies the transition to the isothermal multicomponent theory.
- The new correct estimate for the size of the near-critical region is given.

The evident weak point of the presented theory is the absence of the surface tension dependence on temperature. This phenomenon will be taken into account in the next publication.

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# Heterogeneous condensation in dense media

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A theoretical description of heterogeneous nucleation kinetics is presented. This description takes into account the perturbation of the vapor phase initiated by the growing droplets. The form of the density profile around the growing droplet is analyzed and some special approximations are given. Then the process of nucleation in the whole system is described. As a result all the main characteristics of the process are determined analytically.

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## I. INTRODUCTION

Among the numerous examples of first order phase transitions the case of condensation stands out because of its relative simplicity. This case is well investigated experimentally and is traditionally regarded as the base for application of new theoretical methods. The classical theory of condensation (see, for example, [1]) gives solid ground for further theoretical constructions. Numerous modifications and reconsiderations (see, for example, [2]) allow one to consider that the case of condensation is well analyzed both theoretically and experimentally.

One cannot state that all problems in the derivation of the stationary nucleation rate are completely solved, but the nucleation rate dependence on supersaturation is reliable at least in its general features. Certainly, there exist some unknown factors involved in the smooth dependence on the parameters of external conditions, but they are not very important in the current consideration.

One has to stress that essentially all investigations so far were intended to determine the rate of nucleation and have not presented the global picture of the phase transition. Theoretical descriptions of the global evolution appeared later than the classical theory of nucleation and they were not so numerous as those intended to get the stationary nucleation rate. One can extract many aspects of the global picture of the phase transition. When there is a sufficient quantity of aerosol in the system (i.e., there are already existing droplets formed on impurities) the evolution description does not require the process of droplet formation to be taken into account. This radically simplifies the problem, and this case was investigated in [3]. The total number of droplets there is already known from external conditions. Here this value will be the matter of investigation.

We shall determine the number of droplets and their size spectrum by solving the complex nonlinear problem. Because of the difficulties of this problem, only some numerical calculations have been presented earlier [4,5]. The scheme of calculations presented in [5] allowed the authors to establish in [4] some dimensionless combinations which essentially simplify the numerical procedure used there and allow rather complex numerical calculations. The sectional model presented in [6] simplifies the calculations once more and allows both nucleation and coagulation to be taken into account. Here we do not consider the process of coagulation, assuming that the probability of this process is very low and it can be observed only long after the end of nucleation.

We have to stress that here we are going to present an analytical theory which does not require computer simulations except for some calculations of universal constants. This has to be done only once. The period of nucleation (i.e., the appearance of new droplets) is difficult to describe analytically and ordinarily one has to suggest some model approximation to estimate the influence of the vapor consumption by the existing droplets. Sometimes this influence is not important and it is shown in [7] that this situation is rather widespread in laminar tube flows. In [7] the theory for this case was given and the methods of describing the global evolution were presented completely.

An analytical method to describe most of the nucleation process was presented in [8] on the basis of the balance equation for some characteristic time scales. The form of the size spectrum was postulated and the parameters of this form were associated with characteristic time scales. Then some special equations to obtain these time scales were formulated, which gives a way to get all the main characteristics of the nucleation process.

Here we are going to determine the form of the size spectrum explicitly taking account of the profile of vapor density around every droplet. The great importance of the problem of vapor exhaustion around the droplet was stressed by Reiss in [9], where the stationary profiles around droplets were obtained. Approximation of the stationary profiles was necessary in [9] to get the rate of droplet growth. It will be shown that to describe the kinetics of nucleation it is essential to use nonstationary profiles of the vapor density around the droplet instead of quasistationary ones. The appearance of contradiction between the approach in [9] and that used below is explained by the fact that in [9] only distances near the droplet were considered. To get the rate of growth it is sufficient to consider only relatively small distances. Below we shall be interested in some large distances which have the scale of the mean distance between droplets.

To start our consideration one has to fix external conditions. We shall analyze condensation after the instantaneous creation of initial supersaturation, which is very often used in experiments. The theoretical investigations of this case are also rather numerous. Among them one can extract the descriptions of metastable phase decay by Wakeshima [10], by Segal' [11], and by Kuni and Grinin [12]. The process of condensation that occurs during a smooth variation of external conditions is considered in [13]. Nevertheless, all the mentioned theoretical descriptions of a global picture of condensation kinetics have ignored an important feature of this process, namely, the exhaustion of a metastable phase near the growing embryo of a new phase has not been taken properly into account. Certainly, this exhaustion is partially taken into account in the expression for the rate of embryo growth in the continuous model (i.e., in the diffusion regime of embryo growth). This effect has been analyzed in both stationary and nonstationary aspects in many publications mainly in the field of mechanics of continuous media. But the presence of a gap in the metastable phase density near a droplet will act on the rate of new droplet formation. This effect was not taken into account in all the mentioned previous theoretical descriptions of global evolution during a first order phase transition. But, as shown in [14], this gap can lead to large numerical effects in the description of the whole process.

The reason that this effect has not been considered before is rather trivial. Even under a spatially homogeneous consumption of the metastable phase the descriptions were rather difficult to solve [13]. The condensation process has usually been described in the free molecule regime of droplet growth where there will be no such gap. This was a serious restriction of the theoretical description.

In some publications devoted to construction of a global picture of the phase transition (see, for example, [15]) the regime of droplet growth was the diffusion regime. This requires consideration of the gap in the density near the growing droplet but the vapor consumption was regarded as homogeneous in space. Since this effect is very important one cannot present a reliable description without taking it into account. Here we shall give a more realistic picture of the phase transition which takes this gap into account but allows an analytical solution.

Qualitatively the picture of the condensation process is rather simple. A process of nucleation (i.e., formation of supercritical embryos of a liquid phase) leads to vapor exhaustion, which stops the process of nucleation, but the supercritical embryos continue to consume the vapor phase. All the surplus material of the metastable phase will be accumulated in the embryos of a new phase. One can say that the process of condensation is now completed.[1]

A global picture of homogeneous condensation with explicit account of the density profiles was presented in [14], where very large numerical effects were observed, but ordinarily the process of nucleation occurs on heterogeneous centers.[2] This fact radically complicates the theoretical description due to the centers' exhaustion. This exhaustion has essentially nonlinear character. For simplicity we shall assume that there is only one type of heterogeneous center and the total number of centers is fixed in time. During the nucleation process some of the heterogeneous centers become the centers of supercritical droplets that are growing irreversibly in time. But the nucleation process diminishes the number of free heterogeneous centers (those unoccupied by droplets). In some cases the total exhaustion of free heterogeneous centers interrupts the nucleation; in some cases partial exhaustion of heterogeneous centers seriously diminishes the nucleation rate. This effect has also to be taken into account in a theoretical description.

A simple analytical description of heterogeneous condensation will be presented here with a proper account of all problems mentioned above. As a result, all the main characteristics of the condensation process will be expressed through some parameters of the external conditions and through the substance parameters by explicit analytical formulas. The error of the description presented will be estimated.

The structure of the theory will be as follows. First we shall analyze the density profile around a solitary droplet and construct some approximations. This has much in common with the case of homogeneous condensation considered in [14] and will be considered briefly. Then we shall construct some models for the kinetics of the process. We have to show that these models estimate the time evolution of the system during the nucleation period from above and from below. Since these models give similar results one can state that an approximate description of the nucleation kinetics is given. The error of the description is thus estimated. When the solution has been obtained we can compare it with the formulas given by the previous approach without density profiles and see the numerical effect of the gap near the growing droplets.

The small parameter of the theory will be the inverse number of molecules inside the critical embryo of a new phase. The small value of this parameter is not a restriction of our theory—it comes from the validity of the thermodynamic approach to calculating the free energy of the critical embryo. There is no other reliable way to calculate the free energy except the thermodynamic approach.[3] To use the thermodynamic approach it is necessary to have at least a few dozen molecules inside the embryo.

Also, we shall require a barrier character of the nucleation. This means that every embryo has to overcome an activation barrier of a particular height to begin to grow irreversibly. This height is less than the critical energy for the homogeneously (purely fluctuationally) formed embryo but still attains several thermal units.[4] Certainly, one can imagine a situation when there is no activation barrier. Then all embryos immediately begin to grow irreversibly. The number of

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[1] Further evolution includes the consumption of some relatively small embryos by some relatively big ones. It will be seen later that when all surplus material is consumed all droplets have approximately the same size, and we do not analyze this process here. A description of the further evolution can be given with the help of the Ostwald ripening theory formulated by Lifshitz and Slezov.

[2] Also, it is simpler to observe the heterogeneous case experimentally.

[3] All microscopic models require very complex calculations that cannot be fulfilled directly.

[4] All energylike values will be measured in thermal units.

droplets (i.e., the irreversibly growing embryos) will be equal to the total number of centers and the kinetics of the process will be relatively simple.

We shall speak only about the density profiles around the droplet and ignore the heat extraction in the nucleation process.[5] In fact, the mathematical structure of the diffusion equation resembles the structure of a heat transfer equation. So all constructions for the condensation heat extraction will be the same as for substance consumption. This effect will lead only to some renormalizations. That is why only a few remarks will be made. Some detailed results can be found in [6].

We shall consider the situation of metastable phase decay. This means that in the initial moment of time all the substance is in the vapor phase. All heterogeneous centers are free from droplets.

## II. PROFILE AROUND THE SOLITARY DROPLET

Due to the external influence in the initial moment of time one can observe a homogeneous mother metastable phase with particle number density $n$ equal to some initial value $n_0$. All heterogeneous centers are distributed rather homogeneously in space with the number density $\eta_{\mathrm{tot}}$. A system of unit volume is considered.

The process of condensation can begin only when $n_0$ is greater than the molecule number density $n_\infty$ in saturated vapor over a plane liquid. The power of the vapor metastability is characterized by the value of the supersaturation $\zeta$ defined as

$$\zeta = \frac{n}{n_\infty} - 1 .$$

The initial value of the supersaturation is denoted by $\zeta_0$.

Almost immediately there will be formed around every center an equilibrium embryo which has $\nu_e$ molecules. The value of $\nu_e$ is relatively small[6] and there is no need to consider the density profile around the equilibrium embryos.[7]

During the condensation process the number of free heterogeneous centers $\eta$ decreases due to the exhaustion of the free heterogeneous centers,

$$\eta = \eta_{\mathrm{tot}} - N,$$

where $N$ is the number of supercritical embryos, which will be called the droplets. Despite the simple form of the last relation the effect is very complex because $N$ depends on time in a very complex manner.

The effects of the density profile will be essential also for account of the heterogeneous centers' exhaustion and one cannot directly apply the results of [13]. One has to determine the effect of the influence of the centers' exhaustion even for the density profile of a solitary droplet.

We shall call the approach where the law of embryo growth is found from the continuous model but there is no account of the profile around the droplets the ''additive approach'' (AA). Then one can formulate the following evident statement.

*Statement 1*. The duration of the nucleation period[8] and the characteristic sizes of the droplets at the end of the nucleation period are greater than those calculated in the AA.

In fact, the existence of the density profile means that part of the substance is going to be consumed from regions where there is no droplet formation. This material is consumed from the gap instead of from unexhausted regions as is supposed in the AA.

Then having repeated all constructions[9] from [13] one can see the following.[10]

*Statement 2*. The characteristic size of the droplets at the end of the nucleation period is many times greater than the size of the critical embryo. The main role in vapor consumption is played by the supercritical embryos.

*Statement 3*. The characteristic duration of the nucleation period is many times greater than the time of relaxation to the stationary state in the near-critical region. Thus one can use the stationary rate of nucleation as a measure of the intensity of droplet formation at every current moment of time.

Because of statement 2 one has to investigate the profile around a growing droplet. The problem is whether one has to consider the interference of profiles around different droplets. To solve this problem one has to use the small parameter of the theory. From statement 3 the rate of nucleation is equal to the stationary one. This can be taken from [1],

$$I_s = Z \eta \exp(-\Delta F),$$

where $\Delta F$ is the height of the activation barrier (in thermal units), $\eta$ is the number of free heterogeneous centers (unoccupied by the supercritical embryos), and $Z$ is the Zeldovic factor. The Zeldovic factor is a smooth function of the supersaturation that is given by

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[5] The validity of this assumption can be ensured by using a passive gas.

[6] In comparison with the characteristic number of molecules inside the droplet during the nucleation period.

[7] In fact the gap is rather small and will disappear rather fast. This leads to a slight variation of the equilibrium embryo characteristics. This variation will act on the gap in reverse, but the final relaxation will be rather rapid.

[8] The period of nucleation is the period of relatively intense formation of droplets. It can be proved that the end of this period is well defined due to the cutoff of the intensity of droplet formation.

[9] In [13] the AA was formulated for external conditions of dynamic type. For the situation of decay the required hierarchical inequalities can be proved in the same way. Note that in [13] there is no special reference to the types of condition when the required estimates are proved.

[10] A barrier character of the nucleation is required here. This means that the magnitude of the activation barrier height has the same order as the free energy of the homogeneous critical embryos (it might be three on four times smaller).

$$Z=\frac{W}{\pi^{1/2}\Delta\nu_e\Delta\nu_c},$$

where $W$ is a kinetic factor, $\Delta\nu_c$ is the half-width of the near-critical region, and $\Delta\nu_e$ is the width of the equilibrium region. During the nucleation period the value of $Z$ can be considered as as constant.

Due to its rather small size it is reasonable to use for the critical embryo the free molecule regime of substance exchange.[11] In this regime the expression for the nucleation rate is well known. One has also to note that the critical embryo is in equilibrium (but an unstable one) with the metastable phase, which implies no profiles of vapor density, and the regime of substance exchange has to be the free molecule one.

Under the free molecule regime $W$ can be calculated as

$$W=3\frac{\zeta+1}{\tau}\nu_c^{2/3}\alpha,$$

where $\nu_c$ is the number of molecules inside the critical embryo, $\alpha$ is the condensation coefficient,

$$\tau\sim 12[(36\pi v_l^2)^{1/3}n_\infty v_T]^{-1}$$

is the characteristic time, $v_l$ is the volume per one molecule in the liquid phase, and $v_T$ is the mean thermal velocity of a molecule.

The value of $\Delta\nu_c$ is the half-width of the near-critical region and it can be rewritten as

$$\Delta\nu_c=\sum_{\nu\leq(\nu_c+\nu_e)/2}\exp(-F_c+F_\nu)\pi^{-1/2},$$

where $\nu$ is the number of molecules inside the embryo, $F_\nu$ is the free energy of the embryo of $\nu$ molecules, and $F_c$ is the free energy of the critical embryo. In the continuous approximation it can be estimated as[12]

$$\Delta\nu_c=\left|\frac{2}{\delta^2F/\delta\nu^2}\right|^{1/2}_{\nu=\nu_c}.$$

The value of $\Delta\nu_e$ can be estimated as

$$\Delta\nu_e=\sum_{\nu\leq(\nu_e+\nu_c)/2}\exp(-F_\nu+F_e)$$

where $F_e$ is the free energy of the equilibrium embryo. Both $\Delta\nu_c$ and $\Delta\nu_e$ are rather smooth functions of the supersaturation.

One can see that $I_s$ is a very sharp function of the supersaturation. This means that a relatively small decrease of the supersaturation leads to an interruption of droplet formation.

At least for $\zeta>\zeta_0/2$ one can show that $d^2\zeta/dt^2>0$ and there is no long tail of the size spectrum at small intensity of droplet formation. This means that an interruption of the intensive droplet formation leads to an interruption of new droplet formation. So the relative decrease of supersaturation during the nucleation process is small. One can arrive at the following statement.

*Statement 4*. During the nucleation period the relative variation of supersaturation is small.

The last statement shows that there is no need to consider the interference of profiles in order to change the rate of droplet growth (and only the rate of growth).

On the basis of the expressions mentioned and the smallness of the relative decrease of supersaturation one can see the validity of the approximation

$$I_s(\zeta)=I_s(\zeta_0)\exp[\Delta F(\zeta_0)-\Delta F(\zeta)]$$

for the nucleation period. Moreover, one can linearize the height of the activation barrier over the supersaturation and get

$$I_s(\zeta)=I_s(\zeta_0)\exp\left(-\left.\frac{d\Delta F(\zeta)}{d\zeta}\right|_{\zeta=\zeta_0}(\zeta-\zeta_0)\right). \tag{1}$$

The validity of the last approximation depends on the particular type of heterogeneous center but it is valid for the majority of heterogeneous center types. For example, this validity can be directly proved for ions.

One can explicitly calculate the derivative in the last expression,[13]

$$\frac{d\Delta F}{d\zeta}=-\frac{1}{\zeta+1}(\nu_c-\nu_e).$$

The smooth character of the last expression shows the validity of Eq. (1) once more.[14]

Then Eq. (1) can be rewritten as

$$I_s(\zeta)=I_s(\zeta_0)\exp\left(\Gamma\frac{\zeta-\zeta_0}{\zeta_0}\right), \tag{2}$$

where

$$\Gamma=-\zeta_0\left.\frac{d\Delta F}{d\zeta}\right|_{\zeta=\zeta_0}=\frac{\zeta_0}{\zeta_0+1}[\nu_c(\zeta_0)-\nu_e(\zeta_0)].$$

The real value of $\Gamma$ is very large.[15] Certainly, one can consider the possibility of compensation between $\nu_c$ and $\nu_e$ in

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[11] Since the characteristic size of the droplet during the nucleation is many times greater that the critical size it is quite reasonable to use the diffusion regime of growth for the characteristic droplets.

[12] $\Delta\nu_e$ is usually smaller than $\Delta\nu_c$ and an explicit summation for $\Delta\nu_c$ is quite reasonable.

[13] Here we assume the vapor to be an ideal gas and suppose the possibility of presenting the free energy of critical and equilibrium embryos as an analytical function of the inverse embryo radius.

[14] A concrete value of the free energy derivative is not essential.

[15] Since the value of $\nu_c$ in going to infinity here the value of $\Gamma$ is also going to infinity.

the expression for $\Gamma$. Then one has to mention that due to the barrier character of nucleation at least $\nu_c - \nu_e \geqslant \Delta \nu_c$. Having estimated $\Delta \nu_c$ as the homogeneous value $\Delta \nu_c \sim \nu_c^{2/3}$ one can see that $\Gamma \gg 1$ in any case.

The small value of $\Gamma^{-1}$ will be very important in further constructions.

We see that the essential dependence on supersaturation occurs through the height of the activation barrier. This allows one to give the interpretation of the stationary rate of nucleation as the probability for the given embryo to overcome the activation barrier. After the interpretation of $I_s$ as a probability we can apply it to an arbitrary spatial point of a spatially inhomogeneous system. To use this interpretation the natural requirement is a weak unhomogenity of a system, namely, the volume of the regions where

$$\frac{\zeta(r) - \zeta(r + \sqrt{4Dt_s})}{\zeta(r)} \ll \Gamma^{-1}$$

is violated has to be relatively small. Here $D$ is the diffusion coefficient, and $t_s$ is the time of relaxation in the near-critical region, which can be estimated according to Zeldovic [1] as

$$t_s \sim \frac{\Delta \nu_c^2}{W}.$$

One can use instead of $t_s$ the time $\Delta \nu_e Z^{-1}$, which can be interpreted as the mean time to overcome the near-critical region.

Both these estimates are valid. Actually we need them only for those regions where the intensity of the droplet formation is not too small in comparison with the initial intensity. Certainly, the required property is observed in these regions.

Now we have to turn to determining the rate of embryo growth. According to statement 2 above, the characteristic size of the droplets is rather large. Then it is more reasonable to use the diffusion regime of droplet growth. At intermediate Knudsen numbers one has to use an interpolation law for the rate of embryo growth (for example, see [17,4]). It will be important that all expressions for the embryo growth lead to an avalanche of substance consumption.

The avalanche character of substance consumption means that the quantity of substance accumulated by a droplet increases strongly in time. The most evident manifestation of the avalanche consumption can be seen in the free molecule regime of substance consumption. The weakest effect can be seen in the diffusion regime of substance consumption. The force of the iteration convergence in [13] is based on this property. The property of avalanche consumption will be extremely important in further constructions also. That is why we take the diffusion regime, to have the worst situation and to grasp errors in all possible cases.

In the diffusion regime of vapor consumption the law of growth for a droplet (i.e., for a supercritical embryo) can be written in the following way:

$$\frac{d\nu}{dt} = \kappa \zeta \nu^{1/3},$$

where

$$\kappa = \left(\tfrac{2}{3}\right)^{-1/3} 4\pi n_\infty D \left(\frac{v_l}{2\pi}\right)^{1/3}$$

is some constant. The last expression is written in the stationary approximation. The nonstationary effects have been investigated in many publications in detail and here they are rather small (see, for example, [9]).

One can see that the rate of droplet growth is proportional to $\zeta$. So the rate of growth can be changed only by a relative variation of $\zeta$. Then according to statement 4 one can see the following.

*Statement 5*. The rate of droplet growth during the nucleation period can be approximated as a constant.

The last statement is extremely important because it allows us to analyze the profile of the density initiated by a solitary droplet.[16] Now we are going to consider this problem.

The approximately constant value of the supersaturation allows us to integrate the law of growth and to get

$$\nu(t) = \gamma t^{3/2},$$

where

$$\gamma = (4\pi)^{3/2} \left(\frac{3v_l}{4\pi}\right)^{1/2} \left(\frac{2\zeta n_\infty D}{3}\right)^{3/2}$$

and $t$ is the duration of irreversible growth for the given droplet. Consider a spherical system of coordinates with the center in the center of the droplet. The diffusion equation is written as

$$\frac{\partial n}{\partial t} = D \Delta n$$

where $\Delta$ is the Laplace operator. The diffusion coefficient $D$ is supposed to be approximately constant (there is a lot of a passive gas and the density of a gas mixture is approximately constant).

The boundary conditions are

$$n|_{r=\infty} = n(\infty),$$

$$n|_{r=R_d} = n_\infty,$$

where $R_d$ is the radius of the droplet. The values $n_\infty$ and $n(\infty)$ are known parameters. The variable $r$ is the distance from the center of the embryo.

The stationary approximation is suitable for the rate of droplet growth. The errors are analyzed in [17] and they are small. But the stationary solution cannot give a reasonable result for the density far from the droplet. The stationary solution is

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[16] The interference of the density profiles will be analyzed later.

$$n(r)=n(\infty)-\frac{R_d}{r}[n(\infty)-n_\infty] \qquad (3)$$

and has a very long tail. This tail leads to the infinite value of

$$G=\int_0^\infty 4\pi r^2[n(\infty)-n(r)]dr,$$

which must be the integrated excess of the substance, which must be in the droplet. This contradiction shows that it is absolutely impossible to use the stationary approximation for the density profile around the droplet. One has to introduce another approach.

One can see that if the first boundary condition is changed to

$$n|_{r=\infty}=n(\infty)(1-\Gamma^{-1})$$

then the rate of embryo growth will not be essentially changed. But the level $n(\infty)(1-\Gamma^{-1})$ is the level when nucleation stops. So one can see that during the nucleation period there is no interaction between droplets through a change of the growth rate. Certainly, two droplets can appear too close and act upon one another but the probability of such a coincidence is very small. That is why one can come to the principle of separate growth of droplets during the nucleation period.

Now one has to prove that at the distances $(5-10)R_d$ from the droplet one can observe a quasistationary profile. One has to note that

$$v_l/v_v \ll 1, \qquad (4)$$

where $v_v$ is the partial molecular volume in the vapor phase. This last ratio is very small (for example, it is 0.001 for water in normal thermodynamic conditions). But unlike $\Gamma^{-1}$ one cannot consider it in all cases as zero. Now one can introduce a formal parameter $l$ which attains some large values

$$l \gg 1$$

but satisfies the condition

$$l^2\frac{v_l}{v_v} \ll 1. \qquad (5)$$

According to Eq. (4) it is possible to do this.

In the region $r \leqslant lR_d$ the stationary profile is established after

$$t_h=\frac{l^2R_d^2}{4D}.$$

It is necessary to show that

$$s\equiv\frac{R_d(t+t_h)-R_d(t)}{R_d(t)} \ll 1.$$

In fact,

$$s\approx\frac{dR_d}{dt}\frac{t_h}{R_d}$$

and

$$s\sim l^2\frac{v_l}{v_v},$$

which is a small value according to Eq. (5). So the stationary form of the profile in the region $r<R_d l$ is proved.

Since $\Gamma \gg 1$ and at least $\Gamma \gg l$ one can see that in the region $r<lR_d$ there is no formation of new droplets. Thus this region is not interesting for the theory and one can observe only the region $r>lR_d$.

The previous notation is rather important; this property allows one to use the model with a point source. One can consider only distances greater than $lR_d$, but at these distances the droplet can be interpreted as a point source of vapor consumption. Certainly, the point approximation of a droplet cannot give an expression for the rate of droplet growth because the boundary condition at $r=R_d$ is absent. But the rate of growth is already known and can be used directly as a known function of time. Thus

$$\frac{d\nu}{dt}=\lambda t^{1/2},$$

where

$$\lambda=2^{5/2}\pi v_l^{1/2}\zeta^{3/2}n_\infty^{3/2}D^{3/2}.$$

The action of a point source of vapor consumption can be described in a simple and suitable manner by the Green function formalism. The Green function $G_r$ for the diffusion equation can be written in the form

$$G_r=\Theta(t)\frac{\exp(-r^2/4Dt)}{(4\pi Dt)^{3/2}}.$$

Then one can get the density profile by a simple integration,

$$n(r)=n(\infty)-\int_0^t\frac{\lambda x^{1/2}}{[4\pi D(t-x)]^{3/2}}\exp\left(-\frac{r^2}{4D(t-x)}\right)dx.$$

After obvious transformations one can come to

$$\frac{\zeta_0-\zeta}{\zeta_0}=\sqrt{2/\pi}\sqrt{v_l/v_v}f(\beta), \qquad (6)$$

where

$$\beta=\frac{r}{\sqrt{4Dt}}$$

and

$$f(\beta)=\int_\beta^\infty\left(\frac{1}{\beta^2}-\frac{1}{x^2}\right)^{1/2}\exp(-x^2)dx.$$

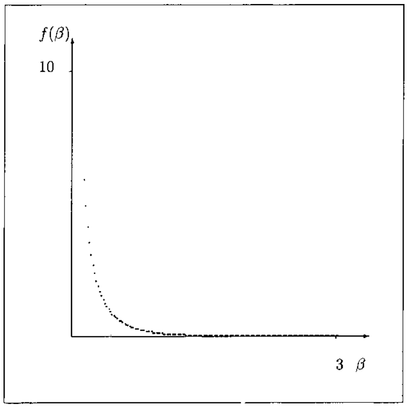

FIG. 1. The form of $f(\beta)$.

It is important that the profile dependence on $t$ and $r$ is now via $\beta$.

The concrete form of $f(\beta)$ is drawn in Fig. 1 in dimensionless units. One can get for $f(\beta)$ an expression through special functions:

$$f(\beta)=\tfrac{1}{2}\Gamma(\tfrac{3}{2})\exp(-\beta^2)\Psi(\tfrac{3}{2},\tfrac{3}{2};\beta^2).$$

Here $\Gamma$ is the Gamma function and $\Psi$ is the confluent hypergeometric function.

One can get the asymptotes for $f(\beta)$ at small and large values of $\beta$. At small values,

$$f(\beta)\sim\frac{\sqrt{\pi}}{2}\frac{1}{\beta}, \tag{7}$$

which corresponds to the stationary solution (3). At large values of $\beta$ one arrives at

$$f(\beta)=\exp(-\beta^2)\frac{1}{2\beta^3}\int_0^\infty x^{1/2}\exp(-x)dx\sim\frac{\exp(-\beta^2)}{\beta^3}. \tag{8}$$

One can see that this asymptote differs radically from the stationary solution, namely this tail behavior gives convergence of the integral for $G$. Certainly, the Green function formalism ensures a precise value for $G$, which is introduced here as an external object.

Now we are going to construct an approximation for the nucleation rate around the growing droplet. One can see that according to Eq. (2) the behavior of the supersaturation is important when $\zeta_0-\zeta\leqslant(2-3)\zeta_0/\Gamma$. When $\zeta_0-\zeta\geqslant(2-3)\zeta_0/\Gamma$ the intensity of droplet formation is negligibly small. From Eq. (1) one can see that

$$I_s(\zeta(r))=I_s(\zeta_0)\exp[-\Gamma\sqrt{2/\pi}\sqrt{v_l/v_v}f(\beta)].$$

Then one can extract the positive parameter

$$\sigma\equiv\Gamma^2\frac{v_l}{v_v}$$

which will be important in further constructions.

Because $\Gamma\gg1$ one can easily see that

$$\sigma\gg1.$$

The last condition is not necessary for further constructions, but it will be rather important for manifestation of the profile effects in the nucleation process. The last condition is also the most doubtful one because $v_l/v_v\ll1$ and one has the combination of two large parameters with generally unknown result. It is necessary to stress that the condition $v_l/v_v\ll1$ is not as strong as $\Gamma^2\gg1$. In the framework of the thermodynamic description $\Gamma\gg1$ is the main condition required and $v_l/v_v\ll1$ is a supplementary condition that slightly simplifies the theory.

In the situation of homogeneous condensation one has a hidden contradiction between the thermodynamic description and the relatively intensive nucleation. Since in homogeneous condensation $\Delta F=F_c\sim\nu_c^{2/3}$ the limit $\nu\rightarrow\infty$ means $\Delta F\rightarrow\infty$ and the rate of nucleation goes to zero. So there is a contradiction between the thermodynamic limit in the critical embryo description and the observable rate of nucleation.[17]

In the case of heterogeneous condensation there is no such contradiction when there are some active centers of condensation. Then the height of the activation barrier has no direct connection with the number of molecules inside the critical embryo. For example, the half-width of the near-critical region estimated from the homogeneous value is $\sim\nu^{2/3}$ and goes to infinity when $\nu\rightarrow\infty$, but the free energy decreases at the boundary of the near-critical region only by one thermal unit. So in a certain sense the case of heterogeneous condensation is preferable for theoretical description.

As a compensation for this advantage one has to note that both statements 1 and 2 are based on a homogeneous estimate for the activation barrier height. These properties can be violated. But since these statements are based on very strong inequalities one can accept their validity.

Now one can analyze the profile of the intensity of droplet formation around the already formed droplet. This profile of the nucleation rate is a rather sharp function which has a steplike behavior.

To show this property we shall introduce two characteristic values of $\beta$ ($\beta_{\mathrm{st}}$ and $\beta_{\mathrm{fin}}$) by the relations

$$f(\beta_{\mathrm{st}})=\sqrt{\pi/2}\sqrt{v_v/v_l}\frac{\exp(-\frac{1}{2})}{\Gamma},$$

$$f(\beta_{\mathrm{fin}})=\sqrt{\pi/2}\sqrt{v_v/v_l}\frac{\exp(\frac{1}{2})}{\Gamma}.$$

In the region $\beta>\beta_{\mathrm{st}}$ the rate of nucleation essentially coincides[18] with the unperturbed value $I_s(\zeta_0)$. In the region $\zeta<\zeta_{\mathrm{fin}}$ the rate of nucleation is negligible in comparison with the unperturbed value, i.e., $I_s(\zeta(r))\ll I_s(\zeta_0)$.

At some moment $t$ the values $\beta_{\mathrm{st}}$ and $\beta_{\mathrm{fin}}$ are related to the space distances $r_{\mathrm{st}}$ and $r_{\mathrm{fin}}$ by the expressions

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[17] This is not very small.

[18] One can easily see the monotonic character of $f(\beta)$.

$$r_{\mathrm{st}}=\beta_{\mathrm{st}}\sqrt{4Dt},$$

$$r_{\mathrm{fin}}=\beta_{\mathrm{fin}}\sqrt{4Dt}.$$

When $\sigma \gg 1$ one can arrive at

$$f(\beta_{\mathrm{st}})\ll 1,$$

$$f(\beta_{\mathrm{fin}})\ll 1$$

and

$$\beta_{\mathrm{st}}\gg 1,$$

$$\beta_{\mathrm{fin}}\gg 1.$$

Then one can use the asymptote (8) and see that

$$\frac{|\beta_{\mathrm{st}}-\beta_{\mathrm{fin}}|}{\beta_{\mathrm{st}}+\beta_{\mathrm{fin}}}=\frac{1}{4\beta_{\mathrm{st,fin}}}\ll 1,$$

$$\frac{|r_{\mathrm{st}}-r_{\mathrm{fin}}|}{r_{\mathrm{st}}+r_{\mathrm{fin}}}=\frac{1}{4\beta_{\mathrm{st,fin}}}\ll 1.$$

The real picture of nucleation occurs on the time scale. At a fixed space point $r$ one can introduce two characteristic times $t_{\mathrm{st}}$ and $t_{\mathrm{fin}}$ by the expressions

$$t_{\mathrm{st}}=\frac{r^2}{4\beta_{\mathrm{st}}^2 D},$$

$$t_{\mathrm{fin}}=\frac{r^2}{4\beta_{\mathrm{fin}}^2 D}.$$

Before $t_{\mathrm{st}}$ one cannot observe any deviation of the nucleation rate from the unperturbed value. After $t_{\mathrm{fin}}$ the rate of nucleation is very small.

One can get for the relative deviation

$$\delta \equiv \frac{t_{\mathrm{fin}}-t_{\mathrm{st}}}{t_{\mathrm{st,fin}}}$$

the expression

$$\delta \sim \frac{1}{\beta_{\mathrm{st,fin}}}.$$

So the relative deviation is small. Even in the situation of small $\sigma$ one can show with the help of asymptote (7) that the value of $\delta$ is rather small.

The steplike behavior of the intensity profile allows one to introduce some characteristic parameter $\beta_{\mathrm{eff}}$ and to consider the region[19]

$$\beta<\beta_{\mathrm{eff}}$$

as the exhausted region where there is no longer nucleation and the region

$$\beta>\beta_{\mathrm{eff}}$$

as the region where the rate of nucleation is unperturbed.[20]

One has to choose $\beta_{\mathrm{eff}}$ carefully. The problem is the possibility of existence of a long tail of the density profile. To grasp the situation of small values of $\sigma$ one has to introduce $\beta_{\mathrm{eff}}$ in an integral manner.

One can introduce the excess of the nucleation rate $\Delta I_s$ by the formula

$$\Delta I_s=I_s\int_0^\infty\left[1-\exp\left(-\frac{\Gamma(\zeta_0-\zeta(r))}{\zeta_0}\right)\right]4\pi r^2\,dr,$$

where $I_s$ is the unperturbed rate of nucleation. On the basis of this expression one can get the excess of $N$ due to the existence of the solitary profile. This value will be denoted $\Delta N_{\mathrm{sol}}$ and can be found as

$$\Delta N_{\mathrm{sol}}=I_s\int_0^t\int_0^\infty\left[1-\exp\left(-\frac{\Gamma(\zeta_0-\zeta(r))}{\zeta_0}\right)\right]4\pi r^2\,dr\,dt'.$$

Having used Eq. (6) one arrives at

$$\Delta I_s=4\pi(4Dt)^{3/2}I_s \times\int_0^\infty\{1-\exp[-\Gamma\sqrt{2/\pi}\sqrt{v_l/v_v}f(\beta)]\}\beta^2\,d\beta.$$

The parameter $\Gamma\sqrt{2/\pi}\sqrt{v_l/v_v}$ has a constant value.

The value $\Delta N_{\mathrm{sol}}$ can be presented as

$$\Delta N_{\mathrm{sol}}=4\pi(4Dt)^{3/2}I_s \times\int_0^t\int_0^\infty\{1-\exp[-\Gamma\sqrt{2/\pi}\sqrt{v_l/v_v}f(\beta)]\} \times\beta^2\,d\beta\,dt'.$$

The steplike approximation of the nucleation profile will lead to

$$\Delta I_s^0(\beta_{\mathrm{eff}})=4\pi(4Dt)^{3/2}I_s\int_0^{\beta_{\mathrm{eff}}}x^2\,dx.$$

The value $\beta_{\mathrm{eff}}$ has to be determined from

$$\Delta I_s^0(\beta_{\mathrm{eff}})=\Delta I_s.$$

Certainly, the value of $\beta_{\mathrm{eff}}$ depends on $\Gamma\sqrt{2/\pi}\sqrt{v_l/v_v}$.

The value of $\beta_{\mathrm{eff}}$ leads to

$$r_{\mathrm{eff}}=2\beta_{\mathrm{eff}}D^{1/2}t^{1/2}.$$

One can state that inside the volume

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[19] At $\sigma\ll 1$ the value of $\beta_{\mathrm{eff}}$ can be greater than $\beta_{\mathrm{st}}$ and $\beta_{\mathrm{fin}}$.

[20] In all cases $\beta_{\mathrm{eff}}>\beta_{\mathrm{fin}}$.

$$V_{\mathrm{eff}}=\tfrac{4}{3}\pi r_{\mathrm{eff}}^3$$

there is no nucleation and outside this volume the rate of nucleation is unperturbed. Thus one can imagine that around every solitary droplet there is an exhausted region (ER) where no nucleation is observed and around the ER there is the unexhausted region (UR) where the nucleation remains unperturbed. The whole space now is divided into two regions.

The volume $V_{\mathrm{eff}}$ grows in time in the following way:

$$V_{\mathrm{eff}}=\frac{32}{3}\pi\beta_{\mathrm{eff}}^3 D^{3/2}t^{3/2}.$$

In the free molecule regime $V_{\mathrm{eff}}$ will grow even faster. For $\beta_{\mathrm{eff}}$ one can get the simple expression

$$\beta_{\mathrm{eff}}^3=3\int_0^\infty\{1-\exp[-\Gamma\sqrt{2/\pi}\sqrt{v_l/v_v}f(\beta)]\}\beta^2\,d\beta$$

or

$$\beta_{\mathrm{eff}}^3=3\int_0^\infty\{1-\exp[-\sigma^{1/2}\sqrt{2/\pi}f(\beta)]\}\beta^2 d\beta.$$

For $\Delta N_{\mathrm{sol}}$ one can obtain

$$\Delta N_{\mathrm{sol}}=I_s(\zeta_0)\int_0^t dt'\,V_{\mathrm{eff}}=I_s(\zeta_0)\int_0^t dt'\,\tfrac{4}{3}\pi r_{\mathrm{eff}}^3.$$

One can easily integrate the last expression and get

$$\Delta N_{\mathrm{sol}}=I_s(\zeta_0)\frac{64}{15}\pi\beta_{\mathrm{eff}}^3 D^{3/2}t^{5/2}.$$

One can see that $\Delta N_{\mathrm{sol}}$ is growing in time rather rapidly. That is, this property illustrates the feature of avalanche consumption during a first order phase transition as applied to heterogeneous nucleation.

For those situations where $\sigma \gg 1$ one can get

$$\beta_{\mathrm{eff}}\approx\beta_{\mathrm{st}}\approx\beta_{\mathrm{fin}}$$

and $\beta_{\mathrm{eff}}$ is determined by the simple equation

$$\exp(-\beta_{\mathrm{eff}}^2)=\beta_{\mathrm{eff}}^3\sqrt{v_v/v_l}\sqrt{\pi/2}\frac{1}{\Gamma}.$$

The last equation can easily be solved by iteration since $\beta_{\mathrm{eff}}\gg 1$ and $\exp(-\beta^2)$ is a very sharp function.

When the principle of separate growth was discussed some remarks were made. The reason given for the absence of interaction between droplets was the low probability of appearing too close to one another due only to the smallness of the space volume. Now one can see that the growing ER also helps to exclude interaction. The essential deviation of supersaturation from the ideal can be seen in the region $r<R_d l$. This means that the distance between the droplets with interference must be of the order $2R_d l$. Then the time distance between the moments of formation of these droplets must be shorter than

$$\Delta t_{\mathrm{init}}\sim\left(\frac{R_d l}{\beta_{\mathrm{eff}}D^{1/2}}\right)^2.$$

This time interval is many times shorter than the duration of the nucleation period.

Rather rapidly after the moment of formation every droplet forms an ER of such a size that it guarantees that the rate of growth of the given droplet cannot be perturbed by vapor consumption initiated by other droplets.

## III. KINETIC MODELS OF GLOBAL EVOLUTION

Now one can construct the picture of nucleation in the whole system. The main problem is to take into account the interference of the density profiles. Interference through the rate of growth is absent, but there is a simple overlapping of profiles. This overlapping leads to deviation of the total nucleation rate over the volume from those calculated taking account of the additive excess around every droplet.

The overlapping of ER's (even when this approximate formalism is used) is very complex and cannot be directly taken into account in a precise manner. Instead of using some long expressions that cannot be explicitly calculated one can act in another manner. First some simple approximate models for the kinetics of the nucleation process will be formulated. These models estimate the nucleation characteristics from below and from above and lead essentially to similar results. So it will be shown that the complex details of ER overlaps have no strong influence on the real characteristics of the phase transition.

First one can consider the common feature of all models. This feature is concerned with the exhaustion of free heterogeneous centers.

The rate of nucleation $I$ depends on time $t$ and on spatial point $r$ (the last behavior is the most complex). So it is reasonable to consider the mean (over space) value of $I$, denoting it by $\langle I\rangle$. For $\langle I\rangle$ one can write the expression

$$\langle I\rangle=\frac{W_{\mathrm{free}}}{W_{\mathrm{tot}}}\frac{\eta}{\eta_{\mathrm{tot}}}I_0, \tag{9}$$

where $I_0$ is the unperturbed rate of nucleation. Here $W_{\mathrm{free}}$ is the volume of the region where the rate of nucleation is unperturbed, i.e., the total UR of the whole system. The value $W_{\mathrm{tot}}$ is the total volume of the system (it equals unity and is written only to clarify the consideration).

Then since

$$N=\int_0^t\langle I\rangle(t')dt'$$

one can get

$$\eta=\eta_{\mathrm{tot}}-\int_0^t\langle I\rangle(t')dt'.$$

In the differential form the last relation can be written as

$$\frac{d\eta}{dt}=-\langle I\rangle$$

and with the help of Eq. (9) it can be rewritten as

$$\frac{d\eta}{dt} = -\frac{\eta}{\eta_{\rm tot}} \frac{W_{\rm free}}{W_{\rm tot}} I_0 .$$

After integration of the last expression one arrives at

$$\eta = \eta_{\rm tot} \exp\left( -\int_0^t \frac{W_{\rm free}(t')}{W_{\rm tot}} \frac{I_0}{\eta_{\rm tot}} dt' \right). \qquad (10)$$

One should note that the heterogeneous centers are not distributed homogeneously with respect to the ER (or UR). Only free heterogeneous centers are distributed homogeneously with respect to the ER. This fact has also to be taken into account.

The problem is to determine the value of $W_{\rm free}$. In different models it will be given in different forms.

### A. The model without overlap

One can write

$$W_{\rm free} = W_{\rm tot} - W_{\rm exh}$$

where $W_{\rm exh}$ is the volume where there is no further formation of droplets. Very approximately one can present it as the sum of all ER's around all already existing droplets,

$$W_{\rm exh} \approx \sum_i V_{\rm eff}$$

(the sum is taken over all already formed droplets). Certainly, the last approximation is rigorous only when there is no overlap of the ER's around different droplets.

Having used the expression for $V_{\rm eff}$ one arrives at

$$W_{\rm exh} = \int_0^t dt' \langle I \rangle (t') \frac{32}{3} \pi \beta_{\rm eff}^3 D^{3/2} (t-t')^{3/2}. \qquad (11)$$

After using the expression for $\langle I \rangle$ one comes to the closed system of nucleation kinetics equations

$$W_{\rm free} = W_{\rm tot} - \int_0^t dt' \frac{\eta}{\eta_{\rm tot}} \frac{W_{\rm free}}{W_{\rm tot}} I_0 \frac{32}{3} \pi \beta_{\rm eff}^3 D^{3/2} (t-t')^{3/2},$$

$$\eta = \eta_{\rm tot} \exp\left( -\int_0^t \frac{W_{\rm free}(t')}{W_{\rm tot}} \frac{I_0}{\eta_{\rm tot}} dt' \right) \equiv \hat{H}(W_{\rm free}). \qquad (12)$$

Now we have to introduce the quasihomogeneous limit. When there is no essential exhaustion of the heterogeneous centers a balance equation for them is not necessary. Only the balance equation for the substance molecules has to be considered. Equation (12) has the same form as in the homogeneous case (after some proper renormalizations). That is why we shall call it the quasihomogeneous equation.

In the quasihomogeneous limit this system can be reduced to

$$W_{\rm free} = W_{\rm tot} - \int_0^t dt' \frac{W_{\rm free}}{W_{\rm tot}} I_0 \frac{32}{3} \pi \beta_{\rm eff}^3 D^{3/2} (t-t')^{3/2},$$

which can be rewritten after the obvious renormalization $t \to at$, $t' \to at'$ where $a = (I_0 \frac{32}{3} \pi \beta_{\rm eff}^3 D^{3/2})^{2/5}$ in the universal form

$$W_{\rm free} = 1 - \int_0^t dt' (t-t')^{3/2} W_{\rm free} .$$

One should note that in the general case the system of nucleation equations can be solved with the help of methods presented in [13]. First one can solve the quasihomogeneous equation (it is a Volterra equation[21] with a rather simple kernel which allows one to apply the Laplace transformation to solve it), and then on the base of the quasihomogeneous equation one can find the final rather precise expression using Eq. (10) as the formula for $\eta$.

Another variant is to solve numerically the universal equation for $W_{\rm free\,hom}$:

$$W_{\rm free\ hom} = 1 - \int_0^t dt' (t-t')^{3/2} W_{\rm free\ hom} .$$

As a result one has the universal function $W_{\rm free\,hom}$. Then one can find $\eta$ as

$$\eta = \eta_{\rm tot} \exp\left( -a^{-1} \int_0^t \frac{W_{\rm free\ hom}(t')}{W_{\rm tot}} \frac{I_0}{\eta_{\rm tot}} dt' \right).$$

The last expression leads to the formula for $\langle I \rangle$:

$$\langle I \rangle = \frac{W_{\rm free\ hom}}{W_{\rm tot}} \exp\left( -a^{-1} \int_0^t \frac{W_{\rm free\ hom}(t')}{W_{\rm tot}} \frac{I_0}{\eta_{\rm tot}} dt' I_0 \right).$$

The justification for such an approach is analogous to [13]. The physical reason is very simple: when there is no exhaustion of heterogeneous centers then the solution is found precisely; when there is an essential exhaustion of centers there is no need to know $W_{\rm free}$ with high precision because the converging force of $\hat{H}$ is extremely high.

Now we shall take into account the effect of overlapping. This can be done rather approximately.

### B. The model with chaotic overlap

The matter under discussion is the correct expression for $W_{\rm free}$, which cannot be found absolutely precisely. Now a reasonable expression for $W_{\rm free}$ will be presented. Certainly, this will lead to a more complex equation, which will be more difficult to solve.

One can use the differential approach to write the expression for $W_{\rm free}$. Having written the obvious relation

$$\frac{dW_{\rm free}}{dt} = -\frac{dW_{\rm exh}}{dt},$$

one has to invent an approximation for $dW_{\rm exh}/dt$. Here the approximation

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[21] The nonlinear generalization.

$$\frac{dW_{\mathrm{exh}}}{dt}\approx\frac{d\Sigma_i V_{\mathrm{eff}}}{dt}\frac{W_{\mathrm{free}}}{W_{\mathrm{tot}}}$$

will be used (the sum is taken over all droplets). It corresponds to the following approach: The probability of the absence of overlap of the new parts of the ER around a given droplet with other ER's is proportional to the free volume of the system. This supposition seems to be rather reasonable.

The value $d\Sigma_i V_{\mathrm{eff}}/dt$ can be rewritten as

$$\frac{d\Sigma_i V_{\mathrm{eff}}}{dt}=\sum_i \frac{dV_{\mathrm{eff}}}{dt}.$$

This can be easily expressed through $\langle I\rangle$ as

$$\sum_i \frac{dV_{\mathrm{eff}}}{dt}=\frac{3}{2}\int_0^t dt'\langle I\rangle(t')\,\frac{32}{3}\,\pi\beta_{\mathrm{eff}}^3 D^{3/2}(t-t')^{1/2} \tag{13}$$

due to Eq. (11). Then

$$\frac{dW_{\mathrm{exh}}}{dt}=\frac{3}{2}\int_0^t\langle I\rangle(t')\,\frac{32}{3}\,\pi\beta_{\mathrm{eff}}^3 D^{3/2}(t-t')^{1/2}dt'\,W_{\mathrm{free}}(t)$$

and

$$\frac{dW_{\mathrm{free}}}{dt}=-\frac{3}{2}\int_0^t\langle I\rangle(t')\,\frac{32}{3}\,\pi\beta_{\mathrm{eff}}^3 D^{3/2}(t-t')^{1/2}dt'\,W_{\mathrm{free}}(t).$$

Having used an expression for $\langle I\rangle$ one arrives at

$$\frac{dW_{\mathrm{free}}}{dt}=-\frac{3}{2}\int_0^t\frac{W_{\mathrm{free}}}{W_{\mathrm{tot}}}I_0\,\frac{\eta}{\eta_{\mathrm{tot}}}\,\frac{32}{3}$$
$$\times\pi\beta_{\mathrm{eff}}^3 D^{3/2}(t-t')^{1/2}dt'\,W_{\mathrm{free}}(t).$$

Together with Eq. (12) the last equation forms the closed system of nucleation equations in the second model.

The previous equation can be integrated, which gives

$$\ln W_{\mathrm{free}}=-\int_0^t\frac{W_{\mathrm{free}}(t')}{W_{\mathrm{tot}}}I_0\frac{\eta(t')}{\eta_{\mathrm{tot}}}\,\frac{32}{3}\,\pi\beta_{\mathrm{eff}}^3 D^{3/2}(t-t')^{3/2}dt'$$
$$+\mathrm{const}.$$

Because of the initial conditions the value of the constant is equal to zero. Having introduced the function $F=-\ln W_{\mathrm{free}}$, one can get for $F,\eta$ the following system of equations:

$$F(t)=\int_0^t\exp[-F(t')]I_0\frac{\eta(t')}{\eta_{\mathrm{tot}}}\,\frac{32}{3}\,\pi\beta_{\mathrm{eff}}^3 D^{3/2}(t-t')^{3/2}dt',$$

$$\eta=\eta_{\mathrm{tot}}\exp\left(-\int_0^t\exp[-F(t')]\,\frac{I_0}{\eta_{\mathrm{tot}}}\,dt'\right).$$

One can see that the system of condensation equations is identical to the system of condensation equations in the AA. It was completely analyzed in [13]. Certainly, the parameters in the system will be different.

The last system can be rewritten after the obvious renormalization as

$$F(t)=\int_0^t\exp[-F(t')](t-t')^{3/2}\theta(t')dt'\equiv\hat{F}(F,\theta),$$

$$\theta(t)=\exp\left(-A\int_0^t\exp[-F(t')]dt'\right)\equiv\hat{\theta}(F),$$

where $\theta(t)=\eta(t)/\eta_{\mathrm{tot}}$ and $A$ is some known parameter. This system can be solved by iterations defined as

$$F_{i+1}=\hat{F}(F_i,\theta_i),$$

$$\theta_{i+1}=\hat{\theta}(F_i)$$

with $F_0=0,\theta_0=1$. For $F_i,\theta_i$ one can get the chains of inequalities

$$F_0<F_2\cdots<F_{2i}<\cdots<F<\cdots<F_{2i+1}<\cdots<F_3<F_1,$$

$$\theta_1<\theta_3<\cdots<\theta_{2i+1}<\cdots<\theta<\cdots<\theta_{2i}<\cdots<\theta_2<\theta_0.$$

Thus one can estimate errors in $F_i$ and $\theta_i$.

One can also use other methods analogous to those described in [13].

The similarity of the condensation equations in the AA and in the second model is extremely important for the transition toward the collective character of vapor consumption, which is analyzed in [13]. The physical reason for the considered model is the chaotic overlap of ER's that is, the chaotic overlap lies at the base of the approximation used here. But due to the spherical form of every ER the overlap is not absolutely chaotic. What can be done in such a situation? In the next model we shall show that the actual type of overlap is not very important.

To finish with the second model we shall show the same method of its solution as for the first model. One can also formulate the quasihomogeneous equation as

$$F_{\mathrm{hom}}(t)=\int_0^t\exp[-F_{\mathrm{hom}}(t')]I_0\frac{32}{3}\,\pi\beta_{\mathrm{eff}}^3 D^{3/2}(t-t')^{3/2}dt'.$$

Then $\eta$ can be approximately found as

$$\eta=\eta_{\mathrm{tot}}\exp\left(-\int_0^t\exp[-F_{\mathrm{hom}}(t')]\,\frac{I_0}{\eta_{\mathrm{tot}}}\,dt'\right).$$

The quasihomogeneous equation can be renormalized. After the renormalization $z\rightarrow at, t'\rightarrow at'$ where

$$a=\left(I_0\frac{32}{3}\,\pi\beta_{\mathrm{eff}}^3 D^{3/2}\right)^{2/5}$$

one can transform the quasihomogeneous equation into the universal form

$$\ln W_{\mathrm{free\ hom}}(t)=-\int_0^t W_{\mathrm{free\ hom}}(t')(t-t')^{3/2}dt'.$$

### C. The model with formation of droplets inside the ER

The third model will show that the role of the overlap is not so essential as might be imagined initially. Suppose that new droplets can also appear in the ER of the already existing droplets. Then instead of Eq. (13) one has to use

$$\sum_i \frac{dV_{\mathrm{eff}}}{dt}=\frac{3}{2}\int_0^t dt' I_0 \frac{\eta(t')}{\eta_{\mathrm{tot}}}\frac{32}{3}\pi\beta_{\mathrm{eff}}^3 D^{3/2}(t-t')^{1/2}.$$

Then

$$\frac{dW_{\mathrm{exh}}}{dt}=\frac{3}{2}\int_0^t \frac{\eta(t')}{\eta_{\mathrm{tot}}} I_0 \frac{32}{3}\pi\beta_{\mathrm{eff}}^3 D^{3/2}(t-t')^{1/2}dt' W_{\mathrm{free}}(t)$$

and

$$\frac{dW_{\mathrm{free}}}{dt}=-\frac{3}{2}\int_0^t I_0 \frac{\eta(t')}{\eta_{\mathrm{tot}}}\frac{32}{3}\pi\beta_{\mathrm{eff}}^3 D^{3/2}(t-t')^{1/2}dt' W_{\mathrm{free}}(t).$$

Together with Eq. (12) the last equation forms the closed system of nucleation equations in the third model.

The material balance equation of the system can be integrated to give

$$\ln W_{\mathrm{free}}=-\int_0^t I_0 \frac{\eta(t')}{\eta_{\mathrm{tot}}}\frac{32}{3}\pi\beta_{\mathrm{eff}}^3 D^{3/2}(t-t')^{3/2}dt'+\mathrm{const}.$$

From the initial conditions the constant in the last equation is equal to zero. Having introduced the function $F=-\ln W_{\mathrm{free}}$ one can get for $F,\eta$ the following system of equations:

$$F(t)=\int_0^t I_0 \frac{\eta(t')}{\eta_{\mathrm{tot}}}\frac{32}{3}\pi\beta_{\mathrm{eff}}^3 D^{3/2}(t-t')^{3/2}dt',$$

$$\eta=\eta_{\mathrm{tot}}\exp\left(-\int_0^t \exp[-F(t')]\frac{I_0}{\eta_{\mathrm{tot}}}dt'\right).$$

This system corresponds to the first iteration in the solution of the second model by the method of iterations described in [13]. These iterations are also mentioned above. For $\eta$ the whole set of iterations has been taken (see details in [13]).

One can slightly modify the model and suppose that in the expression for $\eta$ one can use the same approximation for $\langle I\rangle$ as in the equation for $W_{\mathrm{free}}$. Then the last system of equations will precisely correspond to the first iteration in the iteration solution. One need not analyze these models in detail following [13] but just note that all these solutions are very similar.

Now one has to explain why the third model is rather accurate. One can do it only with the help of results obtained in [16]. There was noted that when the power of the kernel $(t-t')$ is rather large the solution of the quasihomogeneous equation depends weakly on the actual value of the power. It is also important that when the power of $(t-t')$ is extremely high the ER of the given (first) droplet formed inside the ER of another (second) droplet cannot go outside the ER of that (second) droplet. The third model is absolutely adequate in this situation. The same feature can be seen directly from the results of the iteration procedure. Combining these two results, one can see that the second model is close to the first iteration (i.e., to the modified third model) in the situation with large power in the kernel where the third model is suitable.

Now it is possible to explain why the overlap is not so important as might be imagined. Since the power of the kernel is large and one can observe avalanche consumption of the vapor phase, one can see the following qualitative picture. (1) During the whole period of nucleation the total ER is small and there is no problem of overlap. (2) At the end of the nucleation period the total ER will occupy the essential part of the volume and a few moments later it occupies all the volume of the system. This process is rather rapid. It stops the nucleation. This picture shows that there is no strong influence of the overlap on the nucleation process (except for the final moments of the nucleation period). But in the final moments only a few droplets can be formed, so it is not very important to know the overlap in the final moments of the nucleation period.

The nucleation description is now complete. One can use both the second and the third models to get the nucleation description. How to solve these equations is also described here. Now we can turn our attention to a more accurate method which does not give an analytical expression for the size distribution of droplets but gives more precise universal results for all essential characteristics of the nucleation period.

### D. The universal solution

The main idea of the theory presented in [13] was to consider the quasihomogeneous equation, to get a universal solution, and then on the basis of this solution to calculate the number of free heterogeneous centers. As a result one can get an expression for $\langle I\rangle$ and can calculate the total number of droplets appearing during the nucleation process.

Here we follow the same idea, but develop it further. It is not necessary to formulate the universal quasihomogeneous equation. Instead of the universal equation one can formulate a universal model.

The model will be the following.

(i) The rate of nucleation $\langle I\rangle$ can be found from

$$\langle I\rangle=I_0\frac{W_{\mathrm{free}}}{W_{\mathrm{tot}}}\frac{\eta}{\eta_{\mathrm{tot}}}.$$

(ii) With intensity $I_0$ the droplet appears at an arbitrary point of the system.

(iii) The value $W_{\mathrm{free}}$ can be found by exclusion of all ER's around the already existing droplets.

(iv) If the point is occupied by the ER of any droplet then the new droplet cannot be formed.

(v) The size $r_{\mathrm{eff}}$ of the ER grows in time according to

$$r_{\mathrm{eff}}=2\beta_{\mathrm{eff}}D^{1/2}t^{1/2}.$$

(vi) The initial conditions are the absence of droplets and the random distribution of centers.

With the proper renormalization of time $t$ and size $r$ one can cancel all coefficients. Then this process will be a universal one and as a result the value of $W_{\mathrm{free}}$ is a universal function of time. Then one can directly apply Eq. (12) and get the number of free heterogeneous centers (after the proper renormalization).[22] This number is the main result of the approximate separation principle. All other quasi-integrals of the further evolution can be obtained in the same manner.

The modification for dynamic conditions [13] requires using instead of $I_0$ the value $I_0 \exp(ct)$ with some parameter $c$ determined by external conditions and changing the lower limit 0 of integration to $-\infty$ [13]. The main constructions of the theory will be exactly the same but the forms of the characteristic curves will be radically changed.

## IV. NUMERICAL RESULTS

Numerical simulation plays at least two important roles here. The first is the standard comparison with the approximate models to observe their quality. The second is more specific and is concerned with some universal dependencies in the nucleation kinetics.

In the additive approach to the nucleation kinetics it was shown that an adequate approach can be presented on the basis of the quasihomogeneous solution [13]. Despite the dynamic conditions considered in [13] this is true in the situation of metastable phase decay also. Recall the reasons for such an approach. The formal reason is the careful analysis of the iteration procedure proposed in [13]. The final result for the total number of droplets appearing in the nucleation process is given by the second iteration (see the iterations of type $a$ in [13]) for the relative number of free heterogeneous centers. This iteration is based only on the first iteration for the supersaturation. There the value of the supersaturation is calculated without taking account of the heterogeneous centers' exhaustion. So one can see that the final result can be obtained on the basis of supersaturation in the quasihomogeneous approximation. This approximation can be more sophisticated than the first iteration, that is, it was used in [13] where the precise quasihomogeneous universal solution was chosen as the basis for the final results.

The physical reason for such behavior is rather simple. The main role in vapor consumption is played by droplets of relatively large sizes. We have already remarked on this fact. Moreover, due to the avalanche character of the vapor consumption the main role is played by the relatively large droplets that are formed in the first moments of time of the nucleation period. When the effect of center exhaustion is already essential in the first moments of the nucleation period[23] then at the end of the nucleation period all centers will already be exhausted. The result is evident—all centers will be the centers of droplets. Because of the high force of convergence in this situation this result can be obtained without any precise information about the behavior of supersaturation (even including the quasihomogeneous case). In the opposite case when the exhaustion of heterogeneous centers during the first moments of the nucleation period is not essential one can use the quasihomogeneous behavior of supersaturation.

This property can be viewed as an approximate separation of the heterogeneous and homogeneous problems. It is based only on the avalanche consumption of the metastable phase. So there are no objections to seeing this effect also with the density profiles considered here. Thus it is rather important to get the solution in the quasihomogeneous situation and to clarify whether it can be presented in a universal form.

The universal form of the quasihomogeneous solution can be easily seen in the situation with density profiles also. In the AA there was no specific space scale because the consumption took place homogeneously at all space points of the system. Here in the situation with density profiles there is an elementary space scale and one can choose the space scale to ensure that the linear size of the ER around the droplet is growing[24] as $t^{1/2}$ without any additional coefficients. The time scale has to be chosen so that in the initial free volume (equal to the total volume of the system) one can see the appearance of one droplet in the unit of time. Since the functional dependencies of the nucleation rate and of the radius of the ER on the time and on the space variables are not identical one can make such a renormalization without any problems. Thus we see that here the pseudohomogeneous case allows a universal description.

The process of exhaustion of the heterogeneous centers destroys this universality and one has to act as in [13].[25] The total number of droplets has to be approximately calculated as

$$N_{\mathrm{total}} = \eta_{\mathrm{tot}} \left[ 1 - \exp\left( - \frac{N_{\mathrm{hom}}}{\eta_{\mathrm{tot}}} \right) \right], \tag{14}$$

where $N_{\mathrm{hom}}$ is the number of droplets appearing in the quasihomogeneous situation (with the same parameters). This formula can also be used for all approximate models described earlier.

For the numerical simulation it was convenient to consider a cubic box of side 10 units. The rate of ER growth is chosen as

$$\frac{dR}{dt} = 100 t^{1/2}$$

where $R$ is the radius of the ER. The rate of nucleation is chosen to have one attempt at new droplet formation in the system during $dt = 0.002$. The spatial position of this attempt is determined by a random procedure. It may lead to a position in one of the ER's and then no droplet will be formed. In

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[22] This will complete the quasihomogeneous approach method.

[23] More precisely one can define these ''first moments of time'' as 2/5 of the nucleation period duration (under the free molecule regime it is 1/4 of the nucleation period duration). The reason for such concrete values can be seen from the iteration procedure.

[24] Certainly the power has to be conserved.

[25] Here we use a slightly simpler and more approximate method.

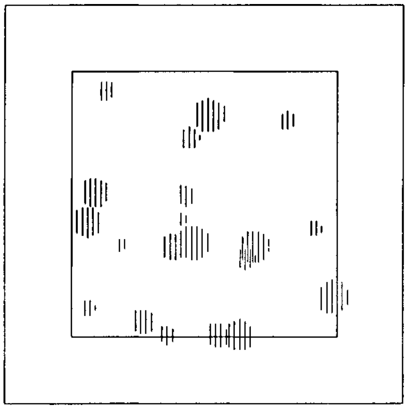

FIG. 2. The cross section of the system at $t=0.5$ for the quasihomogeneous situation.

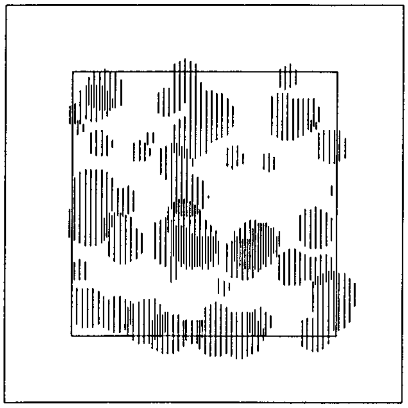

FIG. 3. The cross section of the system at $t=1$ for the quasihomogeneous situation.

the opposite situation when the point indicated is outside the ER's of all droplets already existing there will be formation of a new droplet.

One has to stress that the random procedure ordinarily used in computer simulations has one specific negative feature. In the standard numerical procedures the next random coordinate is calculated on the basis of the previous ones. So if the current coordinate lies near the center of an already existing ER then the next coordinate will also be near the center of another ER. These correlations lead to the necessity to consider a large system. In the system under consideration the number of droplets appearing in the quasihomogeneous situation will be near 500. Nevertheless the mean square fluctuation will be about 20.

The correlations mentioned are not the only source of fluctuations.[26] Careful consideration shows that the error introduced by the substitution of zero boundary conditions for periodic ones has the same power as the mean square error. This can be seen directly by numerical simulation. It is explained by the obvious fact that the characteristic overlap of profiles is about the mean profile size. We shall call this feature the property of ''moderate overlap.'' This fact can be proved analytically.

The mean value of the total droplet number is equal to 504.8 (under zero boundary conditions). This value has to be put into the previous formula.

The avalanche character of vapor consumption is illustrated by Figs. 2–4. Three different moments of time $t=0.5$, 1, and 1.5 are chosen as characteristic values. The space cross section of the system is drawn. The dashed regions correspond to the ER's of the droplets already existing. The black regions correspond to the overlap of ER's.[27]

Now the effects of exhaustion of the heterogeneous centers will be considered. The number of heterogeneous centers in this system is arbitrary. Certainly the effects of their exhaustion will be important when the number of centers is small (in comparison with $N_{\mathrm{hom}}=504.8$). Pictures for $\eta_{\mathrm{tot}}=50$ are drawn in Figs. 5–7 for $t=1.5$, 3, and 6. One can see that the number of ER's is smaller than in the quasihomogeneous case. The size of the ER's when the free volume is almost exhausted is larger than in the quasihomogeneous case. The time necessary to cover the whole volume with ER's is greater than in the quasihomogeneous case. This does not mean that the duration of the nucleation period is longer (simply, all centers will be exhausted and this means the end of nucleation). Moreover, the duration of the nucleation period in the situation with a relatively small number of heterogeneous centers will be shorter than in the quasihomogeneous case.

One can also see that the avalanche character of the vapor consumption in the whole system (not by a solitary droplet) here will be smoother than in the quasihomogeneous case. Certainly, in the quasihomogeneous case the appearance of some new ER's helps to consume the vapor phase in the avalanche manner. But in the situation with a small number of centers there is no need to consider the process carefully because the exhaustion of centers leads to the obvious result of condensation—the number of droplets equals the number of centers.

It is evident that the main object of our interest will be the quasihomogeneous case. The relative rate of nucleation in this case is shown in Fig. 8. Here the rate of nucleation is averaged over $100dt\equiv 0.2$ and over 16 attempts. So the rate of nucleation here is a rather smooth function.

The relative rate of nucleation is compared in Fig. 8 with the models described above. The rate of nucleation defines the spectrum of sizes when the role of the size of the embryo is played by some characteristic that has a rate of growth independent of the size. For the diffusion regime this characteristic is the number of molecules to the power $\frac{2}{3}$.

One can see in Fig. 8 three different curves and some solitary points. The solitary points correspond to the numerical simulation of the quasihomogeneous case and the three curves correspond to the three models in the quasihomogeneous case.

The shortest spectrum is for the first model. This line is doubled. This occurs because the ideal variant of the first model is also drawn. This ideal variant corresponds to

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[26] To prevent these correlations one has to use some special random procedures.

[27] For technical reasons, this occurs only when the distance between the neighboring centers is odd.

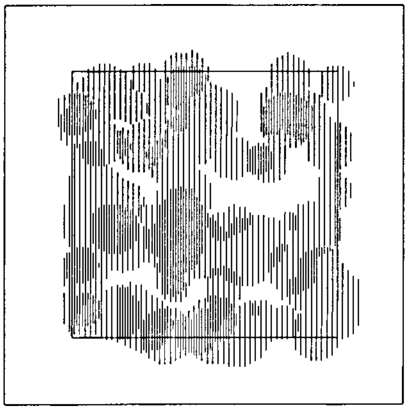

FIG. 4. The cross section of the system at $t=1.5$ for the quasi-homogeneous system.

$W_{\mathrm{free}}/W_{\mathrm{total}}\equiv 1$ in the subintegral function. The coincidence of the two lines means that the main role in the first model is played by the relatively large droplets that were formed at $W_{\mathrm{free}}=W_{\mathrm{total}}$.

The longest spectrum corresponds to the second model. This curve is very close to the intermediate curve which corresponds to the third model. The approximate coincidence of the second and third models shows that both of them are valid and the role of the relatively large droplets here is the main one. One also sees that even the first model is not too far from the real solution. This allows us to present rigorous estimates for the nucleation rate.

Now we going to present rigorous analytical estimates from below and from above for the evolution during the nucleation period. Certainly the first model is an estimate of the real process from below. It gives a number of droplets about 20% less than the numerical simulation. An estimate for the nucleation rate from above can be obtained in the following way. From the first model it follows that until $t=0.52$ (this case is essentially drawn in Fig. 2) the rate of nucleation is near the ideal value and the deviation is less than 15%. So one can say that the period $0<t<0.52$ corresponds to the absence of overlap (the first model is the estimate from above). Thus one can consider the process where the total volume is exhausted only by the ER's of the droplets appearing at $0<t<0.52$ in a random manner. The distribution of the centers of the ER's of such droplets is also random. This model certainly gives an estimate from above for the nucleation process. A simple calculation shows that the total number of droplets is only 25% greater than the result of the estimate from above. As a conclusion one can state that two suitable estimates from below and above are obtained.

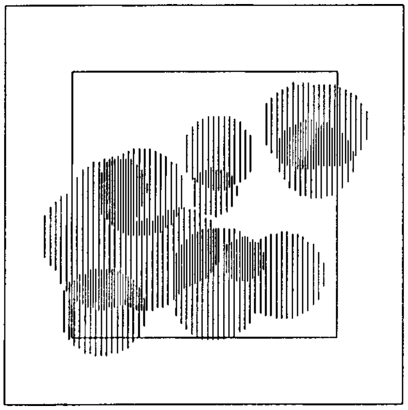

FIG. 6. The cross section of the system at $t=3$ for $\eta_{\mathrm{tot}}=50$.

The proximity of the last estimate to the real solution justifies the supposition that the main role in vapor consumption belongs to the droplets of relatively large sizes appearing when the system is essentially free of ER's. This supposition can also be justified in an analytical manner.

One can see that the second and third models are rather close to the real solution but do not coincide with it. There are at least two reasons for the deviation. The first is the presence of strong correlations in a real system—if two ER's overlap in some moment of time then the power of the overlap can only grow in time. It does not have a random character as stated in the second and third models.

This effect can be taken into account in a rather simple manner. It is sufficient to consider two spheres and calculate the power of the overlap as a function of distance and time (it is a simple geometrical problem). Unfortunately the answer can be written only in a very complicated form. If we have two ER's with radii $R_1$ and $R_2$ with a distance $l$ between their centers and $l>\max(R_1,R_2)$, then the volume of overlap is

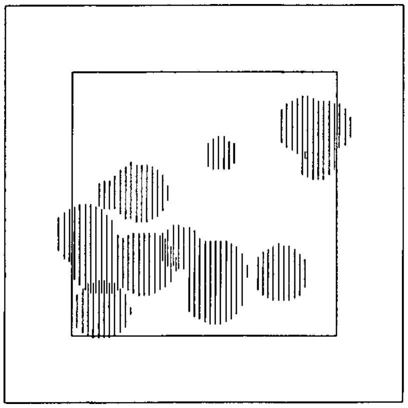

FIG. 5. The cross section of the system at $t=1.5$ for $\eta_{\mathrm{tot}}=50$.

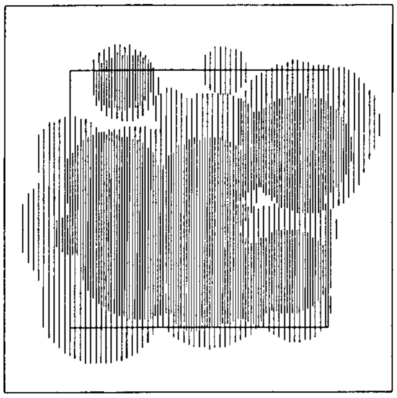

FIG. 7. The cross section of the system at $t=6$ for $\eta_{\mathrm{tot}}=50$.

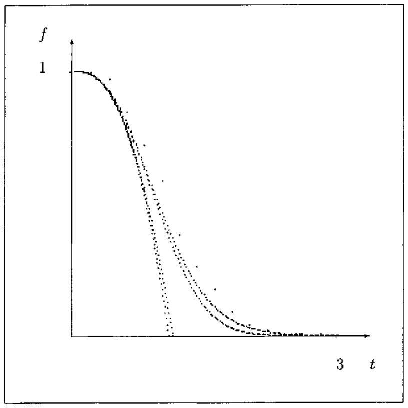

FIG. 8. Comparison of different models in the quasihomogeneous situation.

$$V_{\mathrm{over}}=\frac{2\pi R_1^3}{3}(1-2\cos\varphi_1+\cos^3\varphi_1)$$

$$+\frac{2\pi R_2^3}{3}(1-2\cos\varphi_2+\cos^3\varphi_2),$$

where

$$\cos\varphi_1=\frac{-R_2^2+R_1^2+l^2}{2R_1 l},$$

$$\cos\varphi_2=\frac{-R_1^2+R_2^2+l^2}{2R_2 l}.$$

Certainly, this result cannot lead to a simple form of the balance equation. It will be difficult to solve it analytically.

The second reason for the deviation is the moderate overlap problem. This property means that actually there is an interaction through overlapping in an ensemble of several droplets. Earlier this property was extracted [18] in terms of a special effective length of the ER. Now we see that this property is rather general. The way to solve this problem proposed in [18] is very complicated and leads to some uncertain relations.

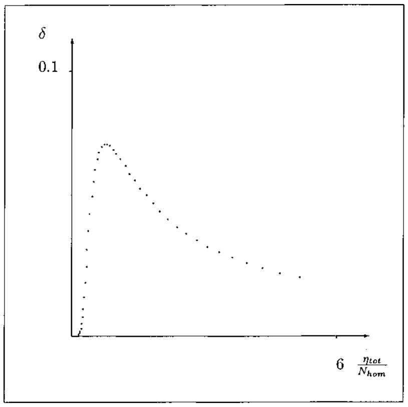

FIG. 9. Relative error of the quasihomogeneous approach in the first model.

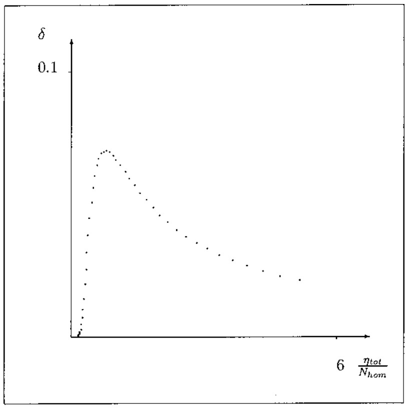

FIG. 10. Relative error of the quasihomogeneous approach in the second model.

How can one overcome all these problems? In fact, one has no need to do it analytically. A simple numerical simulation takes into account all these effects and gives a universal solution. Really we need only one number—the total number of droplets that have formed. This can be given by the numerical simulation. Then one can forget about all the mentioned difficulties.

Now one can analyze the heterogeneous case explicitly. A suitable approximation is given by Eq. (14). One has to substitute instead of $N_{\mathrm{hom}}$ the number of droplets given by the corresponding model.

The relative error of approximation (14) is drawn in Fig. 9 for the first model, in Fig. 10 for the second model, and in Fig. 11 for the third model. It is rather small for all models. For the third model it is practically negligible. This is because the third model is based on the approximation of chaotic overlap.

One can perform the same analysis for the numerical simulation. In Fig. 12 the relative error of (14) for numerical simulation is drawn. Here in Eq. (14) the value $N_{\mathrm{iom}}=504.8$ from the numerical simulation is used. The result is compared with a computer simulation of heterogeneous condensation. This simulation is rather simple. One can take the procedure for the quasihomogeneous case but place the center of the new droplet with probability $\eta/\eta_{\mathrm{tot}}$. Every time this point is outside the ER we reduce $\eta$ as $\eta\to\eta-1$.

One can see that the relative error is very small. We do not use an average over many attempts (this is the reason why there is no smooth curve) to see that the error of Eq. (14) has the scale of the mean square error of the numerical simulation.[28] So there is no need to use a more sophisticated approach.

The solution of the problem is now completed. Generalization for conditions of dynamic type is absolutely analogous to [14]. The convergence due to avalanche consumption is weaker and one has to use instead of the approximation (14) a more sophisticated procedure described in [13]. The universal constants used in [13] have to be calculated by numerical simulation with the density profiles taken into account. Generalization to the arbitrary regime of droplet

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[28] Here there is a system with 500 droplets.

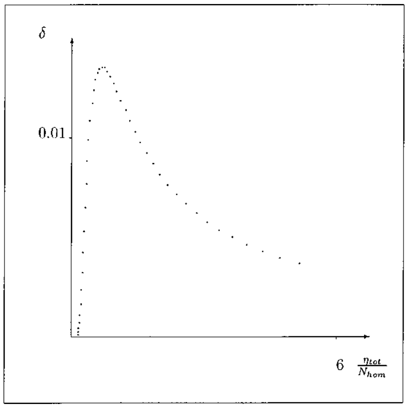

FIG. 11. Relative error of the quasihomogeneous approach in the third model.

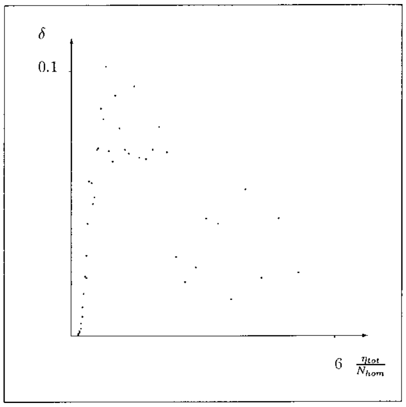

FIG. 12. Relative error of the quasihomogeneous approach in the universal simulation.

growth can be done as in [14]. The generalization is based on the similarity of the functional forms obtained here and in the AA. This similarity lies at the base of the universality property formulated in [16,18].

One can see that the theory of condensation with profiles taken into account presents a picture that is quite different from the AA. Nevertheless, in many situations the result of experiment coincides with the result of the AA. One has to explain this coincidence although it is a rather formal one. In any experiment it is more convenient to have a small system and to get many droplets. The rate of nucleation has to be taken as a rather high one. So the supersaturation is relatively high and the parameter $\sigma^{-1}$ is not a real small parameter of the theory.[29] Thus as shown in [18] the AA gives the correct qualitative result despite the wrong basis of consideration. The reason lies in the fact that at small $\sigma$ most of the material is in the tail of the profile. The tail of the profile is rather thin and can be taken into account by the AA. The correction term for the AA at small $\sigma$ can also be found in [18].

An important feature to mention is the movement of the embryo boundaries. This problem has been widely discussed in the determination of the rate of regular growth for supercritical embryos. In different systems the effect of the boundary movement on the rate of growth is different. We note that in the theory presented here the rate of the embryo growth is an external value which is supposed to be known.[30]

Another problem is to take adequate account of the effect of boundary movement in the method of constructing the ER. If part of the volume is occupied by the liquid phase of the given embryo, one cannot use the Green function of an empty space in an absolutely precise manner. In the first part of this paper we already showed that the effect is small. Here we shall present abstract arguments for this conclusion.

To use the thermodynamic approach the initial power of the mother phase metastability has to be relatively small. Together with the Maxwell rule this leads to the following final result for the phase transition: Only a relatively small part of the system volume is occupied by the new phase. This is not in contradiction with the property that the whole volume is occupied by ER's. The final state of the system is an essentially saturated mother phase and a small volume (distributed over the whole system) occupied by a new phase. As a result one can see that the process of substance consumption (extraction) leads to saturation in a volume relatively large in comparison with the volume of the new embryo phase. The mother phase cannot be undersaturated (then the embryos would disappear). Since even the mother phase has to be spread over almost all the volume of the system, the mean distance between two neighboring embryos of the new phase is many times greater than the mean size of the embryo. Thus one can state that the embryo produces an effective perturbation over relatively large distances in comparison with the size of the embryo. To have an interruption (a relative interruption in comparison with the ideal nucleation rate) of the new phase formation, one needs a very small reduction of the power of metastability.[31] This reduction can be attained only at distances which are very large in comparison with the embryo linear size.[32] Thus one can use the point source approximation as was done in the first part of this paper and forget about the boundary movement.[33] The negligible character of the boundary movement is now proved for all possible systems.

The heat extraction and account of all other intensive parameters of the description can be performed as in [6].

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[29] It is not necessary for the consideration presented here, but it has to be small for a thermodynamic description of the critical embryo.

[30] It is really known for essentially all systems.

[31] The relative reduction has to be $\Gamma^{-1}$ where $\Gamma \gg 1$ is the scale of the number of molecules in the critical embryo.

[32] Because the profile is sharper than in the stationary solution.

[33] The effect of the boundary movement on the embryo growth rate is taken into account as an external parameter.

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# Heterogeneous condensation on the centers with continuous activity in dynamic conditions

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**Abstract**

A system with a metastable phase and a pseudo continuous set of the heterogeneous centers is considered. An analytical theory for kinetics of the process of condensation in such a system is constructed. The free energy of formation of the critical embryo is assumed to be known in the capillary (macroscopic) approach as well as the solvatation energy of the embryo. The theory is based on the quasistationary approximation for the nucleation rate which has been justified analytically. An effective iteration procedure is presented. The iterationa are calculated analytically. The approximate universal form of the spectrum is established.

# 1 Introduction

The theory considered here completes the program of construction of the theory of the aerosol formation announced in [14]. It will be based on the capillary approximation of the height of the activation barrier. This approximation lies in the base of the classical theory of the homogeneous nucleation. All necessary bibliographic remarks can be found in [14].

Speaking about the activity of the heterogeneous centers we mean that the different activity initiates the different height of the activation barrier $\Delta F$, i.e. the difference between the free energy of the critical embryo $F_c$ and the free energy of solvatation $G$. The set of the different activities of the heterogeneous centers can be so dense that we can regard it as the pseudo continuous one. In the case of the "solid nucleus of condensation with the weak interaction" the continuous size of the nucleus ensures the continuous set of $\Delta F$.

The ordinary external conditions for the phase transition have the smooth character in time. The external action on the system leads to formation of the droplets of the new phase. The process of condensation violates the thermodynamic parameters of the system. When the external action on these parameters has the smooth behavior in time we shall say that condensation occurs under the dynamic conditions.

Nevertheless the theory of the heterogeneous condensation in the dynamic conditions has been constructed only for one type of the heterogeneous centers. So, the task to construct the kinetic theory for the system with a continuous set of the heterogeneous centers is rather essential. It will be completely fulfilled here.

We shall use the physical assumptions analogous to [14] which are necessary to construct the mathematical model:

- the thermodynamic description of the critical embryo,
- the random homogeneous space distribution of the heterogeneous centers,
- the free-molecular regime of the droplets growth,
- the homogeneous external conditions for the temperature and for the pressure,

- rather a high activation barrier.

As far as the most interesting characteristics of this process are the numbers of the heterogeneously formed droplets on the centers with a different activity we shall estimate the accuracy of the theory by the error of the obtained solutions for these values[1]. The unit volume is considered. All energy-like values are measured in the thermal units.

The publication has the following structure:

- In the first part the system of the equations of condensation is constructed.
- In the second part the explicit calculation of the iterations is presented.
- In the third part the conception of the universal spectrum is developed.
- In the last part some realistic spectrum of activities is considered and the principle of the self-consistency of the spectrum of the activities is presented.

We shall define the activity of the heterogeneous center as some parameter $w$ which is proportional to the height of the activation barrier

$$\Delta F(w) = \Delta F \mid_{w=0} - \lambda w \tag{1}$$

with some positive coefficient $\lambda$. Note that the choice of the initial point $w = 0$ is rather arbitrary now. We suppose $\Delta F(w) \gg 1$ for all essential types of the heterogeneous centers[2].

The total number of the heterogeneous centers with the given activity $w$ will be marked by $\eta_{tot}(w)$. Naturally $\eta_{tot}(w)$ is rather a smooth function of $w$. We shall suppose that $\eta_{tot}$ in the essential region is near some constant value or it can be well approximated by the polinom which power isn't too high. This value is constant in time.

The density of the molecules in the equilibrium vapor is marked by $n_\infty$, the density of the molecules in the real vapor is marked by $n$. The power of the metastability will be characterized by the value of the supersaturation

$$\zeta = \frac{n - n_\infty}{n_\infty}$$

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[1] But not for the total number of the droplets.

[2] When this condition is violated the kinetics of the process can be described by the trivial modification of the theory presented below.

We shall define the super-critical embryos as the "droplets". Every droplet is described by the number of the molecules $\nu$ , or by the linear size

$$\rho = \nu^{1/3}$$

Due to the free-molecular regime of the droplets growth we have

$$\frac{d\rho}{dt} = \zeta \alpha \tau^{-1}$$

where $\alpha$ is the condensation coefficient and $\tau$ is some characteristic time between the collisions in the saturated vapor obtained from the gas kinetic theory.

Let us introduce the size $z$ according to

$$z = \int_{t_*}^{t} \zeta \alpha \tau^{-1} dt' \tag{2}$$

Here $t_*$ is some characteristic moment of time which belongs to the period of the intensive formation of the droplets. The choice of $t_*$ is rather arbitrary. One can use for example the choice described in [8]. Until the beginning of the coalescence [3],[4] which isn't considered here equation (2) ensures the growth of $z$ in time and can be inverted

$$t(z) = \int_0^z \tau \alpha^{-1} \frac{dx}{\zeta(x)} + t_* \tag{3}$$

Hence, all values dependent on time become the values dependent on $z$ and the relative size

$$x = z - \rho$$

can be introduced. During the whole evolution the droplet has one and the same value of the variable $x$. Considering $t(x)$ as the moment when the droplet with the given $x$ has been formed (as a droplet) we can consider all functions of time as the functions of $x$ . Hence, we can see that the kinetic equation is reduced to the fact that every droplet keeps the constant value of $x$. To reconstruct the picture of the evolution one must establish the dependencies $t(z)$ and $\zeta(x)$.

The values at the moment $t_*$ will be marked by the lower index "*". The positions of the region of the intensive formation of the droplets are essentially different. But one can introduce $t_*$ as the moment corresponding to the maximum af the supersaturation.

## 2 The system of the equations of condensation

We shall mark by the argument $\infty$ the total values of the magnitudes formed during the whole condensation process.

Introduce the value of
$$\zeta_{ideal} = \frac{n_{tot}}{n_\infty} - 1$$
where $n_{tot}$ is the total number of the molecules in the system.

We must take into account the reduction of $\zeta_{ideal}$ to some value $\Phi$ due to the consumption of the vapor molecules in the process of solvatation [9] [10] [11]. Moreover, according to [11] the ideal supersaturation can be changed by the external supersaturation. In any case we shall assume this value as the known one and mark it by $\Phi$. In some rough approximation $\zeta_{ideal} \approx \Phi$.

We shall mark by $\eta^{tot}$ the total number of the heterogeneous centers of all types:
$$\eta^{tot} = \int dw \eta_{tot}(w) \qquad (4)$$
where $\eta_{tot}(w)$ is the total number of the heterogeneous centers of the given type (the density of the total value of the heterogeneous centers).

The following statements are valid in the further consideration:

- (1) The main role in the vapor consumption during the evolution is played by the super-critical embryos, i.e. by the droplets.
- (2) The quasistationary approximation for the nucleation rate is valid during the period of the essential formation of the droplets for those sorts of the heterogeneous centers which aren't completely exhausted in this process.

The justification of the second statement[3] uses the estimate for times $t_i^s$ of the relaxation to the stationary state in the near-critical region which can be found in [1], [5] (for the investigation of the heterogeneous barrier the consideration is the same one).

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[3] The second statement isn't valid for those sorts of the heterogeneous centers which are going to be completely exhausted. But there the result is obvious. Note that the periods of the intensive formation of the droplets on the centers with the different activities don't coincide.

Let $f_s$ be the stationary value of the distribution of the sizes of the heterogeneously formed droplets measured in the units of $n_\infty$. It can be presented in the following form

$$f_s = f_\zeta(\zeta(x), w)\eta(x, w) \tag{5}$$

where $\eta(x, w)$ is the density on activities of the number of the heterogeneous centers which are free from the super-critical embryos and $f_\zeta$ is given by the following formula [6]

$$f_\zeta = \frac{W_c^+ \exp(-\Delta F(\zeta, w))\tau}{\pi^{1/2}\Delta_e\nu\Delta_c\nu\zeta\alpha n_\infty} \tag{6}$$

where $W^+$ is the number of the molecules in the vapor which interact with the droplet in the unit of time, $\Delta_e\nu$ is the width of the equilibrium distribution

$$\Delta_e\nu = \sum_{\nu=1}^{\nu=(\nu_c+\nu_e)/2} \exp(-F(\nu) + G)$$

and $\Delta_c\nu$ is the halfwidth of the near-critical region

$$\Delta_c\nu = \frac{2^{1/2}}{\mid (\frac{\partial^2 F}{\partial \nu^2})_{\nu=\nu_c} \mid^{1/2}}$$

Index "$c$" marks the values for the critical embryo and "e" - the values for the equilibrium embryo. Certainly, $\Delta_c\nu$ and $\Delta_e\nu$ are some smooth functions of $w$ and we shall neglect this dependence.

We shall mark by $n_\infty g(w)$ the density of the distribution on activities of the total number of the molecules of the condensated substance in the heterogeneous droplets formed on the centers of the activity $w$. To simplify the formulas we shall use

$$\theta(w) = \eta(w)/\eta_{tot}(w)$$

We obtain for $g_i, \theta_i$ the following equations

$$g(z, w) = \int_{-\infty}^{z} (z - x)^3 f_\zeta(\zeta(x), w)\eta(w)dx \tag{7}$$

$$\theta(z, w) = \exp(-n_\infty \int_{-\infty}^{z} f_\zeta(\zeta(x), w)dx) \tag{8}$$

As far as we measure the accuracy of the theory in the terms of the error in the droplets number we define these values as the following ones:

$$N(z,w) = \eta_{tot}(w)(1-\theta(z,w)) \tag{9}$$

The total number of the droplets is

$$N^{tot} = \int \eta_{tot}(w)(1-\theta(z,w))dw = \int N(z,w)dw \tag{10}$$

For the majority of the types of the heterogeneous centers the following approximations of the nucleation rates are valid during the period of the essential formation of the droplets[4]

$$f_\zeta(\zeta(x),w) = f_\zeta(\Phi_*,w)\mid_{w=0} \exp(\Gamma\frac{(\zeta-\Phi_*)}{\Phi_*})\exp(w\lambda) \equiv f_{\zeta\ *}\exp(\Gamma\frac{(\zeta-\Phi_*)}{\Phi_*})\exp(w\lambda) \tag{11}$$

where

$$\Gamma = -\Phi_*\frac{d\Delta F(\zeta)}{d\zeta}\mid_{\zeta=\Phi_*}\mid_{w=0} \tag{12}$$

$$f_{\zeta\ *} = f_\zeta(\Phi_*,w)\mid_{w=0}$$

and $\Delta F$ is the height of the heterogeneous activation barrier[5]. The validity of these approximations can be justified for the heterogeneous embryos with the interaction between the center and the molecules of the condensated phase weaker or equal than the reciprocal to the space distance. So, we can imagine this as a hard sphere with a weak interaction on which the embryo is formed.

The dependence of $\Gamma$ on $w$ is rather weak. So we can put

$$\Gamma(w) = \Gamma\mid_{w=0} \tag{13}$$

for any essential part of the spectrum of the activities. The applicability of the last approximation is based on the following qualitative model. It

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[4] Note that the position of the regions of the intensive formation of the droplets on some sort essentially depends on the activity of the centers. the following approximation isn't valid for the regions of the intensive formation on the active centers. But for these centers the result is evident - all centers are going to become the centers of the droplets.

[5] The validity of these approximations may fail in the situations of the extremely long spectrums (see later). But the square form of the behavior of the supersaturation near the maximum will be attained earlier.

is known that $\Gamma$ is approximately $\Phi_*(\nu_c - \nu_e)/(\Phi_* + 1)$. When the supersaturation is sligtly changed then the value of $\nu_e$ doesn't undergo some big variations and the variation of $\Gamma$ occurs mainly due to the variation of $\nu_c$. The behavior of the value $\nu_c$ resembles the analogous behavior in the homogeneous case. As a result we can justify not only the approximation concerning the dependence on the supersaturation, but also the dependence on the activity.

A natural question about the essential part of the spectrum appears here. The process of condensation on the centers with some relatively high activity occurs earlier than the supersaturation attains maximum. These centers form the droplets which can be included in the value of the external supersaturation in the manner of [11] [16]. For these centers the number of the formed droplets coincides approximately with the number of the heterogeneous centers - all centers are now the centers of the droplets.

The action of this part of the spectrum on the further evolution can be treated in the terms of the external supersaturation $\Omega$ (see [11]). The nontrivial statement that the process of formation of the droplets on the centers with the intermediate activity occurs near the maximum of the supersaturation lies in the base of such a method of description. This fact can be analytically proved.

The centers with some relatively low activity remain practically unexhausted (when the spectrum $\eta_{tot}$ has no singularities they can not play any important role in condensation). The singularities can be described in this region in a manner from [11] [16]. So only some centers with the intermediate activity are essential near the maximum of the supersaturation. In the scale of the activities this region corresponds to the variation of $w$ by the value of the order of $\lambda^{-1}$.

Now we shall formulate the system of the balance equations for the functions $g(x, w)$, $\theta(x, w)$ and

$$G(x) = \int dw g(x, w)$$

where the integral is taken over the whole spectrum of the heterogeneous centers. In principle we can write that the region of integration goes from $-\infty$ up to $\infty$ but in fact this integration must be carried out in the region which covers the essential region of the spectrum[6]. In this region it is necessary to

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[6] The extraction of this region is quite analogous to the case of the decay on the spectrum of activities.

have relatively smooth behavior of $\eta_{tot}$. This value must be approximately constant

$$\eta_{tot} \approx const$$

or must be well approximated by the polinom on the activities:

$$\eta_{tot} = P_n(w)$$

We assume the total number of the heterogeneous centers to be constant in time.

Using the conservation laws for the heterogeneous centers and for the molecules of the condensing substance we get for $g, \theta$ the following equations

$$g(z,w) = f_* \int_{-\infty}^{z} (z-x)^3 \exp(-\Gamma \frac{\zeta - \Phi_*}{\Phi_*}) \theta dx \exp(w\lambda) \qquad (14)$$

$$G(z) = \int dw g(z,w) \qquad (15)$$

$$\theta(z,w) = \exp(-\frac{f_* \exp(\lambda w) n_\infty}{\eta_{tot}} \int_{-\infty}^{z} \exp(-\Gamma \frac{\zeta - \Phi_*}{\Phi_*}) dx) \qquad (16)$$

$$\Phi = \zeta + G(z) \qquad (17)$$

where $f_* = f_{\zeta\ *} \eta_{tot}$

These equations form the closed system of the equations for condensation kinetics. This system will be the subject of our investigation.

We shall consider this system of equations during the period when the centers with the intermediate activity are going to become the centers of the droplets. We shall call this period as the period of the intensive formation of the droplets (PIFD).

We assume that the ordinary [8] linearization of the ideal supersaturation is valid during PIFD[7]

$$\Phi(x) = \Phi_* + \frac{\Phi_*}{\Gamma} c x \qquad (18)$$

---

[7] One can analytically show that the duration if PIFD is rather short. Namely

$$\frac{\Phi(z) - \Phi_*}{\Phi_*} \leq \frac{1}{\Gamma}$$

with some positive parameter $c$.

After the substitution of this linearization into the system of the condensation equations this system transfers to

$$g(z,w) = f_* \int_{-\infty}^{z} (z-x)^3 \exp(cx - \frac{\Gamma}{\Phi_*} G(x)) \theta(x,w) dx \exp(w\lambda) \tag{19}$$

$$G(z) = \int dw g(z,w) \tag{20}$$

$$\theta(z,w) = \exp(-\frac{f_* \exp(\lambda w) n_\infty}{\eta_{tot}} \int_{-\infty}^{z} \exp(cx - \frac{\Gamma}{\Phi_*} G(x)) dx) \tag{21}$$

The spectrum of sizes can be found as the following one

$$f(x,w) = f_* \exp(\lambda w) \exp(-\Gamma \frac{\zeta - \Phi_*}{\Phi_*}) \theta(x,w) \tag{22}$$

and when the linearization is taken into account:

$$f(x,w) = f_* \exp(\lambda w) \exp(cx - \frac{\Gamma}{\Phi_*} G(x)) \theta(x,w) \tag{23}$$

# 3 Iteration procedure

Such systems as the already obtained one can be solved by the iteration procedure. It can be constructed by the following way: For the initial approximations we choose:

$$g_0(z,w) = 0 \qquad \theta_0(z,w) = 1 \tag{24}$$

The recurrent procedure is defined according to

$$g_{i+1}(z,w) = f_* \int_{-\infty}^{z} (z-x)^3 \exp(cx - \frac{\Gamma}{\Phi_*} G_i(x)) \theta_i(x,w) dx \exp(w\lambda) \tag{25}$$

$$G_i(z) = \int dw g_i(z,w) \tag{26}$$

$$\theta_{i+1}(z,w) = \exp(-\frac{f_* \exp(\lambda w) n_\infty}{\eta_{tot}} \int_{-\infty}^{z} \exp(cx - \frac{\Gamma}{\Phi_*} G_i(x)) dx) \tag{27}$$

The chains of inequalities analogous to [7] guarantees the convergence of the iterations and some estimates analogous to [7] can be established here.

The direct calculation of the iterations gives

$$g_1(z,w) = f_* \frac{6\exp(cz)}{c^4} \exp(\lambda w) \tag{28}$$

$$\theta_1(x,w) = \exp(-f_{\zeta\ *} n_\infty \exp(\lambda w) \frac{\exp(cx)}{c}) \tag{29}$$

$$G_1(x) = f_{\zeta\ *} \frac{6\exp(cx)}{c^4} \int dw \exp(\lambda w) \eta_{tot} \tag{30}$$

The last integral causes some problems with convergence. When $\eta_{tot} = const$ it can not be calculated. At least there are two possibilities to overcome this difficulty.

The first possibility is a more formal one. Certainly, in every system $\eta_{tot}(w) = 0$ when $w$ is greater than some maximum value $w_{max}$. So, formally the integral exists and it is equal to some constant. This constant is generally unknown, but one can act in the manner like it was done with the supersaturation in [8]. In [8] the value of $\Phi_*$ was not the matter of consideration in the iteration method, but was included in the set of the undefined parameters. After the final form of the size spectrum was established an equation on parameters was studied. The form of the spectrum can play a role of some ansatz with several parameters. The same procedure can be inserted here. The reason is that we can observe the separation of the functions containing $w$ from the terms containing the other parameters of the condensation process. This fact remains valid also in the second iteration which is rather a good approximation for the final solution as it can be analytically proved on the base of the analysis of the iteration procedure.

The second possibility seems to be more physical one because it allows to combine the current problem with the problem of the correct definition of the region of rather active and exhausted centers. Really we have not separated the region included into the external supersaturation from the region which isn't included into the external supersaturation. Note, that in the dynamic conditions the spectrum of sizes of the droplets formed on some fixed sort of the heterogeneous centers has well defined boundaries. The sizes (and the times of formation) of the droplets which are essential in the vapor consumption can be also well localized. Namely, the spectrum is essentially situated in the region

$$-\frac{1}{c} \le z \le \frac{1}{c} \tag{31}$$

and the region of the droplets essential for the vapor consumption during PIFD is essentially covered by the interval[8]

$$-\frac{8}{c} \leq z \leq 0 \tag{32}$$

As a result one can state that for $z \sim -a/c$ where $a \sim 8$ one can get the start of PIFD for the centers which are in the process of nucleation near the maximum of the supersaturation.

Note that the moment $t_*$ can be taken as a moment of the maximum of the supersaturation. Really, when the maximum of intensity of formation (or the moment of formation of the half of the droplets) lies far from maximum of the supersaturation, then the result of nucleation of this sort of centers is rather obvious: the supersaturation is equal to the ideal (or external) supersaturation

$$\zeta = \Phi$$

the total number of the droplets is equal to the total number of the heterogeneous centers

$$N_{tot} = \eta_{tot}$$

and the moment of formation of the spectrum on the centers of some fixed sort which can be considered as a monodisperse one can be found from

$$\theta(z, w) = 1/2$$

which is equivalent to

$$f_{\zeta\ *} \exp(\lambda w) n_\infty \exp(cz) = c \ln 2$$

where the first two terms can be changed by some slightly other amplitude of the spectrum and the parameter $c$ can be reconsidered as far as the derivative can vary.

The simplest regularization by the cut-off is the following one. We must substitute the value of $\eta_{tot}$ by the value $\eta_{init}$ calculated as

$$\eta_{init} = \eta_{tot}\theta(x = -a, w)$$

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[8] See the analysis of the second figure from [16].

after the calculation of $\theta(-a, w)$ which can be calculated on the base of the ideal supersaturation, i.e. in the first iteration. As far as

$$\theta_1(-a, w) = \exp(-f_{\zeta\ *} n_\infty \exp(\lambda w) \frac{\exp(-ca)}{c})$$

the value of $f_*$ must be changed by

$$f_* = f_{\zeta\ *} \eta_{tot}(w) \exp(-f_{\zeta\ *} n_\infty \exp(\lambda w) \frac{\exp(-ca)}{c})$$

# 4 Calculation of the iterations

Let us calculate the iterations. Then the expression for $G$ will be the following

$$G_1 = f_{\zeta\ *} \int_{-\infty}^{\infty} \eta_{tot}(w) \exp(\lambda w) \exp(-A \exp(\lambda w)) dw \frac{6 \exp(cz)}{c^4}$$

where

$$A = f_{\zeta\ *} n_\infty \frac{\exp(-ca)}{c}$$

When $\eta_{tot} = const$ the integral can be taken which leads to

$$G_1 = f_{\zeta\ *} \eta_{tot} \frac{1}{\lambda A} \frac{6 \exp(cz)}{c^4}$$

Note that the integral can be taken in the final limits which allows to take into account only the finite region of activities as far as an approximation of the total number of heterogeneous centers by the composition of the Heavisaid's functions.

When $\eta_{tot}$ is approximated by the polinom it is easy to note that each monom in the integral leads to some elementary functions with some universal constants. This fact can be seen from the simple translation of the variable in

$$\int_{-\infty}^{\infty} w^m \exp(\lambda w) \exp(-A \exp(\lambda w)) dw$$

to the variable

$$\lambda w + \ln(A)$$

Here the integration must be fulfilled in the infinite limits. These integrals can be expressed through $\Psi$-function and its derivatives when the argument is put to 1.

The second approximation for $\theta$ leads to the following result:

$$\theta_2(z,w) = \exp(-f_{\zeta\ *} n_\infty \exp(\lambda w) \int_{-\infty}^{z} \exp(cx - B\exp(cx))dx)$$

where

$$B = \frac{\Gamma}{\Phi_*} f_{\zeta\ *} \frac{6\eta_{tot}}{c^4} \frac{1}{\lambda A}$$

Note that the integral can be taken here also in the finite limits. After the integration we get

$$\theta_2(z,w) = \exp(-f_{\zeta\ *} n_\infty \exp(\lambda w) \frac{1}{cB}(1 - \exp(-B\exp(cz))))$$

Note that $\eta(w) = \eta_{init}(w)\theta(z,w)$.

Particularly, for the final values one can get

$$\theta_2(\infty,w) = \exp(-f_{\zeta\ *} n_\infty \exp(\lambda w) \frac{1}{cB}) \tag{33}$$

This value of $B$ is obtained in the approximation $\eta = const$. For the further consideration only the analytical structure of $B$ is important. Namely, in any case (and also in the case $\eta_{tot}(w) = P_n(w)$) we have for $G$ the expression with the following analytical structure

$$G_1 \sim const(z,w)\exp(cz)$$

So, $B$ is some constant and this fact ensures the possibility of the further calculation of the iterations.

The next step is the calculation of the total number of the droplets appeared in the considered period which can be done by the simple integration

$$N^{tot} = \int_{-\infty}^{\infty} dw N_{tot}(w)$$

Note that instead of

$$N^{tot} = \int_{-\infty}^{\infty} dw \eta_{tot}(w)(1 - \theta_2(\infty,w))$$

which can not be integrated we must take

$$N^{tot} = \int_{-\infty}^{\infty} dw \eta_{init}(w)(1 - \theta_2(\infty,w))$$

which gives the integral with no problems of convergence. To calculate the last integral note that

$$\theta_2(-a,w) = \exp(-f_{\zeta\ *} \exp(\lambda w) n_\infty \int_{-\infty}^{-a} \exp(cx - \frac{\Gamma}{\Phi_*} G) dx)$$

Consider now the case $\eta_{tot} = const$. After the evident renormalization of the variables of integration the integral can be reduced to $\int_{-\infty}^{\infty} \exp(-\exp(x))(1-\exp(-H\exp(x)))dx$ where $H$ is some constant. This value can be approximately calculated by the following procedure. Decompose the internal exponents and get

$$\int_{-\infty}^{\infty} \exp(-\exp(x))(1-\exp(-H\exp(x)))dx =$$
$$\int_{-\infty}^{\infty} \frac{1}{\sum_{i=0}^{\infty} \frac{\exp(ix)}{i!}} (1 - \frac{1}{\sum_{i=0}^{\infty} \frac{\exp(ix) H^i}{i!}}) dx = \tag{34}$$
$$\int_0^{\infty} \frac{\sum_{i=0}^{\infty} \frac{y^i H^{i+1}}{(i+1)!}}{\sum_{i=0}^{\infty} \frac{y^i}{i!} \sum_{i=0}^{\infty} \frac{y^i H^i}{i!}} dy$$

Note, that it is necessary to left the serial in the denominator.

The necessary accuracy will be ensured by the first three terms in the decompositions of

$$\int_0^{\infty} \frac{\sum_{i=0}^{\infty} \frac{y^i H^{i+1}}{(i+1)!}}{\sum_{i=0}^{\infty} \frac{y^i}{i!} \sum_{i=0}^{\infty} \frac{y^i H^i}{i!}} dy \approx \int_0^{\infty} \frac{\sum_{i=0}^{2} \frac{y^i H^{i+1}}{(i+1)!}}{\sum_{i=0}^{3} \frac{y^i}{i!} \sum_{i=0}^{3} \frac{y^i H^i}{i!}} dy$$

Then an integral from the rational function can be simply calculated (also in the finite limits).

Now the integrals

$$I_j \equiv \int_0^{\infty} \ln^j y \frac{\sum_{i=0}^{\infty} \frac{y^i H^{i+1}}{(i+1)!}}{\sum_{i=0}^{\infty} \frac{y^i}{i!} \sum_{i=0}^{\infty} \frac{y^i H^i}{i!}} dy \approx \int_0^{\infty} \ln^j y \frac{\sum_{i=0}^{n-1} \frac{y^i H^{i+1}}{(i+1)!}}{\sum_{i=0}^{n} \frac{y^i}{i!} \sum_{i=0}^{n} \frac{y^i H^i}{i!}} dy$$

will be calculated. These integrals appear when the polynomial approximation for $\eta_{tot}$ is accepted.

Consider the function

$$f(y) = \ln^{i+1} y \frac{\sum_{i=0}^{n-1} \frac{y^i H^{i+1}}{(i+1)!}}{\sum_{i=0}^{n} \frac{y^i}{i!} \sum_{i=0}^{n} \frac{y^i H^i}{i!}}$$

as the function of a complex variable. Integrate this function along the closed path $\Omega$ constructed in the following manner: the big circumference with an infinite radius; two straight lines $]y+i0, \infty+i0[$, $]y-i0, \infty-i0[$; the little circumference with a zero radius. The integrals along the circumferences are going to the zero. The integrals along the straight lines give:

$$\int [\ln^{j+1} y - (\ln y + 2\pi i)^{j+1}] \frac{\sum_{i=0}^{n-1} \frac{y^i H^{i+1}}{(i+1)!}}{\sum_{i=0}^{n} \frac{y^i}{i!} \sum_{i=0}^{n} \frac{y^i H^i}{i!}} dy$$

which can be reduced to $I_j$ and $\sum_{k<j} e_k I_k$ with some known coefficients. On the other hand this integral can be reduced to

$$\sum res(\ln^{j+1} y \frac{\sum_{i=0}^{n-1} \frac{y^i H^{i+1}}{(i+1)!}}{\sum_{i=0}^{n} \frac{y^i}{i!} \sum_{i=0}^{n} \frac{y^i H^i}{i!}})$$

inside $\Omega$. As the result we have the recurrent procedure which allows us to calculate all $I_j$.

Now let us see how the corrections due to the cut-off can be introduced in the value of $g(z,w)$. In the first approximation we have:

$$g_1(z,w) = \frac{6f_*}{c^4} \exp(\lambda w)(\exp(cz) - \exp(-ca))$$

The value of $G_1$ in the approximation $\eta_{tot} = const$ is given by

$$G_1 = f_{\zeta\ *} \frac{6\eta_{tot}}{c^4} \frac{1}{A\lambda} (\exp(cz) - \exp(-ca))$$

Note that it can be calculated for the finite band of the spectrum of the activities. The calculation under the polinomial approximation for $\eta_{tot}$ can be done in the same manner.

Instead of the pre-exponential factor one can put some other function. The separation of this expression into two factors depended on $w$ and on $z$ is obvious.

For $\theta_2$ we get:

$$\theta_2(z,w) = \exp(-f_{\zeta\ *} n_\infty \exp(\lambda w) \int_{-\infty}^{z} \exp(cx - B(\exp(cx) - \exp(-ca)))dx)$$

and after the simple calculation:

$$\theta_2(z,w) = \exp(-f_{\zeta\ *} n_\infty \exp(\lambda w)\exp(B\exp(-ca))\frac{1}{cB}(1-\exp(-B\exp(cz))))$$

The final value is the following:

$$\theta_2(z,\infty) = \exp(-f_{\zeta\ *} n_\infty \exp(\lambda w)\exp(B\exp(-ca))\frac{1}{cB})$$

It differs from (33) only by the remormalisation of the amplitude thanks to $\exp(B\exp(-ca))$.

The value of $N^{tot}$ is calculated in the same manner.

Note that one can change $-\infty$ to $-a$ and repeat all calculations in the same manner.

The analytical estimates show that the second iteration gives rather a good approximation for the process. The reason is quite similar to [8]. Really, one can simply integrate all estimates from [8] to justify the validity of the obtained expressions.

Another important remark must be given. One can see that all obtained values have the separation of the expressions (or arguments of exponents) in two terms: the first one depended on $w$ and the second one depended on $z$. This reduction can not be observed in all high iterations. It is responsible for the absence of the cross influence of exhaustion of the heterogeneous centers with the different activity in the first iterations. The similar property is absent in the situation of decay [14], [15]. Here such a cross influence can be neglected because the equation on the parameters of condensation balances the time of formation with the characteristic intensity of formation and leads to the fact that the characteristic width of the size spectrum is always approximately equal to $\frac{1}{c}$. The probability to form the droplet on the center is always determined only by the supersaturation and by the value of activity (and not by the total number of centers of the given sort).

# 5 Universal solution

Now the problem of the construction of the universal solution will be considered. The idea of the universal solution [2] lies in the fact that after formation of the spectrum of the droplets the further evolution of the process depends only from the first three (and zero) momentums of the distribution function. So if one can choose some variables in which the solution (the distribution function) is the universal function (undepended on the parameters of the problem) then the expressions for the momentums have rather a simple analytical structure combining some parameters of the problem with the universal constants.

For the process of the homogeneous condensation the universal solution was obtained in [2]. For the process of the heterogeneous condensation the universal solution is absent, but some pseudo universal solution can be considered as the base for the further iterations [7].

We shall rewrite the system of the condensation equations in the terms of $\zeta$ and $\Phi$

$$\Phi_* + \frac{\Phi_*}{\Gamma} cz = \zeta + G$$

$$G = \int dw g(w)$$

$$g(w) = f_* \int_{-\infty}^{z} (z-x)^3 \exp(\frac{\Gamma}{\Phi_*}(\zeta - \Phi_*))\theta(w,x) dx \exp(\lambda w)$$

$$\theta(w) = \exp(-f_{\zeta\ *} n_\infty \exp(\lambda w) \int_{-\infty}^{z} \exp(\frac{\Gamma}{\Phi_*}(\zeta - \Phi_*)) dx)$$

Introduce the function

$$\delta = \frac{\Gamma}{\Phi_*}(\zeta - \Phi_*)$$

Then after the substitutions

$$\lambda w \to w$$

$$px \to x$$

$$\frac{\Gamma}{\Phi_*} G \to G$$

$$\frac{\Gamma}{\Phi_* \lambda} g \to g$$

one can get

$$\frac{c}{p} z = \delta + G$$

$$G = \int dw g(w)$$

$$g(w) = \frac{f_* \Gamma}{\lambda \Phi_* p^4} \int_{-\infty}^{z} (z-x)^3 \exp(\delta) \theta(w,x) dx \exp(w)$$

$$\theta(w) = \exp(-f_{\zeta\ *} \frac{n_\infty}{p} \exp(w) \int_{-\infty}^{z} \exp(\delta) dx)$$

Let us choose $p$ as

$$\frac{f_* \Gamma}{\lambda \Phi_* p^4} = 1$$

and now there are no parameters in the expression for $g$. If the moment of $t_*$ is chosen as the moment when the supersaturation attains the maximum, then

$$\frac{c}{p} = \int dw 3 \int_{-\infty}^{z} (z-x)^2 \exp(\delta) \theta(w,x) dx \exp(w)$$

Then

$$f_{\zeta\ *} \frac{n_\infty}{p} = \frac{f_*^{3/4} n_\infty \lambda^{1/4} \Phi_*^{1/4}}{\eta_{tot} \Gamma^{1/4}}$$

An ordinary and natural condition to establish the zero point of activity can be written as the following one:

$$\theta(w=0, z=\infty) = \frac{1}{2}$$

which gives

$$f_* \frac{n_\infty}{p} = \frac{\ln 2}{\int_{-\infty}^{\infty} \exp(\delta(x)) dx}$$

and there are no parameters in the last equation.

As the result there are no parameters in the system of the condensation equations and the solution has the universal form. It can be analytically proved that it is a unique solution. All consequences now coincides with analogous conclusions from [2]

Note that there is a property of a very smooth dependence of the number of droplets on the $f_*$. So we can get the equation on the parameters of the process in some rough approximation (see the iteration procedure) and then use the universal law.

The last model has the evident disadvantage. The equation for $G$ demonstrates no convergence. Really, we can substitute the expression for $g$ into the expression for $G$ and fulfil the integration over $w$. Then we come to

$$G = A_{00} \int_{-\infty}^{z} (z-x)^3 \frac{\exp(\delta(x))}{\int_{-\infty}^{x} \exp(\delta(x')) dx'} dx$$

where

$$A_{00} = \frac{f_* \Gamma}{\lambda \Phi_* p^3 n_\infty f_{\zeta\ *}}$$

The evident necessary asympote $G \rightarrow 0$ when $z \rightarrow -\infty$ leads to $\delta(z) \rightarrow \frac{c}{p} z$ when $z \rightarrow -\infty$. Then the exponents can be cancelled and the subintegral expression has the asymptote $(z-x)^3$ which doesn't ensure the convergence. Then we need some regularizations. The most evident one is to notice that after the process of any appearing of the droplets the constant value of $\eta$ transforms into

$$\eta_{new} = \eta_{old} \exp(-Q \exp(w))$$

where $Q$ is some constant.

We shall use this value as the initial one and after the analogous transformations we can come to

$$G = \frac{f_* \Gamma}{\lambda \Phi_* p^4} \int_{-\infty}^{z} (z-x)^3 \frac{\exp(\delta(x)}{Q + \frac{f_* n_\infty}{p} \int_{-\infty} z \exp(\delta(x')) dx'} dx$$

The coefficient $\frac{f_* n_\infty}{p}$ can be made equal to some constant (may be 1) due to the choice of the scale of activities. This choice states some concrete value of $Q$ (which has the same dependence on the choice as $\frac{f_* n_\infty}{p}$ has). The limit $Q \rightarrow 0$ corresponds to the already observed situation. Now we have more general equation taking into account the power of the previous deformation of the activity spectrum. Evidently the solution depends on the parameter $Q$ and isn‘t universal. We see the further inclusion of the distribution into some more general set of the solutions for the various powers of the deformations of the spectrums by the previous nucleation.

Due to the problems of convergence for $Q = 0$ we must describe the form of the spectrum explicitly. We are going to show that the size spectrum has the universal character.

When $Q$ is going to zero the region where $Q$ is unessential starts at $z_l$ corresponding to

$$\int_{-\infty}^{z_l} \exp(\delta(x)) dx \sim (p/c) \exp(c z_l / p) \approx Q$$

and becomes larger. The asymptote $(z-x)^3$ of the subintegral expression is attained from $z_l$ till some $z$ with no respect to $Q$. So, the asymptotic region becomes larger. Certainly, we can integrate the asymptote explicitly and come to $(z - z_l)^4/4$. Only due to the linear size this asymptote provides the main quantity of the substance in the droplets. As a result we have the following expression for the behavior of $f_\zeta$

$$f_\zeta \sim \exp(z - \alpha(z - z_l)^4)$$

where the scale of $z$ is chosen to put $c/p = 1$ and $\alpha$ is some constant. The value of $\alpha$ can be determined from the requirement that *max* $f_{\zeta\ *}$ (the maximum of the supersaturation) is attained at $z = 0$. Then

$$\alpha = -z_l^{-3}/4$$

The expression for $f_{\zeta\ *}$ can be presented in the following form

$$f_{\zeta\ *} \sim \exp(-\alpha z_l^4) \exp(-(z/\Delta)^2) \exp(-4\alpha z^3 |z_l|) \exp(-\alpha z^4)$$

where $\Delta$ is the characteristic halfwidth

$$\Delta = (2|z_l|/3)^{1/2}$$

One can see that at the characteristic scale $z \approx \Delta$ the arguments of the third and the forth exponents have the characteristic values $z_l^{-1/2}$ and $z_l^{-1}$ respectively. Thus, these terms can be neglected and the form of $f_{\zeta\ *}$ is the gaussian one:

$$f_{\zeta\ *} \sim \exp(-(z/\Delta)^2)$$

and it has no parameters after the evident rescaling[9] $z \to z/\Delta$. So, we see that the universal gaussian form of $\exp(\delta)$ ensures the universal expression for $\theta$

$$\theta = \exp(-\exp(w) \frac{\ln 2}{\sqrt{\pi}} \int_{-\infty}^{z} \exp(-x^2) dx)$$

This universal form will be attained earlier then $Q = 0$ (where the property of convergence disappears) and has the true physical sense.

Figure 1 shows the forms of the size spectrums in some different situations presented in the normalized coordinates. The curves "a", "b", "c", "d" are the solutions of the following equation

$$z = A_1 \int_{-\infty}^{z} (z - x)^3 \frac{\exp(\delta(x))}{Q + \int_{-\infty}^{x} \exp(\delta(x')) dx'} dx$$

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[9] This rescaling excludes the unphysical parameter $z_l$.

for the different values of $Q$ ( "a" : $Q = 10$ "b" : $Q = 1$ "c" : $Q = 0.001$ "d" : $Q = 0.0001$ ). The curve "a" practically coincides with "b", the curve "c" practically coincides with "d" for all $x$. The curve "e" is the spectrum of the gaussian type $\exp(-x^2)$. The curve "f" is the universal form of the first iteration $\exp(x - \exp(x))$ after the renormalization in order to have the same position of the maximum of the curve and to conserve the integral over the spectrum. This curve practically coincides with "a", "b" but only for the negative values of the argument.

One can prove that for all possible values of $Q$ the spectrum lies between the first iteration and the Gaussian spectrum. It can be seen that the difference between the first iteration and the Gaussian curve is rather small (less than 0.2) and lies in the frames of the accuracy of the modern experiment[10]. Note that the value of $A_1$ must be chosen to ensure the position of the maximum of the supersaturation near $max\ \delta = 0$. For $Q \rightarrow 0$ the quantity of the substance in the droplets isn't small due to the known power asymptote and one have to remove the choice of $t_*$ from the previous condition that the $max\ \delta$ is attained at $z = 0$ to the new condition $max\ \delta = 0$. In the concrete calculations one needn't to fulfil this condition precisely but only in a very approximate way as far as the form of the spectrum doesn't change essentially for the different choice of the $max\ \delta$ near zero. This property can be shown analytically and is illustrated by Figure 2.

Figure 2 demonstrates the weak dependence of the form of spectrum on the choice of the base point for the linearizations, i.e. the choice of $t_*$. This property is important for the justification of the conception of the universal spectrum and can be proved analytically. This property is also necessary for the simplification of the numerical calculations. For $Q = 10$ the two values of $A_1$ have been chosen. This corresponds to the different manners of the choice of $t_*$ or the choice of $max\ \delta$. Two curves for $\delta$ for different $A_1$ are shown in the part "a" of this illustration. The upper curve corresponds to $A_1 = 0.5$, the lower curve - to $A_1 = 1$. In the part "b" the size spectrums for these situations are drawn in the normalized coordinates. They coincide and one can see only one curve drawn in the part "b".

Note that the limit $Q \rightarrow 0$ is analogous to the situation of the "wide spectrum" considered in [15]. Here we have some additional difficulties. These

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[10] This ensures the weak sensitivity to the choice of the parameter $a$. It is necessary to the self-consistency of the presented theory.

difficulties appear from the asymptote $(z-x)^3$ for the subintegral expression. As a result the relative quantity of the substance in the droplets is greater than $\Gamma^{-1}$, the spectrum is going to be formed during the period with duration essentially longer than $c^{-1}\tau/\zeta$, the quasistationary approximation isn't valid during all the period of the droplets formation. So, one has to reconsider the approximations which form the base of the concrete constructions.

The simplification goes from the asymptote $(z-x)^3$. Really, this asymptote doesn't depend on the concrete form of the free energy and the derivatives of the free energy. So, the quasistationarity and exponential approximation (11) aren't so essential (they are going to fail namely at this asymptote). The big quantity of the substance in the droplets require to reconsider the condition of the choice of $t_*$ as it is done above. The essential duration of the period of the droplets formation may lead to some new approximations and, thus, change the form of the asymptote $(z-x)^3$. But the consideration of the process remains quite analogous to the already fulfilled one. One of such examples is given in the next section.

The opposite situation corresponds to the validity of the iteration procedure with the ideal supersaturation taken as the external one[11]. Note that the final results for $\theta$ and for the spectrum are obtained (in the second approximation) on the base of the supersaturation calculated without the appropriate account of the exhaustion of the centers, i.e. in the pseudohomogeneous situation. The same situation occurs when we study the condensation on the separate sort of the heterogeneous centers [8], [7]. This analogy leads to the three important consequences. To establish the first one note that the "pseudohomogeneous" base for the final results evidently has some universiality. In [7] the universiality can be broken by the change of the regime of the consumption of the vapor by the droplets. The result of [8] is more approximate, but it is based on the form of the first iteration which can not be depended on the regime of the vapor consumption. So, the universiality here is more general. The analogy of the forms of the "pseudohomogeneous" spectrums allows to give the definition of the relative activity also to the centers in the the process of condensation on the centers of the separate sort. The point $w = 0$ corresponds to $\theta_{final} = 1/2$. The value of $w$

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[11] Certainly, with the corresponding choice of the renormalization of $\theta_{init}$ and the choice of the "external" supersaturation the iteration procedure remains valid in all cases with the linear "external" supersaturation.

can be reconstructed from $\theta_{final}$ as

$$w = \ln(\frac{\ln \theta_{final}}{\ln(1/2)})$$

The invariant $\ln \theta / \exp(w)$ can be also observed for an arbitrary $z$. Hence, the condensation occurs in a hierarchical manner[12]. Then one can consider the distribution $f(x, w)$ over the two variables $x$ and $w$ obtained in the process of condensation on the heterogeneous centers with the spectrum of activities as the formal generalization of the distribution in the process of condensation on the heterogeneous centers of the separate sort. Now the distribution has the universal functions as the base. This base doesn't depend on the process of the exhaustion of the heterogeneous centers. The dependence on $w$ is rather explicit

$$f(x, w) \sim \exp(\delta(x)) \exp(-w \int_{-\infty}^{x} \exp(\delta(x'))dx' \frac{\ln 2}{\int_{-\infty}^{\infty} exp(\delta(x'))dx'})$$

The factor $\exp(\delta)$ is the universal base for this distribution. That's why we prefer to present it in Figure 1 and to call it simply the spectrum. The last expression is precisely valid for $\delta$ calculated on the base of the precise solution. As for approximations for $\delta$ one can take $\delta$ from the pseudohomogeneous situation in two manners (from [8] and from [7]). The first one corresponds to the first iteration and doesn't depend on the regime of the vapor consumption. The second one is more precise but depends on the regime of the vapor consumption. Note that the last expression contains an unessential approximation because it is based on the pseudohomogeneous situation. The negligible character of correction can be seen simple from the result of the iteration procedure in the situation with one sort of the heterogeneous centers. Hence, one can state the natural inclusion of the specific condensation on a sort of the heterogeneous centers into the practically universal distribution appeared from the process of the condensation on the heterogeneous centers with the spectrum of activities.

The second consequence is connected with the fact that now we know the ansatz necessary for the realization of the first opportunity (alternative to

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[12] Certainly, the shift and the zero roint $w = 0$ depend on the parameters of the process including $\eta_{tot}$.

the regularization of $\theta$). One can use the form of $\delta$ obtained in the pseudohomogeneous situation in the first iteration or from the universal homogeneous precise solution.

The third consequence can be noticed in frames of the modified method of the steepens descent [16]. Really, the form of the external supersaturation can be essentially nonlinear[13]. Then we have to use the modified method of the steepens descent. The generalization is evident. Due to the negligible effect of the account of the exhaustion of the heterogeneous centers in all steps except the final formulas which can be seen from the iteration method (in the nonlinear case all analogous estimates can be given) we can simply integrate (summarize) the amplitudes of the distribution[14] over the activity, then get the result for the psudohomogeneous situation and then apply the final formulas for the number of the heterogeneous centers on the base of the supersaturation.

One can analytically show for $Q \geq 1$ that the differences in the forms of the spectrums between the real solution and the first iteration, between the real solution and the pseudohomogeneous universal precise solution decrease when $Q$ increases. Also one can prove that for $Q \geq 1$ the difference between the external supersaturation and the real supersaturation at some arbitrary moment of time decreases[15] when $Q$ increases. So, the results of Figure 1 show that the required limit corresponding to the practically universal spectrum is attained already when $Q \geq 1$.

One can analytically show that the form of the spectrum lies between the gaussian iteration and the first iteration (or between the gaussian form and the universal precise pseudohomogeneous solution). We can see from Figure 1 that the difference in the form of the spectrum is rather small for all situations. This can lead us toward the general approximate universiality. So, the analogy with the ideas of the universiality in the previous considerations is now stated.

Certainly, in the case of the condensation on the separate sort of the heterogeneous centers the spectrum (as $\theta \exp(\delta)$) isn't universal. But the

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[13] In a very specific global form of the activity spectrum $\eta_{tot}$. One can prove that in any case one can restrict the expression for the external supersaturation during the period of the intensive formation of the droplets on the centers with the intermediate activity by the constant, linear and square terms.

[14] The characteristic values of the distribution at $t_*$.

[15] And also at $t_*$.

difference between the forms of the spectrum isn't so important. One can show analytically that the form[16] of the spectrum changes continiously from the case of the relatively small number of the heterogeneous centers up to the pseudohomogeneous case and lies between these two limit cases. Really, when the relative number of the heterogeneous centers is small the first iteration $\exp(x - \exp(x))$ gives the precise expression for the spectrum. In the pseudohomogeneous case the same first iteration is the base for the result which lies prctically near the precise solution (this is the base point for the effectiveness of the iteration method [8]). So, the form of the spectrum doesn't essentially variate. It can be also treated as as some universal form. Hence, this case also allows the universal description. Namely this is the base for the applicability of the iteration procedures from [8], [7].

## 6 Advantages of the model

The results of the iteration procedure can give not only the description of the process of the heterogeneous condensation but also the information about the form of the activity spectrum. From the first point of view this question appears to be an external one to the process of condensation.

Experimental results [13] show that the spectrums of the activities are rather smooth and have the form

$$\varphi(v) \sim v^{-(1+s)}$$

where $s$ is some small positive parameter. Here $v$ has the sense of the activity introduced in a slightly another manner. Namely, the free energy can be approximately written as the function of $v$ in the leading term as

$$F = -\ln(\zeta + 1)\rho^3 + const\rho^2 + constv \ln \nu + const$$

which leads to the approximate applicability of the linearization of $\Delta F = F_c - G = F(\rho_c) - F(\rho_e)$ as function of $w$ together with the identification of $v$ as $w - w_0$ with some characteristic value of the parameter $w_0$. Then $\eta_{tot}$ can be presented as

$$\eta_{tot}(w) = \eta_{tot}(w_0)(w - w_0)^{-(1+s)} \tag{35}$$

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[16] After renormalization and as the function of a rescaled variable.

The positive value of $s$ ensures the convergence of the total number of the heterogeneous centers[17]

$$\eta^{tot} = \int_{w}^{\infty} \eta_{tot}(w) dw$$

Define the class of the "long tail spectrums" (LTS) as the spectrums with extremely long tails in the active region. This spectrum shows an example of such a spectrum. Here we shall develop the theory for condensation on such spectrums.

To present the most simple variant we shall assume that for $f_{\zeta_*}$ an approximation of the known form is adopted

$$f_{\zeta_*} = f_{\zeta_{**}} \exp(\frac{\Gamma}{\zeta_{**}}(\zeta_* - \zeta_{**})) \qquad (36)$$

with some constant value of the known parameter $\Gamma$. Here $\zeta_*$ can be treated as a value corresponding to the moment when some sort of the heterogeneous centers is exhausted and $\zeta_{**}$ is the base for approximations. Require that

$$\theta(z = 0, w) = 1/2$$

which leads to

$$\frac{\Gamma}{\zeta_{**}}(\zeta_* - \zeta_{**}) + \lambda w = -\ln[\frac{f_{\zeta_{**}} n_\infty}{c \ln 2}]$$

The last approximation is valid when the relative variation of $\zeta$ is small. In such a region we can put $c$ in the r.h.s. of the last equation to some constant value and get for the size spectrum

$$\mid f(z) \mid = \mid \eta_{tot}(w \mid_{w=\frac{const - cz}{\lambda}}) \mid \frac{c}{\lambda}$$

where the dependence $\ln c$ is assumed to be unessential. Then one can see that in the case of (35) the convergence of the integral for $G$ can be attained only if $s > 3$ (note that $c \rightarrow const \sim \frac{d\Phi}{dx}$ when $w \rightarrow \infty$). This result shows that LTS can not be effectively spread. More rigorously speaking, the contradiction can be overcome by noticing that this effect is only due to approximation (36). Certainly, $G$ is restricted by the value $\eta_{tot} z_{max}^3$ where

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[17] The infinite tail must be cut off at the centers which must be already exhausted in the previous processes.

$z_{max}$ is the coordinate of the droplets which are imaginary formed when the supersaturation attains some slightly positive value. Nevertheless in such a situation all global features of the free energy appear which doesn't allow to get any effective method to all types of the heterogeneous centers. The leading idea will be that some of heterogeneous centers had been exhausted in the previous processes of condensation occurred earlier. Then the balance equation will be the following

$$\frac{d\Phi}{dx} = c\frac{\Phi}{\Gamma} + 3\int_{-d}^{z}(z-x)^2 f(x)dx$$

where $d$ is some boundary parameter of size spectrum initiated by boundary of activity spectrum. This equation can be solved. In the case of $\eta_{tot} \sim const$ we have

$$\frac{d\Phi}{dx} = c\frac{\zeta_{**}}{\Gamma} + 3\int_{-d}^{z}(z-x)^2 c(x)dx\frac{const}{\lambda} \tag{37}$$

Note that here $c\frac{\zeta_{**}}{\Gamma}$ is the derivative of the real (not the ideal) supersaturation on $x$. Having differentiated this equation three times[18] we get the ordinary linear differential equation with some constant coefficients, which has the known solution.

Now a new principle of the self-consistency of the activity spectrum will be elaborated. We have noticed that active centers have been exhausted in the previous processes of condensation. But the description of the previous processes of condensation is quite analogous to the description of the given process. As the result we have for spectrum of the heterogeneous centers

$$\theta = \exp(-const\exp(\lambda w)\int_{-\infty}^{z}\exp(-\Gamma\frac{\zeta-\Phi_*}{\Phi_*})dx)$$

with the analytical structure

$$\theta(z\to\infty) = \exp(-const\exp(\lambda w)) \tag{38}$$

But this structure is already known - it is the structure of the final and the start results for $\theta$ in the already investigated process. So, our start form was absolutely correct[19]. Also it is very important that the structures before and

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[18] Now we are going to get the equation for the unknown function $c(x)$ so we have to keep the derivatives of $c(x)$

[19] One can repeat all calculations with the new value of parameters initiated by the previous process of consumption of the heterogeneous centers.

after the process coincide in their analytical form. This statement will be called as the principle of the self-consistency of the spectrum of the activities.

Hence, our initial conditions satisfies this principle. The process of condensation conserves the analytical form of the spectrum of the activities and the result of the process can be regarded as some shift in the scale of activities. Only some parameters are changed. We needn't to repeat the calculations as far as they are absolutely the same ones.

However, in (37) when $d \gg 1$ we needn't to know the details of the cut-off of the spectrum and can use the cut-off by the Heavisaid's function.

The last point of discussion is the possibility of the linearization of the external supersaturation. One can analytically prove the following statement:

- In the description of condensation on the centers of the intermediate activity the two manners of description cover all possible situations[20]. These manners of description are the following:

  1). The supersaturation is absolutely determined by the consumption of the vapor by the droplets formed on the centers with high activity.

  2). The linearization of the external supersaturation is possible during the period of formation of the droplets on the centers with the intermediate activity.

The first manner of description is obviously trivial. The second is completely described here. Note that in the case when the spectrum has some pseudo singularities the last statement isn't valid and the special description is necessary. This description can be attained by the combination of the methods presented in [16] with this theory.

# 7 Concluding remarks

Now the theory of aerosol formation is completed. As a base for some concrete results the classical theory of nucleation was chosen. Meanwhile the validity of this theory remains the matter of discussion[21]. Note that this theory is

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[20] The natural requirement for the activity spectrum is that the activity spectrum must be a smooth function with the cut-off (or without the cut-off) like (38).

[21] Note that formally we can put the discrepancy between the predictions of the classical theory and the real rate of nucleation into the values of the microscopic corrections.

necessary only to calculate the amplitude of the distribution. In the situation of the dynamic conditions the manner of the choice of $t_*$ leads to the algebraic equation of the following form:

$$f_* = Smooth\ known\ function(\Phi_*; explicit\ external\ parameters)$$

So, the microscopic corrections to the free energy aren't important for the process of condensation under the dynamic conditions. In the situation of the metastable phase decay the amplitude value of the spectrum is rather artificial. It is given explicitly by the initial supersaturation and one can not exclude the sharp dependence on the microscopic corrections to the free energy. Here any other concrete formula can be used instead of the expression from the classical theory for the nucleation rate in the stationary approximation. Note that the form of the spectrum doesn't essentially depends on the value of the amplitude. That's why we don't pay any serious attention to the solution of the algebraic equations on the parametrs of the process and to the calculation of the concrete numerical results. We have concentrated our attention on the universal depencies which form the base for the common knowledge in the field of the first order phase transitions. Namely the universiality is the main result of our investigation. Note that the universiality also takes place in the process of the condensation under the dynamic conditions.

The theory presented in these four publications can be easily reformulated when we assume that the rate of appearance of the critical embryos is proportional to

$$F_1 \exp(F_2)$$

where $F_1$ and $F_2$ are the smooth functions of the supersaturation and $F_2$ has the big absolute values. Evidently all reasonable recipes for the rate of nucleation satisfyes the last ansatz. We kept the classical stationary flow only due to the tradition. The range of applicability of the presented theory is wider than the case of condensation. The possibility of the linearization of the ideal power of metastability during the period of the intensive formation of the super-critical embryos seems to be quite natural. The sharp increasing of the intensity of the metastable phase consumption by the separate supercritical embryo is also a natural requirement. This theory is based only upon these assumptions. All positions used in the construction of the mathematical model (exept the absence of coalescence) can be missed[22] by the obvious

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[22] The thermal effects can be taken into account in the manner analogous to [8].

generalization conserving the mathematical structure. The requirement of the homogeneous character of the external action and of the nucleus distribution can be attained by the consideration of an arbitrary hydrodynamic element. As the result one can conclude that the general theory for the kinetics of formation of the dispersed embryos of a new phase on the dispersed unpurities in a metastable phase is constructed.

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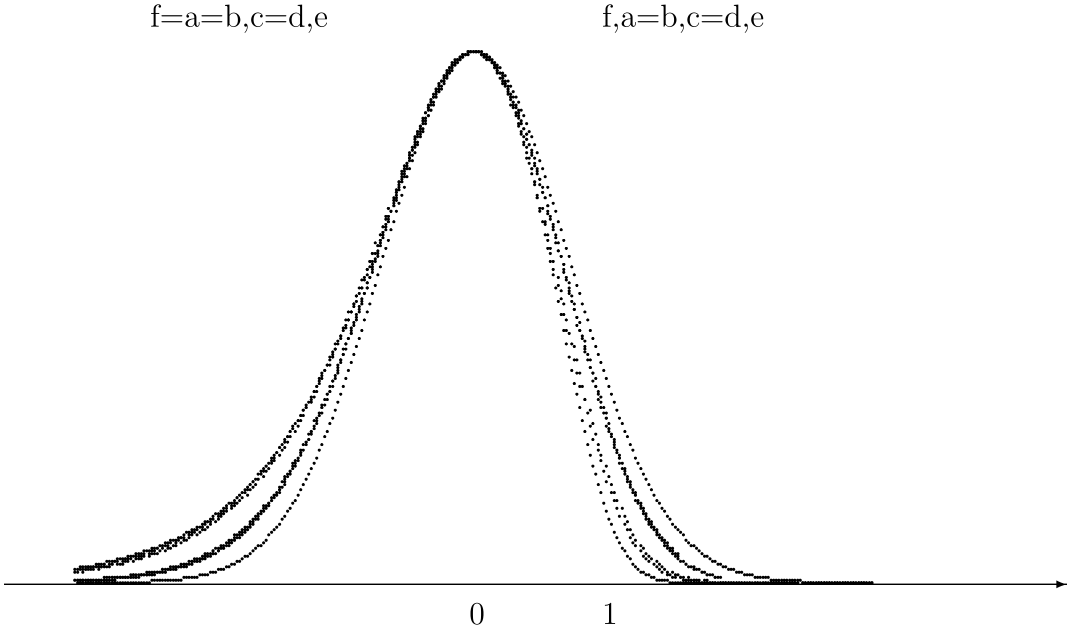

*Figure* 1

*Form of spectrum under the different powers of deformation.*

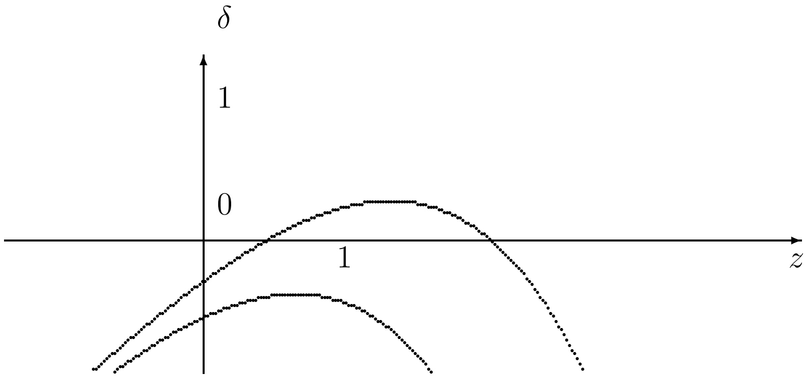

*Figure 2, part a*

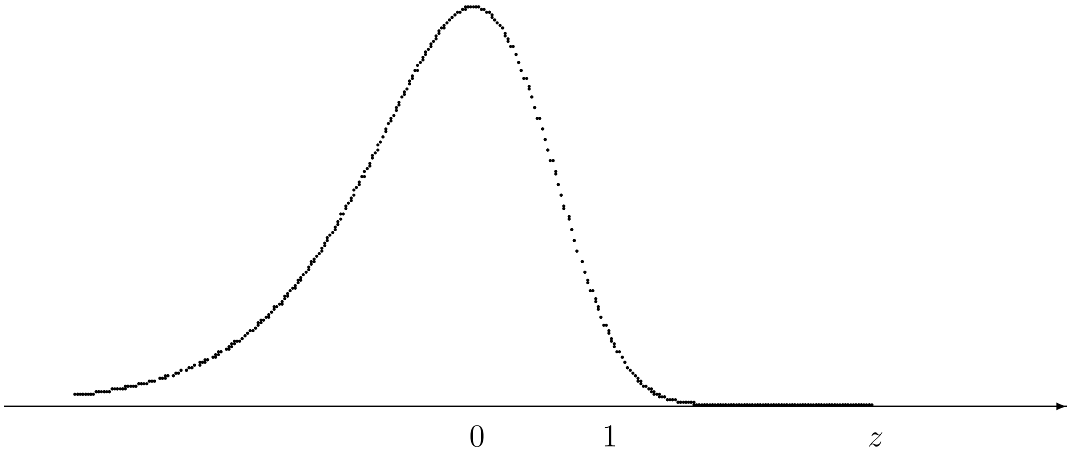

*Figure 2, part b*

*Weak dependence of the spectrum on the base of approximations.*

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# FORM OF THE SPECTRA OF NUCLEUS DIMENSIONS IN FIRST-ORDER PHASE TRANSITIONS

**V. B. Kurasov**[*]

*We study a generalization of the analytic theory of first-order phase transitions to the cases of arbitrary droplet growth, of nonisothermal processes, and of heterogeneous centers in the system. We show that in all these cases, the spectra of droplet dimensions are similar. The same forms of the spectra are also obtained for the stationary condensation process in a spatially inhomogeneous system.*

**Keywords:** first-order phase transition, kinetics, condensation, nucleation, universality

## 1. Introduction

**1.1. Choice of the critical nucleus description.** The process of the phase transition from a supersaturated vapor to the state of liquid droplets is considered as a model of the first-order phase transition. The theoretical description of this process is based on classical nucleation theory [1]–[4]. The main result of the theory is the expression for the stationary nucleation rate, which is inversely proportional in the leading term to the exponential of the free energy of the critical nucleus. Meanwhile, the free energy of the critical nucleus, which plays the role of an external parameter in classical nucleation theory, has not been studied sufficiently well. Numerous papers present different values of this quantity. We note that the concept of how to calculate the free energy was revised significantly in [5]–[9]. We also note that all the proposed modifications of classical nucleation theory could not bring the theory into complete agreement with the experiments in which the nucleation rate is determined.

The development of the theoretical description shows that there is no clear picture even in the problem of fixing the nucleus mass center. Although there is significant progress in understanding the thermodynamic value of the free energy [10], the configuration integrals were calculated directly in recent publications [11]–[14]. Under this approach, the value of the free energy is determined by the model parameters of the Hamiltonian. If the theory of simple liquids is used to calculate the free energy in the framework of density functional theory [15], then the parameters of the liquid state model give a specific value of the free energy of the critical nucleus. In this case, the free energy and hence the nucleation rate turn out to be extremely complicated functions of the model parameters of the substance.

The number of the parameters introduced also increases because of the microscopic corrections stipulated by the curvature of the nucleus surface. The modern theory of curved surfaces [16] cannot give plausible results for the nucleation rate without introducing rather many external parameters determined by the substance.

Nevertheless, one property of the free energy of the critical nucleus can be established with certainty and, moreover, analytically. This free energy is a sufficiently smooth function of the thermodynamic parameters of the system and of the degree of metastability of the condensing substance.

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The exact solution of the kinetic equation with known kinetic coefficients can also give significant corrections [17] to the preexponential term in the nucleation rate. But these corrections are sufficiently small compared with the inaccuracy in determining the free energy. Therefore, the main problems arise in calculating the free energy.

The main aspects of classical nucleation theory are so natural that the qualitative conclusions of this theory are beyond doubt. This theory well predicts the dependence of the nucleus formation rate on the degree of metastability and on the natural thermodynamic parameters, although the discrepancy between the theory and experiments increases for rather small dimensions of the critical nuclei (because the so-called capillary approximation can no longer be used). Therefore, a reasonable universal alternative to classical nucleation theory has never been proposed.

Nevertheless, to determine the preexponential factor in the expression for the nucleus formation rate (or the logarithmic correction to the free energy) with sufficiently good relative accuracy is impossible today. But we can state that this factor is a relatively slow function of the thermodynamic parameters describing the system.

We note that this property can be explained in the framework of ensemble theory in statistical mechanics. The relative difference between the thermodynamic quantities calculated in the framework of different thermodynamic ensembles is rather small. For example, the difference between the additive thermodynamic quantities calculated in the canonical and in the large canonical ensemble is of the order of $\log \nu/\nu$, where $\nu$ is the number of particles in the system[1] (in this case, the nucleus of critical dimensions is taken to be such a system). There is a many-fold difference between the nucleation rates. To prescribe exactly how to calculate the free energy of the critical nucleus, it is necessary to choose the description variables (or to choose the special volume of the arising nucleus [11]–[14]), i.e., to choose a statistical ensemble. The last publications in both the classical approach [11]–[14] and the density functional theory [18] can be interpreted precisely in the framework of the problem of choosing an ensemble. Unfortunately, there is no obvious method for choosing the correct ensemble in the modern state of the theory. In what follows, we use the fact that the preexponential factor in the expression for the nucleation rate depends on the thermodynamic parameters of the description rather weakly.

**1.2. Kinetic problems.** In this paper, we attempt to overcome these difficulties in the framework of studying the kinetic problems of the global evolution of a system under the phase transition. The theory constructed to describe the stationary nucleation rate permits studying the global picture of the phase transition. At the beginning, the results of this study were at most qualitative [19] and were intended to ensure the proper experimental conditions. Later, some realistic models of global evolution appeared. Among them, we note the kinetics of the homogeneous decay of the metastable phase [20] and the kinetics of the homogeneous phase transition under smooth external conditions [21], [22].

It was discovered in [22] that all the characteristics of the global picture of the phase transition weakly depend on the microscopic corrections to the free energy of the critical nucleus. This result opens new perspectives for classical nucleation theory. Earlier, the main efforts were in studying the stationary nucleation rate, which was the desired quantity in the experiment. Because the free energy is usually of the order of several tens of units, even relatively small errors in the value of the free energy lead to significant errors in determining the nucleation rate. The main result in [22] is that there is a strong equalizing feedback, which yields a weak dependence of the phase transition characteristics on the microscopic corrections to

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[1] A partial compensation between the volume and surface contributions to the free energy can be observed. As a result, this thermodynamic quantity is proportional to $\nu^{2/3}$ (but not to $\nu$), where $\nu$ is the number of molecules in the critical nucleus. Some traces of this compensation are also observed in the difference between the corresponding minimum work for nucleus formation in different ensembles. But this difference nevertheless remains proportional to $\log \nu$.

the work of formation, i.e., on relatively small corrections to the free energy. The same conclusion concerns the problem of choosing an ensemble. This property was established only for the collective absorption of substance from the metastable phase. The collective absorption means that each droplet absorbs substance from a volume containing sufficiently many other droplets. Precisely this simplification permits analyzing such a nonlinear problem analytically [23].

Variations in the vapor absorption conditions were analyzed formally in [24], [25] using a simple change of the droplet growth rate. What actually happens is that the revision of the substance absorption conditions must be accompanied with a study of the form of the vapor density profile in the vicinity of the growing droplet. There is no density profile only in the case of purely free-molecule absorption of substance [26] (precisely these conditions were studied in [21], [22]).

An analysis of the form of the spectra of droplet dimensions raised the question whether there exist variables in which the solution can be represented as a function independent of the external conditions and the characteristics of the substance. In [27], such variables were found in the homogeneous condensation case. The specific form of the balance equation [27] shows that the choice of such variables is rather simple. This property is extremely important for understanding the nature of the phase transition, but this property was established in [27] only for the case of the collective vapor absorption.

The case of heterogeneous condensation on heterogeneous centers of the same type does not admit any choice of such variables [28]. It seems that in such a situation, the spectra being of the same form is of no use. But the results obtained in [27] show how the similarity of the forms of the dimension spectra in the homogeneous case can be used to study the case of heterogeneous nucleation at heterogeneous centers of the same type.

The next stage in generalizing the kinetic picture to arbitrary conditions of substance absorption was to take the vapor density profiles arising around the droplets into account [26]. It is natural to assume that a growing nucleus of the new phase first depletes the ambient metastable phase in the immediate vicinity of its boundary. In the diffusion process, the density is being equalized, but the constantly increasing intensity of the metastable phase consumption does not allow the final equalization. Hence, considering the density profile of the metastable phase is essential. Earlier, this process was studied only in the case where the density profiles of the metastable phase were absent.

One of the properties used to justify the theory in the case of density profiles was a sharp increase in the vapor absorption intensity with time. The same fact underlies an approximate coincidence of the main characteristics of the process calculated using the first iteration and the exact solution. This characteristic feature is very important in our study.

In [26], the process kinetics was constructed only for the special homogeneous condensation case. This brings up the problem of generalizing the constructions developed in [26] to the case of arbitrary first-order phase transitions. As a result, the possibility of repeating such methods permits showing that the forms of the spectra of the nucleus dimensions are similar in very different situations. In this connection, the goal of this paper is to show that the similarity of the forms of the dimension spectra is a general characteristic feature of first-order phase transitions.

In Sec. 2, the theory of density profiles [26] is generalized to the case of nonisothermal condensation effects. In Sec. 3, we show that the forms of the spectra are similar under different conditions of absorption of the metastable phase. The dependences obtained are generalized to the heterogeneous condensation case in Sec. 4 and to the case of stationary condensation in a spatially inhomogeneous system in Sec. 5.

In this paper, we study a system of unit volume with homogeneous external conditions (except for Sec. 5). All the quantities having the dimensions of energy are expressed in natural thermal units. The accuracy of the theory is estimated using the relative error in the total number of droplets, which is the most important characteristics of the condensation process.

**1.3. Density profiles of the metastable phase in the homogeneous nucleation kinetics.** In what follows, we draw analogies to the approach used in [26]. It is therefore expedient to discuss the main points of the theoretical description of the homogeneous transition kinetics given in [26].

First, we construct the density profile of the metastable phase around a solitary growing nucleus of the new phase. The influence of the other nuclei is ignored. We prove that the other nuclei cannot significantly affect the growth rate for the nucleus under study. Then its growth rate turns out to be a known variable. In [26], the nucleus is interpreted as a point source of substance absorption with a prescribed intensity. In this case, the density profile can be easily obtained based on the Green's function formalism. The form of the density profile thus obtained has the remarkable property that the entire ambient volume can be divided into the domain where the nucleus formation intensity is not perturbed by the nucleus under study and the domain where the nucleus formation intensity is negligibly small (the depleted domain). The laws for the variation of the dimensions of these domains were obtained in [26]. It turns out that the dimensions of the depleted domain increase with time at a rapidly increasing rate. This permits saying that variations in the metastable phase absorption are of the avalanche type and permits formulating kinetic models of the global evolution of the entire ensemble of nuclei.

The problem (posed in [26]) of describing the evolution of an ensemble of growing droplets and of determining the intensity of constant formation of new droplets is rather too complicated to be stated as a solution of some closed equation (the method proposed in [27] in the case of collective absorption of the metastable substance). Instead of this, several models were introduced in [26] in which either the physical effects decreasing the substance consumption or the effects increasing this consumption were not taken into account. These models give similar estimates of the upper and lower bounds for the total amount of the new phase nuclei already formed. The approximate coincidence of the results given by these models shows that the description of the process is rather good. The true result is thus obtained with a sufficiently high relative accuracy.

The last stage in the construction of the theory must be an analysis of the formal passage to the collective consumption of the metastable phase by the nuclei. In [26], the required passage is rather simple in this case because the functional forms of the equations in one of the models coincide with the integral balance equation obtained for the collective consumption of the metastable phase. It remains only to verify the variations in the numerical values of the parameters in these equations.

To generalize this approach to the general case, we need to follow the above program. Taking all the steps of this program, we obtain the above result about the similarity of the spectra of the nucleus dimensions or, equivalently, of the distribution functions of the new phase nuclei with respect to the dimensions. By the dimension of an nucleus, we mean its spatial characteristics whose rate of growth is independent of the value of this dimension. In this case, the distribution function of the nuclei with respect to this dimension moves in time as a whole along the dimension axis. Precisely in this case, we can speak about the form of the spectra of the nucleus dimensions as about some characteristics that does not change with time.

## 2. Thermal effects in condensation

A first-order phase transition is inevitably accompanied by a release (or an absorption) of the condensation heat in the transition of each molecule from the initial to the new phase. Nonisothermal condensation effects are therefore typical of first-order phase transitions. Naturally, in some cases, there is so much passive substance in the system that the thermal effects do not manifest themselves at all.

To include the nonisothermal condensation effects in the kinetic picture of the process described in [26], we must first determine the stationary nucleation rate. We assume that a near-critical nucleus acts under the free-molecule conditions of substance exchange. Then in the framework of classical nucleation theory, the nucleation rate $I_s$ can be found using the renormalizations presented in [29] and [30], which we discuss later.

It is convenient to describe the degree of metastability by the supersaturation $\zeta$, which is the ratio of the vapor molecule density $n$ to the saturated vapor molecule density $n_\infty$. For the stationary nucleation rate, we have the renormalization

$$I_{\mathrm{s}} = \frac{I_0}{1-k}, \tag{1}$$

where $I_0$ is the nucleation rate with the thermal effects neglected, the parameter $k$ is determined by

$$k = \frac{\alpha\beta^2}{c(1+p)}, \tag{2}$$

$\beta$ is the average condensation heat of a single molecule in the units of $k_{\mathrm{B}}T$, $T$ is the absolute temperature (we can assume here that $T$ is equal to the temperature $T_0$ of the medium), and $c$ is the molecular heat capacity. The parameter $p$ is determined as

$$p = \left(\frac{m}{m_{\mathrm{g}}}\right)^{1/2} \frac{n_{\mathrm{g}} c_{\mathrm{g}}}{nc}, \tag{3}$$

where $n_{\mathrm{g}}$ and $c_{\mathrm{g}}$ are the concentration and the molecular heat capacity of the passive gas and $m$ and $m_{\mathrm{g}}$ are the masses of a condensing substance molecule and of a passive gas molecule. Special forms of renormalizations are inessential; in what follows, only their smooth character is important.

It is now necessary to find the relation between the supersaturation and the ideal saturation at any arbitrary instant of the nucleation stage, i.e., of the stage at which nuclei of the new phase arise. By the supersaturation $\zeta$ in a system, we mean the ratio of the density of molecules in the metastable phase to the density of molecules in the phase that are in phase equilibrium at the same temperature. By the ideal supersaturation $\Phi$, we mean the value of $\zeta$ that would exist in the system without taking nuclei of the new phase into account. In [26], homogeneous condensation was studied using the approximation

$$I_{\mathrm{s}}(\zeta) = I_{\mathrm{s}}(\Phi_*) \exp\left(\Gamma \frac{\zeta - \Phi_*}{\Phi_*}\right), \tag{4}$$

where $\Phi_*$ is the ideal supersaturation at an instant $t_*$ belonging to the stage of new phase nuclei creation. This approximation is based on the properties (see the introduction) of the following smooth dependence: the preexponential factor of the equilibrium distribution and the free energy of the critical nucleus are functions of the thermodynamic parameters of the system and of the degree of metastability of the original phase. This approximation is therefore sufficiently general. The parameter $\Gamma$ is approximately equal to the number of molecules in the critical nucleus of the new phase and is a large value (under the conditions for applicability of the capillary approximation). The form of this approximation also holds for the renormalizations mentioned above because they are sufficiently smooth. The parameter $\Gamma$ remains a large value. The relative variation in the supersaturation $\zeta$ at the nucleation stage is then sufficiently small. Now the supersaturation is also caused by a variation in the vapor molecule density $n$ and by a variation in the temperature $T$, which results in a variation in the saturated vapor molecule density $n_\infty$ according to the Clapeyron–Clausius equation

$$n_\infty(T) = n_\infty(T_0) \exp\left(\beta \frac{T - T_0}{T_0}\right). \tag{5}$$

It is easy to show that variations in $n$ and $n_\infty$ cannot be compensated in the expression for the supersaturation. These variations are therefore also relatively small. This permits writing the approximate form of the supersaturation variation as

$$\Delta\zeta = \frac{\Delta n}{n_\infty} + \frac{\Delta T}{n_\infty}\frac{\beta n}{T_0}, \tag{6}$$

where the variations are deviations from some values indicated by the subscript 0. It is convenient to take the characteristics of the medium to be these values. Also in this case, the other droplets therefore do not significantly affect the growth rate for this particular droplet at the nucleation stage.

Renormalization (1) is valid under the "purely free-molecule conditions of substance exchange" [26], which, in this case, are indicated by the condition $\Delta\zeta < \zeta/\Gamma$ imposed on the boundary of the incipient droplet. The left-hand side of this condition is the decrease in the supersaturation because of the vapor absorption and heat condensation. By an incipient droplet, we mean an nucleus whose linear dimension is two to three times larger than the critical nucleus. This regime is natural for the near-critical nuclei.[2]

The existence of nonisothermal condensation effects means that a temperature profile arises around a growing nucleus of the new phase. To find the temperature profile, along with the diffusion equation

$$\frac{\partial n}{\partial t} = D_f \Delta n, \tag{7}$$

where $D_f$ is the diffusion coefficient, we consider the heat equation

$$\frac{\partial T}{\partial t} = D_t \Delta T, \tag{8}$$

where $D_t$ is the thermal conductivity.

In the context of the constructions in [26], it is necessary to use the law describing the growth rate of a supercritical nucleus of the new phase, i.e., the time variation in the number $\nu$ of molecules in the nucleus of the new phase. A sufficiently precise expression for $d\nu/dt$ was obtained in [29]. In this case, the relative deviation of the temperature is determined by the relation

$$\frac{\beta}{k}\frac{\Delta T}{T_0} = 1 - \exp\left(\frac{dF}{d\nu} + \beta\frac{\Delta T}{T_0}\right). \tag{9}$$

We see that for a supercritical nucleus, the derivative of the free energy $F$ of the nucleus formation at a fixed temperature is now independent of $\nu$,

$$\frac{dF}{d\nu} \to -\log(\zeta + 1). \tag{10}$$

Then the renormalization factor in the growth law becomes independent of $\nu$, and we obtain the old functional dependence established in the nonisothermal situation [26], but with somewhat different parameters. As a consequence, all the facts given in the section *Statements* in [26] remain valid.

The next step is to construct the Green's function formalism for the diffusion and heat equations. Because the vapor molecule absorption rate is assumed known, the heat release amount $\beta k_{\mathrm{B}} T \nu$ is also known as well as the heat release rate. The problems of heat conduction and diffusion are now separated.

In [26], the sharp (time-dependent) profile of the nucleus formation intensity was obtained as a function of time at a given spatial point (except the points belonging to the domain whose relative volume is sufficiently small). This means that the nucleation rate based on this profile can be approximately represented as a function proportional to the Heaviside function of a shifted argument. This property cannot disappear because of a variation in the numerical values of the coefficients in the expressions for the temperature

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[2] The main problem is that the conditions for the critical nucleus are not in equilibrium. The nucleus temperature is different than that of the medium. In this case, it is possible to study only an analytic continuation of the free energy. This procedure is justified because the nucleus is quasi-isolated, but, of course, this is an approximate procedure. Precisely this fact explains why, in contrast to [29], only weak nonisothermal effects were studied in [30].

profile (the boundary conditions are also absolutely similar), and the nucleation rate based on this profile is proportional to a step function. The profiles of the nucleus formation intensity based only on the substance depletion or only on the medium heating are therefore proportional to step functions.

According to approximation (4) for the nucleus formation intensity, precisely the supersaturation profile is interesting. It follows from (6) that the profile of $\zeta$ can be approximately represented as the superposition of the profiles of $n$ and of $T$. We thus obtain the superposition of sharp profiles, and the nucleation profile is a step function. The functional dependence of this profile on $\nu$ and on time remains the same, but the characteristic constants vary. The subsequent considerations in [26] are based only on this property. All other constructions are absolutely similar.

In [26], the continuous passage to the collective vapor consumption is specified by the functional forms of the equations for the collective vapor consumption and for the existence of the density profiles being the same. We have the same situation here. In the integrands, the functions specified by the growth conditions are also the same. Even if they did not coincide, the desired property could be found based on the first iteration, which is already sufficiently precise and is free from the crossed influence of the depletion initiated by different conditions of the substance absorption. This coincidence simplifies the desired approach, which becomes quite similar to the situation studied in [26].

A generalization of the model to nonisothermal effects is based only on the obvious features of the description in the continuous model. The same picture is also observed for all other variables (affecting the nucleation rate) in the description of the nucleus. The role of the parameter $T$ can be played by another thermodynamic parameter.[3] Of course, it is necessary to verify the validity of approximation (4) with a large and approximately constant value of the parameter $\Gamma$.

In what follows, including the nonisothermal effects in the general procedure, we can therefore speak only about the substance absorption and foresee the possibility of this generalization.

## 3. Universal spectrum of dimensions

The dynamic conditions are distinguished by the smooth-in-time behavior of the ideal supersaturation, i.e., by the supersaturation that would be formed in a system in which droplets neither originate nor grow. The ideal supersaturation is independent of the vapor absorption and heat release and is determined only by the external conditions. It is natural to assume that the ideal supersaturation is a smooth function of time. Under the dynamic external conditions with the collective consumption of the metastable phase substance, the evolution equation can be written (in the framework of one of the models proposed in [26]) in the form

$$cz - \varphi(z) = A \int_{-\infty}^{z} K(z-x) e^{\varphi(x)}\, dx \tag{11}$$

with the parameters $c$ and $A$, the unknown function $\varphi(x)$, and the known function $K$. The function $K$ is derived from the growth laws given in [26]. It is known that this equation can be solved by the iteration method and that the rate of convergence of the iterations depends on the rate of the relative increase in the function $K$ [28]. We hence study the relative increase in $K$ in our situation. In [26], this problem was solved under the diffusion conditions for the substance absorption. This yields some known function $K$, denoted by $K_{\text{diff}}$. By completely similar constructions on the basis of the free-molecule conditions of growth, we obtain another expression for $K$, denoted by $K_{\text{free}}$. In an arbitrary situation, the relative increase in $K(z)$

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[3] We note that an analysis of the construction of the expression for the stationary rate of nonisothermal nucleation shows that any other thermodynamic variable can be used instead of the temperature. The only requirement is that the Clapeyron–Clausius equation be satisfied approximately and, moreover, for very small deviations of the nucleus characteristics from the medium characteristics.

is bounded by two limit cases, namely, by the relative increase in $K_{\text{free}}(z)$ and by the relative increase in $K_{\text{diff}}(z)$. Naturally, this property appears only after the equation is made "dimensionless" [26].

In the case of the power-law growth

$$\frac{d\nu}{dt} \sim \nu^{\alpha}, \tag{12}$$

the function $K$ has the form

$$K(y) \sim (y)^{(1-\alpha)^{-1}}. \tag{13}$$

Then the evolution equation can be made completely "dimensionless." By a simple scale transformation, we eliminate all the parameters except $c$ in this equation. Choosing $t_*$ as the instant at which the supersaturation attains its maximum ($z = 0$) [21], we obtain the equation

$$c \sim \frac{1}{1-\alpha} \int_{-\infty}^{0} (z-x)^{(1-\alpha)^{-1}-1} e^{\varphi(x)}\, dx. \tag{14}$$

The solution $\varphi(z)$ is independent of the parameters determined by a specific substance and the external conditions. The dimension spectrum $f(x)$ is proportional to $e^{-\varphi(x)}$ and is also independent of the parameters. Naturally, the dependence on $\alpha$ remains, and we begin to study this dependence.

We can mention a simpler possibility for describing the process, which is based on the first iteration in the iteration method for solving integral equation (11) (this description method corresponds to one possible model):

$$\varphi_{i+1}(z) = cz - A \int_{-\infty}^{z} K(z-x) e^{\varphi_i(x)}\, dx, \quad i = 0, 1, 2, \ldots, \quad \varphi_0 = cz. \tag{15}$$

Moreover, the iterations of the dimension spectrum $f_i(x)$ are described as $f_i \sim e^{\varphi_i(x)}$, and the number $N_i(z)$ of droplets is obtained by integrating $f_i$ from $-\infty$ to $z$. The first iteration has the form

$$\varphi_1(z) = cz - A \int_{-\infty}^{z} K(z-x) e^{cx}\, dx. \tag{16}$$

The functional in the right-hand side of the evolution equation is monotonic. We hence have $N_{2i+1}(z) < N(z) < N_{2i}(z)$. We can estimate the accuracy of the iterations because

$$\frac{d\big(\big|N_i(\infty) - N_{i+1}(\infty)\big| N_i^{-1}(\infty)\big)}{d\alpha} < 0. \tag{17}$$

A similar estimate also occurs under the general conditions of growth of the new phase particles. Indeed, if we introduce the characteristic radius $R_{\text{k}}$ of a droplet and the free path length $R_{\text{free}}$ in a pair (the latter is divided by the condensation coefficient), then we easily obtain

$$\frac{d\big(\big|N_i(\infty) - N_{i+1}(\infty)\big| N_i^{-1}(\infty)\big)}{d(R_{\text{k}} R_{\text{free}}^{-1})} < 0. \tag{18}$$

Some special calculations under the diffusion conditions[4] imply the estimate

$$\frac{N_1(\infty) - N_2(\infty)}{N_2\,(\infty)} \le 0.19. \tag{19}$$

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[4] By these conditions, we mean conditions with some renormalization related to the choice of $t_*$ according to [28], which also permits taking the heterogeneous case into account.

We can see that the first iteration gives a sufficiently precise result under all conditions.

The first iteration can be written as

$$\varphi_1 \sim cz - e^{cz} A_1, \qquad A_1 = A \int_{-\infty}^{0} K(y) e^{cy}\, dy \tag{20}$$

for any choice of the function $K$. The constant $A_1$ is determined by the fact that the parameter $t_*$ corresponds to the supersaturation maximum and to the amplitude value of the spectrum:

$$\left. \frac{d\varphi_1}{dz} \right|_{z=0} = c - A_1 c e^{cz}|_{z=0} = 0. \tag{21}$$

It follows from (21) that

$$A_1 = 1 \tag{22}$$

under all the vapor absorption conditions. The dimension spectra for all the vapor absorption conditions therefore have the form

$$\varphi \sim e^{x - e^x}, \tag{23}$$

and this is a universal function of the natural variable $cx$.

We now discuss the earlier approaches. In [23], the value of $t_*$ was chosen separately for each iteration. Different iterations were thus assigned different choices of $t_*$, which led to certain difficulties in comparing the iterations as was necessary for obtaining estimates of the accuracy. In [23], attempts to obtain a final estimate for the accuracy failed because the approximations constructed there were displaced and hence the estimate of their upper and lower bounds, obtained according to [28], could not be used. In the present paper, the choice of $t_*$ is the same for all iterations.[5] The value of $t_*$ can be determined after the last ("exact") iteration is calculated. In other words, the form of the dimension spectra is determined up to the same displacement of $z$ and $x$. This displacement can be determined after the last ("exact") iteration is calculated. In the first iteration, we obtain the universal form of the spectrum. This result is sufficiently close to the exact solution of the integral equation (we can obtain a common estimate under all the vapor absorption conditions if we take into account that the diffusion conditions for droplet growth are the worst for the convergence of the iterations). In [23], it was assumed that an expression similar to the second iteration describes the process with sufficient accuracy. As a result, the possible universality of the spectrum was lost. Moreover, in the paper cited above, only purely free-molecule conditions of vapor absorption (in the terminology of [26]) were studied.

## 4. Heterogeneous condensation

The heterogeneous condensation at centers of the same type does not allow any choice of variables in which the solution is independent of the external conditions and the substance characteristics [27]. At the same time, it is possible to satisfy a similar requirement for the centers with continuous activity in the case of power-law droplet growth.

In [27], only the collective regime of the metastable phase absorption was studied. In what follows, we obtain the evolution equations in the general case. The study of the profile of the vapor density around a solitary droplet formed at a heterogeneous center is completely similar to the study of the vapor density around a droplet formed homogeneously [26]. Hence, we can again divide the entire volume into the domain

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[5] The value of $t_*$ and all the values at an instant $t_*$ must be considered external parameters in the iteration procedure.

where the nucleus formation rate is practically equal to the ideal rate (i.e., obtained in the absence of droplet formation) and the domain where the nucleation rate is negligibly small.

The heterogeneous centers are homogeneously distributed in the system, but they are distributed inhomogeneously with respect to the depletion domains [26] around the supercritical nuclei. At the center of each depleted domain, there is a heterogeneous center. All other centers are distributed approximately homogeneously. Moreover, it is necessary to take into account that the rate of decrease in the degree of metastability is strongly time dependent, similar to the dependence used to justify the evolution models in [26]. The nucleus formation intensity is proportional to the number $\eta$ of free heterogeneous centers and to the volume $W$ where the nucleation rate is practically unaffected by the vapor absorption by the existing droplets. To the integral terms in all three models [26], it is necessary to add the number $\eta$ of the free heterogeneous centers determined as

$$\eta(t) = \eta(-\infty)\exp\biggl(-D\int_{-\infty}^{t} I_{\mathrm{s}}(\Phi_*)\exp\left(\frac{\Gamma}{\Phi_*}ct\right)(1-W)\,dt\biggr) \tag{24}$$

for the first model, as

$$\eta(t) = \eta(-\infty)\exp\biggl(-D\int_{-\infty}^{t} I_{\mathrm{s}}(\Phi_*)\exp\left(\frac{\Gamma}{\Phi_*}ct\right)W\,dt\biggr) \tag{25}$$

for the second model, and as

$$\eta(t) = \eta(-\infty)\exp\biggl(-D\int_{-\infty}^{t} I_{\mathrm{s}}(\Phi_*)\exp\left(\frac{\Gamma}{\Phi_*}ct\right)\,dt\biggr) \tag{26}$$

for the third model. Here, $D$ denotes the known constant depending on the characteristics of the condensing substance. These equations correspond to the depletion of the heterogeneous centers whose total number is assumed to be fixed, which is quite natural for a relatively short-term nucleation stage.

For the condensation at the centers of the same type under diffusion conditions, it is necessary to close the system of equations with the following relations for the first, second, and third models [26] respectively:

$$W \sim \int_{-\infty}^{t} c_v(t-t')^{3/2} I_{\mathrm{s}}(\Phi_*)\exp\left(\frac{\Gamma}{\Phi_*}ct'\right)(1-W)\eta(t')\,dt', \tag{27}$$

$$\log W \sim \int_{-\infty}^{t} c_v(t-t')^{3/2} I_{\mathrm{s}}(\Phi_*)\exp\left(\frac{\Gamma}{\Phi_*}ct'\right)W(t')\eta(t')\,dt', \tag{28}$$

$$\log W \sim \int_{-\infty}^{t} c_v(t-t')^{3/2} I_{\mathrm{s}}(\Phi_*)\exp\left(\frac{\Gamma}{\Phi_*}ct'\right)\eta(t')\,dt', \tag{29}$$

where $c_v$ is a constant.

A generalization to the general conditions for nucleus growth can be obtained by replacing $c_v(t-t')^{3/2}$ with a certain function $K(t-t')$, which can be constructed as follows. Integrating $d\nu/dt$, we find $\nu(t)$ (and $t(\nu)$). This dependence permits selecting a variable $y$ characterizing the droplet, which depends on $\nu$ and whose rate of growth is constant. The variable $y$ for the droplets formed at $t = t_*$ is denoted by $z$, and the variable $x$ is defined as $x = z - y$. The form of the function $K$ is determined by the dependence of $\nu$ on $y$. The droplets with the coordinate $x$ were formed at $t(x)$. The droplets formed at $t_*$ have the characteristics $z$ at the instant $t$. Then the correspondence $t(z)$ is established, and the coordinates $z$ and $x$ become equivalent. The variables $z$ and $x$ play the same role as the variables $t$ and $t'$.

These models can be compared sufficiently simply. The procedure is similar to that in the homogeneous condensation case [26] with only one difference. The third model now corresponds to the final solution of the second model with the first iteration for $W$ rather than to the first iteration for the second model.

The iteration procedure for the second model with two parameters $D$ and $E$ (the parameter $E$ is similar to the parameter $A_1$ already considered) can be written as

$$\log W_{i+1} = E \int_{-\infty}^{t} K(t-t') I_{\mathrm{s}}(\Phi_*) \exp\left(\frac{\Gamma}{\Phi_*} ct'\right) W_i(t') \eta_i(t')\, dt', \tag{30}$$

$$\eta_{i+1}(t) = \eta(-\infty) \exp\biggl(-D \int_{-\infty}^{t} I_{\mathrm{s}}(\Phi_*) \exp\left(\frac{\Gamma}{\Phi_*} ct\right) W_i\, dt\biggr), \tag{31}$$

$$\eta_0 = \eta(-\infty), \qquad W_0 \sim 1. \tag{32}$$

An analysis of this procedure shows that as $D \to 0$, it is included in the corresponding iteration scheme for homogeneous condensation. We can see that the derivative satisfies the inequality

$$\frac{d\bigl(\bigl|N_2(\infty) - N_3(\infty)\bigr| N_3^{-1}(\infty)\bigr)}{dD} < 0 \tag{33}$$

or is sufficiently small in absolute value, which estimates the error of the iteration procedure just as in the homogeneous case. We note that an extremely weak violation of inequality (33) is possible, which does not result in significant effects. The first iteration has the form

$$-\log W_1 \sim \exp\left(\frac{\Gamma}{\Phi_*} ct\right) R, \tag{34}$$

$$\eta_1 = \eta(-\infty) \exp\left(-D I_{\mathrm{s}}(\Phi_*) \frac{\Phi_*}{\Gamma c} \exp\left(\frac{\Gamma}{\Phi_*} ct\right)\right), \tag{35}$$

where the parameter

$$R = E \int_{-\infty}^{0} K(-t') I_{\mathrm{s}}(\Phi_*) \exp\left(\frac{\Gamma}{\Phi_*} ct'\right) dt' \eta(-\infty) \tag{36}$$

is constant.

The dimension spectrum $f(x)$ in the first approximation is given by the formula

$$\begin{aligned} f_1 = W_1 \eta_1 I_{\mathrm{s}}(\Phi_*) \exp\left(\frac{\Gamma}{\Phi_*} lx\right) \sim \\ \sim \eta(-\infty) \exp\left(\frac{\Gamma}{\Phi_*} lx - Q \exp\left(\frac{\Gamma}{\Phi_*} lx\right) + R \exp\left(\frac{\Gamma}{\Phi_*} lx\right)\right), \end{aligned} \tag{37}$$

where the parameters $l$ and $Q$ are determined by the expressions

$$l = \left.\frac{d\Phi}{dz}\right|_{t=t_*}, \tag{38}$$

$$Q = D I_{\mathrm{s}}(\Phi_*) \frac{\Phi_*}{\Gamma c}. \tag{39}$$

This iteration approximation takes the depletion of the heterogeneous centers into account only in the renormalization, which distinguishes relation (37) from the similar relation in the homogeneous case.

In the heterogeneous case, it is impossible to treat $t_*$ as the instant of the supersaturation maximum because the depletion of the heterogeneous centers can result in droplet formation without any decrease in the supersaturation. In this case, $t_*$ is taken to be the time when half the entire amount of droplets has already formed.

If we use the modified expression

$$f_i = W_{i-1}\eta_i I_{\mathrm{s}}(\Phi_*) \exp\left(\frac{\Gamma}{\Phi_*} lx\right), \quad i = 2, \tag{40}$$

for $f$, then there are no difficulties in calculating the number of droplets. Because $\eta_i$ can be found analytically, it is also possible to calculate $\int f_i \, dx$ analytically,

$$\int_{-\infty}^{t_0} W_i(t) I_{\mathrm{s}}(\Phi_*) \exp\left(\frac{\Gamma}{\Phi_*} ct\right) \exp\left[-DI_{\mathrm{s}} \int_{-\infty}^{t} \exp\left(\frac{\Gamma}{\Phi_*} ct'\right) W_i(t')\, dt'\right] dt \sim$$

$$\sim \frac{1}{D}\left[1 - \exp\left[-D \int_{-\infty}^{t_0} I_{\mathrm{s}}(\Phi_*) \exp\left(\frac{\Gamma}{\Phi_*} ct'\right) W_i(t')\, dt'\right]\right], \tag{41}$$

which corresponds to the balance equation for heterogeneous centers. Then the integral of the dimension spectrum can be written as

$$\int_{-\infty}^{t_0} f(t)\, dt \sim \eta(-\infty) - \eta(t_0). \tag{42}$$

In the second approximation, the dimension spectrum is given by the formula

$$f_2(t) = W_1 \eta_2 I_{\mathrm{s}}(\Phi_*) \exp\left(\frac{\Gamma}{\Phi_*} ct\right). \tag{43}$$

After the renormalization $\Gamma ct/\Phi_* \to t$, we obtain

$$f_2 \sim I_{\mathrm{s}}(\Phi_*) e^t e^{-Re^t} \eta(-\infty) \exp\left[-\frac{D}{R} \frac{\Phi_* I_{\mathrm{s}}(\Phi_*)}{\Gamma c} \left[1 - e^{-Re^t}\right]\right]. \tag{44}$$

The displacement $y = t + \log R$ implies

$$f_2 \sim \frac{I_{\mathrm{s}}(\Phi_*)}{R} \eta(-\infty) e^y e^{-e^y} \exp\left[-\Delta[1 - e^{e^y}]\right], \tag{45}$$

where

$$\Delta \equiv \frac{D}{R} \frac{\Phi_* I_{\mathrm{s}}(\Phi_*)}{\Gamma c}. \tag{46}$$

It seems possible to take the instant of the maximum nucleation intensity (but not of the supersaturation maximum) to be $t_*$ and to thus obtain a relation for $\Delta$. In this case, the value of $\Delta$ would be expressed only in terms of numerical constants, and the form of the spectrum $f_2$ would be independent of the process parameters. But the displacement introduced in passing to $y$ does not allow any further displacement required by the choice of $t_*$, and it is therefore impossible to obtain the universal spectrum of dimensions. Once again, this fact is illustrated by the expression for the total number of droplets in the second approximation

$$N_{\mathrm{tot}\,2} \sim \int_{-\infty}^{\infty} f_2(t)\, dt \sim \eta(-\infty)\left[1 - \exp\left[-DI_{\mathrm{s}}(\Phi_*) \frac{\Phi_*}{\Gamma c} \frac{1}{R}\right]\right], \tag{47}$$

which contains a dependence on the parameters.

We now study the nucleation process for the continuous spectrum of heterogeneous center activity. It is possible to describe the heterogeneous center activity by the parameter $w$ contained in the expression for the probability of droplet formation at a heterogeneous center,

$$I_{\mathrm{s}} = I_+ e^w \exp\left(\frac{\Gamma}{\Phi_*} ct\right) \eta(w,t), \tag{48}$$

where $I_+$ is the base amplitude of the spectra. The variable $\eta(w,-\infty)$ plays the role of the density of the distribution of the total number of heterogeneous centers with respect to activity. We assume that in the range of activities important for the nucleation, this variable depends on $w$ rather weakly.

The evolution equation in the second model under the diffusion conditions becomes

$$-\frac{dW}{dt} \sim \frac{3}{2} \int dw\, I_+ e^w \int_{-\infty}^{t} c_v (t-t')^{1/2} W(t') \exp\left(\frac{\Gamma}{\Phi_*} ct'\right) \eta(w,t')\, dt'\, W(t). \tag{49}$$

Integrating this equation together with the equation for $\eta$, we obtain the system of equations

$$F = \int dw\, P e^w \int_{-\infty}^{t} (t-t')^{3/2} e^{t'-F} \theta_w \, dt, \tag{50}$$

$$\theta_w = \exp\left[-Be^w \int_{-\infty}^{t} e^{t'-F}\, dt'\right], \tag{51}$$

where

$$B = I_+ \frac{\Phi_*}{\Gamma c}, \qquad P = \left(\frac{\Phi_*}{\Gamma c}\right)^{5/3} \eta(w,-\infty) I_+ c_v, \tag{52}$$

for the functions $F = -\log W$ and $\theta_w = \eta(w,t)/\eta(w,-\infty)$ depending on the variables $w$ and $t \to t\Gamma c/\Phi_*$.

We first choose the reference point for $t$ and $w$. Because the number of heterogeneous centers is unbounded, we can take $t_*$ to be the instant of the supersaturation maximum. The reference point for $w$ is chosen from the condition $\theta(w=0,\infty) = 1/2$. Under this choice, we obtain the expressions for the constants $P$ and $B$:

$$P = \left[\int dw\, e^w \frac{3}{2} \int_{-\infty}^{0} (-t')^{1/2} e^{t'-F(t')} \theta_w(t')\, dt'\right]^{-1}, \tag{53}$$

$$B = \log 2 \left[\int_{-\infty}^{0} e^{t'-F(t')}\, dt'\right]^{-1}. \tag{54}$$

Obviously, the variables $P$ and $B$ become independent, and the system does not contain parameters. The solution also does not contain parameters. The droplet distribution as a function of the variables $t$ and $w$ has the form

$$f \sim e^{t-F(t)} \theta_w(t) \tag{55}$$

and depends on the substance absorption conditions.

These relations are similar to the relations obtained as a result of formally generalizing the growth law in the model of the collective substance absorption. This fact ensures a natural inclusion and a continuous passage to the solutions obtained under the purely free-molecule conditions of substance absorption [26].

We also note that the regularization is dimensionless in the study of the condensation in the case of the continuous spectrum of heterogeneous centers. Indeed, it is possible to take $\theta_{w1}(t=-t_{00})$ as the initial value ($t_{00}\sim 5$ is not a parameter; it is only the universal dimension of truncation). We then have

$$\theta_{w1}(-t_{00}) = e^{-Be^{w}e^{-t_{00}}}. \tag{56}$$

Taking this initial condition into account, we obtain

$$F = \int dw\, Pe^{w}e^{-Be^{w}e^{-t_{00}}}\int_{-t_{00}}^{t}(t-t')^{3/2}e^{t'-F(t')}\theta_w(t')\,dt', \tag{57}$$

$$\theta = \exp\biggl[-Be^{w}\int_{-t_{00}}^{t}e^{t'-F(t')}\,dt'\biggr] \tag{58}$$

with the same parameters. For $P$ and $B$, we have other expressions, namely,

$$B = \log 2\biggl[\int_{-t_{00}}^{0}e^{t'-F(t')}\,dt'\biggr]^{-1}, \tag{59}$$

$$P = \biggl[\int dw\, e^{w}e^{-Be^{w}e^{-t_{00}}}\frac{3}{2}\int_{-t_{00}}^{t}(t-t')^{3/2}e^{t'-F(t')}\theta_w(t')\,dt'\biggr]^{-1}. \tag{60}$$

We stress that the value of the regularization parameter $t_{00}\sim 5$ already appears after the renormalization and the displacement of $t$ toward the instant of the maximum supersaturation. This analysis can be used under all the droplet growth conditions.

All the dependences obtained are exact under the natural assumption that $\nu_{\mathrm{c}}\to\infty$ (here $\nu_{\mathrm{c}}$ is the number of molecules in the critical nucleus). They do not contain any parameters of the substance and of the external conditions. We can therefore say that the spectra of droplet dimensions have identical forms. But they still depend on the substance absorption conditions. We now derive an approximate form of the dimension spectra for the new phase nuclei that is the same under all conditions.

We now construct the system of equations under arbitrary nucleus growth conditions. For this, we replace $c_v(t-t')^{3/2}$ with $K(t-t')$. The rate of increase in the function $K$ with time turns out to be bounded below by the diffusion conditions and bounded above by the free-molecule conditions. These estimates can be obtained by analyzing the Boltzmann equation.

The system of condensation equations has the form

$$F = \int dw\, A_0e^{w}\int_{-\infty}^{t}K(t-t')e^{t'-F(t')}\theta_w(t')\,dt', \tag{61}$$

$$\theta_w = \exp\biggl[-Be^{w}\int_{-\infty}^{t}e^{t'-F(t')}\,dt'\biggr], \tag{62}$$

where

$$A_0 = \frac{\Phi_*}{\Gamma c}\eta(-\infty)I_+ \tag{63}$$

and the factor arising after the renormalization is included in $K$. The iteration procedure is determined by the relations

$$F_{i+1} = \int dw\, A_0e^{w}\int_{-\infty}^{t}K(t-t')e^{t'-F_i(t')}\theta_{wi}(t')\,dt', \tag{64}$$

$$\theta_{w\,i+1} = \exp\biggl[-Be^{w}\int_{-\infty}^{t}e^{t'-F_i(t')}\,dt'\biggr], \tag{65}$$

$$F_0 = 1, \qquad \theta_{w1} = 1. \tag{66}$$

In reality, to calculate the iterations, it is expedient to regularize the total relative number $\theta_{w\,\mathrm{tot}}$ of heterogeneous centers,

$$\theta_{w\,\mathrm{tot}} = e^{-Qe^{w}}, \tag{67}$$

where

$$Q \sim Be^{-t_{00}}. \tag{68}$$

We then have

$$F_1 = Se^{t} \tag{69}$$

with the constant parameter

$$S = \int dw\, A_0 e^{-A_1 e^{w}} e^{w} \int_0^{\infty} K(\rho) e^{-\rho}\, d\rho$$

and

$$\theta_{w2} = \exp\left[-Be^{w}\frac{1}{S}\left(e^{-Se^{t_{00}}} - e^{-Se^{t}}\right)\right]. \tag{70}$$

The parameter $S$ contains some information about the droplet growth conditions. Under a special choice of $t = 0$ and $w = 0$ in the second approximation, we have

$$S = 1, \qquad B = \frac{\log 2}{e^{-e^{-t_{00}}} - e^{-1}}. \tag{71}$$

In this case, the expression for the spectrum of droplet dimensions, which has the form

$$f(w,t) \sim A_0 e^{w} e^{t - Se^{t}} \exp\left[-Be^{w}\int_{-\infty\,(-t_{00})}^{t} e^{t' - Se^{t'}}\, dt'\right], \tag{72}$$

does not contain any parameters,

$$\frac{f}{\max_{(t)} f} \sim e^{w} e^{t - e^{t}} \exp\left[-\frac{\log 2}{q - e^{-1}} e^{w}\left(q - e^{-e^{t}}\right)\right], \tag{73}$$

where $q = 1$ or $q = e^{-e^{-t_{00}}}$.

Some estimates of the accuracy of the second iteration can be obtained similarly to those already considered. This analogy is based on the absence of crossed effects of center depletion in the second iteration approximation. It follows from estimate (19) that the crossed depletion effects are sufficiently weak. It can then be seen that the dimension spectra are also similar in the case of heterogeneous condensation.

A similar argument can also be used to study the condensation at heterogeneous centers of the same type. Indeed, it follows from (19) that the second iteration is already sufficiently precise. But the number of droplets in the second iteration is just an integral of the dimension spectra in the first approximation, which, as shown above, is independent of the parameters. This property can be established for each $w$.

It is possible to show that for the variables in which the equations are dimensionless in the homogeneous case, the form of the dimension spectrum varies from the first iteration to the exact solution in the homogeneous case as the portion of centers depleted in the condensation process increases. In an arbitrary situation, the form of the dimension spectrum is bounded above and below by the exact solution in the homogeneous case and by the first iteration, which are sufficiently close to each other. This permits speaking about a relative similarity of the spectra for different values of the degree of depletion of heterogeneous centers.[6] Therefore, the spectra in the process of condensation at heterogeneous centers of the same type are also similar and independent of the conditions of the substance absorption by droplets.

We return to the condensation at heterogeneous centers with an activity spectrum. We now know that all the functions $f_w(x) \equiv f(w, x)$ (as functions of $x$) have approximately the same form. This form varies continuously from the form of the first iteration for $w \ll 1$ to the form of the exact solution (if it is possible to speak about the exact solution) for $w \gg 1$, i.e., the form of the function $f_w$ (as a function of $x$) is always bounded by the exact solution and the first iteration, which means that this form remains practically the same. Starting from the form of the spectrum in the first approximation $f \sim f_* e^{cx - e^{cx}}$, we can speak about the amplitude $f_*$ and about the half-width $1/c$. We then note that the half-width is the same for all $f_w$. The amplitude also does not vary as $w \to -\infty$ and decreases as $e^{-w}$ as $w \to \infty$. It remains to describe the dependence of the position of the maximum on $w$. As $w \to -\infty$, it is proportional to $w$; as $w \to \infty$, it remains constant and corresponds to droplets arising at $t = t_*$. Therefore, its separate parts in the spectrum $f(w, x)$ are also similar to each other. Different sections $f_w$ reproduce each other.

The same idea can also be used to study the kinetics of decay of the metastable phase. In this case, the rectangular approximation is used as the central approximation of the spectrum. Precisely as under the dynamic conditions, this approximation is the formal limit as the power in the integral term in the substance balance equation tends to infinity. In the language of free volumes [26], this means that $W$ varies instantaneously from 1 to 0. The formal generalization of the models is quite similar to that in [26].

## 5. Condensation in inhomogeneous systems

We can now use the theory to study the stationary process of condensation in inhomogeneous systems. Widely known examples of such systems are condensation in the atmosphere and condensation in a diffusion chamber. For simplicity, we study an inhomogeneous system in the form of a diffusion chamber [31]. Earlier, the theory was constructed only for collective substance absorption [32], which cannot occur in a diffusion chamber.

We study the vapor absorption by a single droplet. We do not consider thermal effects; they are similar to those studied above. The ordinate axis is denoted by $h$, and the Stokes law is used for the stationary particle velocity,

$$\left(\frac{dh}{dt}\right)_{\mathrm{st}} = V_0 \rho^2 \tag{74}$$

with the characteristic constant $V_0$, where

$$\rho = \nu^{1/3} \tag{75}$$

and $\nu$ is the number of molecules in a droplet.[7] The variable $\rho$ is the linear dimension of a droplet. It is possible to show that the stationary approximation can be used for the droplet velocity in the majority of cases.

We first consider the free-molecule conditions of substance absorption, which permits considering both the case where the density profiles exist and the case where they do not exist. We can write the growth rate as

$$\frac{d\nu}{dt} = V_1 \rho, \tag{76}$$

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[6] It is possible to show that the spectrum is bounded above by the exact solution if there is no depletion of centers and bounded below by the first iteration.

[7] The theory can also be constructed if the law of droplet motion differs from the stationary law.

where $V_1$ is a constant. (In what follows, all known constants whose calculation can be reduced to algebraic transformations are denoted by the symbol $V$ with some subscript.) We then obtain the relation

$$\frac{dh}{dt} = V_2 \frac{d\nu}{dt} \tag{77}$$

or

$$\frac{d\nu}{dh} = V_2^{-1}. \tag{78}$$

In the study of vapor absorption by a single droplet, we can assume that there is approximately no nucleation in some domain of cylindrical form and that the nucleation outside this domain is unaffected. Moreover, we can use the expression for the nucleation rate known from classical nucleation theory. In this case, the nucleation rate is used in the probability interpretation.

It follows from (78) that the diffusion is small with respect to $h$ because the vapor absorption intensity per unit path of the droplet remains the same for the entire evolution process. Instead of studying the three-dimensional case, we can then solve the problem on the plane. The diffusion from the bottom of the cylinder exists, but its effect is negligible (the bottom corresponds to the instant of formation of an essentially supercritical nucleus, which begins to grow regularly). The radius of this cylinder can be obtained using the Green's function formalism. In fact, we need not know this radius because the profile spreads with time because of diffusion. We thus obtain the case of collective vapor consumption in which the influence of the profile is negligible. We must recall here that the functional form of the evolution equation for the second model and the equation for the collective substance absorption are similar, which permits obtaining the form of the spectrum of droplet dimensions. We must also take the integral character of the definition of the depleted domain boundary into account [26]. Therefore, we can speak formally about the depletion domain boundary and about the collective character of the vapor absorption.

We study the global evolution of the system. All the functions now depend only on $h$. The intensity $j dh$ of the vapor absorption on a sufficiently short interval $dh$ is known [27] and has the form

$$j \sim \int_{-\infty}^{z} e^{V_4 (n(x) - n_{\mathrm{id}*})}\, dx, \tag{79}$$

where $n$ is the molecular density of the condensing substance, $n_{\mathrm{id}}$ is the unperturbed value of $n$, and $*$ indicates a certain spatial point similar to the instant $t_*$. In relation (79), the integrand is the nucleus formation rate, whose functional behavior can be approximated by an expression of form (4). Then the right-hand side of the last expression contains the total number of droplets that have formed before the height $z$ is attained. As shown above, all of them consume vapor at the same intensity per unit path (but, of course, they move at different velocities).

We can show that the main consumers of the vapor are supercritical nuclei, i.e., droplets. We can also show that the quasistationary approximation of the nucleus formation rate can be used in the case where this is actually necessary.

Because the diffusion equation is linear, we can write it directly for the deviation $\Delta n$ of the density $n$ from the unperturbed value $n_{\mathrm{id}}$. In the study of the metastable substance consumption by a single nucleus, the diffusion with respect to $h$ is not taken into account. In the study the global evolution, it is necessary to use other scales of lengths and characteristic times. The diffusion in the horizontal plane occurs on the level of the description of vapor absorption by a single droplet, but in the study of the behavior of the entire system, there is no diffusion in the horizontal plane, which corresponds to the case of homogeneous boundary conditions in this plane. The stationary diffusion equation can be written as

$$D_l \frac{\partial^2 \Delta n}{\partial h^2} = -j, \tag{80}$$

where $D_l$ is the diffusion coefficient. After two integrations[8] with the asymptotic expansions as $n \to n_{\mathrm{id}}$ and with $\partial n/\partial z \to \partial n_{\mathrm{id}}/\partial z$ as $x \to -\infty$, we obtain

$$\Delta n = -V_5 \int_{-\infty}^{z} (z-x)^2 e^{V_6(n(x)-n_{\mathrm{id}\,*})}\, dx. \tag{81}$$

Because $V_6 n_{\mathrm{id}\,*} \gg 1$, we can show that the relative dimensions of the domain of the intensive nucleus formation in the diffusion chamber are sufficiently small. In this connection, we can consider only the linearization[9]

$$n_{\mathrm{id}} = n_{\mathrm{id}\,*} + V_7 z \tag{82}$$

for $n_{\mathrm{id}}$. By changing the scale, we can make the coefficient $V_7$ be equal to 1.

Substituting (82) in (81), we obtain the equation already studied in [27] for the power two in the homogeneous limit; this equation was considered in the preceding sections. Therefore, all the above conclusions also hold here.

We now describe the condensation approximately in a more general situation. Previously, we studied the free-molecule conditions, which led to formula (77). We now consider the opposite conditions, i.e., the diffusion conditions, which permit studying all possible conditions of substance absorption and estimating the errors. In this case, we have

$$\frac{d\rho}{dh} = \frac{V_8}{\rho} \tag{83}$$

and

$$\frac{d\nu}{dh} = t^{-1/2} = h^{-\alpha}, \qquad \alpha = \frac{1}{4}, \tag{84}$$

or

$$\frac{(d\nu/dh)_{h=h_a}}{(d\nu/dh)_{h=h_b}} = \left(\frac{h_b}{h_a}\right)^{\alpha}. \tag{85}$$

To obtain these formulas, we use the stationary Stokes law for the droplet velocity. Expression (74) is an approximation. If there are deviations from the stationary conditions, then the velocity is bounded below by this expression. The absorption cylinder no longer has a constant section; its radius $r_0$ depends on $h$ as

$$\frac{(dr_0/dh)_{h=h_a}}{(dr_0/dh)_{h=h_b}} = \left(\frac{h_b}{h_a}\right)^{\alpha/2} \tag{86}$$

(without the vertical diffusion taken into account). The small value $\alpha/2$ permits using the quasistationary approximation and neglecting the vertical diffusion. All conclusions remain valid, and we obtain a description similar to that of the nonstationary condensation in a homogeneous system. Instead of the power two in integral relation (81), we obtain the power 3/2 recalling the condensation in the homogeneous case. The first iteration in this case sets the foundation for more precise expressions.

We consider the scope of the model considered above. The stationary conditions can be observed only for the fog-type condensation. This means that the elementary volume must contain many droplets. We determine the dimensions of this volume. After the spectrum parameters are found, we can determine the dimension $h_0$ of the domain of intense nucleus formation. This dimension yields the characteristic time $t_0$

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[8] The role of the variables $z$ and $x$ is similar to their role in the preceding calculations. Now $z$ is identified with the current value of $h$.

[9] Because $V_6$ is sufficiently large (of the order of $\Gamma/\Phi_* n_{\mathrm{id}*}$), the dependence on relative variations in the molecular density is significant, and we cannot assume that $n_{\mathrm{id}}$ is constant.

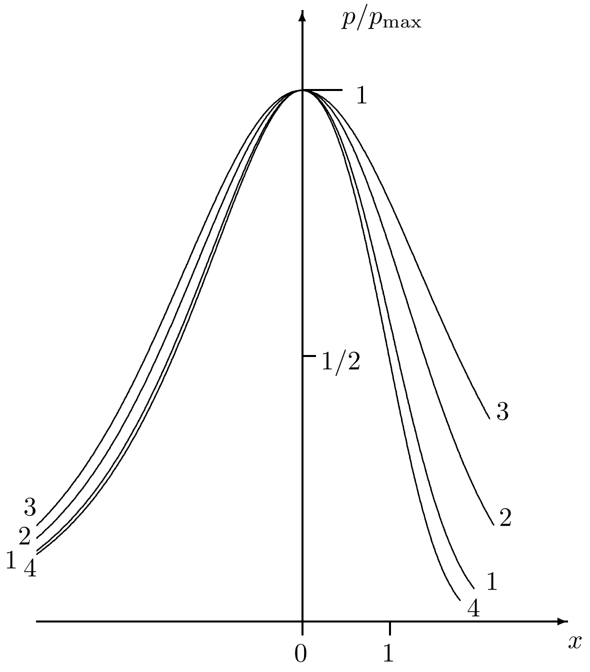

**Fig. 1**

during which a droplet exists in the domain under study. Then the characteristic horizontal dimension is equal to $\sqrt{D_l t_0}$, which leads to the volume $V_0 = h_0 D_l t_0$. The number of droplets in this volume must be large. If the number of droplets in this volume is $N$, then the fluctuations are estimated as $\sim \sqrt{N}$. It is desirable that the relative weight of fluctuations be less than the errors of the second iteration.

The similarity of the forms of the spectra shows that small fluctuations cannot significantly affect the characteristics of the condensation process. The situation is similar to that in the case of nonstationary condensation in a spatially homogeneous system, where the influence of microscopic corrections to the free energy is significant.

## 6. Conclusions

The above consideration is based on the assumption that the forms of the spectra of droplet dimensions are the same in different situations. This assumption permits both deriving systems of equations for the condensation kinetics and obtaining concrete results.

In the case of collective vapor absorption, the construction of the system of equations is independent of the form of the dimension spectrum. If the density profiles exist, then the situation is different, and the fact that the spectra are the same in different models plays an important role in their justification [26]. Analytic results show that the solution of the homogeneous system (or the second model) and of the first iteration (or the third model) are close to each other. This is illustrated in Fig. 1, where the forms of the dimension spectra are presented for different powers in the integral terms of the balance equations. Curve 1 corresponds to the power three, curve 2 corresponds to the power 3/2, curve 3 corresponds to the analytic solution in the case of the power one, and curve 4 shows the form of the first iteration. The ordinate axis is the ratio of the distribution of $p$ to its maximum value $p_{\max}$. The abscissa axis is the deviation $x$ of the dimension linearly increasing with time from the value corresponding to the distribution maximum (this deviation is measured in units of the distribution half-width).

The general character of the laws established above permits considering a weak dependence of the results on microscopic corrections to the free energy [27] a general feature of first-order phase transitions.

The equations (and hence the solutions) in the case of stationary condensation in an inhomogeneous system and in the case of nonstationary condensation in a homogeneous system are the same. This permits considering the nonstationary condensation in an inhomogeneous system a simple superposition of the cases already described. A similar superposition was already studied for the multicomponent condensation [33].

Theoretically calculating the form of the spectrum of the new phase nuclei permits finding this function experimentally. For this, it suffices to measure only the linear dimensions of droplets at some instant and to find the dependence of the linear dimension on time. It is then easy to determine the new variable as a function of the linear dimension (whose rate of variation is constant in time) and to recalculate the distribution function with respect to the linear dimension as the distribution function with respect to this new variable. Precisely this function must have the universal form obtained in this paper. Technically, performing such experiments is simpler than performing the now classic experiments of observing the stationary nucleation rate, in which it is necessary to ensure that the metastable phase appears and disappears instantaneously for the system to be stationary during the nucleation period. The fact that there are no experimental data concerning the process described in the present paper can be easily explained: in this case, the experiment would give fragmentary information, which is in no way related to the properties of the substance. An efficient study of this information is impossible without theoretical investigations.

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# Theoretical description of nucleation in multicomponent system

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**Abstract**

The full theoretical analysis of the kinetics of multicomponent nucleation is presented. The relief of the free energy with surface excesses was analyzed, the valleys and ridges were described, their mutual interaction was studied. The new possibility to change the valley of nucleation is shown. The possibility to have one common valley instead of several neighbor ones which leads to the radical change in the height of the effective activation barrier and to the new value for the nucleation rate.

# Introduction

Historically the problem of determination of the stationary rate of nucleation was primary investigated in one-dimensional approximation [1], [2]. The unique variable characterizing an embryo of a new phase was a number of molecules inside the embryo. Meanwhile, it is evident that the embryo has at least several characteristics, which have to be taken into account to give the adequate description of the nucleation process. That's why it is necessary to study the description of the nucleation process on the base of several characteristics of the embryo.

One can not pretend to take into account all characteristics of an embryo and to give the nucleation description on the base of all embryo characteristics. The kinetic aspects of the embryo formation are also far from clear interpretation. Even the mathematical structure of the theory of multi-dimension nucleation is far from complete understanding. So, it is worth to start with the simple cases of multidimension description.

The simplest and the most evident example of multi-dimension description is a multicomponent nucleation. It means that the nucleation in mixture of vapors is studied. Here kinetic coefficients are determined extremely clear, the free energy of the embryo is also rather well known in general features.

The history of investigations of the binary nucleation is very rich. The number of publications concerning the binary nucleation is now greater than devoted to other domains of the nucleation theory. But already in the case of binary nucleation there appear many problems to solve. So, it is worth paying attention namely to multicomponent nucleation.

Until nowadays there is still no universal self consistent analytic approach which makes use of all previous theories or directly shows their errors. This task will be the goal of the present paper.

At first one has at least to mention approaches, which pretend to give original recipes for the stationary nucleation rate. Certainly, the classical expression for the free energy given by the standard thermodynamics has to be the starting point of a theory. In our analysis we ignore approaches suggesting some artificial correction terms or some reconsiderations without a solid thermodynamic base.

The microscopic corrections to the free energy given by classical thermodynamiocs [3], [4] are not the subject of our investigation, we consider only a task to describe nucleation at the relatively low supersaturations. Even this question is out of a true solution. We do not consider a normalising factor in an equilibrium distribution which evidently appear in the expression for the nucleation rate. This will be a subject of a separate investigation.

The first essential contribution to establish the binary nucleation rate was made by H.Reiss [5] who determined the rate of nucleation on the base of a steepest descent line in a near critical region. Solution of a kinetic equation presented by Reiss was corrected by Stauffer [6]. In the last paper the correct formula for the rate of nucleation in the square approximation of the free energy in the neighborhood of the critical embryo was given. Earlier the general ideas for the problem of overcoming the activation barrier in the multicomponent case were formulated by Langer [7] but one can not state that the publication [6] is a direct consequence of [7]. One has to stress that the constant direction of a flow in a neighborhood of the critical point was simply postulated in [6]. This constancy can be proven only with the help of the boundary conditions which was done in [8] where direct solution of the kinetic equation was presented.

As it became clear after the solution of Trinkaus [9] the problem to determine the nucleation rate requires to decide whether the transition over the barrier really occurs at the critical point ( the saddle point - here and later the critical point means the coordinates of the critical embryo). When there is a strong hierarchy between kinetic coefficients of absorption of different components one can see that flow of embryos can pass aside the critical region (the region near the critical point), but over the ridge far from critical point.

Solution of Stauffer implies the square approximation of the embryos free energy near the critical point. Solution of Trinkaus implies the linear approximation of the height of special activation barrier. But as it will be seen later there is no contradiction between approximations - both are suitable in corresponding situations.

Further analytical progress is associated with the appearance of many variations. Among them one can outline the refined Stauffer's solution presented by Berezhkovski and Zitserman [10] and conception of the genuine saddle point proposed by Li et al. [11]. One has to stress that these contributions did not radically change the already known formulas for nucleation rate but slightly corrected some known results. In this context it is also necessary to mention the publications of Shi and Seinfeld [12] and Wu [13].

Here we do not analyze the theories connected with the reconsidered free energy of the embryos formation taking their history from the famous publication of Lothe and Pound [14] and modifications of this approach to the case of multicomponent nucleation. Any new expression for the free energy will cause the new value of the nucleation rate but the mathematical structure of the derivation of the nucleation rate remains the same.

In the middle of 1990-ies the serious set of attempts to analyze the binary nucleation problems was presented in [15], [16].

In the last years one can outline the publications which analyze the same problems which have been already mentioned. The problem of boundary conditions was revised in publication of Wilemski and Fisenko [17]. The authors put the natural boundary conditions directly at the boundaries of a whole pre-critical region where these conditions are evident. But then it is necessary to solve the kinetic equation in the whole pre-critical and the near-critical region which was done in [17] only numerically.

The set of papers by Li, Nishioka, Maksimov [11] is devoted to give the definition of the generalized saddle point which can be used both in the situation where the flow goes over the standard saddle point and in the situation of hierarchy where the solution of Trinkaus [9] takes place. This idea is certainly attractive but as it will be shown in this publication sometimes the nucleation occurs in a more complex way and can not be described in terms of the genuine saddle point even approximately. Moreover, the point of the Trinkaus' solution depends not only on the free energy but also on the derivatives along special directions.

The problem of transition of the binary case to the unary one was studied in [18] where the full analysis of this problem was given. Here we are not interested in this transition because the embryo with one molecule of a rare component can not be considered on the base of a standard thermodynamics in an approximation of a homogeneous liquid which is adopted in this publication.

Here we do not analyze numerous publications which combine the standard known approach with some artificial additions. Such combinations are rather typical for publications of Djikaev with coauthors (see, for example, [19]). In [19] the values of kinetic coefficients from the first passage time analysis are formally injected in the standard solution presented in [20] and the final formulas are presented. One has to mention that the first passage time analysis is based on some unknown characteristics (for example, the height of activation barrier for a molecule to penetrate inside the embryo) which can not lead to concrete results.

All mentioned publications in the binary nucleation do not make any profit from the topology of the relief of the free energy of the embryo. This task was solved in [20] where the structure of relief of the free energy in the capillary approximation was studied. It was shown that the relief of the free energy can be characterized as the straight channels, ridges and saddle points. In this publication the results of [20] will be widely used.

The formulation of the capillary approximation faces the difficulty known as the Renninger-Wilemski's paradox [21], [22]. Because of publications by Oxtoby and Kashiev [24] the thermodynamic background of the surface excesses is completely studied. To overcome this difficulty one has to write the Gibbs' absorption equation and to introduce surface excesses of components of the surface of tension. This leads to the difference of concentration in the surface layer and in the bulk of the embryo which was noted in [20]. But there further conclusions for kinetics of the process have not being made.

The structure of the free energy relief with surface excesses was investigated in [23] but only in thermodynamic aspects of the problem. The kinetic features have not been considered in [23].

In [8] the kinetic equation was solved in the neighborhood of the critical embryo. The progress achieved in [8] was the appropriate formulation and account of boundary conditions. Certainly earlier the boundary conditions were mentioned in [9] but they were put in the infinitely far points where the structure of a free energy can not be seen in all details. Namely the necessity to conserve the boundary conditions at the low boundary of a near-critical region determines the conservation of the square form of the free energy in transformation presented in [8].

Having summarized the development of theoretical investigations in the binary nucleation one can state that despite the essential progress in this field there are still many problems to consider.

It is rather natural to construct the global picture of the nucleation including the case of the hierarchy between kinetic coefficients, surface excesses, etc. The unification of the free energy topological features with the already mentioned approaches is the main goal of this publication. This approach leads to many rather essential features of nucleation presented below. Moreover, some striking features changing the rate of nucleation in the order of magnitude will appear.

The structure of this paper is the following

- In the first part the main ideas of the capillary approximation are formulated and the free energy is constructed. Here the surface excesses are taken into account. The variables providing the simple form of the free energy are shown and their connection with the numbers of molecules in the embryo is established.

- The second part is devoted to the description of the near-critical region. It is shown that this region has the form similar to the case of the absence of the surface excesses. Here the hierarchy of evolution will be shown.

- The third part is devoted to the analysis of the Reiss' solution and the Stauffer's one. The plausible way to see the Reiss' formula will be shown. The moderate value of the difference between the Reiss' and the Stauffer's solution is justified. This is important for the possible ignorance of the slow or rapid variables of correcting order.

- The forth section analyzes the jump of the embryos from one channel to another one. The situation of the near-equilibrium falling transition is considered here. The solution is found also in the discrete model.

- The fifth section considers the conception of the common valley. The equilibrium common valley transition is analyzed. It will be shown the new height of activation barrier. This value seriously differs from all known results.
- The sixth section analyzes the general picture picture of the nucleation rate formation. The case of the equilibrium saturation of the destination valley is studied.
- All results are summarized in the conclusion.

# 1 Thermodynamic basis

## 1.1 Capillary approximation

The main object involved in determination of the nucleation rate is the free energy of the isolated embryo. To give the description of the embryo one has to fix the variables of the state of the embryo. Assuming the thermal equilibrium of the embryo one can describe the embryo only by the numbers of molecules $\nu_i$ inside the embryo. These variables are extracted by following properties

- In elementary acts of evolution $\nu_i$ are changed separately. The step of change is one unit.
- Although the free energy even in capillary approximation is not diagonal the form of expression for the free energy is relatively simple.

In the capillary approximation the energy $F$ ordinary taken in the thermal units is the sum of the bulk part $B$ and the surface part $\Omega$.

$$F = -B + \Omega$$

The ordinary expressions for $B$ and $\Omega$ are following

$$B = \sum_i \nu_i \mu_i$$

$$\Omega = \gamma S$$

Here the sum is taken over all components of the embryo, $\mu_i$ are the differences of the chemical potentials counted from the equilibrium values (with a negative sign), $S$ is the square of the surface of tension, $\gamma$ is the renormalized surface tension.

The difference between the precise value of the free energy and the value in the capillary approximation referred as "correction terms" (*c.t.*) is supposed to be relatively small in comparison with $B + \Omega$. This situation takes place when the number of molecules

$$\nu_{tot} = \sum_i \nu_i$$

inside the embryo is very (strictly speaking infinitely) big

$$\nu_{tot} \gg 1 \qquad (1)$$

The inverse number of molecules (i.e. $\nu_{tot}^{-1}$) will be the small parameter of the theory. So,

$$F = -B + \Omega + c.t.$$

where *c.t.* indicates correction terms with a property

$$|c.t.| \ll |F|$$

Ordinary the decomposition of correction terms on inverse radius $r^{-1}$ of the embryo converges and $F$ has the form

$$F = -B + \Omega + \sum_{k=-1}^{\infty} c_k r^{-k} + c_0 \ln r$$

Here $c_k$ are the coefficients. One can also consider the last decomposition as an asymptotic decomposition. We shall accept the validity of this decomposition.

Ordinary this decomposition is taken with a finite number of terms

$$F = -B + \Omega + \sum_{k=-1}^{1\div 2} c_k r^{-k} + c_0 \ln r \qquad (2)$$

From the last decomposition it follows

$$|d\ c.t.| \ll |dF|$$

The last inequality is important in the justification of the linearization of the free energy.

While speaking about the capillary approximation one has to imply a whole set of assumptions beside the pure thermodynamic consideration. There are several ordinary used approximations included into the capillary approximation. These approximations are the following

- The surface tension is attributed to the dividing surface calculated on the base of the volume separation, i.e.

  $$S = (\sum_i v_i \nu_i)^{2/3}$$

  where $v_i$ are the volumes in a liquid phase. The formal factor $4\pi/(4\pi/3)^{2/3}$ is ordinary included into the effective surface tension.

- Values $v_i$, $\gamma$ are taken from the case of a bulk liquid.

- To give expressions for $\mu_i$ one has to use some model. The most widely used model is the model of a liquid solution. The validity of this model requires

  $$\nu_i \gg 1$$

  for every component. Certainly one can use other models and ignore these limitations. When $\nu_j = 1$ for some component, one can consider this component as a heterogeneous center. That's why the extension of the approximation of the regular solution up to $\nu_i = 1$ in [18] causes questions.

  In this paper we shall use the model of solution.

  To give a formula for chemical potential one can define a supersaturation as

  $$\zeta_i = \frac{n_i}{n_{i\infty}}$$

  where $n_i$ is the molecular number density in the existing vapor and $n_{i\infty}$ is the molecular number density of the vapor saturated over the pure bulk liquid of component $i$ with a flat surface. Then

  $$\mu_i = \ln(\zeta_i) - \ln \xi_i - \ln f_i(\{\xi\})$$

  Here it is supposed that the vapor is an ideal gas which gives the value for the first term in the r.h.s. as $\ln(\zeta_i)$. Ordinary it is assumed that the concentrations $\xi_i$ form a set $\{\xi\}$ of concentrations and the coefficients of activity $f_i$ can depend on the whole set of activities.

For approximation of ideal solution all coefficients

$$f_i = 1$$

To know $f_i$ one has to construct some model of solution or to use some experimental data.

- A special question concerns the definition of concentration. Ordinary the concentration is determined as

  $$\xi_i = \frac{\nu_i}{\sum_j \nu_j} \tag{3}$$

  Sometimes this definition is also included into the ordinary auxiliary approximations of the capillary approach.

  This question is directly linked with the Wilemski-Renninger's paradox [21].

All assumptions made above are necessary for formula for the free energy in capillary approximation.

The presented formula for the free energy is rather transparent, but it faces the difficulty known as the Wilemski-Renninger's paradox. The difficulty is the following:

- It is known that in the critical embryo the Kelvin's relation

  $$\frac{\mu_i}{v_i} = invariant$$

  has to be observed. This follows from the general thermodynamics and from the sense of chemical potentials.

  The last relation gives an equation for the concentration in the critical embryo.

- One can come to the same equation on concentration also by direct differentiation of expression for the free energy. For simplicity assume that $v_i$ do not depend on concentration. This gives

  $$\frac{\partial F}{\partial \xi_i} = 0$$

i.e.

$$0 = -\mu_i - \sum_j \frac{\partial \mu_j}{\partial \nu_i}\nu_j + \frac{2}{3}\gamma(\sum_j v_j \nu_j)^{-1/3} v_i + S\frac{\partial \gamma}{\partial \nu_i}$$

Here it is supposed that $v_i$ do not depend on concentration.

One has to recall that the coefficients of activity $f_i$ satisfy the Gibbs-Duhem's equations

$$\sum_i \xi_i d\mu_i = 0$$

which put a restriction on the coefficients of activity.

$$\sum_i \xi_i d \ln f_i = 0$$

Moreover the Gibbs-Duhem equation can be written as

$$\sum_j \frac{\partial \mu_j}{\partial \nu_i}\nu_j = 0$$

Then the differentiation becomes very simple and leads to

$$\frac{\partial F}{\partial \xi_i} = 0 = -\mu_i + \frac{2}{3}\gamma(\sum_j v_j \nu_j)^{-1/3} v_i + S\frac{\partial \gamma}{\partial \nu_i}$$

Then one can come to the widely known Kelvin's equation only if the derivative $\partial\gamma/\partial\xi_i$ is zero. So, the formal recipe is to forbid the differentiation of the surface tension on concentration. Since the last equation comes from the foundations of thermodynamics it means that something is irrelevant in the previous formula for the free energy.

In the case when $v_j$ depend on concentration we have

$$\frac{\partial F}{\partial \xi_i} = 0 = -\mu_i - \sum_j \frac{\partial \mu_j}{\partial \nu_i}\nu_j + \frac{2}{3}\gamma(\sum_j v_j \nu_j)^{-1/3}[v_i + \sum_j \frac{\partial v_j}{\partial \nu_i}\nu_j] + S\frac{\partial \gamma}{\partial \nu_i}$$

But the Gibbs-Duhem equation has to be here the following one

$$-\sum_j \frac{\partial \mu_j}{\partial \nu_i}\nu_j + \frac{2}{3}\gamma(\sum_j v_j \nu_j)^{-1/3} \sum_j \frac{\partial v_j}{\partial \nu_i}\nu_j = 0$$

which leads to the same conclusions.

> As the result there appeared a formal recipe not to differentiate the surface tension. At first it was the artificial recipe but later the justification of this recipe was given on the base of the Gibbs dividing surfaces formalism.
>
> To resolve this difficulty one has to add to the free energy some new contributions connected with the surface excesses. It will be done later.

Now we return to consideration of the properties of $F$.

The leading idea here is the extraction of the mentioned small parameters $\nu_i^{-1}$. Recall that conditions are rather far from the second order phase transition. If we accept that the surface layer has a finite thickness $d$, then in the limit $r \to \infty$ (where $r$ is the radius of the embryo) one can see that correction terms ($c.t.$) are really relatively small in the following sense

$$|B| \gg |c.t.| \qquad |\Omega| \gg |c.t.|$$

$$|\frac{\partial c.t.}{\partial \nu_i}| \ll |\frac{\partial B}{\partial \nu_i}| \qquad |\frac{\partial c.t.}{\partial \nu_i}| \ll |\frac{\partial \Omega}{\partial \nu_i}|$$

$$|\frac{\partial^2 c.t.}{\partial \nu_i^2}| \ll |\frac{\partial^2 \Omega}{\partial \nu_i^2}|$$

These inequalities are valid for absolute values.

These inequalities is a new result and they will be widely used below. Their validity can be proven analytically.

## 1.2 The form of the free energy

To see the structure of the free energy one can introduce the extensive variable

$$V = \sum_i v_i \nu_i$$

Certainly $V$ is a volume of the embryo. Then

$$F = \gamma V^{2/3} - b(\xi) V$$

with the generalized chemical potential

$$b = \frac{\sum_j \mu_j \xi_j}{\sum_j v_j \xi_j}$$

The generalized chemical potential allows an interpretation

$$b = \frac{< \mu >}{< v >}$$

as the ratio of the mean chemical potential excess and the mean volume per one molecule in the embryo.

One can take also as an extensive variable the total number of molecules inside the embryo

$$\nu_{tot} = \sum_i \nu_i$$

Then the free energy can be written in a following way

$$F = \gamma(\sum_i v_i \xi_i)^{2/3} \nu_{tot}^{2/3} - \nu_{tot} \hat{b}(\xi)$$

where

$$\hat{b}(\xi) = \sum_i \mu_i \xi_i$$

and the renormalized surface tension

$$\hat{\gamma} = \gamma(\sum_i v_i \xi_i)^{2/3}$$

appears.

One has also to mention the possibility to take as external variable the surface energy in the power 3/2, i.e.

$$\varsigma = \gamma^{3/2} \sum_i v_i \nu_i$$

used in [20]. Then the free energy has the form

$$F = -b_p(\xi)\varsigma + \varsigma^{2/3}$$

where the generalized chemical potential is

$$b_p = \frac{\sum_j \mu_j \xi_j}{\sum_i \gamma^{3/2} v_i \xi_i} = \frac{b}{\gamma^{3/2}}$$

The third possibility used in [20] is the most preferable because here the free energy has the most simple form and in the "surface" term the factor depending on concentration is absent.

The question to discuss is what we shall take as an extensive variable - the variable proportional to the volume or the value proportional to the number of molecules? Thermodynamics does not give an answer because asymptotically these values are proportional.

But the problem to take into account the Renninger-Wilemski's paradox remains here our of attention. To overcome this difficulty one has to include into description the surface excesses of components. To take these excesses one has to choose the surface accurately. The most preferable choice is to choose as the surface the surface of tension because the surface tension can be attributed to this surface without corrections. At this surface all components have the surface excesses $\psi_i$ but the surface tension can be attributed namely to this surface. In the first (rough) approximation these values are proportional to the square $S$ of the surface of tension

$$\psi_i = \varrho_i S$$

Parameters $\varrho_i$ are supposed to be independent on $S$ and have to be given by the theory of a liquid state.

The square of the surface of tension can be approximately calculated as

$$S = (\sum_i v_i(\nu_i - \psi_i))^{2/3}$$

Certainly, there exists a difference between a surface of tension and the surface covering the volume of the embryo. But since the sense has only $S\gamma$ one can attribute this difference to the value of $\gamma$.

Here we omit the constant factor having included it into the surface tension $\gamma$. Hence,

$$\psi_i = \varrho_i(\sum_i v_i(\nu_i - \psi_i))^{2/3}$$

The last relation is not a formula for $\psi_i$ but an equation. It can be solved by iterations. These iterations are based on a small parameter $\psi_i/\nu_i$. The smallness of these parameters at $\nu_i \to \infty$ is evident. The first approximation

$$\psi_i = \varrho_i(\sum_i v_i\nu_i)^{2/3}$$

is already suitable as a leading term under the conditions (1). The second iteration

$$\psi_i = \varrho_i(\sum_i v_i(\nu_i - \varrho_i(\sum_j v_j\nu_j)^{2/3}))^{2/3}$$

will refine the solution. The complexity of dependence of $\psi_i$ on $\nu_i$ is the certain difficulty.

The value of concentration $\xi_i$ has now to be redefined as

$$\xi_i = \frac{\nu_i - \varrho_i S}{\sum_j (\nu_j - \varrho_j S)}$$

As an extensive variable it is natural to choose the straight analog of $\varsigma$, namely

$$\varsigma = (S\gamma)^{3/2} = \sum_i v_i(\nu_i - \psi_i)\gamma^{3/2}$$

But this choice does not lead to the "true" form of the free but to

$$F = -\sum_j \lambda_j \mu_j - \sum_j \varrho_j \mu_j \frac{\varsigma^{2/3}}{\gamma(\xi)} + \varsigma^{2/3}$$

with

$$\lambda_i = \nu_i - \psi_i$$

Here the dependence $\gamma$ on $\{\xi\}$ is the source of difficulties. Certainly,

$$\frac{\lambda_i}{\lambda_j} = \frac{\xi_i}{\xi_j}$$

One can introduce another set of variables. Now instead of $\varsigma$ one has to choose the extensive variable

$$\kappa = S^{3/2}(\gamma - \sum_i \varrho_i \mu_i)^{3/2}$$

In these variables the free energy $F$ has the form

$$F = -\kappa b_g(\xi) + \kappa^{2/3} \tag{4}$$

with the generalized chemical potential

$$b_g = \frac{\sum_i \lambda_i \mu_i}{\kappa}$$

or

$$b_g = \sum_i \xi_i \mu_i \frac{\sum_j \lambda_j}{\kappa}$$

One has to show that $b_g$ does not depend on $\kappa$. To fulfill this derivation one can come to

$$b_g = \sum_i \xi_i \mu_i \frac{\sum_j \lambda_j}{S^{3/2}(\gamma - \sum_k \varrho_k \mu_k)^{3/2}}$$

or

$$b_g = \sum_i \xi_i \mu_i \frac{\sum_j \lambda_j}{(\gamma - \sum_k \varrho_k \mu_k)^{3/2} \sum_l v_l \lambda_l}$$

It can be also presented as

$$b_g = \sum_i \xi_i \mu_i \frac{1}{(\gamma - \sum_k \varrho_k \mu_k)^{3/2} \sum_l v_l \xi_l} \qquad (5)$$

The last relation evidently shows that $b_g$ is really a function of $\xi$. The dependence on $\kappa$ is absent.

One can use expression (5) to clarify the Renninger-Wilemski's paradox. According to the Gibbs' absorption relation

$$d\gamma = d \sum_j \varrho_i \mu_i$$

the derivative of the surface tension on concentration is cancelled by the corresponding derivatives of $\varrho_i$ on $\xi$. So, if we write $b_g$ without surface excesses as

$$b_g = \sum_i \xi_i \frac{1}{\gamma^{3/2} \sum_j v_j \xi_j}$$

we have to forbid the differentiation of $\gamma$ on concentration. Now the Renninger-Wilemski's paradox is explained. It is necessary to stress that the reason is not the formal Gibbs' absorption equation, but the difference of concentrations in the bulk solution from the integral values.

Although the the new variables ensure the simple form of the free energy their connection with "initial" variables $\nu_i$ is rather complex. One has to see how on the base $\kappa$, $\xi_i$ it is possible to reconstruct $\nu_i$. The procedure is the following:

- On the base of $\xi_i$ we know $\mu_i$, then we get $\gamma - \sum_i \varrho_i \mu_i$.
- This gives a value of

$$S = \kappa^{2/3} / (\gamma - \sum_i \varrho_i \mu_i)$$

- On the base of $S$ having presented $S$ as
  $$S = \sum_i v_i \lambda_i = \sum_i v_i \xi_i \sum_j \lambda_j$$
  we get $\sum_i \lambda_i$.

- Since $\lambda_i = \xi_i \sum_j \lambda_j$ we get all $\lambda_i$.

- Then
  $$\nu_i = \lambda_i + \varrho_i(\xi) S$$
  and we know all $\nu_i$.

The inverse transformation can not be made by explicit formulas, the problem to find[1] $\varrho$ on the base of $\nu$ has been considered above. When $\varrho$ is found then $\lambda$ is known. This gives $\xi$ and $\kappa$.

The main new facts found here are the following:

- The variables giving the simple expression for the free energy with surface excesses are found.

- The recipe to get the initial variables on the base of the new ones is given

## 1.3 The structure of the free energy relief

The functional form (4) has some consequences analogous to those considered in[2] [20]. But now this form takes into account the surface excesses of an embryo. Here the form (4) ensures the following properties of the free energy of an embryo

- One can see the channels of nucleation defined by equations
  $$\frac{\partial b_g}{\partial \xi_i} = 0$$
  $$\frac{\partial^2 b_g}{\partial \xi_i^2} < 0$$
  Along these channels the equilibrium density of distribution has a maximum (but the real distribution coincides with the equilibrium one only in the part of the pre-critical region)

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[1] When the index is absent it means that the whole set is considered.

[2] In [20] the free energy without surface excesses was considered.

- Because of the Gibbs-Duhem's equation the variables $\xi_i$ in differentiating of $b_g$ are separated. This leads to the approximately zero value of the cross derivatives $\partial^2 b_g / \partial \xi_i \partial \xi_j$.

- One can see the separation lines of nucleation defined by equations

$$\frac{\partial b_g}{\partial \xi_i} = 0$$

$$\frac{\partial^2 b_g}{\partial \xi_i^2} > 0$$

  Along the separation lines the equilibrium density of distribution has a minimum.

- In one channel there is only one saddle point. Certainly, this takes place only in the capillary approximation. This saddle point has a coordinate $\kappa_c$ determined from the following equation

$$\kappa_c = (\frac{2}{3 b_g(\xi_c)})^3$$

  Here $\xi_c$ is the coordinate of the channel.

- The amplitude value of the free energy $F_c$ in the channel is given by the formula

$$F_c = \frac{1}{3} \kappa_c^{2/3}$$

  Here one can see the Gibbs' equation and now it is clear that namely $\kappa^{2/3}$ is the true surface energy, but not $\gamma S$ as it seems from the first point of view. One has to attribute to the surface energy all energy like contributions with the space dimension 2 (or 2/3 in relative units).

- All channels are independent - the embryos starting from the origin of coordinates will use only one separate channel to go to the supercritical region where they begin to grow irreversibly. The nucleation flow will mainly go through the channel with minimal $\kappa_c$ or maximal $b_g$. This remark concerns the case where there is no strong hierarchy between kinetic coefficients of absorption.

One can see that the picture of nucleation is rather simple, but this simplicity was observed for the free energy with the surface excesses for the first time here. This is the new result of this section.

## 1.4 The form of the near-critical region

As it has been mentioned at the beginning the set of natural variables is $\nu_i$. The elementary kinetic act of absorption leads to the change

$$\nu_i \to \nu_i \pm 1$$

So, it is necessary to establish connection between $\kappa, \xi$ and $\nu$ at least approximately.

Denote by the subscript $o$ the values when all surface excesses are zero. Then the theory is very simple and one can get the connection between $\kappa_o, \xi_o$ and $\nu_o$ in a very transparent manner. From $\nu_0$ to $\kappa_0, \xi_0$ one can get by

$$\kappa_0^{2/3} = \gamma \sum_i v_i \nu_{i0}$$

$$\xi_{i0} = \nu_{i0} / \sum_j \nu_{j0}$$

Inverse transformation is given by the chain formulated above. So, it is quite easy to write the kinetic equation for the case of the absence of excesses.

The above consideration shows the role of the case with zero excesses. Hence, this case will be the base to construct the description in the general case.

Return now to the general case.

One can define the near-critical region as the region where

$$|F - F_c| \leq 1$$

This is quite analogous to the one component case. But here we consider the near-critical region associated with the given channel. Then it is necessary that this region has to be closer to this point than the separation lines.

One can define the positive size $\Delta\kappa$ of the near-critical region along the channel of nucleation as

$$F(\kappa_c \pm \Delta\kappa, \xi_c) = F_c - 1$$

Here $\xi_c$ is the coordinate of some channel. Certainly, we get two values $\Delta_1\kappa$ and $\Delta_2\kappa$ corresponding to the positive and to the negative shift. In the square approximation of the free energy

$$\Delta_1\kappa = \Delta_2\kappa = 3\kappa^{2/3} \qquad (6)$$

When $\nu_i \gg 1$ for all $i$ the square approximation is rather accurate.

Analogously one can define the characteristic sizes $\Delta\xi_i$ according to relation

$$F(\kappa_c, \xi_c \pm \Delta\xi_i) = F_c + 1$$

Certainly, we get two values $\Delta_1\xi_i$ and $\Delta_2\xi_i$ corresponding to the positive and to the negative shift. In the square approximation

$$\Delta_1\xi_i = \Delta_2\xi_i = |\frac{\partial^2 b_g}{2\partial\xi_i^2}|^{-1/2}\kappa^{-1/2} \tag{7}$$

When $\nu_i \gg 1$ for all $i$ and there is no singular behavior of generalized chemical potential then the square approximation is valid.

Certainly, it is necessary that the channels have to be separated, i.e. the height of the separation line has to be several thermal units higher than the height of the channels. This has to take place at $\kappa$ near the critical value.

We define the reduced near-critical region as the region where $|\kappa - \kappa_c| \leq \Delta\kappa$, $|\xi_i - \xi_{ic}| \leq \Delta\xi_i$. This definition differs from the ordinary definition of the near critical region as extracted by condition $|F - F_c| \leq 1$.

In the multi-dimensional case there exists long tails near lines $F = F_c$. To illustrate it one can use the square approximation, then the curves $F = F_c+1$ and $F = F_c - 1$ are hyperbolic ones with common asymptotics which are straight lines.

We shall define the tails as the regions corresponding to $|F - F_c| \leq 1$ and $|\xi_i - \xi_{ic}| > \Delta\xi_i$, $|\kappa - \kappa_c| > \Delta\kappa$.

Actually, the following statements can be proven analytically:

- One can show that the tails do not play any essential role in formation on the total nucleation flow.
- Then it is possible to reduce the near-critical region up to the following domain

$$|\xi_i - \xi_{ic}| \leq \Delta\xi_i$$

$$|\kappa - \kappa_c| \leq \Delta\kappa$$

Here and later we shall imagine the reduced near-critical region speaking about the near-critical region.

Now one can see that the relative sizes of the near-critical region are small

$$|\xi_i - \xi_{ic}| \ll \xi_i$$

$$|\kappa - \kappa_c| \ll \kappa$$

Ordinary this smallness is implied when the kinetic coefficient of absorption is supposed to be a constant value. Here this smallness will help to prove the following main result of this section:

- **In the near-critical region the function $F - F_c$ as a function of variables $\kappa - \kappa_c$, $\xi_i - \xi_{ic}$ for every $i$ has practically the same behavior as the function $F_o - F_{co}$ as a function of variables $\kappa_o - \kappa_{co}$, $\xi_{io} - \xi_{ico}$. At least the relative difference is small:**

  $$\frac{|(F(\nu_i - \nu_{ic}) - F_c) - (F_o(\nu_{io} - \nu_{ico}) - F_{co})|}{(F_o(\nu_{io} - \nu_{ico}) - F_{co})} \ll 1$$

  The explanation and the idea of the proof is rather simple. Really, the correction terms to which the excesses belong begin to be essential only when the surface term cancels the bulk term. But as it clear from the sequential differentiation this can take place only in the first derivative. Starting from the second derivative the contribution from the bulk term is zero and this compensation can not take place. This effect is taken into account by the shift of $\nu_{ic}$ instead of $\nu_{ic0}$. So, here the influence of correction termms is negligible.

The last result allows to write the kinetic equation in $\nu_i$ variables taking into account the surface excesses by a simple shift. This takes place only in the near-critical region. This result is new.

## 1.5 The place of the Renninger-Wilemski's effect

The "paradox" of Wilemski and Renninger occupies so important place in the multicomponent nucleation that from the first point of view it seems that this is the real effect taking place in the leading term of capillary approximation. Below it is shown that this effect has an order of correction. To see this effect one can redefine $\kappa$ as $S^{3/2}$ and forget about excesses.

Really, from equation

$$\frac{\partial F}{\partial \xi}|_{\kappa=fixed} = \frac{\partial \gamma}{\partial \xi} \kappa^{2/3} + \frac{\partial b_g}{\partial \xi} \kappa \gamma^{3/2}$$

it is seen that the first term $\frac{\partial\gamma}{\partial\xi}\kappa^{2/3}$ with the derivative $\frac{\partial\gamma}{\partial\xi}$ has a correction order $\kappa^{2/3}$

$$\frac{\partial\gamma}{\partial\xi}\kappa^{2/3} \sim \kappa^{2/3}$$

in comparison with the second term $\frac{\partial b_g}{\xi}\kappa\gamma^{3/2}$ having the order $\kappa$

$$\frac{\partial b_g}{\xi}\kappa\gamma^{3/2} \sim \kappa$$

We extract this result which is explicitly outlined for the first time here because of its importance for the reconstruction of the logical self-consistency of thermodynamics. Only the correcting order of the term with the derivative of the surface tension allows to ignore it in the main order and to return the leading role of the ordinary capillary approximation.

Since the formal recipe to resolve the Renninger-Wilemski's paradox is to forbid the differentiation of $\gamma$ on concentration then the equation on concentration will be different. It would cause the impression that there is a shift in a leading term. The correct answer is that this result causes the shift in $F_c$ which has a correction order as it follows from the last equation.

The necessity to develop the theory with surface excesses is evident because the surface excesses will essentially shift the position of the near-critical region. The shift is many times greater than the size of the near-critical region. The shift has the order $\kappa$ (because there is another equation on concentration - the derivative of $\gamma$ on $\xi$ is cancelled) while the size of the near-critical region has the order $\kappa^{1/2}$.

One can treat the surface tension as a coefficient in the first correction term proportional to the surface of the embryo. The coefficients at $\kappa^{1/3}, \ln\kappa, \kappa^{-1/3}$, etc. depend on intensive variables (concentrations is one example). Their derivatives will be cancelled by derivatives of corresponding excesses. The structure will resemble the Renninger-Wilemski's paradox. But here the dimension of "surface" will be $\kappa^{1/3}, \ln\kappa, \kappa^{-1/3}$, etc. This effect will be called as "generalized cancellation of derivatives on intensive variables".

One to note that the same procedure can be effectively applied for all other correction terms. Rigorously speaking to determine the form of the near-critical region one has to take the expression for $F$ with correction terms up to the order which causes the shift of position of the near-critical region. Now it is clear that the effect of all correction terms will be quite similar to the already described one.

# 2 Channels and separation lines

## 2.1 Similarity of the near-critical relief

Although the Renninger-Wilemski's effect has a correction order it is worth taking it into account. The main reason is the following:

- The relative sizes of the near-critical region is very small. Really, from (6) it follows that
$$\frac{\Delta\kappa}{\kappa_c} \sim \kappa_c^{-1/3} \ll 1$$
and the relative size in $\kappa$-scale is small. From (7) it follows that
$$\Delta\xi_i/\xi_i \sim \kappa^{-1/2}$$
and the relative size in the $\xi_i$ scale is small also. Then it is clear that the relative size in $\nu_i$ scale will be
$$\nu_i/\nu_{ic} \sim \nu_i^{-1/3}$$
Namely these estimates allow to put in the near-critical region the kinetic coefficient $W_i^+$ of absorption of the molecule of $i$-th component to the constant value $W_{ic}^+$ corresponding to the critical embryo
$$W_i^+ \approx W_{ic}^+$$

So, the relatively small error in the determination of the coordinates $\nu_i$ can remove embryo out of the near-critical region which makes the consideration of kinetic equation without surface excesses in the near-critical region useless.

Beside this one has to take into account that the elementary transitions are written in the $\nu$-scale
$$\nu_i \to \nu_i \pm 1$$
and the free energy is written explicitly (with the surface excesses account) in variables $\kappa$, $\xi_i$. So, it is necessary to have the a very precise transformation between $\nu_i$ and $\kappa, \xi_i$. This forms the problem.

Although the transformation from $\kappa, \xi_i$ to $\nu_i$ exists it is very complex. The inverse transformation has not been found explicitly. So, it is necessary to establish the approximate connection. The following statement establishes this connection

- The function $F - F_c$ as a function of $\nu_i - \nu_{ic}$ approximately coincides in the near-critical region with the behavior of $F_0 - F_{0c}$ as a function of $\nu_i - \nu_{ic0}$:
$$F_0(\nu_{ic0} + y_i) - F_{c0} \approx F(\nu_{ic} + y_i) - F_c$$

This property can be called as the approximate similarity of the free energy relief.

Here this fact is established for $\{\nu_i\}$ variables while earlier the same conclusion was made for $\kappa, \{\xi\}$ variables.

The idea of the proof of this property is based on the simple remark that the terms produced by the surface excesses can be important only when the terms produced by the bulk and surface contributions are cancelled. In the near-critical region this occurs only in the first derivative over $\nu_i$ at the critical embryo. Cancellation in high derivatives is impossible[3]. Here we use the form $F = \sum_i \mu_i \nu_i - \gamma S$ and differentiate it over $\nu_i$. This ensures the similarity of relief.

Now one can propose the following sequence of actions

- at first one has to solve equations for the characteristics of the critical embryo
- then one has to solve the kinetic equation without excesses but in shifted coordinates.

Certainly, the similarity of relief takes place both in $\nu_I$ coordinates and in $\kappa, \xi_i$ coordinates.

Analogously one can one can prove the small relative role of microscopic corrections in the value of $dF_c/d\zeta_i$ which is used in construction of the global evolution of the phase transition. Here the formula (2) has to be used and it has to be taken into account that the coefficients in this formula are constant.

## 2.2 The form of pre-critical region

One can see the following important property:

- **The critical embryo can not have** $\xi_i = 0$

---

[3] Since the high derivatives of the bulk contribution are zero.

It can be seen from the explicit form of $\mu_i$

$$\mu_i = \ln \zeta_i + \ln \xi_i + \ln f_i(\xi)$$

Recall that here $\zeta_i$ is the supersaturation of $i$-th component defined as

$$\zeta_i = \frac{n_i}{n_{ii}}$$

$n_i$ is the molecular number density of vapor of $i$-th component, $n_{ii}$ is the molecular number of the pure saturated vapor of $i$-th component. The second term is caused by the standard entropy of mixing, the third term characterizes the deviation of mixture from the ideal solution, here $f_i$ is the phenomenological coefficient of activity.

Then one can see that at $\xi_i \to 1$ the situation of dilute solution takes place. Then the Henry's law states that the situation is close to the ideal solution, then $f_i = 1$ and there are no correction terms. Then one can see that

$$\frac{db_g}{d\xi_i}|_{\xi_i=1} = \infty$$

and the condensation into the pure component is forbidden. Analogously

$$\frac{db_g}{d\xi_i}|_{\xi_i=0} = -\infty$$

Earlier the analogous estimates were formulated in [20] for $\xi_{i0}$. Then from (6) and (7) it follows that the widths $\Delta\nu_i$ along $\nu_i$ satisfy

$$\Delta\nu_i \gg 1$$

for all $i$. These estimates ensure the possibility of continuous description of evolution in the kinetic equation.

In the absence of the strong hierarchy between coefficients of absorption one can define the pre-critical region by two conditions

- by inequality
$$F < F_{cm} - 1$$
where $F_{cm}$ is the minimal activation barrier among different channels.
- by requirement that this region has to be continuous and the origin belongs to this region.

One can prove that in this region the quasi stationary equilibrium state takes place. Here the absence of the hierarchy of kinetic coefficients plays the principal role.

Now one can investigate the form of the pre-critical region in $\nu_i$ variables. It looks like a star and the needles are going along the bottoms of channels. Certainly due to restrictions $\nu_i \geq 0$ there is only one quarter of a star. In $\kappa, \{\xi\}$ variables it looks like a brush.

If in every channel we put the value $F_c$ corresponding to this channel, the shortest needle is the main one. The shortest needle (in $\kappa, \xi$ plane) corresponds to the lowest barrier and, hence, it is the main needle through which the nucleation takes place.

If the level $F_c$ is chosen as $F_{cm}$ and it is one and the same for all channels then the main needle is the longest one

To see the relaxation to the equilibrium distribution we need to determine the minimal diameter of this star. It is given by the following relation

$$-\kappa_{min} b_{g\ min} + \kappa_{min}^{2/3} = F_{cm} - 1$$

Here $b_{g\ min}$ is the minimal value of $b_g$. So, if $|b_{g\ min}|$ does not go to infinity, one can easily see the finite value of $\kappa_{min}$ and the connection of channels.

The last consideration solves the problem of connection of channels of nucleation. The problem was that the behaviour of channels near the origin where the surface excesses can play the leading role was unclear. So, one could not say whether the channels are connected or no. Now the concrete position of channels near origin is not important.

The only condition is the restriction on $b(\xi)$ - this function can not go to $-\infty$ at some concentrations.

## 2.3 Characteristic sizes of near-critical region.

Consider the variables parallel to $\xi_i, \kappa$ and having the scale of $\nu_i$. These variables are

$$\nu_{par} \simeq \frac{\kappa n}{\gamma^{3/2} \sum_i^n v_i}$$

$$\nu_{i\ perp} \simeq \nu_{par} \xi_i$$

Here it is supposed that all $v_i$ have the same order of values. The total number of components $n$ is not supposed to be a big parameter.

Then the halfwidths along $\nu_{par}$ and $\nu_{i\ perp}$ satisfy the following estimates

$$\Delta\nu_{par} \sim \kappa^{1/6}\Delta\nu_{i\ perp}$$

$$\Delta\nu_{par} \sim \kappa^{2/3} \sim \nu_{tot}^{2/3}$$

$$\Delta\nu_{perp} \sim \kappa^{1/2} \sim \nu_{tot}^{1/2}$$

The time of establishing of the stationary state along $\nu_{par}, \nu_{i\ perp}$ is given by

$$t_{r\ par} sim (\frac{W^+}{\Delta^2\nu_{par}})^{-1}$$

$$t_{r\ iperp} \sim (\frac{W^+}{\Delta^2\nu_{i\ perp}})^{-1}$$

Here all kinetic coefficients of absorption are supposed to have one and the same order of value which is marked by $W^+$.

Then we come to the following strong inequality

$$\frac{t_{r\ par}}{t_{r\ iperp}} \sim \kappa^{1/3} \gg 1$$

This equation states the hierarchy in the near critical region. Earlier this hierarchy was established in [25] for the situation without surface excesses. Here it is done for the presence of the surface excesses.

To see this property the main effort was spent to show the similarity of forms of the free energy relief. Then one can come to the hierarchy rather automatically.

The mean characteristic time $t_u$ to overcome the near-critical region for the embryo at the bottom the channel at the boundary of the near-critical and pre-critical regions has the order of $t_{r\ par}$

$$t_u \sim t_{r\ par}$$

Then we come to the following strong inequality

$$\frac{t_u}{t_{r\ iperp}} \sim \kappa^{1/3} \gg 1$$

It means that along $\nu_{i\ perp}$ there is a quasi equilibrium.

## 2.4 Advantages of hierarchy

On the base of hierarchical inequalities one can see that along $\nu_{i\ perp}$ or $\xi_i$ there is quasi equilibrium. Then the distribution function $n(\{\nu_i\})$ which can be transformed into $n(\nu_{par}, \{\nu_{i\ par}\})$ can be presented as

$$n(\nu_{par}, \{\nu_{i\ par}\}) = N_{par}(\nu_{par}) n_{eq}(\{\nu_{i\ perp}\})$$

where $N_{par}$ plays the role of the amplitude of the known equilibrium distribution and $n_{eq}$ is given by

$$n_{eq}(\{\nu_{i\ perp}\}) \sim \exp(-F(\nu_{par}, \{\nu_{i\ perp}\}))$$

or more convenient

$$n_{eq}(\{\nu_{i\ perp}\}) \sim \exp(F(\nu_{par}, \{\nu_{i\ perp}\}) - F(\nu_{par}, \{\nu_{i\ perp\ b}\}))$$

where $b$ marks the coordinate of the bottom of the channel.

Then there remains only the task to determine the amplitude $N_{par}$. This is a simple one-dimensional problem of nucleation. One can easily solve it.

Reduction the problem of nucleation to the one dimensional case allows to solve more complex situations. At first one can see that when the characteristic width of equilibrium distribution seriously changes it leads to the change of the effective free energy in $N_{par}$. Really the effective free energy looks like

$$F_{eff} = F - \ln \Delta_{eq}\nu$$

where

$$\Delta_{eq}\nu = (\sum_{\nu_{perp}} n_{eq}(\nu_{perp}))^{-1}$$

In the majority of cases the summation in the last formula can be replaced by integration

$$\Delta_{eq}\nu = (\int_{-\infty}^{\infty} n_{eq}(\nu_{perp}) d\nu_{perp})^{-1}$$

Here the region of integration is formally put to an infinite one, actually one has to integrate over the region near the bottom of the channel where $n_{eq}$ is essential.

The further simplification is the following: one can take the last integral in square approximation for the equilibrium distribution:

$$n_{eq}(\{\nu_{i\ perp}\}) \sim \exp(-F_b) \prod_j \exp(-\frac{\partial^2 F(\nu_{par}, \{\nu_{i\ perp}\})}{2\partial\nu_{j\ perp}^2}|_{\nu_{i\ perp}=\nu_{i\ perp\ b}} (\nu_{j\ perp} - \nu_{j\ perp\ b})^2)$$

This allows to take integrals explicitly.

Then the effective free energy is given by

$$F_{eff} = F - \sum_j \ln \frac{\pi^{1/2}}{\sqrt{\frac{\partial^2 F(\nu_{par},\{\nu_{i\ perp}\})}{2\partial \nu^2_{j\ perp}}|_{\nu_{i\ perp}=\nu_{i\ perp\ b}}}}$$

Later one has to solve one-dimensional nucleation problem with the effective free energy instead of the initial free energy. As it will be shown later by demonstration of the plausible derivation of Reiss' formula one has to be very attentive at this step.

Ordinary in the near-critical region the value $\Delta_{eq}\nu$ is constant and there is no peculiarities in behavior of $F_{eff}$. Certainly, in the square approximation the is an explicit solution of Stauffer. But the approach based on hierarchy leads to final analytical results in more complex and may be exclusive cases. Really, here the square approximation was taken only as an illustration.

One has to clarify the place of the presented approach in the task to determine the nucleation flow. Ordinary to justify the total square approximation in the near critical zone and to use the Langer-Stauffer's approach one has to adopt some approximations including the smooth behavior of the derivative of $b_g$ near the bottom of the channel. But there is no clear evidence of the regular behavior of $b_g$ near the bottom. So, the approach based on the hierarchy is preferable.

On the base of hierarchy one can also see many interesting and important facts:

- At first we see that the quasi-unary condensation can not be described in terms of the square approach. A direct transformation of the formulas appeared in the Langer-Stauffer's approach does not lead to the formulas of the unary nucleation. This occurs because inevitably the square approximation has to be violated. So, we come to **the impossibility of description of the quasi-unary nucleation in terms of the standard Stauffer's binary nucleation approach.**

- The next consequence of general results is the impossibility of situation of the inverse direction proposed by Zisterman-Berezhkovskii, where [10] the Stauffer's approach meets difficulties. Really, now it is clear that valleys have to be directed to the origin, but not at the perpendicular direction as it is supposed in the consideration of Zisterman and Berezhkovskii.

One has to mention that the thermodynamics is rather formal and can give essential corrections to the initial variant of the theory if some other expressions for chemical potentials and surface energy are taken. Certainly, these expressions have to be the matter of discussion. But one can not deny the possibility to come to the situation where the square approximation is not suitable and one has to follow the approach suggested here.

Here we suppose that these expressions are already given. They are some external information for the theory developed here.

# 3 Stauffer's and Reiss' solutions

The main goal in the investigation of the multicomponent nucleation is to get essential corrections in comparison with the already known approaches. For this purpose we shall examine the formulas of Stauffer and Reiss for the nucleation rate.

## 3.1 Kinetic equation

Consider the binary case. Introduce the Reiss' variables $x$, $y$ as the variables when the free energy in the critical region has the form

$$F = F_c - x^2 + y^2,$$

where $F_c$ is the free energy in the saddle point. These variables can be obtained from $\nu_1$, $\nu_2$ by rotation and rescaling[4].

Instead of rotation and rescaling it is more convenient to introduce the separated variables directly. The variables $\kappa$, $\xi$ are the stable and unstable ones. One can come to

$$\frac{\partial^2 F}{\partial \xi \partial \kappa} = -\frac{d b_g(\xi)}{d\xi},$$

which is vanished in the saddle point. It means that the square form of the free energy in $\kappa, \xi$ variables looks like

$$F = -A(\kappa - \kappa_c)^2 + B(\xi - \xi_c)^2 + F_c$$

---

[4] May be some part of the Lorenz transformation with an arbitrary parameter has been made. So, these variables aren't completely fixed.

without the cross term. Here $A$ and $B$ are some positive constants

$$A = -(\frac{\partial^2 F(\kappa,\xi)}{2\partial\kappa^2})_c \quad B = (\frac{\partial^2 F(\kappa,\xi)}{2\partial\xi^2})_c$$

Then in the coordinates

$$\tilde{x} = \sqrt{A}(\kappa - \kappa_c) \quad \tilde{y} = \sqrt{B}(\xi - \xi_c)$$

one gets

$$F = F_c - \tilde{x}^2 + \tilde{y}^2$$

Now we shall seek for the similar variables obtained by the linear transformations.

The variables $x$, $y$ can be obtained from $\nu_1$, $\nu_2$ by the linear transformation

$$x = c_{11}(\nu_1 - \nu_{1c}) + c_{12}(\nu_2 - \nu_{2c}),$$

$$y = c_{21}(\nu_1 - \nu_{1c}) + c_{22}(\nu_2 - \nu_{2c})$$

(which isn't orthogonal) with the known coefficients

$$c_{11} = [-\frac{1}{2}(\frac{\partial^2 F}{\partial\kappa^2})_c]^{1/2}(\frac{\partial\kappa}{\partial\nu_1})_c,$$

$$c_{12} = [-\frac{1}{2}(\frac{\partial^2 F}{\partial\kappa^2})_c]^{1/2}(\frac{\partial\kappa}{\partial\nu_2})_c,$$

$$c_{21} = [\frac{1}{2}(\frac{\partial^2 F}{\partial\xi^2})_c]^{1/2}(\frac{\partial\xi}{\partial\nu_1})_c,$$

$$c_{22} = [\frac{1}{2}(\frac{\partial^2 F}{\partial\xi^2})_c]^{1/2}(\frac{\partial\xi}{\partial\nu_2})_c.$$

The variables $x, y$ practically coincide with $\tilde{x}$, $\tilde{y}$. The difference has an order of a small parameter.

The estimates for coefficients $c_{11}, c_{21}, c_{12}, c_{22}$ are

$$c_{11} \sim \kappa_c^{-2/3},$$

$$c_{12} \sim \kappa_c^{-2/3},$$

$$c_{21} \sim \kappa_c^{-1/2},$$

$$c_{22} \sim \kappa_c^{-1/2}.$$

The estimates

$$\Delta\kappa \sim \kappa^{2/3} \sim \nu_{tot}^{2/3} \sim \Delta\nu_{par}$$

$$\Delta\nu_{perp\ i} \sim \kappa^{1/2} \sim \nu_{tot}^{1/2}$$

in positive powers of a big parameter $\kappa$ (or $\nu_{tot}$) allows to use the Fokker-Planck's approximation.

In the Fokker-Planck's approximation the kinetic equation for the distribution function $n$ can be written in the following form

$$\partial_t n(\nu_1, \nu_2) = W_1 \partial_1 [n \partial_1 F + \partial_1 n] + W_2 \partial_2 [n \partial_2 F + \partial_2 n],$$

where $W_1$, $W_2$ are the kinetic coefficients, i.e. the numbers of the first sort molecules and the second sort molecules which are absorbed by the embryo in the unit of time. Here

$$\partial_1 \equiv \partial/\partial\nu_1, \qquad \partial_2 \equiv \partial/\partial\nu_2$$

and $\partial_t \equiv \partial/\partial t$. The differentiation on the number of the molecules of the given sort in marked by the index near the symbol of the partial differentiation.

Now we rewrite the kinetic equation in the variables $x$, $y$. Note that

$$\partial_1 = c_{11}\partial_x + c_{21}\partial_y$$

$$\partial_2 = c_{12}\partial_x + c_{22}\partial_y$$

where $\partial_x = \partial/\partial x$ and $\partial_y = \partial/\partial y$.

The distribution $n(x, y)$ is proportional to the distribution $n(\nu_1, \nu_2)$ with coefficient $\partial(\nu_1, \nu_2)/\partial(x, y)$ and one has to take this difference into account in final calculations. In the near-critical region the coefficients of kinetic equation are approximately constants.

To simplify the treatment one can use notations

$$\partial_{x1} = c_{11}\partial_x, \quad \partial_{x2} = c_{12}\partial_x, \quad \partial_{y1} = c_{21}\partial_y, \quad \partial_{y2} = c_{22}\partial_y.$$

Then one can get the equation

$$\begin{aligned}\partial_t n = &W_1(\partial_{x1} + \partial_{y1})[n(\partial_{x1} + \partial_{y1})F + (\partial_{x1} + \partial_{y1})n] \\ &+ W_2(\partial_{x2} + \partial_{y2})[n(\partial_{x2} + \partial_{y2})F + (\partial_{x2} + \partial_{y2})n]\end{aligned}$$

Since the structure of terms like $n(\partial_{x1}+\partial_{y1})F$ coincide with the structure of $(\partial_{x1}+\partial_{y1})n$ one can simply miss the last term and reconstruct it in the final expressions. Then

$$\partial_t n = K_1\partial_x(n\partial_x F+\partial_x n)+K_2[\partial_x(n\partial_y F+\partial_y n)+\partial_y(n\partial_x F+\partial_x n)]+K_3\partial_y(n\partial_y F+\partial_y n)$$

where

$$K_1 = W_1 c_{11}^2 + W_2 c_{12}^2$$

$$K_2 = W_1 c_{11} c_{21} + W_2 c_{12} c_{22}$$

$$K_3 = W_1 c_{21}^2 + W_2 c_{22}^2$$

To stress the hierarchy one can introduce the coefficients

$$R = K_1, \quad k = -\frac{K_1}{K_2}, \quad q = \frac{K_3 K_1}{K_2^2}$$

Then finally

$$\partial_t n(\nu_1,\nu_2) = R[\partial_x[n\partial_x F + \partial_x n] - k^{-1}[\partial_x[n\partial_y F + \partial_y n] + \partial_y[n\partial_x F + \partial_x n]]$$

$$+k^{-2} q \partial_y [n\partial_y F + \partial_y n]]$$

For $R$, $k$, $q$ one can get the following expressions

$$R = W_1 c_{11}^2 + W_2 c_{12}^2,$$

$$k = -\frac{W_1 c_{11}^2 + W_2 c_{12}^2}{W_1 c_{11} c_{21} + W_2 c_{12} c_{22}},$$

$$q = \frac{(W_1 c_{21}^2 + W_2 c_{22}^2)(W_1 c_{11}^2 + W_2 c_{12}^2)}{(W_1 c_{11} c_{21} + W_2 c_{12} c_{22})^2}$$

The last coefficient can be also written as

$$q = 1 + W_1 W_2 (\frac{c_{11} c_{22} - c_{12} c_{21}}{W_1 c_{11} c_{21} + W_2 c_{12} c_{22}})^2.$$

The value of $R$ isn't important because it can be changed by the time rescaling. One can see the estimate

$$k \sim \nu_c^{-1/6}$$

which shows that $k$ is a small parameter. The scale of $q$ is arbitrary, but one can outline situations where $q - 1 \ll 1$.

The boundary conditions for the last equations are the following

$$\begin{aligned} n/n^e = 1 \qquad x \ll -1 \qquad -\infty < y < \infty, \\ n/n^e = 0 \qquad x \gg 1 \qquad -\infty < y < \infty \end{aligned} \tag{8}$$

The plausible but not rigorous consideration corresponding to the solution proposed by Reiss is the following one

- The main operator of kinetic equation is the last term in r.h.s.
- It ensures the relaxation over the stable variable and the kinetic equation becomes the one dimensional one.
- The consideration of the evolution only over the unstable variable leads to the reduction of the kinetic equation to

$$\partial_t n(\nu_1, \nu_2) = R\partial_x[n\partial_x F + \partial_x n]$$

The solution of the last equation leads to the results of Reiss. But in the cited paper of Reiss the hierarchy was not observed. Hence, the analysis there was less plausible.

## 3.2 The influence on the characteristics of the process

One needs the transformation of kinetic equation which conserves the boundary conditions, since the variables in the boundary conditions (8) are already separated. This transformation is the Lorenz' transformation.

Introduce the Lorenz' transformation via formulas

$$\psi = \frac{x + \alpha y}{\sqrt{1-\alpha^2}}, \qquad \eta = \frac{y + \alpha x}{\sqrt{1-\alpha^2}}$$

This transformation conserves the form of the free energy in the critical region:

$$F = F_c - \psi^2 + \eta^2$$

The kinetic equation is transformed to

$$\partial_t n(\nu_1, \nu_2) = R(1-\alpha^2)^{-1}k^{-2}[[(k-\alpha)^2 + \alpha^2(q-1)]\partial_\psi[n\partial_\psi F + \partial_\psi n] -$$

$$[(k-\alpha)(1-k\alpha)-\alpha(q-1)][\partial_\psi[n\partial_\eta F+\partial_\eta n]+$$
$$\partial_\eta[n\partial_\psi F+\partial_\psi n]]+[(1-k\alpha)^2+q-1]\partial_\eta[n\partial_\eta F+\partial_\eta n]].$$

Parameter $\alpha$ which has the absolute value less than 1 has to be chosen to vanish the cross term. The equation for the choice of $\alpha$ is the following

$$(k-\alpha)(1-k\alpha)=\alpha(q-1)$$

Then

$$\partial_t n(\nu_1,\nu_2)=A\partial_\psi[n\partial_\psi F+\partial_\psi n]+C\partial_\eta[n\partial_\eta F+\partial_\eta n]$$

where

$$A=\frac{R}{k^2}(1-\alpha^2)^{-1}[(k-\alpha)^2+\alpha(k-\alpha)(1-k\alpha)]$$
$$C=\frac{R}{k^2}(1-\alpha^2)^{-1}[(1-k\alpha)^2+\frac{(k-\alpha)(1-k\alpha)}{\alpha}]$$

The parameter of the Lorenz' transformation is given by

$$\alpha=\frac{1}{2k}[k^2+q-\sqrt{(k^2+q)^2-4k^2}].$$

After the decomposition at small $k$ one can come to

$$\alpha=\frac{1}{q}k. \tag{9}$$

in the leading term. One can see that it is small. So, it is difficult to see the effect of the Stauffer's consideration on the direction of the flow. But one can not directly put $\alpha=0$ because there is a small parameter $k$. Expression for $A$ will be

$$A=R\frac{q-1}{q}. \tag{10}$$

The ratio $1/q$ is not small. So the correction to the Reiss' formula is essential. The direct substitution $\alpha=0$ leads to

$$A|_{\alpha=0}=R$$

which is the Reiss' result and it is not precise.

## 3.3 Some consequences for the binary nucleation

The question to discuss here is the rate of the deviation of the Reiss' formula for the nucleation rate from the analogous result of Stauffer.

In the derivation of the expression for $q$ no suppositions about $W_1$ and $W_2$ have been made. At first the situation with the moderate ratio $W_1/W_2$ will be discussed.

As far as

$$\frac{\partial\xi}{\partial\nu_1} = \frac{\partial(1-\xi)}{\partial\nu_2} = -\frac{\partial\xi}{\partial\nu_2} \tag{11}$$

we see that the partial cancellation can take place in expression for $q$ only in

$$W_1 c_{11} c_{21} + W_2 c_{12} c_{22}$$

but not in

$$c_{11}c_{22} - c_{12}c_{21}$$

So $q$ is big enough to lead to result near the Reiss' formula $A = R$. This shows that the Reiss' formula is not so bad although it is not a true result.

The precise coincidence of Reiss' and Stauffer's results takes place when $q = \infty$, i.e. when

$$W_1 c_{11} c_{21} + W_2 c_{12} c_{22} = 0$$

The last relation taking into account (11) can be rewritten as

$$W_1 \frac{\partial\kappa}{\partial\nu_1} = W_2 \frac{\partial\kappa}{\partial\nu_2}$$

In the rough approximation corresponding to:

- the capillary approximation itself,
- the Gibbs-Duhem' equation in the capillary approximation
- the negligible dependence of $v_i$ on $\kappa$ in capillary approximation

one can see that the last relation transforms to

$$W_1 v_1 = W_2 v_2$$

where $v_i$ is the volume per molecule in a liquid phase. This condition is the condition of precise applicability of the Reiss' result. It differs from condition

$$W_1 = W_2$$

announced in paper [10] analyzing the theory of Stauffer.

It is clear that the last condition is wrong which opens a question of the formal validity of the Stauffer's derivation. Really, formally regarding one molecule of the first substance as several particles, one can attain the applicability of Reiss' result by such an artificial way. For condition $W_1 v_1 = W_2 v_2$, this trick fails.

Let us extract the conditions when $A$ essentially differs from $R$. It can be only when

$$q \approx 1$$

The last condition can be satisfied only when $W_1 \ll W_2$, $W_1 \gg W_2$. Namely, this situation occurs when there is the rapid component. *The essential variation of the nucleation rate in comparison with the Reiss' formula is possible only under the hierarchy of the kinetic coefficients.* This situation requires a separate analysis.

As an illustration here we shall show the result in a square approximation of the free energy, although one can analytically prove that the existence of a rapid component throws the main nucleation flow away from the near-critical region and another approximations for the free energy have to be used.

Under the hierarchy one can see the evident rapid component and formulas can be simplified. The simplification can be made also directly in the final formulas and the expression for $A$

$$A = W_2 \frac{(c_{11}c_{22} - c_{12}c_{21})^2}{c_{21}^2}$$

is proportional to $W_2$. Then

$$A = W_2 \left(-\frac{1}{2}\frac{\partial^2 F}{\partial \kappa^2}\right)\left[\frac{\partial \kappa}{\partial \nu_1} + \frac{\partial \kappa}{\partial \nu_2}\right]^2$$

In the further considerations of this section this simplification is not used.

## 3.4 Conclusions based on hierarchy

In the post critical region one can assume the derivative on the unstable variable to be locally a constant and reduce the kinetic equation to

$$\partial_t n = R[\partial_x(\partial_x + h) - k^{-1}(\partial_x(\partial_y + 2y) + \partial_y(\partial_x + h)) + k^{-2} q \partial_y(\partial_y + 2y)]n,$$

where $h$ is the constant coefficient corresponding to the first derivative on the unstable variable and the values of $R$,$k$, $q$ are changed since the derivatives are taken now in the local current point. Renormalize the scale over the unstable variable as to put $h = 1$. Certainly, the hierarchy takes place after the renormalization.

We are interested in the stationary solution and shall seek it in the form

$$n = Q(x)\exp(-(y-y_0)^2) \tag{12}$$

with the constant mean value $y_0$ and some function $Q(x)$. The derivative $dQ(x)/dx$ can be neglected. Then

$$[-k\partial_y h + q\partial_y(\partial_y + 2y)]n = 0$$

For $y_0$ one can get taking into account

$$\partial_y \exp(-(y-y_0)^2) = -2(y-y_0)\exp(-(y-y_0)^2),$$

$$\partial_y(\partial_y + 2y)\exp(-(y-y_0)^2) = -4y_0(y-y_0)\exp(-(y-y_0)^2)$$

the following relation

$$\frac{kh}{q} = 2y_0. \tag{13}$$

So the solution is obtained.

Consider this solution. We see that the deviation of the rapid parameter is small also in the post critical region and the possible hidden parameter can not be extracted.

Due to the slope of the free energy surface on $\kappa$ the minimum of the free energy in the cross section depends on the slope of this cross section. But since the slope of the free energy surface on $\kappa$ is small the deviation of the minimum is small also. This deviation can be considered as the deviation of the mean value of the rapid variable and leads to the absence of the possibility to extract this variable in the post critical region also.

The analogous method can be applied also for the near-critical region. In the near-critical region one can make the substitution

$$n = P(x)\exp(-(y-y_0(x))^2),$$

where $y_0$ is now the function of $x$. One can determine $y_0$ according to

$$(\partial_x - 2x)n = -J_x,$$

there the r.h.s. is constant. Then

$$\partial_x n = -J_x + 2xn. \tag{14}$$

The linear character of the last equation ensures the linear dependence of $y_0$ on the unstable variable. As far as the flow is reciprocal to the halfwidht (along the trajectory $y_0$) one can get the equation on the flow. The linear dependence of $y_0$ on $x$ ensure the linear character of the transformation which is analogous to the Lorenz' transformation.

This way of considerations can be applied to the more general situations without the square form of the free energy. Then the trajectory isn't the straight line and the solution is some approximation based on the hierarchy.

The last question to solve is a real position of the near-critical region.

When the deviation of the flow from the steepens descent situation is essential there is the danger to violate the square form of the free energy. The boundary conditions for kinetic equation in the critical region in reality have to be observed at

$$n/n^e = 1 \qquad x \sim -1 \qquad -1 < y < 1,$$

$$n/n^e = 0 \qquad x \sim 1 \qquad -1 < y < 1.$$

After the Lorenz' transformation

$$n/n^e = 1 \qquad \psi \sim -1 \qquad -1 < \eta < 1,$$

$$n/n^e = 0 \qquad \psi \sim 1 \qquad -1 < \eta < 1.$$

Rigorously speaking one has to put the equilibrium conditions at the line where $F = F_c - 1$ which is invariant to Lorenz' transformation. But actually, to ensure the finite relaxation time and the constant values of kinetic coefficients one has to cut-off the tails and to go to the boundary of the reduced near-critical region. But this boundary is not invariant to Lorenz' transformation.

The last definition of the boundary conditions has to be considered as the main one.

But here the reduced near-critical region is stretched along one of the lines $F = F_c$ where the transition occurs. The square approximation in such stretched region can be invalid.

## 3.5 Conclusions

The main new results of the consideration made above are the following:

- The hierarchy of terms in kinetic equation is shown. Earlier the hierarchy was observed only for halfwidths of the near critical region [25].
- The plausible way to derive the Reiss' formula was demonstrated. Since this formula is wrong, this deviation demonstrates the impossibility to neglect in kinetic equation all terms except the main one.
- The moderate value of the error made by Reiss is established. Earlier there was a strong conviction that the error of the Reiss' approach can be enormous, which was illustrated by numerical examples in [6]. Now it is clear that the big error can be only in the cases of strong hierarchy between kinetic coefficients ($W_1 \gg W_2, W_2 \gg W_1$) when the nucleation flux goes mainly far from the saddle point.
- The simplified relations for $\alpha$ (see (9)) and for the nucleation rate (see equation (10) for $A$) have been derived.
- The super-critical region is studied and the expression for the distribution function over the stable variable (12), (13) in this region is derived.

One can see that the precise result is rather complex. It can not be achieved by a simple superposition of naive solutions based on hierarchy. One has also to mention that even in hierarchy $W_1 \gg W_2$ the result differs from the naive one.

But the main result is the absence of the really important corrections in comparison with a naive approach. All obtained corrections are rather small and mainly less than the microscopic corrections in real situations. Below, we shall seek essential corrections in the case of hierarchy.

# 4 Nucleation rate in the situation with hierarchy

The case of hierarchy certainly requires a special consideration going outside the local approximations in the neighborhood of a saddle point of the embryos free energy.

There are many substances for which the densities $n_{\infty i}$ have the different orders of the values. For example,

$$\frac{n_{\infty H_2O}}{n_{\infty H_2SO_4}} > 10^5$$

in the everyday thermodynamic conditions.

Assume that there are two groups of substances: the substances with a slow exchange and the substances with a rapid exchange. Suppose

$$W_a^+ \ll W_b^+$$

The components of the first group will be marked by the index "a" and the components of the second group will be marked by the index "b". At first we shall consider the situation of two components and later the generalization will be evident.

Here the variable $\tilde{v}$ is the following one

$$\tilde{v} = \sum_a v_{la}\nu_a \quad . \tag{15}$$

## 4.1 Direction of a flow

Extract the conditions when the flow is parallel to $\nu_b$. We construct a simple model which will show some estimates.

The quantity of the embryos at the bottom with a fixed slow component can be estimated from above by

$$N_{above} = \Delta\nu n_0 \exp(-F_b)$$

where $F_b$ is the free energy at the bottom $\Delta\nu$ is the effective width of the bottom. The normalizing factor $n_0$ in some situations of the overcoming of the few activation barriers can differ from the standard one. That's why we keep a special definition for this factor.

The quantity of the embryos in the critical region which change the number $\nu_a$ in the unit of time is

$$I_A = W_a^+ \Delta\nu n_0 \exp(-F_b)$$

The flow over the ridge is $J_s$. So, the necessary condition is the following

$$W_a^+ \Delta\nu n_0 \exp(-F_b) \ll J_s \quad . \tag{16}$$

One can adopt for $J_s$ the following expression

$$J_{sb} = W_b^+ n_0 \exp(-F_t)/\Delta\nu \pi^{1/2} \qquad (17)$$

where $F_t$ is the free energy at the top of the ridge and put $\Delta\nu$ as

$$\Delta\nu = (\frac{\partial^2 F(\nu_a, \nu_b)}{2\partial\nu_b^2})^{-1/2}|_{\nu_a=\nu_{ac}, \nu_b=\nu_{bc}} \quad . \qquad (18)$$

It is necessary that the transition occurs earlier than the near-critical region is attained. Then it is possible to put

$$F_b = F_c - 1$$

at the boundary of the near-critical region. At the same boundary one can also put

$$F_t = F_c + 1$$

The inequality (16) comes to

$$W_a^+ \ll \frac{W_b^+}{\exp(2)(\Delta\nu)^2 \pi^{1/2}} \quad . \qquad (19)$$

Practically the same condition can be obtained by the comparison of the characteristic time between the transitions of the embryo along $\nu_a$ which is

$$t_{tr} \sim (W_a^+)^{-1}$$

and the time of the relaxation in the bottom

$$t^s = \frac{(\Delta\nu_b)^2}{W_b^+} \quad .$$

## 4.2 The normalizing factor

Here we shall see that there is no equilibrium distribution in the whole pre-critical region.

Extract the condition when there will be the equilibrium distribution at the level with the fixed $\nu_a$ of the pre-critical region. The quasi equilibrium distribution has the form

$$n = n^q = n_0^q \exp(-F(\nu_a, \nu_b))|_{\nu_a=const} \quad . \qquad (20)$$

The normalizing factor $n_0^q$ differs from the standard normalizing factor because there is an equilibrium along the band but there is no equilibrium between bands.

To establish the equilibrium it is sufficient to have the intensity of the contact between the neighbor bands greater than the intensity of the overcoming over the activation barrier. So, it is necessary to determine the height of the activation barrier. Choose as $\nu_b$ the value of $\nu_{be}$, corresponding to the minimum of the free energy at the band

$$\nu_{be} \ : \ min_{\nu_b} F(\nu_a, \nu_b) = F(\nu_a, \nu_b) \ \ . \tag{21}$$

Then the intensity of the contact can be estimated by $W_a^+ n_0 \exp(-F(\nu_a, \nu_{be})$.

One can due to (19) assume that the transition to the post critical region occurs along $\nu_b$, i.e. inside the band[5]. Beside $\nu_{be}$ one can introduce $\nu_{bx}$ as the point inside the band where the free energy has the maximum

$$max_{\nu_b} F(\nu_a, \nu_b) = F(\nu_a, \nu_{bx}) \equiv F_x(\nu_a) \ \ . \tag{22}$$

Under the square approximation the transition along $\nu_b$ can not occur because this variable is the stable one. Then $\nu_{b\ x}$ can not be defined. But if the component $\nu_b$ is supersaturated over the pure plane liquid then the condensation into the pure liquid is possible and $\nu_{b\ x}$ must exist. This shows that the square approximation can not be used here.

The transition into the super critical region can occur under the arbitrary $\nu_a$. But the probability of such transition is very low for all $\nu_a$ when $\exp(-F_x(\nu_a))$ strongly differs from $\exp(-F_c)$, i.e. out of the critical region. But it can be greater than the intensity to come to the next band. The intensity of the establishing of the equilibrium (not the quasi equilibrium) at the next band[6] is less than the intensity of the transition over the ridge. This intensity is given by

$$J = J_s = n_0^q \exp(-F_x(\nu_a)) W_{bx}^+ / \Delta_x \nu_b \pi^2 \ \ , \tag{23}$$

where

$$W_{bx}^+ = W_b^+(\nu_a, \nu_{bx}); \qquad \Delta_x \nu_b = (\frac{\partial^2 F(\nu_a, \nu_b)}{2 \partial \nu_b^2})^{-1/2} |_{\nu_b = \nu_{bx}} \ \ . \tag{24}$$

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[5] The value $\Delta \nu_b$ depends on $\nu_a$ weakly.

[6] The intensity of transition to the next band.

There is no need to establish the equilibrium along the whole band with the small $\nu_a$. The value of $\nu_{bx}$ for small $\nu_a$ can be very big, the barriers of the nucleation can be very high, but it is necessary to have the equilibrium only near the bottom, i.e. at $\nu_b$ near to $\nu_{be}$. The establishing of the equilibrium along the whole pre-critical region of the band is necessary only for the bands where the intensity of the transition to the post critical region is essential (comparable with the intensity of the transition between the bands). According to the previous considerations there is the quasi equilibrium along such bands.

Introduce the number of embryos in the band

$$N(\nu_a) = n_0^q \exp(-F(\nu_a, \nu_{b\ e}))\Delta_e \nu_b \quad , \tag{25}$$

where

$$\Delta_e \nu_b = \sum_{\nu_b=0}^{\nu_{bx}} \exp(-F(\nu_a, \nu_b) + F(\nu_a, \nu_{be})) \tag{26}$$

has a sense of characteristic width. The last formula in a continuous limit can be transformed to

$$\Delta_e \nu_b = \int_0^{\nu_{bx}} \exp(-F(\nu_a, \nu_b) + F(\nu_a, \nu_{be})) d\nu_b \quad . \tag{27}$$

At the ends of the interval of integration the equilibrium distribution can be violated but there the subintegral function goes to zero. As far as $\exp(-F)$ as function of $\nu_b$ is rather sharp near the maximum then the number of the embryos going from the band with $\nu_a$ to the band with $\nu_a - 1$ can be approximated by $W_a^-(\nu_a, \nu_{be})N(\nu_a)$. The number of the forward transitions is $W_a^+(\nu_a - 1, \nu_{be})N(\nu_a - 1)$. Then one can write the balance equation at the band

$$\begin{aligned} \frac{\partial N}{\partial t} = W_a^+(\nu_a - 1, \nu_{be})N(\nu_a - 1) + W_a^-(\nu_a + 1, \nu_{be})N(\nu_a + 1) - \\ W_a^+(\nu_a, \nu_{be})N(\nu_a) - W_a^-(\nu_a, \nu_{be})N(\nu_a) - J(\nu_a) \quad . \end{aligned} \tag{28}$$

For $J(\nu_a)$ one can get

$$J(\nu_a) = N \frac{W_{bx}^+ \exp(F(\nu_a, \nu_{be}) - F_x(\nu_a))}{\Delta_e \nu_b \Delta_x \nu_b} \quad . \tag{29}$$

One can see that the absence of the equilibrium distribution in the whole pre-critical region is the characteristic feature of the transition far from the saddle point.

### 4.3 Valley zone and ridge zone

For every $\nu_a$ in the pre-critical region there will be $\nu_{be}$. The curve $\nu_{be}(\nu_a)$ will be called the valley in $\nu_a, \nu_b$ plane.

For every $\nu_a$ in the region under consideration there will be $\nu_{bx}$. The curve $\nu_{bx}(\nu_a)$ will be called the ridge in $\nu_a, \nu_b$ plane.

Since there is a slope of the ridge and the valley in $\nu_a$ direction it is necessary to specify the set of variables.

In the set of variables $\kappa, \xi$ the channel of nucleation is the straight analog of a valley. But the channel of nucleation does not coincide with the the valley in $\nu_a, \nu_b$ plane.

The line analogous to the ridge, i.e. the ridge in $\kappa, \xi$ plane will be the separation line defined as

$$\frac{\partial F(\kappa, \xi)}{\partial \xi} = 0$$

$$\frac{\partial F(\kappa, \xi)}{\partial \xi} < 0$$

The values at the channel of nucleation here will be marked by the subscript $h$ and at the separation line the values will be marked by the subscript $s$.

We see that effectively the flow is directed along $\nu_b$. The problem to get $J(\nu_a)$ is purely a one dimensional problem. So, in the band $\nu_a = const$ there exists the valley $\nu_b \approx \nu_{b\ e}$ zone and the ridge $\nu_b \approx \nu_{b\ x}$ zone. Precise definitions are the following

- The ridge zone in $\nu_b$ scale is determined by conditions

  $$F(\nu_a, \nu_b) \geq F(\nu_a, \nu_{bx}) - 1$$

  Certainly, $F(\nu_a, \nu_b) \leq F(\nu_a, \nu_{bx})$. This zone has to be near the given ridge.

- The valley zone in $\nu_b$ scale is determined by conditions

  $$F(\nu_a, \nu_b) \leq F(\nu_a, \nu_{be}) + 1$$

  Certainly, $F(\nu_a, \nu_b) \geq F(\nu_a, \nu_{be})$. This zone has to be near the given valley.

To find the value of the flow $J(\nu_a)$ one has to solve kinetic equation in the ridge zone. To find the normalizing factor like it was done in heterogeneous nucleation it is necessary to consider the valley zone and to solve kinetic equation in this region.

The problem under consideration is the influence of the surface excesses on the forms of the free energy in the ridge zone and the valley zone. Fortunately some simplifying properties will be established below which help to escape from the explicit inclusion of surface excesses in the kinetic equation.

For the ridge zone these properties are the following

- Define by the subscript 0 the values without surface excesses
- In the ridge zone for arbitrary $s$ corresponding to the ridge zone

$$F(\nu_a, \nu_{bx} + s) - F(\nu_a, \nu_{bx}) \approx F(\nu_a, \nu_{bx0} + s) - F(\nu_a, \nu_{bx0})$$

For the valley zone these properties are the following

- In the valley zone for arbitrary $s$ corresponding to the valley zone

$$F(\nu_a, \nu_{be} + s) - F(\nu_a, \nu_{be}) \approx F(\nu_a, \nu_{be0} + s) - F(\nu_a, \nu_{be0})$$

One can analogously define the channel zone and the separation zone.

- The separation zone is determined by conditions

  $$F(\kappa, \xi) \geq F(\kappa, \xi_s) - 1$$

  The value of $\kappa$ is fixed here. Certainly, $F(\kappa, \xi) \leq F(\kappa, \xi_s)$. The separation zone has to be near the given separation line.

- The channel zone is determined by conditions

  $$F(\kappa, \xi) \leq F(\kappa, \xi_h) + 1$$

  The value of $\kappa$ is fixed here. Certainly, $F(\kappa, \xi) \geq F(\kappa, \xi_h)$. The channel zone has to be near the given channel line.

One can analytically prove the following properties for the separation zone

- In the separation zone for arbitrary $s$ corresponding to the separation zone
$$F(\kappa,\xi_s+s)-F(\kappa,\xi_s)\approx F(\kappa,\xi_{s0}+s)-F(\kappa,\xi_{s0})$$

One can analytically prove the following properties for the channel zone

- In the channel zone for arbitrary $s$ corresponding to the channel zone

$$F(\kappa,\xi_h+s)-F(\kappa,\xi_h)\approx F(\kappa,\xi_{h0}+s)-F(\kappa,\xi_{h0})$$

The method of a proof of all these properties is quite analogous to the already presented for the near-critical region. These properties allow to solve kinetic equations in these regions by some shift renormalizations and solutions in the absence of the the surface excesses.

## 4.4 Discrete case

Consider the stationary solution. The last equations form the system of algebraic equations. Note that the sufficient equations are those where $W_a^+N$ has the order of $J$. The equations with $W_a^+N\gg J$ can be taken into account by the boundary condition $n=n^q=n^e$ for $\nu_a$ which is less than some $\nu_{amin}$, where $J$ begins to be comparable with $W_a^+N$. More precisely this question will be discussed later.

Formally one has to put this condition at $\nu\ll\nu_{amin}$. Then one has to solve equations and to see where the condition $n\approx n^e$ will be violated. It is very easy to do having calculated $J(\nu_a)$ on the base of $n^e$ to get

$$n\approx n^e-\int_{-\infty}^{\nu_a}J(\nu_a')d\nu_a'$$

or having expelled the unphysical region

$$n\approx n^e-\int_{1}^{\nu_a}J(\nu_a')d\nu_a'$$

This will give the necessary estimate.

In the region where $W_a^+N\ll J$ the solution is rather simple

$$n\ll n^e \quad . \tag{30}$$

This condition will be seen automatically at some $\nu_a$ and since $n/n^e$ is a decreasing function of $\nu_a$ it will take place later. So, one has to investigate only few equations of the type

$$W_a^+(\nu_a - 1, \nu_{be}) N(\nu_a - 1) + W_a^-(\nu_a + 1, \nu_{be}) N(\nu_a + 1)$$
$$-W_a^+(\nu_a, \nu_{be}) N(\nu_a) - W_a^-(\nu_a, \nu_{be}) N(\nu_a) = J(\nu_a) \quad . \tag{31}$$

The total flow is defined as

$$J_{int} = \sum_{\nu_a = \nu_{amin}}^{\nu_{amax}} J(\nu_a) \quad , \tag{32}$$

where $\nu_{amax}$ marks the upper boundary of the equations sufficient for the consideration.

In the limit when there is only one sufficient equation[7]

$$J_{int} = W_a^+ \int_0^{\nu_{bx}} n_0 \exp(-F(\nu_a, \nu_b)) d\nu_b \quad = W_a^+ N_{tot}(\nu_a) \tag{33}$$

where the total number of droplets at $\nu_a$ is

$$N_{tot}(\nu_a) = \int_0^{\nu_{bx}} n_0 \exp(-F(\nu_a, \nu_b)) d\nu_b$$

The discrete situation is the most frequent one. But namely this situation has not been considered earlier.

## 4.5 Differential model

Consider the opposite situation when among (31) there are so many equations that it is difficult to solve the algebraic equations. Then it is reasonable to come to the differential form. The condition of the validity of the differential form coincides with the condition of the big number of the essential equations. Then

$$J(\nu_a) = -\frac{\partial}{\partial \nu_a} \{ (W_a^+(\nu_a, \nu_{be}) - W_a^-(\nu_a, \nu_{be})) N(\nu_a) \} +$$
$$\frac{\partial^2}{2 \partial \nu_a^2} \{ (W_a^+(\nu_a, \nu_{be}) + W_a^-(\nu_a, \nu_{be})) N(\nu_a) \} \quad . \tag{34}$$

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[7] Having attained $\nu_a$ all embryos come automatically to the super critical region. Then it is possible to write the expression for the transition on $\nu_b$.

With account of (29) one can get

$$N\frac{\exp(F(\nu_a,\nu_{be})-F_x(\nu_a))}{\Delta_e\nu_b\Delta_x\nu_b}W^+_{bx} =$$
$$\frac{\partial}{\partial\nu_a}\{(W^+_a(\nu_a,\nu_{be})(1-\exp(\frac{\partial F(\nu_a,\nu_{be})}{\partial\nu_a})))N(\nu_a)\} + \tag{35}$$
$$\frac{\partial^2}{2\partial\nu_a^2}\{(W^+_a(\nu_a,\nu_{be})(1+\exp(\frac{\partial F(\nu_a,\nu_{be})}{\partial\nu_a})))N(\nu_a)\} \quad .$$

One can note that

- The hierarchy of the halfwidths of the near-critical region shows that the quasi-unary nucleation in the square approximation in the neighborhood of the saddle point is impossible.

So, the change of approximation to a linear one is absolutely necessary. This conclusion is very essential for further consideration.

One can use the following approximations

$$J = J_0 \exp(cy) \quad , \tag{36}$$

$$y = \nu_a - \nu_{a0} \quad , \tag{37}$$

$$c = \frac{\partial F(\nu_a,\nu_{be})}{\partial\nu_a}|_{\nu_a=\nu_{a0}} - \frac{\partial F(\nu_a,\nu_{bx})}{\partial\nu_a}|_{\nu_a=\nu_{a0}} \quad , \tag{38}$$

$$J_0 = J(\nu_a)|_{\nu_a=\nu_{a0}} \quad . \tag{39}$$

It means that the linear approximation for $F(\nu_a,\nu_{bx}) - F(\nu_a,\nu_{be})$ is adopted. The supposition made in this paper radically changes from the supposition of Trinkaus. This difference will be discussed in a special part of this paper.

One has to note that

$$\frac{\partial F(\nu_a,\nu_{be})}{\partial\nu_a}$$

differs from

$$\frac{\partial F(\nu_a,\nu_b)}{\partial\nu_a}$$

and

$$\frac{\partial F(\nu_a,\nu_{bx})}{\partial\nu_a}$$

differs from

$$\frac{\partial F(\nu_a, \nu_b)}{\partial \nu_a} \quad .$$

When we use $\frac{\partial F(\nu_a,\nu_{be})}{\partial \nu_a}$ we imply the differentiation along the bottom of a valley. When we use $\frac{\partial F(\nu_a,\nu_{bx})}{\partial \nu_a}$ we imply the differentiation along the top of a ridge.

Then one can get

$$I \exp(cy) N = -W_a^+(1-\epsilon)\frac{dN}{dy} + W_a^+(1+\epsilon)\frac{d^2N}{2dy^2} \quad , \tag{40}$$

where

$$I = \frac{W_{bx}^+ \exp(F(\nu_{a0}, \nu_{be}) - F_x(\nu_{a0}))}{\Delta_e \nu_b \Delta_x \nu_b} \quad , \tag{41}$$

$$W_a^+ = W_a^+(\nu_a, \nu_{be}) \quad , \tag{42}$$

$$\epsilon = \exp(\frac{\partial F(\nu_a, \nu_{be})}{\partial \nu_a}) \quad . \tag{43}$$

It is supposed that $\epsilon$ depends on $\nu_a$ rather weakly. We suppose that $\epsilon$ is locally a constant value. This supposition is many times weaker than the previous approximation.

Since $\frac{\partial F(\nu_a,\nu_{be})}{\partial \nu_a}$ is small the value of $\epsilon$ is close to 1 and $1-\epsilon$ is very small. Then the value $1+\epsilon$ is close to 2. Then the relative deviation of $\frac{\partial F(\nu_a,\nu_{be})}{\partial \nu_a}$ have no importance.

Then one can get

$$x = cy \quad , \qquad N \exp(x) + A\frac{d^2N}{dx^2} + B\frac{dN}{dx} = 0 \tag{44}$$

with the known values of $A$, $B$.

After the transition to $\tilde{\psi} = \exp(x)$ one can get

$$A\tilde{\psi}^2 N'' + (A+B)\tilde{\psi}N' + \tilde{\psi}N = 0 \tag{45}$$

with the known solution

$$N = \tilde{\psi}^{-B/(2A)} Z_{B/A}(\frac{2}{\sqrt{A}}\tilde{\psi}^{1/2}) \quad , \tag{46}$$

where $Z_i$ is the cylinder function. One has to choose the solution vanishing at $\infty$.

The known value of $N$ allows to determine the total intensity of the embryo formation and the integral can be taken analytically.

## 4.6 Applicability of solution

Our solution corresponds to the solution derived by H. Trinkaus in [9]. But this correspondence is only a formal one. Recall the derivation by Trinkaus in [9]. Trinkaus proposed the linearization of the free energy $F$ ($G$ in terms of Trinkaus) around $\hat{n}_2$ (this value is analogous to $\nu_{a0}$).

Now we shall analyze the possibility of linearization of $F$ in the vicinity of $\nu_{a0}$. This linearization can be considered in the global sense and in the local sense when linearization is done over one coordinate while the other coordinate determines the values of coefficients in this linearization.

Linearization in the global sense can not exist because the second derivative at the ridge and the second derivative at the valley must have different values. Only then the value of

$$\Delta F(\nu_a) \equiv F(\nu_a, \nu_{bx}) - F(\nu_a, \nu_{be})$$

will be a real activation barrier. The exponent of the last value is the leading term in the expression for the flow.

Linearization in the local sense can not be valid also. It is absolutely clear that the linearization over $\nu_b$ can not be made because it is necessary to have a valley and a ridge for $F$ as a function of $\nu_b$. So, it can not be linearized. Another possibility is to fulfill linearization over $\nu_a$ while coefficients depend on $\nu_b$. The last possibility is the most preferable one.

The careful analysis of the last possibility shows the impossibility of linearization. Really, since the ridge in $\nu_a, \nu_b$ scale is relatively close to the ridge in $\kappa$, $\xi$ scale one can see that the behavior of $F$ as a function of $\nu_a$ at $\nu_b$ slightly greater than $\nu_{bx}$ is the following one: At first $F$ increases until the ridge in $\nu_a, \nu_b$ will be attained. Later with increase of $\nu_b$ the value of $F$ will decrease. This behavior is the direct consequence of the slope of the channels of nucleation in $\nu_a, \nu_b$ plane. So, the linearization is impossible.

The only possible variables, in which the approximate local linearization is valid are variables $\kappa, \xi$. One can see that there $F$ can be linearized far from the critical point

$$\partial F(\kappa, \xi)/\partial \kappa = 0$$

at every $\xi$. The linearization is made only along $\kappa$. But these variables have not been even mentioned in [9].

It has been already analytically shown that we are far from the critical point. Namely this allows the linearization in a local sense along $\kappa$.

The critical point which is the nearest to the origin of coordinates is situated in the channel in $\nu_a, \nu_b$ picture. This is the real saddle point. But since we are far from the main saddle point it means that we are far from every critical point.

Now we shall see that the linearization of the free energy in $\kappa, \xi$ variables is possible. Really,

$$\frac{\partial F(\kappa,\xi)}{\partial \kappa} = -b_g(\xi) + 2\kappa^{-1/3}/3$$

The second derivative is

$$\frac{\partial^2 F(\kappa,\xi)}{\partial \kappa^2} = -2\kappa^{-4/3}/9$$

The size of characteristic region in which the linearization is necessary can be estimated as

$$\Delta\kappa = (b_g(\xi) - 2\kappa^{-1/3}/3)^{-1}$$

So, the necessary condition is

$$|(-b_g(\xi) + 2\kappa^{-1/3}/3)^{-2} 2\kappa^{-4/3}/9| \ll 1$$

Since we are far from the critical point one can neglect the compensation in $(-b_g(\xi) + 2\kappa^{-1/3}/3)$ and get

$$|(2\kappa^{-1/3}/3)^{-2} 2\kappa^{-4/3}/9| \ll 1$$

or

$$\kappa^{-2/3} \ll 1$$

The last inequality is evident.

The last property is important for our needs. We are interested in the linearization of the free energy of the ridge and of the valley. Really, the particular case of the last derivation is the possibility of linearization of $F$ along the ridge and the valley in $\kappa, \xi$ scale, i.e. along the channel and along the separation line.

The last step is to go from $\kappa, \xi$ picture to $\nu_a, \nu_b$ picture. We see that the slope of the valley and the ridge in $\kappa, \xi$ picture along $\kappa$ is very small. Since the slope is proportional to $|\frac{\partial F(\kappa,\xi)}{\partial \kappa}|$ it can be seen from

$$|\frac{\partial F(\kappa,\xi)}{\partial \kappa}| = |-b_g(\xi) + 2\kappa^{-1/3}/3| \sim 2\kappa^{-1/3}/3 \ll 1$$

So, the characteristic distance where the height of the valley, the height of the ridge and, thus, the height of the activation barrier (in fact it can be proven that there is no compensation) undergo the variation of one thermal unit is

$$D_1 = \kappa^{1/3}$$

One can see that $D_1 \ll \kappa$ and it means that the relative size of the transition region has to be small.

This slope has to compared with the characteristic halfwidth along $\nu_b$ or the characteristic size $D_1$ has to be compared with the half-width along $\xi$ multiplied on $\kappa$. We have

$$D_2 = (\frac{\partial^2 F(\kappa,\xi)}{2\partial\xi^2})^{-1/2}\kappa = (\frac{\partial^2 b_g(\xi)}{2\partial\xi^2})^{-1/2}\kappa^{1/2} \sim \kappa^{1/2}$$

We see that

$$D_2 \ll D_1$$

The slope at the boundary of halfwidth is

$$\frac{\partial^2 F(\kappa,\xi)}{\partial\xi^2} D_2/\kappa \sim \kappa^{1/2}$$

and it is rather essential.

We introduce the distance $D_3$ where the slope

$$S_l = \frac{\partial^2 F(\kappa,\xi)}{\partial\xi^2} D_3/\kappa^2 \sim D_3/\kappa$$

has the order of the slope of the ridge $\partial F/\partial\kappa \sim \kappa^{-1/3}$, i.e. $\kappa^{-1/3}$. Then we get

$$D_3 \sim \kappa^{2/3}$$

We see that the order of $D_3$ is the same as the order of $D_1$ and it is relatively small

$$D_3 \ll \kappa$$

It means that the deviation of the separation line in $\kappa,\xi$ scale from the ridge in $\nu_a,\nu_b$ scale is relatively small.

Since $F_h$, $F_s$ allow linearization as functions of $\kappa$ or of $\nu_a$ we come to a conclusion that the linearization of $F_e$, $F_r$, $\Delta F$ (this value is a function of one variable) as a function of $\kappa$ or of $\nu_a$ is quite possible.

## 4.7 Simplified solution

Since $\partial F(\nu_a, \nu_{be})/\partial \nu_a \ll 1$ one can put $\epsilon = 1$. Then $B = 0$ and one come to the universal solution

$$N \sim Z_0(\frac{2}{\sqrt{A}}\tilde{\psi}^{1/2}) \tag{47}$$

This is the universal function $Z_0$ of the variable

$$\frac{2}{\sqrt{A}}\exp(cx/2)$$

Finally we get a universal solution.

## 4.8 Discussion

The multidimensional case is quite analogous to the two-dimensional one. In the multidimensional nucleation one has to consider some channel of nucleation. One has to extract the set of fast variables $\{\nu_b\}$ and the set of slow variables $\{\nu_a\}$.

For the set $\{\nu_a = fixed\}$ one can establish $J_{\{\nu_a\}}$ by the consideration of the evolution in the set $\{\nu_b\}$. It can be done by the standard methods from the previous sections.

After the calculation of $J_{\{\nu_a\}}$ one can define the direction. It will be the quasi-integral on $\nu_a$. This defines the first coordinate. The second coordinate is the direction of the bottom of the valley in the cross section $\{\nu_b = const\}$. The further consideration is absolutely analogous.

The new results formulated above are the following:

- In the paper of Trinkaus [9] only the differential case was considered. The discrete case was not considered there. Really, the height of the pseudo-activation barrier can change rather rapidly with increase of $\nu_a$. This leads to the preference of discrete model.

  As for the half-widths of the bottom of the channel and of the top of the ridge in calculation of $J$ there are inequalities which guarantee the possibility of the differential description. Really, these half-widths increase like $\kappa^{1/2}$ (see the standard estimates for the half-widths along the stable variables). But if even these variables will be not so big nothing will be changed because they variate slowly in comparison with the exponent of the height of the pseudo-activation barrier. So, the mathematical structure of the balance equation will be the same.

- Here the surface limited growth is considered while in [9] the diffusion limited growth was used. It seems that because the transition occurs earlier than the saddle point will be attained the embryos are small enough and the surface limited growth is preferable.

- It is shown that the absence of the equilibrium distribution in the precritical region is the driving force of the transition far from the saddle point. This fact stresses once more the importance of the formulation of the boundary conditions and outlines the paper [8] where the boundary conditions were used for the situation without hierarchy of kinetic coefficients.

- The hierarchy of the halfwidths of the near-critical region (more accurate the near-saddle region) shows that the quasi-unary nucleation in the square approximation in the neighborhood of the saddle point is impossible. So, the change of approximation to a linear one is absolutely necessary. Moreover, it is impossible to see the transition of the Stauffer's solution to Trinkaus' one on the analytic level of explicit formulas.

Beside the mentioned disadvantages of the differential approach one can mention the disadvantage connected with the position of the basic point $\nu_a^*$ for decompositions of the height of the ridge and depth of the valley. An ordinary chosen point for such decompositions is

$$W_a^+ = J(\nu_a)/N(\nu_a) \tag{48}$$

The presence of this point awakes the idea of the Genuine Saddle Point [11]. It is reasonable to put the point of decomposition at

$$n(\nu_a^*) = n_{eq}(\nu_a^*)/2 \tag{49}$$

The shift between $\nu_a^*$ determined by (48) and (49) will be called "the soft shift".

The greater is $|c|^{-1}$, the greater is the soft shift. But the applicability of differential approach requires

$$|c| \ll 1$$

The last parameter ordinary comes from two decompositions: one of the height of the ridge[8]

$$F_r(\nu_a) = F_r(\nu_{a0}) + k_r(\nu_a - \nu_{a0})$$

---

[8] Take a cross section $\{\nu_b = const\}$.

with parameter $k_r$ and another of the depth of the valley[9]

$$F_e(\nu_a) = F_e(\nu_{a0}) + k_e(\nu_a - \nu_{a0})$$

with parameter $k_e$.

Ordinary

$$k_e > 0$$

(the opposite sign means that the saddle point is already behind)

$$k_r < 0$$

(the opposite sign means that energetically it was more profitable to cross the ridge earlier[10]). Then in

$$J \simeq J_0 \exp(-k_r(\nu_a - \nu_{a0}) + k_e(\nu_a - \nu_{a0})) = J_0 \exp(c(\nu_a - \nu_{a0}))$$

parameters $k_e$ and $k_r$ can not be compensated. Ordinary both linear approximations are necessary.

Then the condition $|c| \ll 1$ leads to

$$|k_r| \ll 1$$

$$|k_e| \ll 1$$

Under the last two inequalities one can see that $N$ becomes many times less than the equilibrium value $N^{eq}$ much earlier than $\nu_a = \nu_{a0}$ and the transition is actually over. So, the point of decompositions has to shifted.

The shift of decompositions has to lead to the basic point situated at the position characteristic for the relatively intensive flow. One of the possible recipes is to choose the point $\nu_a^*$ of decomposition according to

$$N(\nu_a) W_a^+ = \int_0^{\nu_a^*} J d\nu_a'$$

The last condition can be approximately rewritten as

$$W_a^+ = \frac{1}{|k_r| + |k_e|} \frac{1 - J(\nu_a^*)}{N}$$

---

[9] Take a cross section $\{\nu_b = const\}$.

[10] Then the cross of the ridge can not disturb the equilibrium distribution. So, the flow is known.

One can start instead of $\nu_a = 0$ from infinity and get a similar estimate. Also it is reasonable to consider

$$W_a^+ = \frac{1}{|k_r| + |k_e|} \frac{J(\nu_a^*)}{2N}$$

as the point for decompositions.

Here naturally appears the length $\Delta$ of the region where the transition occurs. It can be estimated as

$$\Delta = \frac{1}{|k_r| + |k_e|}$$

So, the soft shift can be greater than this region.

We continue to consider the problems of the differential approach.

- Another problem is the smallness of $|k_e|$, $|k_r|$. Because of the monotonous character of derivatives of the free energy along channels and ridges it can be attained only near the saddle point. But here the square approximation has to be used and the Stauffer's solution will be the answer.

  Certainly, if the value of $\nu_a$ is extremely big one can observe small values of derivatives rather far from the saddle point. But, although even here the discrete approach is preferable as it will be shown later.

Now the simplified approximate method for continuous case will be presented. In equation

$$\frac{d^2N}{dx^2} - k_e \frac{dN}{dx} = N \frac{\exp(F_r - F_e)}{\Delta\nu_e \Delta\nu_r} \frac{W_{bx}^+}{W_a^+}$$

one can put $k_e \frac{dN}{dx}$ to zero because of the smallness of $|k_e|$.

Also because of the smallness of $|k_e|$, $|k_r|$ one can put very approximately

$$\frac{\exp(F_r - F_e)}{\Delta\nu_e \Delta\nu_r} \frac{W_{bx}^+}{W_a^+}$$

to some constant (let it be $I_0$). Then

$$\frac{d^2N}{dx^2} = NI_0$$

Solution of the last equation is evident

$$N = A\exp(-\sqrt{I_0}x) + B\exp(\sqrt{I_0}x)$$

The requirement $N \to 0$ at $x \to \infty$ leads to

$$N = A\exp(-\sqrt{I_0}x) \tag{50}$$

But this solution has a bad behavior at $x \to -\infty$. So, in this region one has to use another approach. At $x \to -\infty$ the flow is very small and $N$ is approximately equal to the equilibrium value $N_{eq}$. Then

$$\frac{d^2N}{dx^2} - k_e\frac{dN}{dx} = N_{eq}\frac{\exp(F_r - F_e)}{\Delta\nu_e\Delta\nu_r}\frac{W_{bx}^+}{W_a^+}$$

Then approximately

$$N = N_{eq} - \int J dx$$

or

$$N = N_{eq} - \int N_{eq}\frac{\exp(-(|k_e| + |k_r|)x)}{\Delta\nu_r\Delta\nu_e}dx\frac{W_{bx}^+}{W_a^+}$$

With the evident approximation for the equilibrium value $N_{eq}$:

$$N_{eq} = N_*\exp(-|k_e|x)$$

with parameter $N_* = N_{eq}(x = 0)$ one can get

$$N = N_{eq} - N_*\int\frac{\exp(-|k_r|x)}{\Delta\nu_r\Delta\nu_e}dx\frac{W_{bx}^+}{W_a^+}$$

Since one can approximately take $\Delta\nu_r\Delta\nu_e$ as a constant value there are no problems with integration. So,

$$N = N_{eq} - N_*\frac{1 - \exp(-|k_r|x)}{|k_r|\Delta\nu_r\Delta\nu_e}\frac{W_{bx}^+}{W_a^+}$$

These two solutions (let it be $N_1$ and $N_2$) have to be stuck together at the point where

$$N_1 = N_2$$

Another method can be formulated if we notice that (50) is valid namely locally because it was derived with a supposition $I_0 = const.$ So, we have to go to the local form by differentiation of (50) which gives

$$\frac{dN}{dx} = -NI_0$$

This equation can be integrated with arbitrary $I_0$ which leads to

$$N \sim \exp(-\int I_0(x')dx')$$

When the evident known functional form

$$I_0 \sim exp(cx)$$

is taken, one can come to

$$N \sim \exp(-\frac{I_{00}}{c}\exp(cx))$$

with parameter $I_{00}$. Certainly, parameters $I_{00}$ and $c$ can be considered here as the fitting parameters.

The functional form announced above resembles $\Theta$-function with a soft transition from 1 to 0. We shall call it as a soft $\Theta$-function and denote it by

$$S(x) = \exp(-\exp(x))$$

This function can be used as a brick in an ansatz

$$Q = \sum A_i S(a_i(x - x_i))$$

which can be very effectively used as an approximate solution in all situations considered below in this paper.

# 5 Interaction of valleys

## 5.1 Coordinates of valley in the $\nu_a, \nu_b$ coordinate system

The coordinate of the valley is given by the condition

$$\frac{\partial F(\nu_a, \nu_b)}{\partial \nu_b} = 0$$

The straight differentiation of the free energy gives

$$\frac{\partial F}{\partial \nu_b} = \frac{d\gamma}{d\xi}\frac{\partial \xi}{\partial \nu_b}S + \gamma\frac{2}{3}S^{-1/2}[v_b + \frac{\partial v_a}{\partial \xi}\nu_a\frac{\partial \xi}{\partial \nu_b} + \frac{\partial v_b}{\partial \xi}\nu_b\frac{\partial \xi}{\partial \nu_b}]$$

$$-b_b - [\frac{\partial b_a}{\partial \xi}\nu_a\frac{\partial \xi}{\partial \nu_b} + \frac{\partial b_b}{\partial \xi}\nu_b\frac{\partial \xi}{\partial \nu_b}]$$

where $S$ is the surface square of the embryo. In simplest approximation it can be written as

$$S = (v_a\nu_a + v_b\nu_b)^{2/3}$$

The standard Gibbs-Duhem's equation looks like

$$\nu_a db_a + \nu_b db_b = 0$$

and leads to

$$[\frac{\partial b_a}{\partial \xi}\nu_a\frac{\partial \xi}{\partial \nu_b} + \frac{\partial b_b}{\partial \xi}\nu_b\frac{\partial \xi}{\partial \nu_b}] = 0$$

This brings the condition for the valley coordinate to

$$\frac{\partial F}{\partial \nu_b} = \frac{d\gamma}{d\xi}\frac{\partial \xi}{\partial \nu_b}S + \gamma\frac{2}{3}S^{-1/2}[v_b + \frac{\partial v_a}{\partial \xi}\nu_a\frac{\partial \xi}{\partial \nu_b} + \frac{\partial v_b}{\partial \xi}\nu_b\frac{\partial \xi}{\partial \nu_b}] - b_b$$

But due to the surface enrichment the concentration differs from

$$\xi = \frac{\nu_a}{\nu_a + \nu_b}$$

and has to be

$$\xi = \frac{\nu_a - S\varrho_a}{\nu_a - S\varrho_a + \nu_b - S\varrho_b}$$

Then the Giibs-Duhem's equation looks like

$$Sd\gamma + \nu_a db_a + \nu_b db_b = 0$$

and leads to

$$\frac{d\gamma}{d\xi}\frac{\partial \xi}{\partial \nu_b}S + [\frac{\partial b_a}{\partial \xi}\nu_a\frac{\partial \xi}{\partial \nu_b} + \frac{\partial b_b}{\partial \xi}\nu_b\frac{\partial \xi}{\partial \nu_b}] = 0$$

and

$$\frac{\partial F}{\partial \nu_b} = \gamma\frac{2}{3}S^{-1/2}[v_b + \frac{\partial v_a}{\partial \xi}\nu_a\frac{\partial \xi}{\partial \nu_b} + \frac{\partial v_b}{\partial \xi}\nu_b\frac{\partial \xi}{\partial \nu_b}] - b_b$$

The careful analysis of the generalization of the Gibbs-Duhem's equation for the embryos shows that the terms

$$\frac{\partial v_a}{\partial \xi}\nu_a\frac{\partial \xi}{\partial \nu_b}+\frac{\partial v_b}{\partial \xi}\nu_b\frac{\partial \xi}{\partial \nu_b}$$

have to vanish together with

$$\frac{d\gamma}{d\xi}\frac{\partial \xi}{\partial \nu_b}S+[\frac{\partial b_a}{\partial \xi}\nu_a\frac{\partial \xi}{\partial \nu_b}+\frac{\partial b_b}{\partial \xi}\nu_b\frac{\partial \xi}{\partial \nu_b}$$

Really, the Kelvin's relation in the saddle point requires that

$$\frac{b_a}{v_a}=\frac{b_b}{v_b} \tag{51}$$

The direct calculation with a non zero value of the last terms gives

$$\frac{b_b}{[v_b+\frac{\partial v_a}{\partial \xi}\nu_a\frac{\partial \xi}{\partial \nu_b}+\frac{\partial v_b}{\partial \xi}\nu_b\frac{\partial \xi}{\partial \nu_b}]}=\gamma(36\pi)^{1/2}\frac{2}{3}S^{-1/2}=\frac{b_a}{[v_a+\frac{\partial v_a}{\partial \xi}\nu_a\frac{\partial \xi}{\partial \nu_a}+\frac{\partial v_b}{\partial \xi}\nu_b\frac{\partial \xi}{\partial \nu_a}]}$$

and one can come to (51) only if these terms vanish.

Generally speaking the Gibbs-Duhem's equation has to written in the form

$$\sum(differentials\ of\ all\ intensive\ variables)*(corresponding\ intensive\ variables)=0$$

Particularly

$$Sd\gamma+\nu_a db_a+\nu_b db_b+\nu_a dv_a+\nu_b dv_b=0$$

Then

$$\frac{d\gamma}{d\xi}\frac{\partial \xi}{\partial \nu_b}S+\gamma\frac{2}{3}S^{-1/2}[\frac{\partial v_a}{\partial \xi}\nu_a\frac{\partial \xi}{\partial \nu_b}+\frac{\partial v_b}{\partial \xi}\nu_b\frac{\partial \xi}{\partial \nu_b}]-[\frac{\partial b_a}{\partial \xi}\nu_a\frac{\partial \xi}{\partial \nu_b}+\frac{\partial b_b}{\partial \xi}\nu_b\frac{\partial \xi}{\partial \nu_b}]=0$$

and

$$\frac{\partial F}{\partial \nu_b}=\gamma\frac{2}{3}S^{-1/2}v_b-b_b$$

One can see that the concentration of valley satisfies the condition

$$\gamma\frac{2}{3b_b(\xi)}(v_a(\xi)+v_b(\xi^{-1}-1))^{-1/3}=\nu_a^{1/3}$$

and it is not a constant value. Moreover, it is evident that valleys in the $\nu_a, \nu_b$ system of coordinates do not coincide with channels in $\kappa, \xi$ system of coordinates. They coincide only in saddle points. The valleys in $\nu_a, \nu_b$ system can appear and disappear, their position in the absence of hierarchy of kinetic coefficients means nothing.

## 5.2 Asymptotics at $\nu_b \to \infty, \nu_a - fixed$

The necessary condition of applicability of solution of Trinkaus is the limit

$$\nu_b \to \infty,\ \nu_a = fixed \quad F \to -\infty$$

The explicit calculation gives

$$\nu_b \to \infty,\ \nu_a = fixed \quad F \to -b_b \zeta_b$$

So, it is necessary that $\zeta_b > 0$. But the last condition is not a necessary condition for nucleation in a gas mixture. The necessary condition is the existence of concentration $\xi$ for which the function $b_a \xi + b_b(1-\xi)$ is negative. So, there exists a situation when there is no behavior necessary for application of the Trinkaus' solution.

When $b_b > 0$ one can see the asymptotic wing with a negative slope. It will be called simply as "wing".

Otherwise there can be a situation when even with $b_b > 0$ nucleation can go from one valley to another (may be more deep) valley and further no transition to $\nu_b \to \infty,\ \nu_a = fixed$ will take place because of the height of a new (further) ridge.

In the case of purely supersaturated vapor of components the wings have to be included in the general picture of relief of the free energy.

## 5.3 Two valleys. Kinetic equation

The previous consideration shows that the most ordinary situation is the jump of embryo from one valley to the neighbor one. In one valley (let it be called as the "source valley" and marked by the subscript $-$) the embryos are in the pre-critical region (i.e. $\kappa < \kappa_c$) and in the other valley (let it be called as the "destination valley" and marked by the subscript $+$) the embryos are in the post-critical region (i.e. $\kappa > \kappa_c$). The transitions take place along lines $\nu_a = const$. Since the increase of $\nu_b$ leads to the increase of $\kappa$ it is quite possible.

The values of $\nu_b$ at the ridge will be marked as $\nu_{br}$. The values of $\nu_b$ at the bottom of the source valley will be marked as $\nu_{be-}$ and the values of $\nu_b$ at the bottom of the destination valley will be marked as $\nu_{be+}$. All these values are taken in the $\nu_a$, $\nu_b$ coordinate system.

Kinetic equations are rather transparent and look like

$$\frac{dN_-}{dt} = W^+_{as}(\nu_a - 1, \nu_{be-})N_-(\nu_a - 1) - W^+_{as}(\nu_a, \nu_{be-})N_-(\nu_a)$$

$$+W^-_{as}(\nu_a + 1, \nu_{be-})N_-(\nu_a + 1) - W^-_{as}(\nu_a, \nu_{be-})N_-(\nu_a) - J_-(\nu_a) + J_+(\nu_a) \tag{52}$$

$$\frac{dN_+}{dt} = W^+_{ad}(\nu_a - 1, \nu_{be+})N_+(\nu_a - 1) - W^+_{ad}(\nu_a, \nu_{be+})N_+(\nu_a)$$

$$+W^-_{ad}(\nu_a + 1, \nu_{be+})N_+(\nu_a + 1) - W^-_{ad}(\nu_a, \nu_{be+})N_+(\nu_a) - J_+(\nu_a) + J_-(\nu_a) \tag{53}$$

Here $N_-$ and $N_+$ are the numbers of embryos with given $\nu_a$ in a valley (in $\nu_a, \nu_b$ system of coordinates), $W_+$ and $W_-$ are direct and inverse absorption coefficients, $J_-$ is the flow from the source valley to the destination valley, $J_-$ is the flow from the destination to the source valley (the inverse flow).

We shall investigate the stationary solution.

One has to take into account that $W^+_a$ and $W^-_a$ are functions of $\nu_b$. They are taken at $\nu_b$ equal to the values at the bottom of valley. This can be done because of the relative narrowness of valleys which goes from representation in $\kappa, \xi$ variables.

## 5.4 Two valleys. Direct and inverse flows

The values of flows $J_-$ and $J_+$ are given by the standard formulas

$$J_- = N_- \frac{\exp(-F_r + F_{e-})}{\Delta_r \nu_b \Delta_{e-} \nu_b} W^+_{bx}$$

$$J_+ = N_+ \frac{\exp(-F_r + F_{e+})}{\Delta_r \nu_b \Delta_{e+} \nu_b} W^+_{bx}$$

Here $F_r$ is a free energy of the embryo at the ridge (in $\nu_a, \nu_b$ coordinates), $F_{e-}$ is the free energy of the bottom of the source valley in $\nu_a$, $\nu_b$ coordinate system, $F_{e+}$ is the free energy of the bottom of the destination valley in $\nu_a$, $\nu_b$ coordinate system.

The value of $\Delta_r \nu_b$ is given by

$$\Delta_r \nu_b = \sum_{\nu_b = \nu_{br1}}^{\nu_{br2}} \exp(-F_r + F(\nu_a, \nu_b))$$

Here $\nu_{br1}$ and $\nu_{br2}$ are chosen as roots of equation

$$F(\nu_a, \nu_b) = (2F_r + F_{e+} + F_{e-})/4$$

closest to $\nu_{br}$ and

$$\nu_{br1} < \nu_{br} < \nu_{br2}$$

The value of $\Delta_{e-}\nu_b$ is given by

$$\Delta_{e-}\nu_b = \sum_{\nu_b=\nu_{be-1}}^{\nu_{be-2}} \exp(F_{e-} - F(\nu_a, \nu_b))$$

Here $\nu_{be-1}$ and $\nu_{be-2}$ are chosen as roots of equation

$$F(\nu_a, \nu_b) = (F_r + F_{e-})/2$$

closest to $\nu_{be-}$ and

$$\nu_{be-1} < \nu_{be-} < \nu_{be-2}$$

The value of $\Delta_{e+}\nu_b$ is given by

$$\Delta_{e+}\nu_b = \sum_{\nu_b=\nu_{be+1}}^{\nu_{be+2}} \exp(F_{e+} - F(\nu_a, \nu_b))$$

Here $\nu_{be+1}$ and $\nu_{be+2}$ are chosen as roots of equation

$$F(\nu_a, \nu_b) = (F_r + F_{e+})/2$$

closest to $\nu_{be-}$ and

$$\nu_{be+1} < \nu_{be+} < \nu_{be+2}$$

In continuous approximation one can get the following equations

$$\Delta_r\nu_b = \int_{\nu_b=\nu_{br1}}^{\nu_{br2}} \exp(-F_r + F(\nu_a, \nu_b))d\nu_b$$

$$\Delta_{e-}\nu_b = \int_{\nu_b=\nu_{be-1}}^{\nu_{be-2}} \exp(F_{e-} - F(\nu_a, \nu_b))d\nu_b$$

$$\Delta_{e+}\nu_b = \int_{\nu_b=\nu_{be+1}}^{\nu_{be+2}} \exp(F_{e+} - F(\nu_a, \nu_b))d\nu_b$$

One can prove that in frames of inequalities lying in the base of capillary approximation the continuous approximation is valid. One can also prove that in the absence of peculiarities in behavior of the free energy it is possible in the capillary approximation to use the square approximation with infinite limits for calculation of the mentioned values. This gives

$$\Delta_r \nu_b = \sqrt{\pi}(-\frac{1}{2}\frac{\partial^2 F(\nu_a,\nu_b)}{\partial \nu_b^2}|_{\nu_b=\nu_{br}})^{-1/2}$$

$$\Delta_{e-} \nu_b = \sqrt{\pi}(\frac{1}{2}\frac{\partial^2 F(\nu_a,\nu_b)}{\partial \nu_b^2}|_{\nu_b=\nu_{be-}})^{-1/2}$$

$$\Delta_{e+} \nu_b = \sqrt{\pi}(\frac{1}{2}\frac{\partial^2 F(\nu_a,\nu_b)}{\partial \nu_b^2}|_{\nu_b=\nu_{be+}})^{-1/2}$$

One can rewrite equations for $J_-$ and $J_+$ as following

$$J_- = N_- I_-$$

$$J_+ = N_+ I_+$$

where $I_+$ and $I_-$ are independent on $N_+$, $N_-$.

Already now one can fulfill the qualitative analysis of the kinetic equations.

## 5.5 Qualitative analysis of the kinetic equations

Consider the region of $\nu_a$ where $W_a^+(\nu_a,\nu_{be-}) \sim I_-$. It is easy to see that at $\nu_a$ corresponding to the possible transition from one valley to another

$$W_a^+(\nu_a,\nu_{be-}) < W_a^-(\nu_a,\nu_{be-})$$

(otherwise the saddle point in the source valley is already over)

$$W_a^+(\nu_a,\nu_{be+}) > W_a^-(\nu_a,\nu_{be+})$$

(otherwise it will be necessary to overcome the saddle point in the destination valley and it will cause the establishing of the equilibrium distribution until the height of the saddle point; moreover there is a straight way without barriers to the origin of coordinates).

It means that

$$F(\nu_a,\nu_{be-}) < F(\nu_a+1,\nu_{be-})$$

$$F(\nu_a,\nu_{be+}) > F(\nu_a+1,\nu_{be+})$$

Moreover one can see that

$$F(\nu_a, \nu_{br}) > F(\nu_a + 1, \nu_{br})$$

(otherwise it is more profitable to overcome the ridge earlier at smaller $\nu_a$).

Practically in the main order

$$\frac{I_-}{I_+} = \exp(+F_{e-} - F_{e+})$$

The ratio $I_-/I_+$ governs the evolution of the process. One can see two characteristic situations here

- Situation

  $$I_- \gg I_+$$

  Here one can see that the solution of the previous section can be directly applied. The destination valley do not affect the distribution in the source valley. So, one can put $J_+ = 0$ and split the system of equations. Only the first equation is essential and solution is really the solution in the situation discussed above.

- Situation

  $$I_- \ll I_+$$

  This situation has no analogs and has to be considered separately.

## 5.6 Situation $I_- \ll I_+$

One can approximately put

$$W_a^+(\nu_a, \nu_{be-}) \simeq W_a^+(\nu_a, \nu_{be+})$$

This is taken only for simplicity.

Approximately, the condition of the beginning of the jump of embryos, which changes $N_-$ is the following

$$I_- \geq W_a^+(\nu_a, \nu_{be-})$$

Then

$$I_+ \gg W_a^+(\nu_a, \nu_{be-})$$

Then the second equation of the system becomes the following

$$J_- = J_+$$

and we have locally in a rough approximation

$$\frac{dN_-}{dt} = W_a^+(\nu_a - 1, \nu_{be-})N_-(\nu_a - 1) - W_a^+(\nu_a, \nu_{be-})N_-(\nu_a)$$
$$+W_a^-(\nu_a + 1, \nu_{be-})N_-(\nu_a + 1) - W_a^-(\nu_a, \nu_{be-})N_-(\nu_a) \tag{54}$$

Then

$$\frac{N_-}{\Delta_{e+}\nu_b} = \frac{N_+}{\Delta_{e-}\nu_b} \exp(-F_{e-} + F_{e+})$$

and approximately

$$\frac{N_+}{N_-} = \exp(F_{e-} - F_{e+})$$

The point where

$$I_- \approx W_a^+(\nu_a, \nu_{be-})$$

will be marked as $\nu_a = y_0$. When $\nu_a$ increases one has

$$I_- \gg W_a^+(\nu_a, \nu_{be-})$$

$$I_+ \gg W_a^+(\nu_a, \nu_{be-})$$

This ensures the quasi-equilibrium and actually the common valley. Later one attains $y_1$ where

$$F_{e-}(y_1) = F_{e+}(y_1)$$

For $\nu_a > y_1$ one has

$$I_- \gg I_+$$

$$J_- = J_+$$

$$N_+ \gg N_-$$

It will be until $y_2$ defined by condition

$$I_+(y_2) = W_a^+(\nu_a = y_2, \nu_{be-})$$

(also the soft shift has to be added). Later all remaining embryos from the source valley go into the destination valley. But their total quantity is already rather small. So, we need not to consider this process in details.

The main conclusion results in the appearance of the common valley with a new free energy $F_0$. Here there is no connection with the absence of excesses. This free energy can not be defined separately from the width of the equilibrium distribution, only the ratio

$$\exp(-F_0)/\Delta_{e0}\nu_b$$

can be determined. But namely this ratio is the equilibrium distribution and in the expression for the nucleation rate.

The last ratio can be determined from

$$\frac{\exp(-F_0)}{\Delta_{e0}\nu_b} = \frac{\exp(-F_{e-})}{\Delta_{e-}\nu_b} + \frac{\exp(-F_{e+})}{\Delta_{e+}\nu_b}$$

Very approximately one can say that

$$\frac{\exp(-F_0)}{\Delta_{e0}\nu_b} = \frac{\exp(-F_{e-})}{\Delta_{e-}\nu_b}$$

when $F_{e-} < F_{e+}$ and

$$\frac{\exp(-F_0)}{\Delta_{e0}\nu_b} = \frac{\exp(-F_{e+})}{\Delta_{e+}\nu_b}$$

when $F_{e-} > F_{e+}$.

## 5.7 Intermediate situation

- Intermediate situation is very rare because it can take place only under the simultaneous realization of two equations

$$I_- = I_+$$

and

$$I_- = W_a^+(\nu_a, \nu_{be})$$

(also the soft shift has to taken into account). But this case in the only one where the interaction of valleys and the exhaustion of the equilibrium distribution play simultaneously.

Solution of this situation is rather simple - it is necessary to solve the system of several algebraic equations. At small

$$\nu_b < y_0$$

where

$$W_a^+(\nu_a, \nu_{be-}) \gg I_-$$

one has to use the boundary condition

$$N_- = N_{-eq} \sim \exp(-F(\nu_a, \nu_{be-})/\Delta_{e-}\nu_b$$

$$N_+ \ll N_{+eq} \sim \exp(-F(\nu_a, \nu_{be+})/\Delta_{e+}\nu_b$$

At big

$$\nu_b > y_0$$

where

$$W_a^+(\nu_a, \nu_{be-}) \ll I_-$$

one has to use another boundary condition

$$N_- \ll N_{-eq}$$

$$I_+ = 0$$

if it will be necessary. So, the task is to solve several simple algebraic equations. Certainly, the discrete approach is preferable in the computation.

To come to the continuous approximation one has to change the finite differences for derivatives which approximately leads to the following kinetic equations

$$\frac{\partial N_-}{\partial t} = W_a^+(\nu_a, \nu_{be-})[k_{e-}\frac{\partial N_-}{\partial \nu_a} + \frac{\partial^2 N_-}{\partial \nu_a^2}] - J_-(\nu_a) + J_+(\nu_a)$$

$$\frac{\partial N_+}{\partial t} = W_a^+(\nu_a, \nu_{be+})[\frac{\partial^2 N_+}{\partial \nu_a^2} + k_{e+}\frac{\partial N_+}{\partial \nu_a}] - J_+(\nu_a) + J_-(\nu_a)$$

Here

$$k_{e-} = -(1 - \exp(\partial F(\nu_a \nu_{be-})/\partial \nu_a)) \approx \partial F(\nu_a \nu_{be-})/\partial \nu_a$$

$$k_{e+} = 1 - \exp(\partial F(\nu_a \nu_{be+})/\partial \nu_a) \approx -\partial F(\nu_a \nu_{be+})/\partial \nu_a$$

Continuous approximation can not be widely spread but can be applied only in rather specific situations. The reasons are similar to those described in analysis of the Trinkaus' solution. The proximity of $dF_r/d\nu_b$ and both $dF_{e+}/d\nu_b$ and $dF_{e-}/d\nu_b$ to zero means the proximity to the saddle point where the linear approximation fails.

The simple approximate method is the iteration one - the values $J_-$ and $J_+$ are calculated on the base of previous approximations and they are treated as known functions. Initial approximations are following:

- when the source valley are deeper than the destination one, then there is the quasi-equilibrium.

- when the destination valley are deeper than the source one, then there is the Trinkaus' solution or the corresponding simplified solution.

This method is very effective and leads to a rather precise solution after one or two iterative steps.

It is necessary to stress here the effectiveness of the method based on the ansatz with the soft Heavisaid's functions.

The main result of this section which was the goal of the whole publication is the radical change of the nucleation rate. The main goal is achieved - the change of the nucleation rate in the orders of magnitudes is shown. One can also see that the rate of nucleation does not depend on the free energy in saddle point but on the mutual position of valleys and ridges and their relative heights. Certainly, the problem to find the nucleation rate includes now the determination of many characteristics and is more complex than in the theories suggesting the recipes based on the value of the free energy in one point. The theory presented here has to be used in order to get the true value of the free energy. Now the problem is transformed in the thermodynamic area - it is necessary to find the free energy of the embryo formed in the mixture of vapors. This problem is complex enough to continue investigations of the binary and multicomponent nucleation.

# 6 Paths of transition

Now one can return to the general situation to see how the real transition from the pre-critical region to the post-critical region will occur.

The problem is to see where the real change of the channels will take place. This problem will be solved here. So, here the analysis will be mainly qualitative. All details of transition between channels will be a subject of a separate analysis.

## 6.1 Approximate position of the valley

To get the approximate position of valley and the ridge one can act without surface excesses.

Consider the channel in coordinates $\nu_a, \xi$. Then

$$\nu_a = \kappa / p(\xi)$$

where $p(\xi)$ is a known function and

$$F = -B(\xi) p(\xi) \nu_a + p^{2/3}(\xi) \nu_a^{2/3}$$

The coordinate of the valley is given by condition

$$\frac{\partial F}{\partial \xi} = 0$$

or

$$-B'(\xi) p(\xi) \nu_a - B(\xi) p'(\xi) \nu_a + \frac{2}{3} p^{2/3}(\xi) \nu_a^{-1/3} p'(\xi) = 0$$

At the saddle point

$$-B(\xi) p'(\xi) \nu_a + \frac{2}{3} p^{2/3}(\xi) \nu_a^{-1/3} p'(\xi) = 0$$

and the saddle point of valley coincides with the saddle point of the channel line, since

$$B'(\xi) = 0$$

Asymptotically at $\nu_a \to \infty$ one can get

$$-B'(\xi) p(\xi) - B(\xi) p'(\xi) = 0$$

One can see that the function $p$ is rather smooth while $B$ is rather sharp. This condition is a definition of a "clear channel". Then one can neglect $B(\xi)p'(\xi)$ in comparison with $B'(\xi)p(\xi)$. This leads to

$$-B'(\xi)p(\xi) = 0$$

and because of $p \neq 0$ the last equation coincides with the coordinate of the channel. So, we see that the valley is near the channel line for every $\nu_a$.

To see the behavior at moderate $\nu_a$ near the critical values one can note that $p'$ attains a moderate value. Really

$$p' = \frac{\partial^2 \kappa}{\partial \nu_a^2} \sim 1$$

(we choose the space scale to have the volume for a molecule in a liquid phase the order of 1). Then one has to take into account that

$$\kappa_c = 2/(3max\ B(\xi)) \gg 1$$

requires $max\ B \ll 1$ Then the term $B(\xi)p'(\xi)\nu_a$ has a small parameter. The term $p^{-1/3}(\xi)\nu_a^{-1/3}p'(\xi)$ has the same order as $B(\xi)p'(\xi)\nu_a$ and, thus, is small. This reduces the coordinate of a value to coordinate of a channel.

The same analysis can be done for every ridge. The general approximate conclusion is that every separation line corresponds to the ridge and their coordinates are similar.

At $\nu_a \to 0$ and $\kappa \to 0$ the leading term is

$$\frac{2}{3}p^{2/3}\nu_a^{2/3}p'$$

which means that the valley does not exist. So, the valley can not directly start at $\nu_a = 0$ in continuous approximation. Fortunately, ordinary this effect takes place at $\nu_a$ less than 1.

All above considerations are very approximate and they are used only to see that qualitatively nothing is changes when we consider valleys instead of channels.

Approximately speaking every channel corresponds to one valley, their coordinates are rather similar.

Precisely speaking one can see many specific peculiarities, for example, the appearance of valleys without corresponding channels. But the probability of such peculiarities is very low. As a rule these valleys are not deep enough and can be treated as negligible ones.

## 6.2 Transition zones

Consider the pair of valleys.

Every valley (index $v$) can be considered as a source valley ($s$). Every valley can be considered as a destination valley ($d$). One can imagine many pairs of source and destination valleys. Every pair has to be investigated.

At first we consider the situation when the channels are neighbor ones. The ridge is the maximum of $F$ at the band $\nu_a = const$ between the concentration $\xi_s$ of a source valley and the concentration $\xi_d$ of a destination valley.

We define $F_v$ as the free energy at the valley, $F_r$ the free energy at the ridge.

Now we shall make use from the approximate functional form for $F_r$, $F_v$ established above

$$F = const_1 \nu_a^{2/3} - const_2 \nu_a$$

One can see the following facts

- Every valley has only one critical $\nu_{avc}$ point determined by

  $$dF_v/d\nu_a = 0$$

- One can define the pre-critical region of the valley where $dF_v/d\nu_a > 0$ and post-critical region of valley where $dF_v/d\nu_a < 0$. There is only one pre-critical region with a size $\nu_a < \nu_{avc}$ and a post-critical region where $\nu_a > \nu_{avc}$.

- Every ridge has only one critical $\nu_{avc}$ point determined by

  $$dF_r/d\nu_a = 0$$

- One can define the pre-critical region where $dF_r/d\nu_a > 0$ and post-critical region of ridge where $dF_r/d\nu_a < 0$. There is only one pre-critical region with a size $\nu_a < \nu_{arc}$ and a post-critical region where $\nu_a > \nu_{arc}$.

The real effect on the nucleation rate occurs when there is a transition from the pre-critical part of the source valley to the post-critical part of a destination valley. Transition from the post-critical part is useless because the embryos can simply continue to grow, they already overcame the barrier. So, there is no need to overcome another one barrier and this case is out of our interest.

At first we suppose that in the whole pre-critical part of the destination channel there is an equilibrium distribution. It means that there is no further change of channels and the destination channel will be the final destination channel. So, there is only one cascade - only one change of the channel. We shall call such processes as one-cascade processes.

One can choose components in such a way that the first component is a rapid one.

Consider the regions where the probability to change the channel is greater than to increase the value of slow components in the old channel. This corresponds to condition

$$W_{sl} \leq W_1 Z_1 \exp(F_r - F_s)$$

Here the kinetic coefficient $W_{sl}$ is the total kinetic coefficient of all slow components, $W_1$ is the kinetic coefficient of a rapid component and $Z_1$ is the corresponding Zel'dovich factor for transition over the ridge. The last inequality can be expressed in terms of the $F_r - F_v$ as

$$F_r - F_v \leq \ln(W_{sl}/(W_1 Z_1)) \equiv \Delta_t$$

The rhs is a very slowly varying function. Approximately it is a constant.

Consider

$$\Delta = F_r - F_v$$

According to the approximate formulas the function $\Delta(\nu_a)$ has the second derivative

$$\frac{d^2\Delta}{d\nu_a^2} = -[p^{2/3}(\xi_r) - p^{2/3}(\xi_v)]\frac{2}{9}\nu_a^{-4/3}$$

which has a constant sign.

Thus, $\Delta$ has no more than maximum (it will be marked by the index "m").

Certainly, the condition $F_r - F_v = \Delta_t$ depends on the scale of $\nu_a$. It is necessary to choose the scale of $\nu_a$-axis to have

$$d\Delta/d\nu_a \sim 1$$

at $\Delta \simeq \Delta_t$. Since $\Delta$ is not a too sharp function of $\nu_a$, it is easy to do. The condition $\Delta < \Delta_t$ can be valid no more than in two zones: one before $\nu_{am}$ another later $\nu_{am}$. Namely, in intervals

$$[0, \nu_{at-}], \quad [\nu_{at+}, +\infty]$$

the last condition is valid.

One can make the following notes:

- The second interval $[\nu_{at+}, +\infty]$ can be absent when

$$B(\xi_r)p(\xi_r) < B(\xi_s)p(\xi_s)$$

- The first interval also can be effectively (not precise) absent when $\nu_{at-} < 1$ which occurs rather often.
- One can come to the situation when valleys are purely isolated.
- One has to keep in mind that the approximate formulas take place only at big $\nu_a$.

The interval $[0, \nu_{at-}]$ will be called as the "pre-transition zone", the interval $[\nu_{at+}, +\infty]$ - as the "post-transition" zone.

Consider the question about the mutual position of the destination and the source channels. The definition of $\kappa$ as even without microscopic corrections $(\sum \nu_i v_i)\gamma^{3/2}$ contains $\gamma$ and $v_i$ and is a very complex function. But in the majority of situations the increase of $\nu_a$ (other $\nu_i$ are fixed) causes the increase of $\kappa$. We shall imply this property to take place. This property will be referred as the property of $\kappa$-convexity. The line $\kappa = const$ as a function of $\nu_a$ is convex.

Certainly, in real systems there can be concave regions, where the growth of $\nu_a$ leads to the change of concentration, the partial volumes change, the surface tension change and the value of $\kappa$ falls. But this situation is exclusive.

Under the property of convexity one can see that the transition will be carried out only by addition of molecules of the first component (ejection is not possible) and will go from the left side to the right side in $\nu_a, \nu_b$ plane.

The precise position of boundaries have to be defined with surface excesses. Also a shift connected with a special renormalization has to be taken into account.

## 6.3 Nucleation conditions and supplying conditions

Here we shall mark $\nu_a$ by $x$.

Conditions for the possibility of nucleation through the post-transition zone are the following ones

- Transition has to be effective, i.e. there has to be a region in the post-critical region in a destination valley $x > x_{dc}$ where $F_d(x) < F_{sc}$ Certainly this region looks like

  $$[x_b, +\infty]$$

  and the beginning of this region has to be smaller than $x_{sc}$:

  $$x_b < x_{sc}$$

- Transition has to be opened, i.e.

  $$x_{t+} < x_{sc}$$

The beginning of transition will be at

$$x_w = max\{x_b, x_{t+}\}$$

There are two possibilities at $x_w$:

- The first possibility

  $$F_d(x_w) > F_s(x_w)$$

  Here the common valley will be formed and the most effective transition will be at $x_u$ defined as

  $$F_d(x_u) = F_s(x_u)$$

- The second possibility

  $$F_d(x_w) < F_s(x_w)$$

  Here the transition from valley to valley occurs like a falling from the high channel to the low channel. Solution looks like the Trinkaus' one.

To see the real process of the channel transition it is necessary to have corresponding conditions at the beginning of transition. These conditions have to be the equilibrium conditions. It is necessary that earlier in the valley there would be no possibility to escape from the valley. One has to analyze such possibility.

To see the transition in the pre-transition zone it is necessary that two conditions take place

- The first condition:

$$F_d(x) < F_s(x_w)$$

- The second condition:

  Transition has to lead to the post-critical region in the destination valley.

We are interested to avoid such intensive transition which can destroy the equilibrium conditions at $x_w$.

Since $F_d$ has to be at the post-critical region, it is a decreasing function of $x$ and it is sufficient to check condition at the boundary:

$$F_d(x_{t-}) < F_s(x_w)$$

In this situation the intensity of the valley transition in the pre-transition zone is so big that there is no equilibrium condition for the transition in the post-transition zone.

Since the transition in the pre-transition zone has to lead to the post-critical zone then the peak of $F_d$ lies inside the transition through the pre-transition zone. So, since

$$maxF_d > maxF_s > F_s(x_w)$$

the transition occurs in a manner of common channel and the real transition takes place at $x_p$ when

$$F_d(x_p) = F_s(x_p)$$

if

$$x_p < x_{t-}$$

If at

$$x = x_{t-}$$

we have

$$F_d > F_s$$

the most intensive transition takes place at $x_{t-}$. This situation is more probable than the precedent one.

What has to be done when the condition

$$F_d(x_{t-}) > F_s(x_{t-})$$

takes place?

Certainly, the transition can take place out of pre-transition and post-transition zones but with a very low probability. To take into account this possibility one has to add to $F_s$ the quantity $F_r - F_s - \Delta_t$, i.e. to go from $F_s$ to $F_r - \Delta_t$. This has to be done out of pre- and post-transition zones.

The point of transition will be near the root of equation

$$F_d = F_r - \Delta_t$$

Let it be at $x = x_y$.

This transition can not violate the equilibrium. So, the transition in the post-transition zone is not destroyed and intensities of this transition and transition in the post-transition zone have to be compared (added).

We shall call this transition as "the saturation transition".

Here the transition is going across the ridge into the valley. The surface excesses can be taken into account very simply by noticing that the forms of ridge and valley profiles remain the old ones and only the shifts of profiles as a whole take place due to the account of excesses.

## 6.4 Details of the saturation transition

Solution of the saturation transition is rather simple. Consider at first the general situation. Let $n_d(\nu_a)$ be the embryos number density in a destination valley, $n_s(\nu_a)$ be the embryos number density in a source valley, The evolution equation for the source valley looks like

$$\frac{\partial n_s}{\partial t} = -\frac{\partial}{\partial \nu_a} W_{as}^{+} n_s^e(\nu_a)[\frac{n_s(\nu_a)}{n_s^e(\nu_a)} - \frac{n_s(\nu_a+1)}{n_s^e(\nu_a+1)}] -$$

$$n_s \frac{Z_s}{\Delta_s} \exp(-F_r + F_s) W_{bx}^{+} + n_d \frac{Z_d}{\Delta_d} \exp(-F_r + F_d) W_{bx}^{+}$$

Here $W_a$ is kinetic coefficient, $n^e$ is the equilibrium distribution, the flow

$$n_s \frac{Z_s}{\Delta_s} \exp(-F_r + F_s) W_{bx}^{+}$$

is the flow from the source valley to the destination valley and

$$n_d \frac{Z_d}{\Delta_d} \exp(-F_r + F_d) W_{bx}^{+}$$

is the flow from the destination valley to the source valley. The value $Z$ is the Zeldovich' factor, $\Delta$ is the normalizing factor.

Analogously one can write equation for the destination valley

$$\frac{\partial n_d}{\partial t} = -\frac{\partial}{\partial \nu_a} W^+_{ad} n^e_d(\nu_a)[\frac{n_d(\nu_a)}{n^e_d(\nu_a)} - \frac{n_d(\nu_a+1)}{n^e_d(\nu_a+1)}] +$$

$$n_s \frac{Z_s}{\Delta_s} \exp(-F_r + F_s) W^+_{bx} - n_d \frac{Z_d}{\Delta_d} \exp(-F_r + F_d) W^+_{bx}$$

In continuous approximation

$$\frac{\partial n_s}{\partial t} = W^+_{as}[\frac{\partial^2}{\partial \nu_a^2} n_s(\nu_a) + \frac{\partial F_s}{\partial \nu_a} \frac{\partial}{\partial \nu_a} n_s(\nu_a)]$$

$$-n_s \frac{Z_s}{\Delta_s} \exp(-F_r + F_s) W^+_{bx} + n_d \frac{Z_d}{\Delta_d} \exp(-F_r + F_d) W^+_{bx} \tag{55}$$

for the source valley and

$$\frac{\partial n_d}{\partial t} = W^+_{ad}[\frac{\partial^2}{\partial \nu_a^2} n_d(\nu_a) + \frac{\partial F_d}{\partial \nu_a} \frac{\partial}{\partial \nu_a} n_d(\nu_a)] -$$

$$n_d \frac{Z_d}{\Delta_d} \exp(-F_r + F_d) W^+_{bx} + n_s \frac{Z_s}{\Delta_s} \exp(-F_r + F_s) W^+_{bx} \tag{56}$$

for the destination valley.

One can assume that

$$\frac{\partial F_d}{\partial \nu_a} = v_d \qquad \frac{\partial F_s}{\partial \nu_a} = v_s$$

are constants. Also it can be assumed that the linear approximations

$$-F_r + F_d = A_d x + \tilde{C}_d \tag{57}$$

$$-F_r + F_s = A_s x + \tilde{C}_s \tag{58}$$

for $x = \nu_a - \nu_{a0}$ are valid. Here $\nu_{a0}$ is some parameter chosen as to belong to effective region of transition.

Then the stationary solutions will satisfy the system of equations

$$\frac{\partial^2}{\partial x^2} n_s + v_s \frac{\partial}{\partial x} n_s - C_s n_s \exp(A_s x) + C_d n_d \exp(A_d x) = 0 \tag{59}$$

$$\frac{\partial^2}{\partial x^2}n_d + v_d\frac{\partial}{\partial x}n_d - C_d n_d \exp(A_d x) + C_s n_s \exp(A_s x) = 0 \qquad (60)$$

with

$$C_s = \exp(\tilde{C_s}) Z_s W^+_{bx}/\Delta_s W_{as}$$

$$C_d = \exp(\tilde{C_d}) Z_d W^+_{bx}/\Delta_d W_{ad}$$

In the second solution because the region in the destination valley is the super-critical one it is possible to neglect $\frac{\partial^2}{\partial x^2}n_d$. Then the second equation is the linear first order differential equation with a known solution. Then after the substitution the first equation becomes the closed the closed equation. Since solution of (60) contains the integral then to get the differential equation it will be necessary to differentiate (59) one time and the resulting differential equation will have the order 3. It can not be solved at least in elementary functions. So, it is necessary to consider simplification based on classification of transitions.

These are three types of transitions - the non-equilibrium falling transition (first type), the equilibrium common valley transition (second type), the equilibrium saturation transition (third type). For different types we shall use different approximations.

For the first type it is possible to neglect

$$C_d n_d \exp(A_d x)$$

in the first equation. Then it becomes the closed equation

$$\frac{\partial^2}{\partial x^2}n_s - v_s\frac{\partial}{\partial x}n_s - C_s n_s \exp(A_s x) = 0 \qquad (61)$$

Then there is no necessity in validity of the linearization (58).

Solution of the last equation is presented above via cylindrical function.

The second equation is not necessary, but to complete the picture one can write it in the form

$$v_d\frac{\partial}{\partial x}n_d + C_s n_s \exp(A_s x) = 0 \qquad (62)$$

with the solution

$$n_d = -\int_{-\infty}^{x} C_s n_s \exp(A_s x')/v_d dx'$$

Certainly, the presentation of the solution via the cylindrical function is not convenient. It is more convenient to fulfill a block transformation and then to solve the system of several algebraic equations. We shall formulate this procedure. Really, one can go from $x$ to $kx$ to have

$$A_s k \approx \ln \alpha$$

where the parameter $\alpha \approx 1.5$. Then with an increase of $x$ by 1 the intensity of transition increases 1.5 times. Then the equation (61) will be

$$k^{-2} \frac{\partial^2}{\partial x^2} n_s + v_s k^{-1} \frac{\partial}{\partial x} n_s - C_s n_s \alpha^x = 0 \tag{63}$$

Now it is possible to consider the interval $-2 < x < 2$ and to come back to the initial discrete form of equation

$$k^{-2}[n_s(x+1) - 2n_s(x) + n_s(x-1)] + v_s k^{-1}[n_s(x+1) - n_s(x-1)]/2 - C_s n_s(x)\alpha^x = 0 \tag{64}$$

These coupled algebraic equations have to be written at $x = -2, -1, 0, 1, 2$. At $x < -2$ one has to put $n_s$ to the equilibrium value. So, there is a system of five coupled equations which can be easily solved.

One can continue analysis. Every band has a separate physical meaning:

- The band $x = 2$ is the starting band.
- At $x = -1$ one can use the smallness of the flow $C_s n_s(x)\alpha^x$ and the smallness of the deviation of $n_s$ from the equilibrium value.
- The point $x = 0$ is the point where $|d/dx[(n_s - n_s^e)/n_s^e]|$ attains maximum and, thus,
  $$d^2/dx^2[(n_s - n_s^e)/n_s^e] = 0$$
- At $x = 1$ one can assume that $n_s$ is already small in comparison with $n_s^e$
- The values at $x = 2$ are the final values.

One can use these features at the characteristic zones to get analytic solutions and then the common solution will be their combination.

These approximations allow to solve this equation analytically by combination of the corresponding analytical band solutions. But the resulting formulas will be very long to use them for calculations. To get concrete results it is more profitable to solve algebraic equations, the precision is rather high while the error is less than one tenth.

Certainly, one can directly solve the initial form of evolution equation described earlier as the discrete model.

The analysis of the first type is completed.

For the transition of the second type it is possible to neglect

$$\frac{\partial^2}{\partial x^2} n_s + v_s \frac{\partial}{\partial x} n_s$$

and

$$\frac{\partial^2}{\partial x^2} n_d - v_d \frac{\partial}{\partial x} n_d$$

Then both equations will be reduced to

$$-C_s n_s \exp(A_s x) + C_d n_d \exp(A_d x) = 0 \tag{65}$$

with the evident equilibrium solution as it was described earlier. The point $x = 0$ is the saddle point, i.e. the point where approximately $F_s = F_d$.

The third type of transition can be described in a following manner:

- Equation (59) leads to the fact that $n_s = n_s^e$. For $n_s^e$ one can take approximation

  $$n_s^e(x) = n_s^e(0) \exp(B_s x)$$

  where

  $$B_s = -\frac{dF_s}{dx}|_{x=0}$$

- Equation (60) looks like

  $$v_d \frac{\partial}{\partial x} n_d - C_d n_d \exp(A_d x) + C_s n_s^e \exp(A_s x) = 0 \tag{66}$$

  and can be easily solved since it is the first order linear equation. The integral can be taken and the result will be expressed via Whittaker or Kummer functions which can be reduced to the Hypergeometric function.

The point $x = 0$ has to be chosen as $\arg(max \frac{dn_d}{dx})$.

Since the result can be expressed only in the form of special functions it is worth solving the discrete model. The method is quite the same and one can come to

$$k^{-2} \frac{\partial^2}{\partial x^2} n_d + k^{-1} v_d \frac{\partial}{\partial x} n_d - C_d n_d \exp(A_d kx) + C_s n_s(0) \exp((B_s + A_s)kx) = 0 \tag{67}$$

The value of $k$ has to be chosen to satisfy

$$k \min(A_d, A_s + B_s) = \alpha$$

Then algebraic equations will be

$$\begin{gathered} k^{-2}[n_d(x+1) - 2n_d(x) + n_d(x-1)] + k^{-1} v_d [n_d(x_1) - n_d(x-1)]/2 \\ -C_d n_d \exp(A_d kx) + C_s n_s(0) \exp((B_s + A_s)kx) = 0 \end{gathered} \tag{68}$$

and have to be written at $x = -2, -1, 0, 1, 2$

Also it is necessary to mention the possibility to solve the discrete model from the very beginning. The starting equation will be

$$\begin{gathered} W_{ad}[n_d(x-1) - \frac{n_d^e(x-1)}{n_d^e(x)} n_d(x) - n_d(x) + \frac{n_d^e(x)}{n_d^e(x+1)} n_d(x+1)] \\ -C_d n_d \exp(A_d x) + C_s n_s^e \exp(A_s x) = 0 \end{gathered} \tag{69}$$

These equations are coupled algebraic equations. The initial condition is $n_d = 0$ at $x \to -\infty$.

Our consideration has to be completed by equation on parameters of transition.

The points of approximations $x = 0$ form the equations on parameters of the process. The possible presence of the special functions can be eliminated by rational approximations for special functions. Then the parameters of th process will be determined by the root of the algebraic equation.

Now one can see the general picture of transition. One can note that the complexity of the phase transition already between two valleys is rather essential. There are at least several possibilities to observe this transition

- Equilibrium transition in the pre-transition zone

- Equilibrium transition out of transition zone
- Equilibrium transition in the post-transition zone
- Falling transition in the post-transition zone

So, the unique approach to get the rate of nucleation is impossible.

One has to stress that already the equilibrium transitions can lead to the absence of equilibrium in valley with bigger $x$, and $\kappa$. This effect has to be taken into account to diminish the intensity of transition in the post-transition zone.

Here it becomes clear that the flow can split and merge. Beside these effects one can see the rapid change of the leading manner of the supercritical embryo formation. This is caused only by kinetic coefficients and, thus, it is reasonable to speak about "the kinetic rupture in the rate of nucleation".

One has to stress that in the saturation transition there is no difference whether the transition occurs in the open or in the forbidden zone. Really, $F_r - F_s$ can be greater than $\Delta_t$:

$$F_r - F_s > \Delta_t$$

and the transition will take place. The only conditions is

- $$F_r(\nu_a) - \Delta_t < F_{mc}$$

  where $F_{mc}$ is the value at the saddle point with a minimal height and

- $$F_d(\nu_a) < F_{sc}$$

  for some $\nu_a > \nu_{acd}$

Rigorously speaking the same consideration can take place for transition of other types.

Then one can come to the situation when both the equilibrium common channel transition and the falling transition can take place. When at some $\nu_a > \nu_{acd}$

$$F_d(\nu_a) = F_s(\nu_a) < F_{mc}$$

we have to examine $F_r$.

If

$$F_r - \Delta_t < F_{mc}$$

we see that the intensity of the common channel transition is greater than the intensity of transition through the saddle point.

Since $F_d$ for $\nu_a > \nu_{acd}$ is a decreasing function this intensity is also greater than the intensity of a saturation transition. Then we have to compare it with the intensity of a falling transition.

If

$$F_r - \Delta_t < F_s$$

we have the common valley transition with intensity greater than the further falling transition.

If

$$F_r - \Delta_t > F_s$$

then the further falling transition will occur with intensity greater than the intensity of the common valley transition.

All this is done without account of the soft shift. To take this shift into account in a rough approximation it is necessary to add to $\Delta_t$ the quantity

$$\ln[\frac{d(F_r - F_s)}{d\nu_a}]^{-1}$$

## 6.5 Other peculiarities of transition

The property of the $\kappa$-convexity is very important in the context of the current analysis because it forbids the possibility to reach the pre-critical region after the transition through the post-transition zone. Otherwise there would be a source of embryos in some region of the destination valley. The property of the $\kappa$-convexity forbid the localization of the flow.

Such a localization of the transition flow can be seen in a multi-valley transition. Consider the situation when there is an intermediate valley (index $i$) and, thus, there are two ridges - one between the source valley and the intermediate valley (index $rs$), another between the intermediate valley and the destination valley (index $rd$). Suppose that for intermediate valley

$$F_{rs} - F_i < \Delta_t$$

$$F_{rd} - F_i < \Delta_t$$

Then one can speak about one effective ridge with a height

$$F_{rr} = max(F_{rs}, F_{rd})$$

Then the property of the ridge convexity disappears and the localization of the transition flow can be seen. One can speak about the

- Injection at the finite zone into the valley.

Earlier we consider only two components in the mixture. So, the inverse transition has to be the backward one. But in the three component mixture one can imagine the curved transitions - at first transition the concentration of the first component increases, at the second transition the concentration of the second component increases. However, it is necessary to have at least two rapid components in the mixture. In some special cases it is possible to return to the same valley but in another place of this valley - may be it is possible to jump from the pre-critical zone to the post-critical one, may be it is possible to make one loop of a spiral. Here the picture will be very picturesque. However, it would be very nice to see the concrete examples of such nucleating systems.

Here we do not consider the transitions from the post-critical zone of one valley to the post-critical zone of the other valley because this transition can not change the rate of nucleation.

Despite the transition will have now a very complex form the elementary bricks remain the same:

- the equilibrium common-valley transition
- the equilibrium saturation transition
- the non-equilibrium falling transition

The possibility to reach the rather transparent classification is based on the following simple approximate structure of every channel/separation line/valley/ridge:

- Every channel/separation line/valley/ridge has a pre-critical zone which is directly (without hills) connected with the origin, post-critical region with the irreversible growth (until infinity) and a small near-critical growth.

The last property takes place for every channel, separation line, valley and ridge.

According to the last analysis the multi-cascade transitions are not effective. Really, the cascade can lead to the post-critical region or to the pre-critical region. When it leads to the post-critical region it will be the last cascade. If it leads to the pre-critical region there is a smooth increasing path along the valley and this path will have at least the same intensity. So, the transition across the ridge is not effective here. As the result we see that there is only one main cascade in the multi-cascade transition.

Here we imply that one cascade can be the saturation transition, the falling transition or the common valley transition. Actually, the saturation transition is also the common valley transformation because here there exists a common valley. Then we shall speak here about the generalized common valley. Then there is the generalized common valley and the falling transition.

Certainly, the multi-common valley can be such a cascade. In this cascade at some may be finite zone several valleys are treated as one common channel. It is also possible that the set of common channels with the given channel can change - at some zone there is one set, at another zone there is another set. But in this common valley under the $\kappa$-convexity there will be only one leading pair of the neighbor channels.

As the result we see that in the binary case there is only one leading cascade which is the falling transition or the generalized common valley.

We have examined only the stationary solutions. The relaxation of the distribution $n$ to the stationary solution can be easily studied since in all situations the stationary solution $n_{st}$ is known. Then one can linearize equation on $n - n_{st}$ and get

$$\frac{\partial n}{\partial t} = Ln$$

where $L$ is a differential operator (or in finite differences) on $\nu_i$. Then one can get the relaxation time as the minimal eigenvalue of the linear operator $L$ in the evolution equation by the iteration procedures

$$Trace(L), \;\; Trace(L^2), \;\; Trace(L^3), \;\; etc.$$

of the standard numerical methods.

In reality all operators in the rhs of kinetic equations are reduced to the square approximations. Then the eigenvalues and eigenfunctions are known. Eigenfunctions are the Hermite's polynomials or the Generalized error-functions.

# Main results

One can see that the problem to get even the stationary rate of nucleation is rather complex. Below we present the sequence of actions to fulfill this task:

1. We determine all channels and find the channel with a minimal activation barrier. Determine its height $F_{cm}$

2. We determine the rate $W_a/W_b$. Choose components to have $W_a < W_b$ If $W_b/W_a < exp(1)$ there will be a Stauffer's solution with $F_{cm}$. If there is an opposite situation one has to continue consideration.

   Suppose that we have the binary case and the $\kappa$-convexity. The last property is rather ordinary but it simplifies the consideration. Then the procedure will be the following

   (a) Instead of channels determine the valleys. D We determine also all ridges. We enumerate valleys to have $\xi_i < \xi_j$ for $i < j$. We enumerate ridges to have $\xi_i < \xi_j$ for $i < j$. For every neighbor valleys we determine the source valley $i$ and the destination valley $i + 1$. Below we shall consider the one-cascade transition.

   (b) We determine the possibility of the saturation transition: there is $\nu_a$ satisfying conditions:

   $$\nu_a < \nu_{acs}$$

   $$\nu_a < \nu_{acr}$$

   $$F_r(\nu_a) - \Delta_t < F_{cm}$$

   If these conditions are satisfied we determine the point of the saturated transition $\nu_a^*$ by equation

   $$F_d(\nu_a^*) = F_r(\nu_a^*) - \Delta_t$$

   This gives

   $$F_* = F_d(\nu_a^*)$$

   (c) We determine the possibility of the common valley transition: there exists $\nu_a$ with properties

   $$\nu_a < \nu_{acs}$$

$$\nu_a > \nu_{acd}$$

$$F_s(\nu_a) = F_d(\nu_a) < F_r(\nu_a) - \Delta_t$$

The last condition determines only one point $\nu_a^{**}$ of the common valley transition with a maximal intensity. This value will be the saddle point of the unified valley. Here we determine

$$F_{**} = F_s(\nu_a)$$

If the equilibrium valley transition takes place there is no need to consider the falling transition. If it does not exist then we consider the falling transition.

(d) The falling transition takes place when there is $\nu_a$ satisfying conditions:

$$\nu_a < \nu_{acs}$$

$$\nu_a > \nu_{acd}$$

$$F_d(\nu_a) < F_s(\nu_a)$$

$$F_r(\nu_a) - F_s(\nu_a) \leq \Delta_t$$

Conditions

$$F_r(\nu_a) - F_s(\nu_a) = \Delta_t \quad F_d(\nu_a) < F_s(\nu_a)$$

determine the point of transition $\nu_a^{***}$ and the free energy

$$F_{***} = F_s(\nu_a^{***})$$

(e) To see what transition is more profitable one has to compare $F_{cs}$, $F_*$, $F_{**}$ and $F_{***}$ and to choose the minimal value

$$F_{ch} = min(F_{cs}, F_*, F_{**} F_{***})$$

This will be the free energy corresponding to this valley as the source valley. Then one has to take the minimum over all valleys and to determine the free energy of nucleation $F_f$. Then the rate of nucleation is rather approximately given by

$$J = \exp(F_f) Z W_a$$

where the Zeldovich' factor $Z$ contains the normalizing factor of the equilibrium distribution.

(f) If there are two approximately equal minimal values of free energies between $F_{cs}$, $F_*$, $F_{**}$ and $F_{***}$ then one has to add the quantity $\ln(d(F_r - F_s)/d\nu)$ to the free energy of the falling transition. Certainly, the last quantity shifts the point of transition but approximately one can take it at the old point.

The analysis presented above gave the following new results

- The free energy of the embryo is found including the surface excesses and the clear interpretation of the generalized chemical potential is given. The variables giving the simple form of the free energy is found and their connection with the initial natural variables is shown (section 1). The similarity of the form of the near-critical energy to the situation without surface excesses is shown (section 1). The correction order of the Renninger-Wilemski's effect is shown (section 1).
- The hierarchy in the near-critical region is shown (section 2).
- The impossibility of the essential difference between the Reiss' formula ad the Stauffer's formula in capillary approximation is shown (section 3).
- The possibility to change valleys during the evolution is shown. The discrete analog of Trinkaus' solution is presented and investigated (section 4).
- The possibility to have one united valley instead of several initial ones is shown. It is shown that the height of the effective activation barrier is changed in comparison with the heights of barriers in the initial channels. Thus, the rate of nucleation will be radically changed (section 5)
- The possibility to change the valley and to reach the post-critical zone already from the pre-critical transition is shown (section 6). This form a special type of the equilibrium saturation transition. This transition also leads to a new special value of effective height of activation barrier.
- All possible transition are classified. It is shown that the tree mentioned types cover the variety of possible transitions.

Here only the main new results are outlined. An application of the presented theory to the concrete binary and multicomponent systems will form the subject of a separate publication.

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# Explicit two cycle model in investigation of stochastic effects in diffusion regime of metastable phase decay

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**Abstract**

The theory for manifestation of stochastic appearance of embryos in the global decay of metastable phase has been constructed. The regime of droplets growth is supposed to be both free molecular one and diffusion one. The deviation for a mean droplets number from the value predicted by the theory based on averaged characteristics have been calculated. The value of dispersion for the distribution of the total droplets number in particular attempt has been also calculated analytically. Comparison with results of numerical simulation has been given and the correspondence between simulation and analytical approximate results is rather good.

The aim of this paper is to give analysis of decay in diffusion regime of the droplets growth in frames of the method given in [1] and corrected in [6]. This method is based on the following approximation

- Until the half of the nucleation period (in the time scale) the supersaturation remains unperturbed and the droplets appear independently.
- In the second half of the nucleation period the droplets appear under the supersaturation changed by the vapor consumption by the droplets appeared in the first part of the nucleation period.

The part of the droplets size spectrum which corresponds to the droplets appeared during the first part of the nucleation period will be called as the first part of spectrum, the remaining part will be the second part of spectrum.

Here this model will be generalized by means of the following changes:

- The duration of the first part of nucleation period will be not exactly the first half but it will be regulated by some parameter $p$ instead of 1/2.

- The regime of growth will be an arbitrary power law of growth (the power type is adopted only to present concrete formulas, it isn't principal here).

- It is supposed that the distribution of droplets in the first part of spectrum can differ from the distribution

  $$P_0(N) \sim \exp(\frac{(N-\bar{N})^2}{2\bar{N}})$$

  of $N$ independently appeared droplets during the period of time corresponding to the mean value $\bar{N}$ of appeared droplets.

  Now instead of the previous distribution the distribution with renormalized dispersion

  $$P_r(N) \sim \exp(\frac{(N-\bar{N})^2}{2\psi\bar{N}})$$

  will be used. Here $\psi$ is parameter of renomalization. This change is initiated by the using of the property of self similarity of spectrums in the first iteration (see [5]) used for investigation of stochastic effects in [6].

The structure of consideration will be the following

- At first we shall present the formal generalized model

- Then the parameter $p$ of the boundary between the first and the second parts will be calculated.

- In the last part the effect of the "growing volumes of interaction" will be described and it will be shown how to include this effect into already presented scheme.

- In Appendix the theory for the free molecular regime of growth will be presented. This theory was given in [6] but now some modifications and improvements have been made. So, a new variant can be found in appendix.

The main object of investigation will be the calculation of dispersion of the droplets distribution since the mean value will be very close to the characteristic calculated in frames of the theory based on the averaged characteristics (TAC), all arguments given for the free molecular regime of the droplets growth remain here practically the same [6], the only principally new feature is to use the theory with explicit profiles of density around the growing droplets [4].

The smallness of fluctuations which will be shown here plays a very important role in transition from the free molecular kinetics to the diffusion kinetics. Really, such transition was shown in [4] only in general features on the level of TAC and the possible giant fluctuations initiated by stochastic appearance of droplets would destroy this transition in frames of the known approaches. Fortunately the giant fluctuations don't appear and the justification of their absence lies in the moderate value of dispersion calculated here.

# 1 Calculation of dispersion

Here we shall analyze the situation with diffusion regime of metastable phase consumption. At it has been already noticed this situation is characterized by the growing volumes of interaction which produces additional difficulties. The growing volume of interaction means that the fixed point in the volume will be under influence of vapor consumers which appeared in a volume $V$ with a center at this point and with a radius $\sqrt{4Dt}$ where $t$ is a time counted from the consumer appearance up to a current moment and $D$ is a diffusion coefficient. Certainly the last value can be regarded only as the rough estimate, the precise expression can be obtained only of the base of precise profiles of a substance gap [4].

At first we briefly follow the way to derive the estimate for dispersion proposed in [1] to use it for diffusion regime of metastable phase consumption. As we have noticed the formalism of a volume of interaction is a rather rough estimate (precise theory has to be based on a form of substance gap from [4]). Thus, the accuracy here is limited. So, in frames of adopted accuracy we shall use here only some rough way to estimate dispersion of a distribution and can use formalism from [1] with appropriate comments and modifications. This way is useful because it allows to understand formulas from [1] which were widely used in above consideration.

Here we suppose that the rate of embryos growth is given by

$$\frac{d\nu}{dt} \sim \nu^s$$

where $\nu$ is the number of molecules inside the embryo and $s$ is a power parameter. We suppose that $s$ takes values which are essentially greater than 0 ($s$ isn't too small in comparison with 1) and essentially less than 1 ($1 - s$ isn't too small in comparison with 1). For the free molecular regime of metastable phase consumption $s = 2/3$, for the diffusion regime $s = 1/3$.

Then the characteristic $\rho$ of a droplet defined as

$$\rho = \nu^{(1/s)+1}$$

grows with velocity independent on it's value

$$d\rho/dt \sim 1$$

The period of nucleation is divided in many elementary intervals with a length $\Delta$ (or $\Delta_i$) in a $\rho$-scale, the average total number of interval in the whole nucleation period is $M$, the number of embryos $N_i$ appeared during every elementary interval is supposed to be big $N_i \gg 1$.

The fact that the total number of intervals is $M$ and their length is $\Delta$ (in estimates we can put it one and the same for all intervals, at least we can take the smallest length and attribute it to all intervals) means that

$$\Gamma \bar{f} (M\Delta)^{(\frac{1}{1-s}+1)} \sim (\frac{1}{1-s} + 1)\zeta(0) \ ,$$

where $\zeta(0)$ is the initial supersaturation, $\bar{f}$ is the initial average amplitude of embryos size spectrum [3], $\Gamma$ is parameter from TAC [3]. Namely the last relation can be derived from the first iteration in TAC. It will be used to express $\bar{f}$ through $M, \Delta$.

During every interval the increase $\delta\rho$ of the value $\rho$ of already existing droplet will be

$$\delta\rho \sim \Delta\zeta(0)/\tau$$

with some characteristic time $\tau$ which will be dropped out in final formulas.

Denote by $N_i$ the number of embryos appeared at $i$-th interval. The value $\bar{N}_i$ is the average $N_i$, $P_i(N_i)$ is the density distribution on $N_i$.

Denote by $N^{(i)}$ the number of embryos appeared at the first $i$-th intervals $\Delta$. The value $\bar{N}^{(i)}$ is the average $N^{(i)}$, $P^{(i)}(N^{(i)})$ is the density distribution of $N^{(i)}$. It is important to stress that $\bar{N}^{(i)}$ isn't equal to $\tilde{N}^{(i)}$ which is the corresponding value completely calculated in frames of TAC (stochastically appeared droplets in the previous moments of time taken into account).

At the first $P$ intervals (i.e. at the first part of nucleation period) the metastable substance consumption is negligible. Here $P = pM$ and $p$ is parameter of constructions. Then for $k < P$ the distribution $P^{(k)}$ of the number of droplets $N^{(k)}$ appeared in the first $k$ intervals is

$$P^{(k)}(N^{(k)}) \sim \exp(-\frac{(N^{(k)} - \bar{N}^{(k)})^2}{2\psi \bar{N}^{(k)}})$$

and it is is a standard Gaussian distribution of $k$ independent subsystems[1].

We introduce here the parameter of renormalization $\psi$ to be able to fulfill calculations suggested in [6] based on the approximate similarity of nucleation conditions [5].

For $k > P$ the expression for $P^{(k)}$ will be formally the following

$$P^{(k)}(N^{(k)}) = \sum_{N_1,\dots\dots,N_P} \prod_{i=1}^{P} \hat{P}_i(N_i)\Omega$$

where

$$\hat{P}_i(N_i) \sim \exp(-\frac{(N_i - \bar{N}_i)^2}{2\psi N_i})$$

$$\Omega = \sum_{N_{P+1},\dots,N_{k-1}} \prod_{j=P+1}^{k-1} \hat{P}_j(N_j)\hat{P}_k(N^{(k)} - \sum_{l=1}^{k-1} N_l)$$

Here the function $\Omega$ is extracted because it corresponds to the second part of spectrum. The function $\Omega$ is superposition of independent subsystems and can be calculated explicitly

$$\Omega \sim \exp(-\frac{(N^{(k)} - \sum_{i=1}^{P} N_i - \sum_{j=P+1}^{k} \bar{N}_j)^2}{2\sum_{j=P+1}^{k} \bar{N}_j})$$

The problem is that the values $\bar{N}_j$ standing in the last expression are unknown now. They are functions of all $N_i$, $\quad i = 1, .., P$ (since the two

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[1] Here and later without any notation we don't keep the preexponential factors before Gaussian distributions, they can be easily reconstructed by integration.

parts model is used). So, the distributions from the first group $i \leq P$ have the influence on $\Omega$. This influence is given through the values $\bar{N}_j$. Now we shall get an expression for this value. At first we recall the exponential approximation which can be found elsewhere (see [3])

$$\bar{N}_j = \bar{N}_1 \exp(-\frac{\Gamma}{\zeta_0} G_j)$$

Here $G_j$ is the number of molecules in a liquid phase at $j$-th interval. For this value we can write

$$G_j = \sum_{i=1}^{j} N_i \rho_i^{(j)\ \frac{1}{1-s}}$$

where $\rho_i^{(j)}$ is the "size" $\rho$ of a droplet appeared at $i$-th interval at the moment corresponding to the $j$-th interval. Then

$$G_j = \sum_{i=1}^{j} N_i ((\Delta\zeta_0/\tau)j - (\Delta\zeta_0/\tau)i)^{\frac{1}{1-s}} = \sum_{i=1}^{j} N_i (j-i)^{\frac{1}{1-s}} (\Delta\zeta_0/\tau)^{\frac{1}{1-s}}$$

and

$$\bar{N}_j = \bar{N}_1 \exp(-\frac{\Gamma}{\zeta_0} (\Delta\zeta_0/\tau)^{\frac{1}{1-s}} \sum_{i=1}^{j} N_i (j-i)^{\frac{1}{1-s}})$$

Now we have to get another expression for

$$K = \frac{\Gamma}{\zeta_0} (\Delta\zeta_0/\tau)^{\frac{1}{1-s}}$$

which appeared in the last relation. One has to clarify the meaning of $M$ as the total number of intervals. Certainly, it is no more than a conditional definition to say that the end of nucleation is the moment when the averaged rate of nucleation falls $e$ times in comparison with initial value. Then the corresponding equation will be

$$\frac{\Gamma}{\zeta_0} G_M = 1$$

We have to calculate $G_M$ in some approximation. Let it be the ideal approximation, i.e. the first iteration [3]. Then

$$K \sum_{i=1}^{M} \bar{N}_1 (M-i)^{1/(1-s)} = 1$$

or

$$K\bar{N}_1 \sum_{i=1}^{M} (M-i)^{1/(1-s)} = 1$$

For $M \gg 1$ summation can be replaced by integration which gives

$$\sum_{i=1}^{M} (M-i)^{1/(1-s)} = \int_0^M (M-x)^{1/(1-s)} dx = \frac{M^{1/(1-s)+1}}{\frac{1}{1-s}+1}$$

and

$$K = (\bar{N}_1 \frac{M^{1/(1-s)+1}}{\frac{1}{1-s}+1})^{-1} \tag{1}$$

Then

$$\bar{N}_j = \bar{N}_1 \exp(-\frac{1}{\bar{N}_1 M^{(\frac{1}{1-s}+1)}} \sum_{i=1}^{j} N_i (\frac{1}{1-s}+1)(j-i)^{\frac{1}{1-s}})$$

Here

$$\frac{1}{\bar{N}_1 M^{(\frac{1}{1-s}+1)}}$$

is simply the scaling factor. One can argue whether the style of calculation of $G_M$ is appropriate. Really we used another approximation which differs from the two cycle model which we are going to use. But there is absolutely no sense how to calculate the last value. One can simply say that our model is to take the first part as $P = pM$ where the definition of $M$ is given by (1). The problem is how to choose $p$.

We continue to simplify expression for $\bar{N}_j, \ j > P$. We recall that the droplets from the first part only consume vapor. Then we come to

$$\bar{N}_j = \bar{N}_1 \exp(-\frac{1}{\bar{N}_1 M^{(\frac{1}{1-s}+1)}} \sum_{i=1}^{P} N_i (\frac{1}{1-s}+1)(j-i)^{\frac{1}{1-s}}) \tag{2}$$

Now we shall simplify the last formula. We make the following transformations:

- we add and subtract $\bar{N}_1$, which is the ideal mean value of droplets appeared during the elementary interval. Then

$$\bar{N}_j = \bar{N}_1 \exp(-\frac{1}{M^{(\frac{1}{1-s}+1)}} \sum_{i=1}^{P} (1 + \frac{N_i - \bar{N}_1}{\bar{N}_1})(\frac{1}{1-s}+1)(j-i)^{\frac{1}{1-s}})$$

and

$$\bar{N}_j = \bar{N}_1 \exp(-\frac{1}{M^{(\frac{1}{1-s}+1)}} \sum_{i=1}^{P} (\frac{1}{1-s} + 1)(j-i)^{\frac{1}{1-s}} -$$
$$\frac{1}{M^{(\frac{1}{1-s}+1)}} \sum_{i=1}^{P} \frac{N_i - \bar{N}_1}{\bar{N}_1} (\frac{1}{1-s} + 1)(j-i)^{\frac{1}{1-s}})$$

We can calculate $\sum_{i=1}^{P} (\frac{1}{1-s} + 1)(j-i)^{\frac{1}{1-s}}$. For $M \gg 1$

$$\sum_{i=1}^{P} (\frac{1}{1-s} + 1)(j-i)^{\frac{1}{1-s}} = (\frac{1}{1-s} + 1) \int_0^P (j-x)^{\frac{1}{1-s}} dx$$

and since we suppose $1/3 < s < 2/3$ we have $1/(1-s) \gg 1$ and

$$\int_0^P (j-x)^{\frac{1}{1-s}} dx = \int_0^j (j-x)^{\frac{1}{1-s}} dx = (\frac{1}{1-s} + 1)^{-1} j^{\frac{1}{1-s}+1}$$

for $j$ which aren't too big in comparison with $P$ (namely the parameter $p$ will be chosen in such a way that $P$ can not be too small in comparison with $M$ and certainly $j$ can not be essentially greater than $M$).

Then

$$\bar{N}_j = \bar{N}_1 \exp(-\frac{1}{M^{(\frac{1}{1-s}+1)}} j^{\frac{1}{1-s}+1} -$$
$$\frac{1}{M^{(\frac{1}{1-s}+1)}} \sum_{i=1}^{P} \frac{N_i - \bar{N}_1}{\bar{N}_1} (\frac{1}{1-s} + 1)(j-i)^{\frac{1}{1-s}})$$

and

$$\bar{N}_j = \bar{N}_1 \exp(-\frac{1}{M^{(\frac{1}{1-s}+1)}} j^{\frac{1}{1-s}+1}) \exp(-\frac{1}{M^{(\frac{1}{1-s}+1)}} \sum_{i=1}^{P} \frac{N_i - \bar{N}_1}{\bar{N}_1} (\frac{1}{1-s} + 1)(j-i)^{\frac{1}{1-s}})$$

Now we linearize the last exponent over

$$\frac{1}{M^{(\frac{1}{1-s}+1)}} \sum_{i=1}^{P} \frac{N_i - \bar{N}_1}{\bar{N}_1} (\frac{1}{1-s} + 1)(j-i)^{\frac{1}{1-s}}$$

This linearization is possible and it differs from linearization over

$$\frac{1}{M^{(\frac{1}{1-s}+1)}} \frac{N_i - \bar{N}_1}{\bar{N}_1} (\frac{1}{1-s} + 1)(j-i)^{\frac{1}{1-s}}$$

made in [1]. The linearization in [1] since we study fluctuations namely in $N_i$ is very doubtful. In our approach we can see the compensation of fluctuation during the period comparable with the whole nucleation period and, thus, the linearization is possible.

It is necessary to stress that after the linearization one can not pretend on the derivation of deviation of the mean value of droplets from the value prescribed by TAC. Contrary to [1] we don't pretend on this but here we are interested only in dispersion. To prove the smallness of deviation of the mean value of total droplets from the value given by TAC one can use other approaches (see [6].

Here we directly use $(\frac{1}{1-s}+1)(j-i)^{\frac{1}{1-s}}$ as the quantity of substance in droplets of a given size (the relative deviation of the size during the elementary interval is small) instead of inappropriate integration over constant distribution (it is stochastic and isn't constant) in [1].

In the zero approximation we get

$$\bar{N}_j = \bar{N}_1 \exp(-\frac{j^{(\frac{1}{1-s}+1)}}{M^{(\frac{1}{1-s}+1)}})$$

In the first approximation

$$\bar{N}_j = \bar{N}_1 \exp(-\frac{j^{\frac{1}{1-s}+1}}{M^{\frac{1}{1-s}+1}})(1 - \frac{1}{M^{\frac{1}{1-s}+1}} \sum_{i=1}^{P} \frac{N_i - \bar{N}_1}{\bar{N}_1}(1+\frac{1}{1-s})(j-i)^{\frac{1}{1-s}}$$

Now we know the influence of embryos of big sizes and can directly analyze the numerator of Gaussian distribution for $\Omega$. We have

$$(N^{(k)} - \sum_{i=1}^{P} N_i - \sum_{j=P+1}^{k} \bar{N}_j) = (N^{(k)} - \sum_{i=1}^{P}(N_i - \bar{N}_1) - \sum_{i=1}^{P} \bar{N}_1 - \sum_{j=P+1}^{k} \bar{N}_j)$$

$$(N^{(k)} - \sum_{i=1}^{P}(N_i - \bar{N}_1) - \sum_{i=1}^{P} \bar{N}_1 - \sum_{j=P+1}^{k} \bar{N}_j) =$$

$$(N^{(k)} - \sum_{i=1}^{P}(N_i - \bar{N}_1) + P\bar{N}_1 - \sum_{j=P+1}^{k} \bar{N}_j)$$

Now we shall derive formula for $\sum_{j=P+1}^{k} \bar{N}_j$. We start with (2) where $\bar{N}_0 \equiv \bar{N}_1$ and get

$$\sum_{j=P+1}^{k} \bar{N}_j = \bar{N}_0 \sum_{j=P+1}^{k} \exp(-\frac{1}{M^{1/(1-s)+1}} \frac{1}{\bar{N}_0} \sum_{i=1}^{P} (\frac{1}{1-s}+1)(j-i)^{1/(1-s)} N_i)$$

Since $M \gg 1$, $P \sim M$

$$\sum_{i=1}^{P}(\frac{1}{1-s}+1)(j-i)^{1/(1-s)}/M^{1/(1-s)+1} \approx j^{1/(1-s)+1}/M^{1/(1-s)+1}$$

So, one can come to

$$\sum_{j=P+1}^{k}\bar{N}_j = \bar{N}_0 \sum_{j=P+1}^{k}\exp(-(j/M)^{M^{1/(1-s)+1}})\exp(-\frac{1}{M^{1/(1-s)+1}}$$

$$\frac{1}{\bar{N}_0}\sum_{i=1}^{P}(\frac{1}{1-s}+1)(j-i)^{1/(1-s)}N_i)\exp(\sum_{i=1}^{P}(\frac{1}{1-s}+1)(j-i)^{1/(1-s)}/M^{1/(1-s)+1})$$

Then

$$\sum_{j=P+1}^{k}\bar{N}_j = \bar{N}_0 \sum_{j=P+1}^{k}\exp(-(j/M)^{M^{1/(1-s)+1}})$$

$$\exp(-\frac{1}{M^{1/(1-s)+1}}\sum_{i=1}^{P}(\frac{1}{1-s}+1)(j-i)^{1/(1-s)}\frac{(N_i-\bar{N}_0)}{\bar{N}_0})$$

Now one can fulfill linearization of exponent over

$$\frac{1}{M^{1/(1-s)+1}}\sum_{i=1}^{P}(\frac{1}{1-s}+1)(j-i)^{1/(1-s)}\frac{(N_i-\bar{N}_0)}{\bar{N}_0}$$

which leads to

$$\sum_{j=P+1}^{k}\bar{N}_j = \bar{N}_0 \sum_{j=P+1}^{k}\exp(-(j/M)^{M^{1/(1-s)+1}})$$

$$(1-\frac{1}{M^{1/(1-s)+1}}\sum_{i=1}^{P}(\frac{1}{1-s}+1)(j-i)^{1/(1-s)}\frac{(N_i-\bar{N}_0)}{\bar{N}_0})$$

The formula is ready.

Then

$$(N^{(k)}-\sum_{i=1}^{P}(N_i-\bar{N}_1)-P\bar{N}_1-\sum_{j=P+1}^{k}\bar{N}_j) = (N^{(k)}-\sum_{i=1}^{P}(N_i-\bar{N}_1)-P\bar{N}_1-$$

$$\bar{N}_0\sum_{j=P+1}^{k}\exp(-(j/M)^{1/(1-s)+1})(1-\frac{1}{M^{1/(1-s)+1}}\sum_{i=1}^{P}(\frac{1}{1-s}+1)(j-i)^{1/(1-s)}\frac{(N_i-\bar{N}_0)}{\bar{N}_0}))$$

The next transformation gives

$$(N^{(k)} - \sum_{i=1}^{P}(N_i - \bar{N}_1) - P\bar{N}_1 - \bar{N}_0 \sum_{j=P+1}^{k} \exp(-(j/M)^{1/(1-s)+1})(1 - \frac{1}{M^{1/(1-s)+1}}$$

$$\sum_{i=1}^{P}(\frac{1}{1-s} + 1)(j-i)^{1/(1-s)} \frac{(N_i - \bar{N}_0)}{\bar{N}_0})) =$$

$$(N^{(k)} - \sum_{i=1}^{P}(N_i - \bar{N}_1) - P\bar{N}_1 - \bar{N}_0 \sum_{j=P+1}^{k} \exp(-(j/M)^{1/(1-s)+1}) +$$

$$\bar{N}_0 \sum_{j=P+1}^{k} \exp(-(j/M)^{1/(1-s)+1}) \frac{1}{M^{1/(1-s)+1}} \sum_{i=1}^{P}(\frac{1}{1-s} + 1)(j-i)^{1/(1-s)} \frac{(N_i - \bar{N}_0)}{\bar{N}_0})$$

Having noticed that

$$\tilde{N}^{(k)} = \bar{N}_1(P + \sum_{j=P+1}^{k} \exp(-\frac{j^{(\frac{1}{1-s}+1)}}{M^{(\frac{1}{1-s}+1)}})$$

is the mean number of droplets $N^{(k)}$ prescribed in the zero approximation by TAC, we come to

$$(N^{(k)} - \sum_{i=1}^{P}(N_i - \bar{N}_1) - P\bar{N}_1 - \bar{N}_0 \sum_{j=P+1}^{k} \exp(-(j/M)^{1/(1-s)+1}) +$$

$$\bar{N}_0 \sum_{j=P+1}^{k} \exp(-(j/M)^{1/(1-s)+1}) \frac{1}{M^{1/(1-s)+1}} \sum_{i=1}^{P}(\frac{1}{1-s} + 1)(j-i)^{1/(1-s)} \frac{(N_i - \bar{N}_0)}{\bar{N}_0}) =$$

$$(N^{(k)} - \sum_{i=1}^{P}(N_i - \bar{N}_1) - \tilde{N}^{(k)} + \bar{N}_0 \sum_{j=P+1}^{k} \exp(-(j/M)^{1/(1-s)+1}) \frac{1}{M^{1/(1-s)+1}}$$

$$\sum_{i=1}^{P}(\frac{1}{1-s} + 1)(j-i)^{1/(1-s)} \frac{(N_i - \bar{N}_0)}{\bar{N}_0})$$

Now we shall change the order of summation and come to

$$(N^{(k)} - \sum_{i=1}^{P}(N_i - \bar{N}_1) - \tilde{N}^{(k)} +$$

$$\bar{N}_0 \sum_{j=P+1}^{k} \exp(-(j/M)^{1/(1-s)+1}) \frac{1}{M^{1/(1-s)+1}} \sum_{i=1}^{P}(\frac{1}{1-s} + 1)(j-i)^{1/(1-s)} \frac{(N_i - \bar{N}_0)}{\bar{N}_0}) =$$

$$(N^{(k)} - \sum_{i=1}^{P}(N_i - \bar{N}_1) - \tilde{N}^{(k)} +$$

$$\sum_{i=1}^{P}(N_i - \bar{N}_0) \sum_{j=P+1}^{k} \exp(-(j/M)^{1/(1-s)+1}) \frac{1}{M^{1/(1-s)+1}} (\frac{1}{1-s} + 1)(j-i)^{1/(1-s)})$$

The last transformation leads to

$$(N^{(k)} - \sum_{i=1}^{P}(N_i - \bar{N}_1) - \tilde{N}^{(k)} +$$

$$\sum_{i=1}^{P}(N_i - \bar{N}_0) \sum_{j=P+1}^{k} \exp(-(j/M)^{1/(1-s)+1}) \frac{1}{M^{1/(1-s)+1}} (\frac{1}{1-s} + 1)(j-i)^{1/(1-s)}) =$$

$$(N^{(k)} - \tilde{N}^{(k)} - \sum_{i=1}^{P}(N_i - \bar{N}_0)(1 -$$

$$\sum_{j=P+1}^{k} \exp(-(j/M)^{1/(1-s)+1}) \frac{1}{M^{1/(1-s)+1}} (\frac{1}{1-s} + 1)(j-i)^{1/(1-s)}))$$

or

$$(N^{(k)} - \sum_{i=1}^{P}(N_i - \bar{N}_1) - \tilde{N}^{(k)} +$$

$$\sum_{i=1}^{P}(N_i - \bar{N}_0) \sum_{j=P+1}^{k} \exp(-(j/M)^{1/(1-s)+1}) \frac{1}{M^{1/(1-s)+1}} (\frac{1}{1-s} + 1)(j-i)^{1/(1-s)}) =$$

$$(N^{(k)} - \tilde{N}^{(k)} - \sum_{i=1}^{P}(N_i - \bar{N}_0) a_i^{(k)})$$

where

$$a_i^{(k)} = (1 - \sum_{j=P+1}^{k} \exp(-(j/M)^{1/(1-s)+1}) \frac{1}{M^{1/(1-s)+1}} (\frac{1}{1-s} + 1)(j-i)^{1/(1-s)})$$

The last definition can be rewritten as

$$a_i^{(k)} = (1 - b_i^{(k)})$$

where

$$b_i^{(k)} = \sum_{j=P+1}^{k} \exp(-(j/M)^{1/(1-s)+1}) \frac{1}{M^{1/(1-s)+1}} (\frac{1}{1-s} + 1)(j-i)^{1/(1-s)}$$

Now we shall analyze denominator of Gaussian distribution for $\Omega$. Here we can use $\bar{N}_j$ in the zero approximation and come to

$$\sum_{j=P+1}^{k} \bar{N}_j = \tilde{N}^{(k)} - P\bar{N}_1$$

The use of zero approximation is based on the following simple estimate. Really, the last linearization is based on the smallness mainly of the parameter which can be simply neglected in denominator since

$$\sum_{j=P+1}^{k} \exp(-(\frac{j}{M})^{1/(1-s)+1})$$

isn't too small.

Now we can directly go to the calculation of $P^{(k)}(N^{(k)})$ for $k > P$. The starting formula is

$$P^{(k)}(N^{(k)}) = \int_{-\infty}^{\infty} d(N_1 - \bar{N}_1) ... \int_{-\infty}^{\infty} d(N_P - \bar{N}_P) \prod_{i=1}^{P} \exp(-\frac{(N_i - \bar{N}_1)^2}{2\psi\bar{N}_1})$$
$$\exp(-\frac{[N^{(k)} - \tilde{N}^{(k)} - \sum_{i=1}^{P} a_i^{(k)} (N_i - \bar{N}_1)]^2}{2(\tilde{N}^{(k)} - P\bar{N}_1)}) \qquad (3)$$

where we because of $\bar{N}_i \gg 1$ have replaced summation by integration. The limits of integration can be infinite ones because of $\bar{N}_i \gg 1$ and estimates predicted by Gaussian distribution.

To fulfill integration we have to use a simple formula

$$\int_{-\infty}^{\infty} \exp(-\frac{x^2}{c}) \exp(-\frac{(lx+d)^2}{b}) dx \sim \exp(-\frac{d^2}{b+l^2c})$$

We have to use this formula $P$ times with

$$x \sim x_i = N_i - \bar{N}_1$$

$$c \sim c_i = 2\psi\bar{N}_1$$
$$l \sim l_i = -a_i^{(k)}$$
$$b \sim b_i = 2(\tilde{N}^{(k)} - P\bar{N}_1)$$

This leads to

$$P^{(k)}(N^{(k)}) \sim \exp(-\frac{(N^{(k)} - \tilde{N}^{(k)})^2}{2D^{(k)}})$$

where dispersion $D^{(k)}$ is given by

$$D^{(k)} = \tilde{N}^{(k)} - (P - \psi \sum_{i=1}^{P} a_i^{(k)^2})\bar{N}_1$$

Now we can calculate dispersion at infinite $k$. Since $M \gg 1$ we can substitute summation by integration. The number of interval corresponds to the variable $z * M$, then $z = 1$ corresponds to the end of nucleation.

Since

$$\tilde{N}^{(\infty)} = \bar{N}_1(P + \sum_{j=P+1}^{\infty} \exp(-(\frac{j}{M})^{1/(1-s)+1})) \approx M\bar{N}_1\alpha$$

$$\alpha \equiv \int_0^{\infty} \exp(-x^{1/(1-s)+1})dx$$

then

$$D^{(\infty)} = \tilde{N}^{(\infty)}(1 - (1-\psi)\frac{P}{M\alpha} - \frac{2\psi}{\alpha}\frac{1}{M}\sum_{i=1}^{P} b_i^{(\infty)} + \frac{\psi}{\alpha}\frac{1}{M}\sum_{i=1}^{P} b_i^{(\infty)^2})$$

One can easily calculate $b_i^{(\infty)}$:

$$b_i^{(\infty)} = \frac{1/(1-s)+1}{M^{1/(1-s)+1}} \sum_{j=P}^{\infty} \exp(-(\frac{j}{M})^{1/(1-s)+1})(j-i)^{1/(1-s)}$$
$$\to (1/(1-s)+1)\int_p^{\infty} \exp(-x^{1/(1-s)+1})(x-y)^{1/(1-s)}dx$$

Also one can note that

$$\frac{1}{M}\sum_{i=1}^{P} \to \int_0^p dy$$

Then

$$D^{(\infty)} = \tilde{N}^{(\infty)}(1 - (1-\psi)\frac{p}{\alpha} - \frac{\Psi}{\alpha}\beta)$$

where

$$\beta = \beta_1 - \beta_2$$

$$\beta_1 = 2(1/(1-s)+1)\int_0^p dy \int_p^\infty dx \exp(-x^{1/(1-s)+1})(x-y)^{1/(1-s)}$$

$$\beta_2 = (1/(1-s)+1)^2 \int_0^p dy(\int_p^\infty dx \exp(-x^{1/(1-s)+1})(x-y)^{1/(1-s)})^2$$

This result can be directly calculated.

## 2 Calculations of parameters of the model

To compare analytical constructions with the real value of dispersion we shall present numerical simulations.

The results for the mean value of droplets calculated in units of the droplets number calculated in TAC as function of the droplets number calculated in TAC are presented in figure 1.

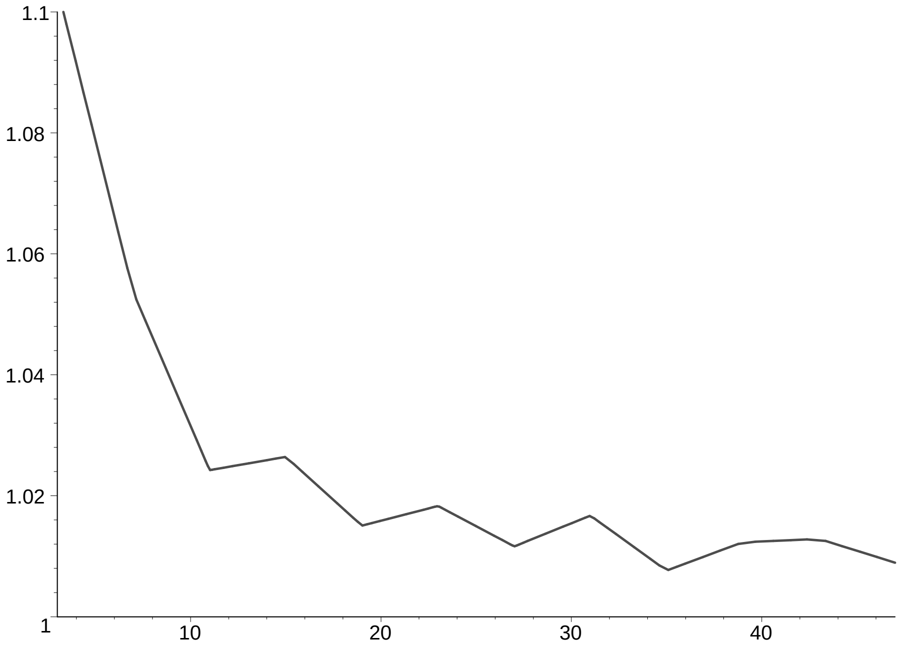

Figure 1: Mean value of the droplets number

The relative dispersion as a function of the mean number of droplets is shown in figure 2.

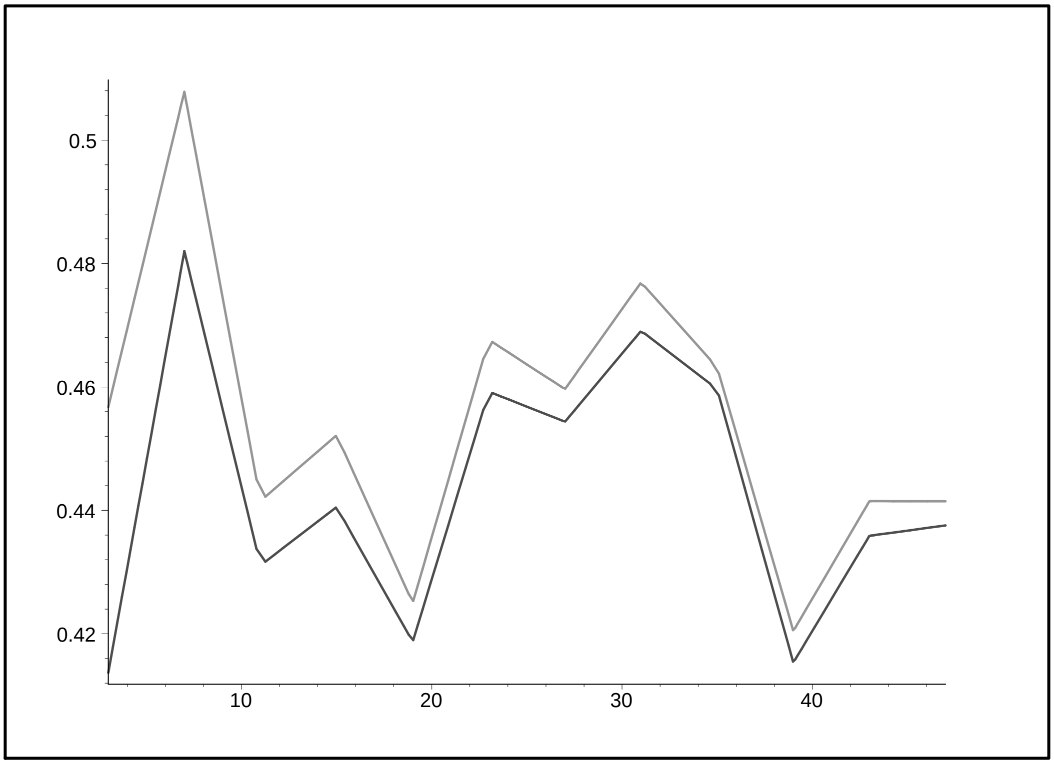

Figure 2: Dispersion

Now we shall perform calculations. We study equation

$$g(x) = \frac{5}{2}\int_0^z \exp(-g(x))(z-x)^{3/2}dx$$

Namely the coefficient $\frac{5}{2}$ corresponds to the final formulas in the previous section.

At first we calculate the form of spectrum. It is shown in figure 3. Two curves are drawn. The upper one in the second iteration approximation, the lower curve is the first iteration approximation. The spectrum lies between these curves.

One can see that the characteristic length of spectrum is $x_0 \approx 1.2 \div 1.25$.

The total number of droplets is $N_{TAC} = 0.9292$. The first iteration gives $N_{first} = 0.8773$.

Now we investigate the two cycle model. The relative number of droplets as a function of the boundary $p$ is shown in figure 4.

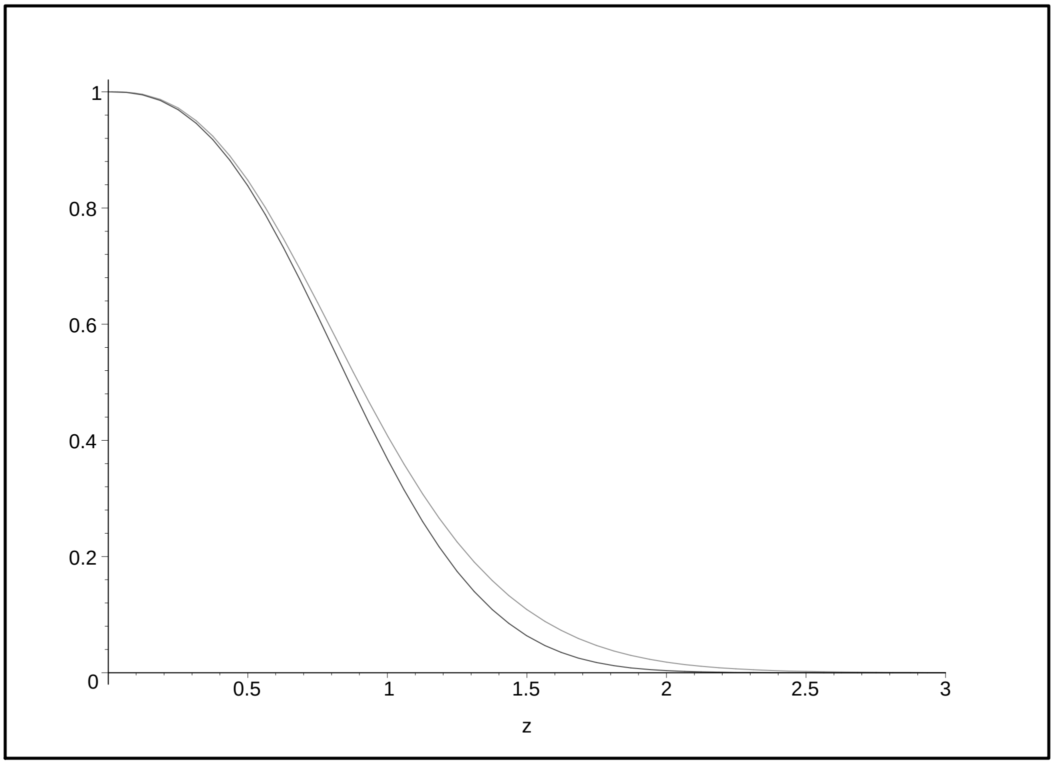

Figure 3: The form of spectrum in TAC

Here two curves are drawn. The upper corresponds to the number of droplets referred to the number of droplets in the first iteration, the lower curve is referred to the precise value of the droplets number. One can see that the deviation of the second curve is two times closer than the deviation of the first curve in the value of minimum. The minimum is attained at $p_0 = 0.64$ which is approximately the 55 percent of $x_0$ (the same part as in the free molecular regime! [6]).

Now we calculate $\beta$. The values $\beta_1$ and $\beta_2$ are drawn in figure 5. One can see that the behavior of $\beta$ is mainly governed by behavior of $\beta_1$.

The ratio $\beta_2/\beta_1$ is drawn in figure 6.

One can see that there is no extremum of the ratio. So, there is no special boundary which provides the quickest convergence of the chain $\beta_1$, $\beta_2$, ... and one has to use $p_0 = 0.64$ going from the most precise approximation for number of droplets as a criterium for such boundary. Also one can see that the ratio is small for all $p$.

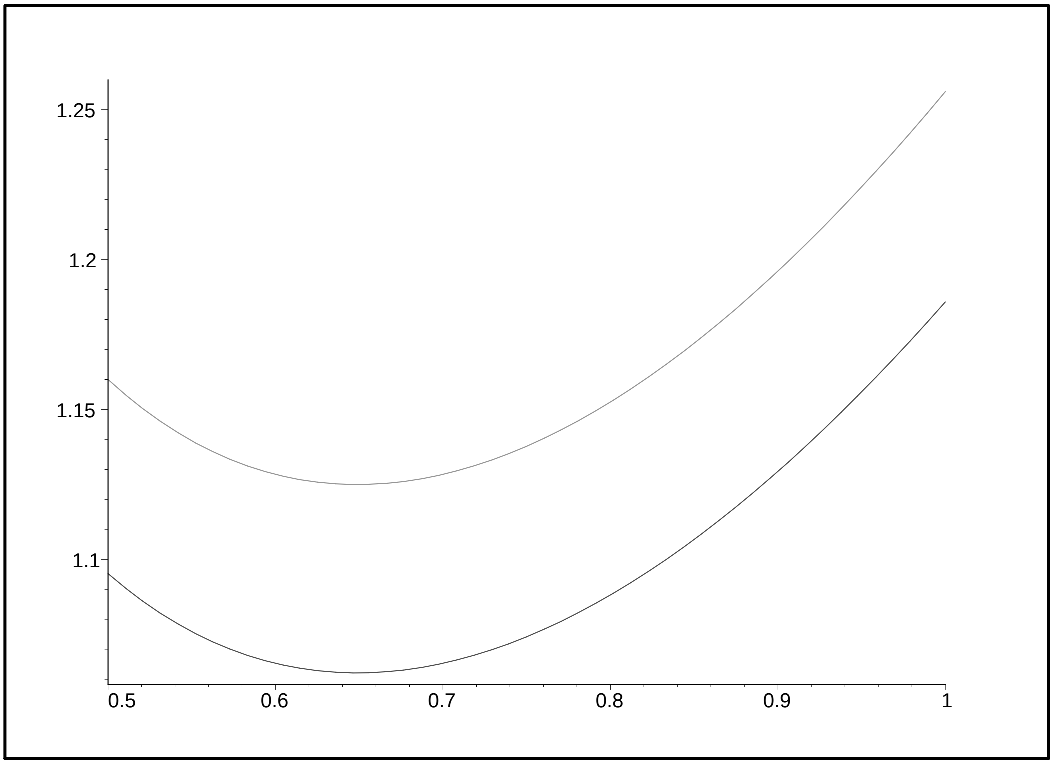

Figure 4: Mean value of the relative droplets number in two cycle model

The value of relative dispersion calculated according to

$$D = 1 - \beta/\alpha$$

is drawn in figure 7.

There are two curves: the upper is dispersion calculated with precise number of droplets, the lower is dispersion calculated with the number of droplets calculated in the first iteration. Both curves have extremum at $p = 0.68$. Even for the lowest curve all values are greater than 0.54 while the real value is 0.44.

If we take into account that $\alpha$ also has to be calculated in two cycle model. Then the value of relative dispersion[2] as a function of the boundary $p$ ini the two cycle model is drawn in figure 8.

One can see that practically nothing has been changed. Minimum is at 0.67, the value of minimum is near 0.6.

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[2] More precisely there is a square of relative dispersion.

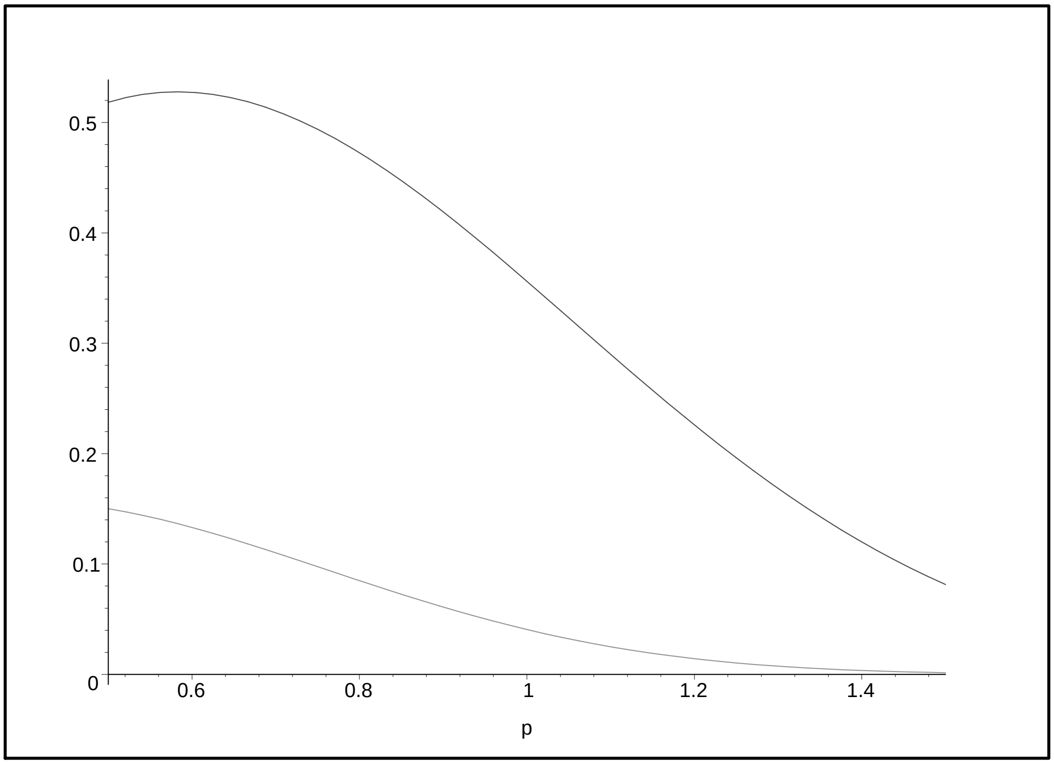

Figure 5: Values $\beta_1$ and $\beta_2$.

Now we try approach based on similarity of nucleation conditions [5]. We start with the infinite upper boundary in formulas for $\beta_1$ and $\beta_2$.

At first we shall show the result for renormalization of dispersion when for $\alpha$ we take the result from the two cycle model. The result is shown in figure 9.

At $p = 0.64$ the value of $\psi$ will be 0.46, at $p = 0.68$ the value of $\psi$ will be 0.43.

When we put $\alpha = 0.92$ which is the result in the precise solutuion we came to the result shown in figure 10. Practically nothing has been changed.

Now we shall restrict the upper limit of integration by $z = 1$ (this is the current moment of observation). At first we draw the number of droplets as function of $p$ in figure 11.

We see that the number of droplets has minimum at $p = 0.43$. This value has to be chosen as $p$ in calculation of dispersion.

Then the value of relative square of dispersion can be calculated and it

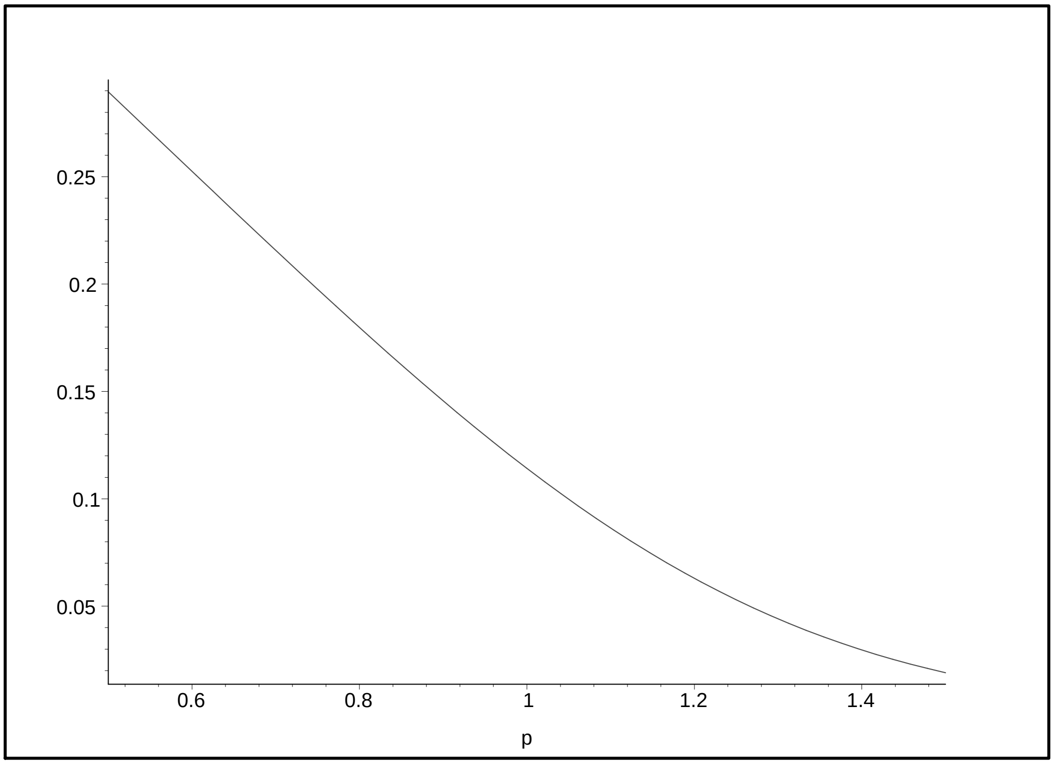

Figure 6: Ratio $\beta_1/\beta_2$

is drawn in figure 12.

We see that at $p = 0.43$ the value of dispersion is near 0.64 and it is far from the expected value. It resembles the calculation without similarity taken into account.

It is interesting to note that in diffusion regime the values of relative dispersion $\psi$ calculated in the model with the upper boundary $\infty$ and with the upper boundary 1 are practically the same. This is true for moderate $p$ (more concrete $p \leq 0.7$).

An explanation of this property is the following: under the free molecular regime of droplets growth the droplets appeared in the first moments of time grow so rapidly that it was very important to know until what sizes (or until what moment) they will grow. So, the duration of the nucleation period was very important. Under the diffusion regime of growth this effect is much more weak. So, the position of the boundary isn't so essential.

For $p \leq 0.5$ the value $1 - \beta/\alpha$ is also close to these values.

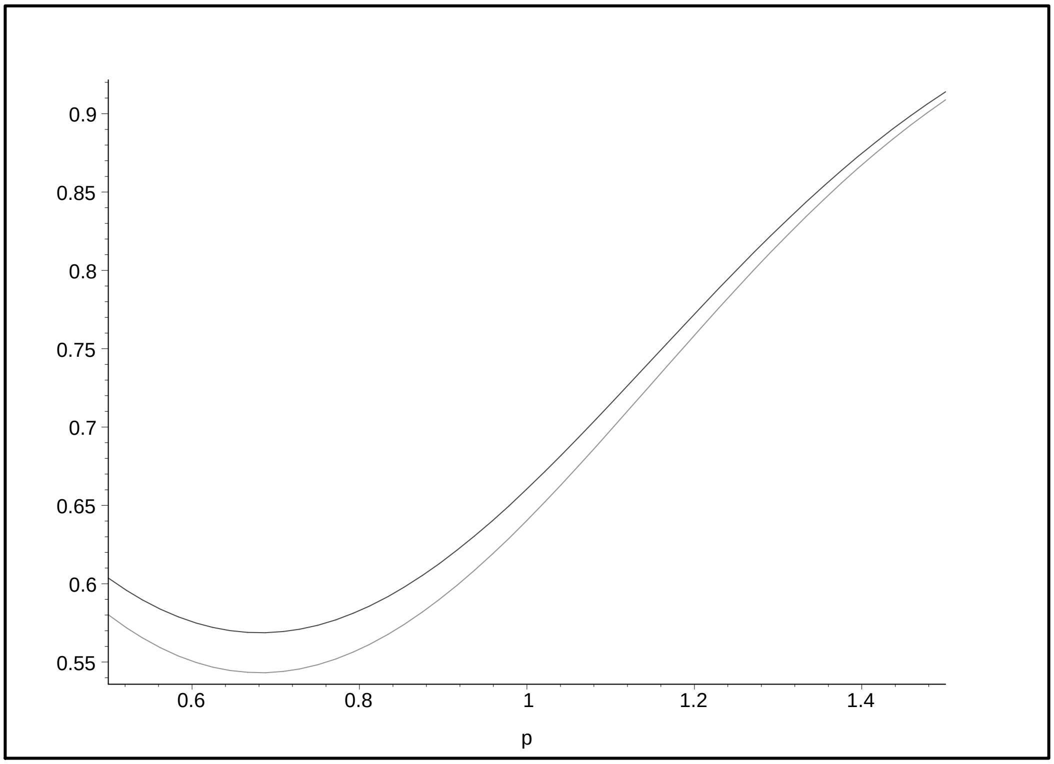

Figure 7: The relative square of dispersion in the two cycle model.

The explanation lies also in collective character of stochastic effects initiated under the diffusion regime of droplets growth.

The question to decide is whether we have to take $p$ from extremum for $\alpha$ calculated with the upper boundary $\infty$ or with the upper boundary 1. From the first view it seems that the boundary 1 is preferable because $\beta_1$ and $\beta_2$ are calculated with the upper boundary 1. But the extremum for $\alpha$ corresponds to the value $\alpha = 0.815$. This value is smaller than $\alpha$ calculated in the first iteration, i.e. $\alpha_1 = 0.8773$ and smaller than this value calculated in the precise solution $\alpha_{pr} = 0.9292$. So, at extremum (it is a minimum) of the model with the upper boundary 1 the deviation from the precise value attains maximum. At the upper boundary $\infty$ the value of $\alpha$ is always bigger than 1 which is greater than $\alpha_1$ and $\alpha_{pr}$. So, here the extremum is really the closest value to precise solution. Then it has a real physical meaning. So, it is reasonable to take $p$ corresponding to the extremum of $\alpha$ with the upper boundary $\infty$.

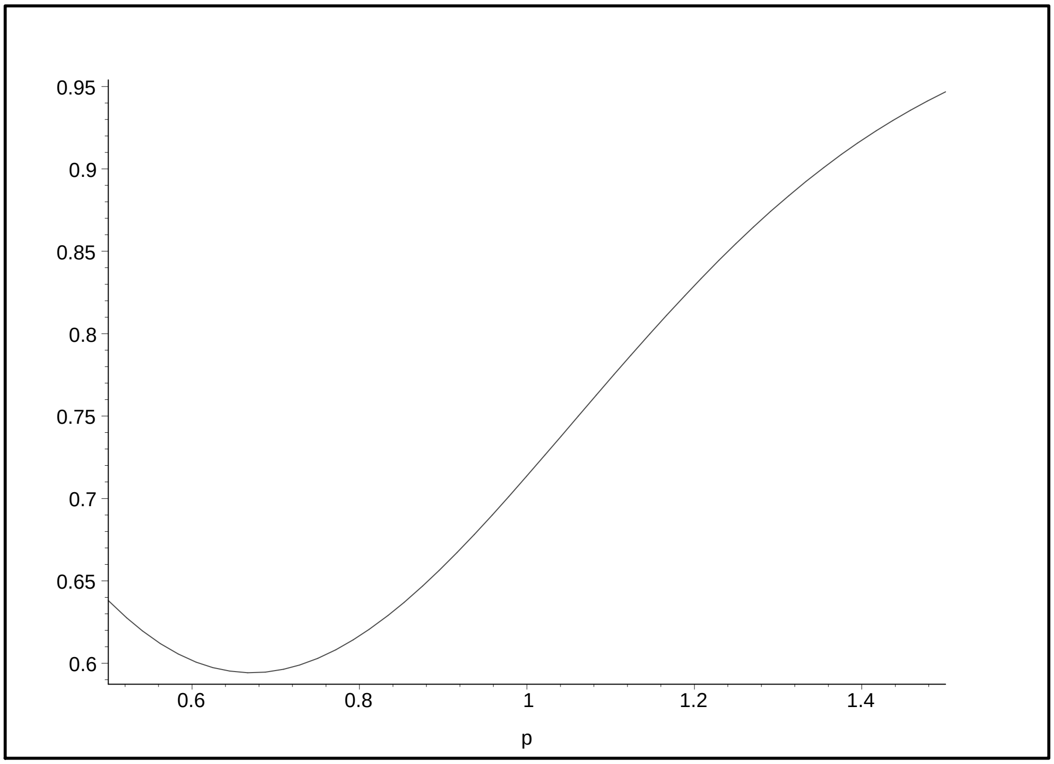

Figure 8: The relative square of dispersion in the two cycle model. Account of the change of the droplets number.

Calculations give $p = 0.65$ and $\psi = 0.49$. This value is calculated on the base of $\beta_1$ and $\beta_2$ with the upper boundary 1. The value $\psi = 0.49$ is rather close to result of numerical simulation $\psi = 0.44$. Certainly, the relative error is one tenth and the methods based on the explicit two cycle models cannot give more precise results.

One can note the following curious result. Evidently, when we calculate $\psi$ for $p = 0.65$ with the upper boundary 1 we come to $\psi = 0.46$ which is practically the necessary result. But this coincidence is no more than an occasional one. When we try the same procedure for the free molecular regime we come to $\psi = 0.55$ (here $\psi = 0.55$) which is far from numerical result $\psi = 0.64$.

Having estimated the value of deviation of $\psi = 0.49$ from $\psi = 0.44$ one has to note that it is much smaller than the deviation of $\psi = 0.59$ of the value $1 - \beta/\alpha$ in its minimum from $\psi = 0.44$. So, the modification made

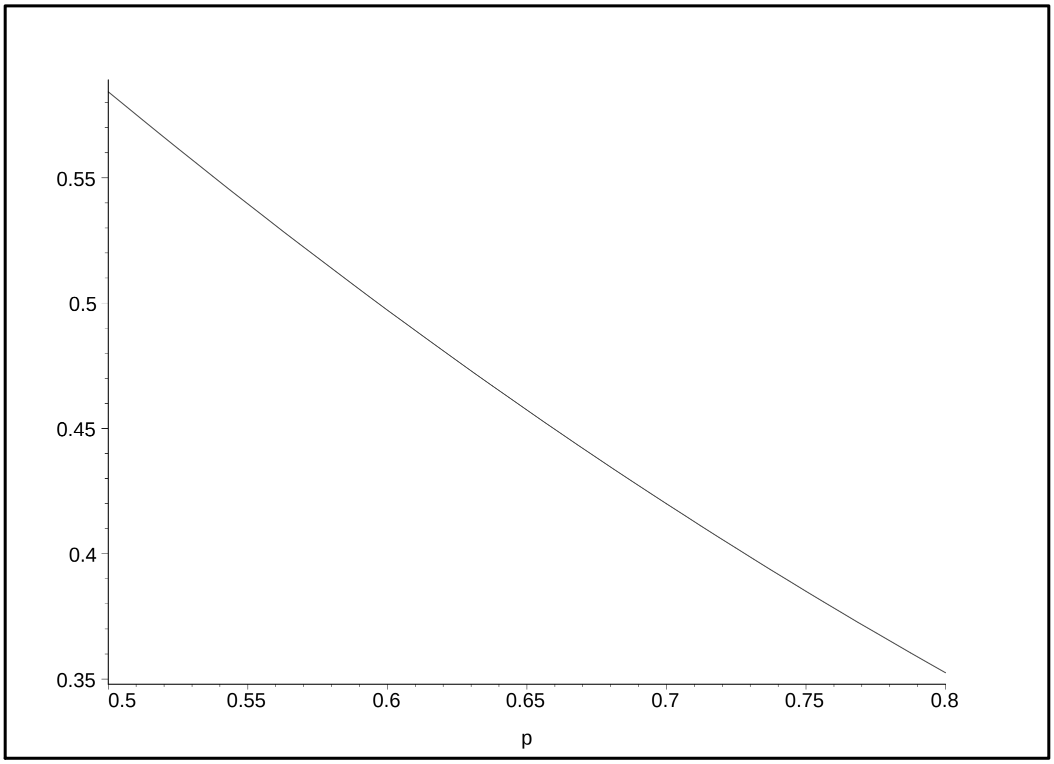

Figure 9: The relative square of dispersion in the similarity model. Account of the change of the droplets number in two period model.

here really have a real sense.

# 3 The effect of growing volumes of interaction

What shall we do to take into account the growth of the volume interaction in diffusion regime of growth? It is necessary to rewrite formula (3). We can substitute in $\exp(-\frac{(N_i-\bar{N}_1)^2}{2\bar{N}_1})$ the denominator $2\bar{N}_1$ by another denominator which corresponds to the growing volume of interaction. Then $\bar{N}_1$ has to be substituted by $\bar{N}_1 const(j-i)^{5/2}$ with some known *const*. It means that the characteristic half-width $\sqrt{\bar{N}_1}$ has to be substituted by $\sqrt{\bar{N}_1 const(j-i)^{5/2}}$. One can not apply directly this substitution in $\exp(-\frac{(N_i-\bar{N}_1)^2}{2\bar{N}_1})$ but only ap-

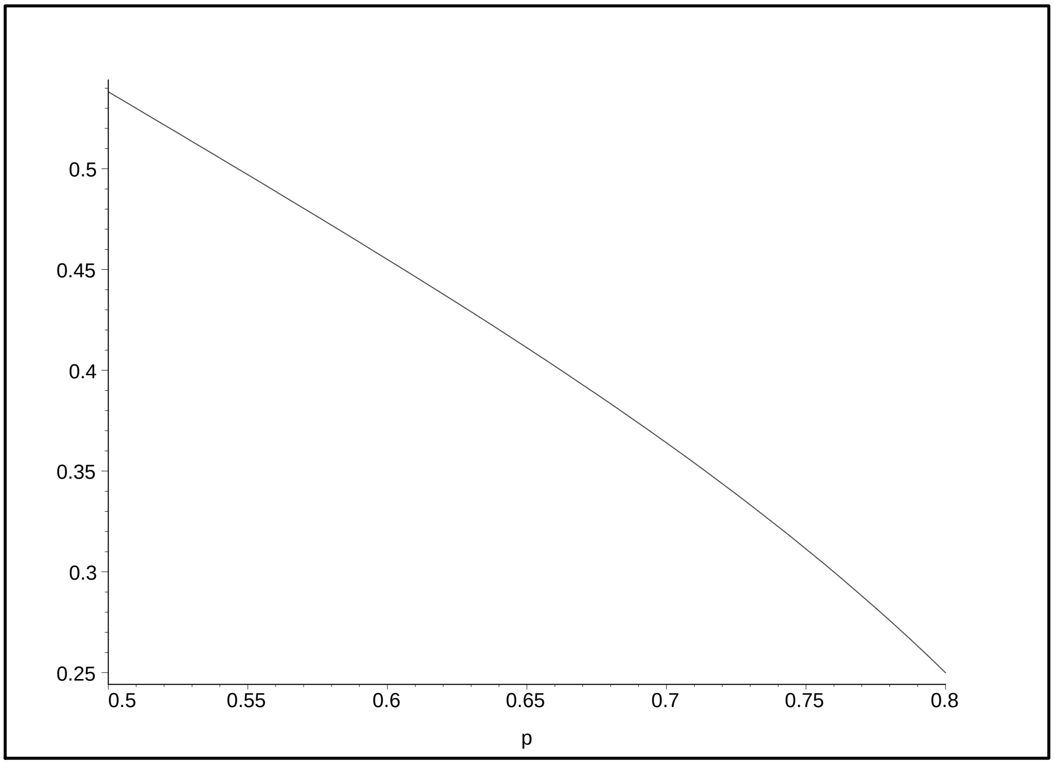

Figure 10: The relative square of dispersion in the similarity model. The droplets number is taken from precise solution.

proximately in expression for $a_i^{(k)}$ which now will be

$$a_i^{(k)} = 1 - \frac{5/2}{M^{5/2}} \sum_{j=P+1}^{k} \exp(-\frac{j^{5/2}}{M^{5/2}})(j-i)^{(\frac{1}{1-s}+1)-5/2}/const$$

with some known *const* and an appropriate renormalization.

In diffusion regime

$$\frac{1}{1-s} + 1 - \frac{5}{2} = 0$$

and there is absolutely no effect. It means that kinetics of nucleation will be absolutely different. It is described in [4]. The most strong effect will take place in the free molecular regime where $\frac{1}{1-s} + 1 - 5/2 = 3/2$

Now we shall estimate the effect of the dispersion variation. We see

$$D^{(\infty)} \sim \tilde{N}^{(\infty)}(1 - \frac{1}{\alpha}(2(\frac{1}{1-s}+1)\int_0^p dx \int_p^\infty dz (z-x)^{\frac{1}{1-s}+1-5/2} \exp(-z^{5/2})$$

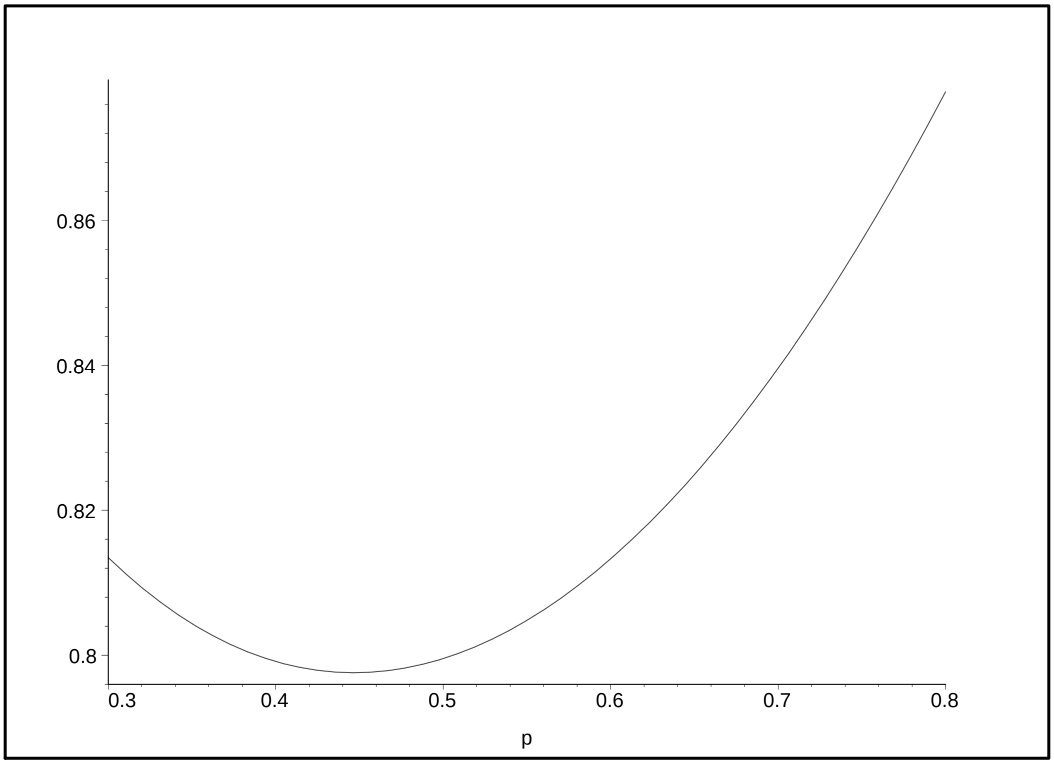

Figure 11: The number of droplets until the current moment.

$$-(\frac{1}{1-s}+1)^2\int_0^p dx(\int_p^\infty dz(z-x)^{\frac{1}{1-s}+1-5/2}\exp(-z^{5/2}))^2))$$

Note that the last relation has to applied to the subsystem with the size $\sqrt{4Dt_n}$ where $t_n$ is the duration of the nucleation period. Then we have to take the superposition of these independent subsystems.

We see that in the majority situations we can approximately neglect $(j-i)^{\frac{1}{1-s}+1-5/2}\approx(j-i)^0=1$ and see that then

$$D^{(\infty)}\approx\tilde{N}^{(\infty)}$$

and there is no effect.

Nevertheless the deviation in the number of droplets from the value calculated on a base of averaged characteristics exists. We have to divide the whole system into subsystems of the size $\sqrt{4Dt_n}$, then determine the number of droplets in this subsystem $\tilde{N}^{subs}_{tot}$ obtained on the averaged characteristics,

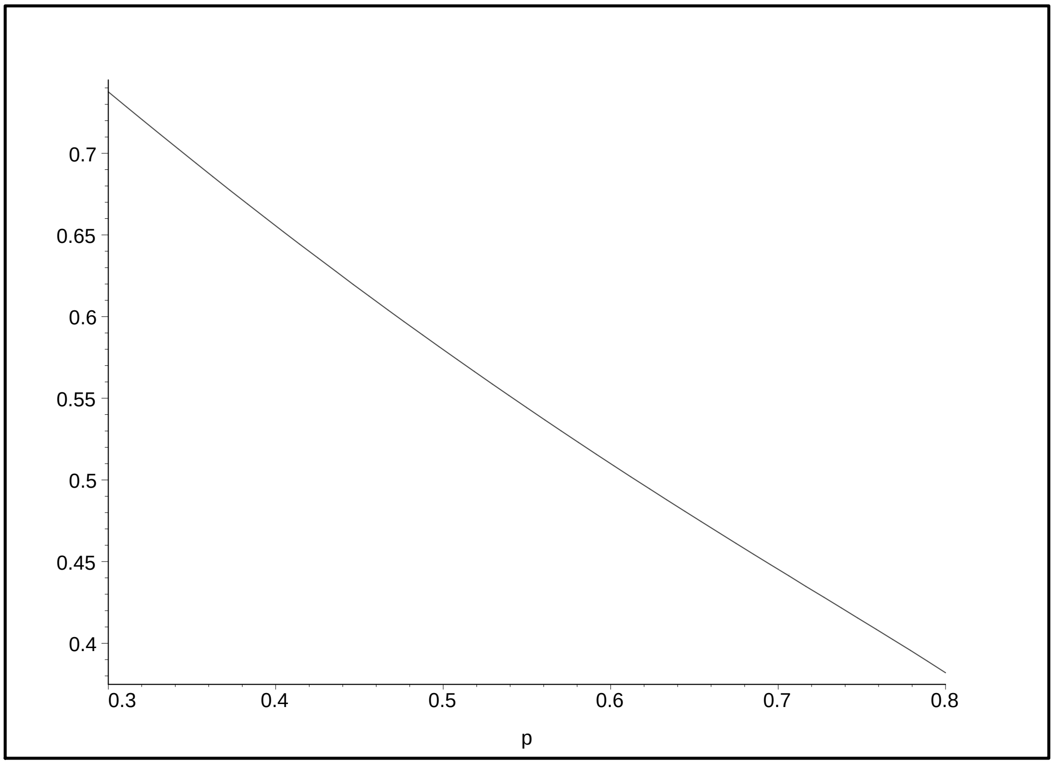

Figure 12: Relative square of dispersion up to the current moment. Account of the change of the droplets number.

then determine the deviation $\delta N_{tot}^{subs}$ from the values calculated in TAC and then the whole deviation in the whole number of droplets $N_{tot}$ from the value based on the averaged value $\tilde{N}_{tot}$ will be

$$\delta N_{tot} = \delta N_{tot}^{subs} \frac{\tilde{N}_{tot}}{\tilde{N}_{tot}^{subs}}$$

These procedures completely solve the problem.

One has also to note that the use of monodisperce approximation [2] leads to the absence of the problem of growing volume because the characteristics governing the nucleation period have been determined only in one moment of time. The problem here is a justification of monodisperse approximation to the calculation of fluctuation effects.

# 4 Appendix

Here we shall present the two cycle model with a fixed boundary in kinetics of the metastable phase decay under the free molecular regime of the droplets growth. This question was completely investigated in [6] but during the last two years our view on this problem was slightly modified and the modern state is described below.

Systematic investigations of the first order phase transitions are performed since Wilson [7]. The classical theory of nucleation [8] gave expressions for all main characteristics of stationary process of nucleation. This allowed to investigate a global picture of the phase transition. A set of papers [9] was devoted to model pictures of the global kinetics of nucleation. Here we shall also consider the global picture of the phase transition. One can note that all cited publications [9] were based on averaged nucleation rates. Here we shall consider stochastic appearance of embryos and outline the stochastic manner of appearance.

Recall briefly the main features of phase transition. Suppose that in initial moment of time there exists a metastable state. Then the embryos of a new phase begin to appear in the metastable system. The average rate of appearance is given by [8]. Then the embryos begin to grow and to consume the vapor, metastability falls and the rate of nucleation, i.e. the rate of appearance of new embryos falls also. The vapor consumption occurs in a time scale in a very sharp avalanche manner.

It is clear that during the nucleation period the new supercritical formations of the new phase appear with some fixed probability, but they appear in stochastic manner. So, the stochastic appearance of relatively big number of droplets leads to very rapid stochastic consumption of vapor. Stochastic appearance of relatively small number of droplets leads to delay of the vapor exhaustion and to excess of droplets appearance in next moments of time. But it seems that this excess can not compensate the opposite effect of the absence of embryos in first moments of time. It seems that the total number of droplets will differ from the average value. This is the naive reason why stochastic effects of nucleation have to be taken into account.

In a system with macroscopic sizes due to a giant value of the Avogadro number there appears some rather big number of droplets. It allows to use the averaged characteristics to construct kinetics of a nucleation process. Precise kinetic approach based on averaged characteristics is described in [3]. In [3] the time evolution is completely constructed.

After the formulation of integral equations (see [3]) one can introduce "elementary intervals of nucleation" - the intervals where the state of the system changes negligibly small. In macroscopic systems the total number of droplets is so big that at every elementary interval there appears a great number of droplets $\Delta N$. On the base of traditional thermodynamics one can state that the relative fluctuation $\delta \Delta N / \Delta N$ of droplets formed at elementary interval is small and has an order of $(\Delta N)^{-1/2}$. This remark completely solves a problem of justification of nucleation description based on averaged characteristics.

Since it is possible to extract elementary intervals where thermodynamic parameters and the nucleation rate have small variations there is no need to take care about the stochastic corrections.

In experimental investigations one can not study quite macroscopic systems because the most popular data is the number of droplets and to fulfill the calculation of this number one can not have too many droplets[3]. After the theory based on the averaged characteristics has been presented it became possible to investigate the stochastic effects in kinetics of nucleation, i.e. the effects of stochastic appearance of droplets. Recently there appears a set of papers [10], [1], [11] where a stochastic effects (the effects of fluctuations of droplets formation) were described and investigated. One can extract two approaches which were formulated in [10] and in [1]. Although [1], [11] were written by the same authors of [10] these authors didn't hesitate that the theories formulated in [1] , [10] gave different results. So, at least one has to analyze approaches [10], [1] and decide whether there is a true result among these approaches and how it can be used to construct the adequate description of the nucleation process.

One has to specify a formulation of the problem of our investigation.

In [1], [10] it was proposed to establish corrections to the total number of droplets $N$ appeared in the system. It was supposed that these corrections are functions of $N$. To demonstrate the error of this approach it is sufficient on one hand to take two identical systems then to calculate them separately and to add results or on the other hand to calculate correction directly for the total system. The results will be different.

One has to determine a real volume to which one has to refer the number of droplets. It is simple to do with the help of results from [4]. In that

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[3] One can not simply calculate the infinite number of droplets. The upper limit of the number of droplets which can be noticed on a photo image is about several dozens.

paper the kinetics of nucleation for diffusion regime of droplets growth was constructed. It was shown that a solitary droplet perturbs vapor up to distances of an order $\sqrt{4Dt}$, where $D$ is a diffusion coefficient, $t$ is a time from a moment of droplet formation up to a current moment. As an estimate one can take as $t$ a time $t_1$ of the whole nucleation period duration[4].

The last remark allows to give a new definition of the volume $V_{el}$ where the number $N_{el}$ of interacting (mainly through the vapor exhaustion) droplets is formed. Namely this value has to be regarded as a volume of a system in approach [10], [1]. This volume is

$$V_{el} = 4\pi(4Dt_1)^{3/2}/3$$

If the sizes of the system are smaller than this value one has to take the volume of the system as this value. But such a small system can be hardly regarded as a macroscopic one. At least one has to analyze carefully the boundary conditions for the system.

Naturally, the droplets appeared at different moments of time perturb initial phase up to different distances. So, one can regard above formulas only as estimates. Some more rigorous equations can be found in [13].

The number of droplets $N_{el}$ isn't too big as $N$ is. So, an analysis of stochastic effects has a real sense. It is interesting now to get all correction terms which are ascending with the number of droplets (but not only a leading term). To solve this task one has to modify approaches from [1], [10].

Complexity of this problem appears here because one can not directly use equations based on the theory with averaged characteristics. In [1], [10] some properties of solution of the theory on the base of averaged characteristics (TAC) were the starting points for constructions. This supposition was adopted without any justification. So, at first we have to decide whether it is possible to start with TAC.

We shall consider the situation of decay of metastable phase. The new dimensionless parameter - the number of droplets destroys the universality observed in [3] for the theory based on averaged characteristics. Moreover, it is difficult even to formulate the system of equations. This radically complicates the problem.

The possibility to use the effective monodisperse approximation formulated in [2] was used in [10] without any justifications. Generally speaking this property can not be directly used to calculate stochastic corrections.

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[4] The nucleation period is a period of intensive formation of droplets.

One has to analyze whether this conclusion leads to an error made in [10]. Here we have to formulate more correct constructions.

Both approaches from [1] and from [10] declared that they used the following property observed in [3] in frames of TAC:

*"The droplets formed at the beginning (i.e. at the first half) of the nucleation period are the main consumers of vapor".*

This property is valid [3], but it is substituted in reality in [10], [1] by the following statement:

*The main source of stochastic effects are the free fluctuations of droplets formed at the beginning (i.e. at the first half) of the nucleation period. They govern the fluctuations of all other droplets.*

The last statement seriously differs from the first one. To get credible results it was necessary to balance the fluctuation effects from the first half of spectrum by the corresponding reaction of remaining part of spectrum. Then, at least this approach needs some special justifications. So, one has to use some new constructions which are presented below.

The application of the model approximation which was in reality done in [1], [11] will lead to some errors. But due to universality of solution [3] the errors can not be be too big. Qualitatively everything is suitable, but precision will be not so high.

The same conclusion will be valid for any approach based on some model behavior of supersaturation (justification is valid for a vapor consumption in TAC, but not for stochastic effects). Namely, in [1] was used an artificial approximation where at the first half of the nucleation period the conditions of nucleation are the ideal ones and at the second half the conditions of nucleation are governed by the droplets formed at the first half. Here in current paper the final result will be more precise and it will be not based on rather spontaneous artificial choice of some parameter as it was done in [1] where this parameter was put to to 1/2. In [1] it is supposed that until some moment (it is chosen in [1] as a half of nucleation period) the droplets are formed under ideal conditions and namely these droplets determine a vapor consumption. In reality this approach taken from [12] (page 310) was used in [1] in slightly another sense. It is supposed that droplets formed during a first half of nucleation period are the main source of stochastic effects. The last statement was not justified in [1] and it is rather approximate. The relative correctness of a result was attained due to specific compensation of different errors of approximations used in [1]. It is necessary to stress that the the mentioned model was used in [12] to justify a strong inequality and the high precision of constructions was not essential. But in [1] this model was the source of numerical result.

All arguments listed above lead to necessity of reconsideration which will be made in this publication. A plan of narration will be the following one

- Having considered the interaction of stochastic deviations of the number of droplets appeared during the elementary intervals of nucleation we shall see that stochastic effects are at least moderate.

- A moderate scale of stochastic effects allows to seek the solution on the base of the theory with averaged characteristics. But we have to take stochastic effects from all droplets formed during the nucleation period.

- The possibility to take into account the influence of stochastic deviations of all droplets can be provided by the property of the self similarity of nucleation conditions during the nucleation period. This property can be considered in two senses - 1) in the local differential sense and 2) in the integral sense in frames of the first iteration in the iteration procedure in TAC [15]. The local property will be used in justification of the smallness of stochastic effects and the integral property will be used to calculate the stochastic corrections of the whole nucleation period.

All analytical results will be checked by computer simulation and a coincidence will be shown.

All mentioned constructions will be valid for an arbitrary first order phase transition. The law of droplets growth here will be a free molecular one, then the linear size of droplet grows with velocity independent from its value. Consideration of other regimes can be formally attained in frames of the current approach by some trivial substitutions, but one has to take into account that the new regime requires new approaches to construct nucleation kinetics as it is shown in [4]. So, one can not agree with [10] where it is stated that one of results is an account of stochastic effects in a diffusion regime of droplets growth. This effect has to be taken into account principally in another manner by application of methods presented in [14].

## 4.1 Some characteristic features of decay kinetics

We begin with the theory based on averaged characteristics. It is supposed to be known [3], that the supersaturation $\zeta$ behavior can be determined after certain renormalizations by the following equation

$$\psi(z) = \int_0^z dx (z-x)^3 \exp(-\psi)$$

on function $\psi$ which is the relative renormalized deviation of supersaturation from the initial value. Variables $x$ and $z$ can be considered as equivalent ones. A good approximation for solution and for a distribution of the droplets number over time (or over liner sizes of droplets) which is proportional to $\exp(\psi)$ is

$$f_1 = \exp(-z^4/4). \tag{4}$$

The form of $f_1$ is given by fig.13. It is seen that approximately at $z_0 = 1.25$

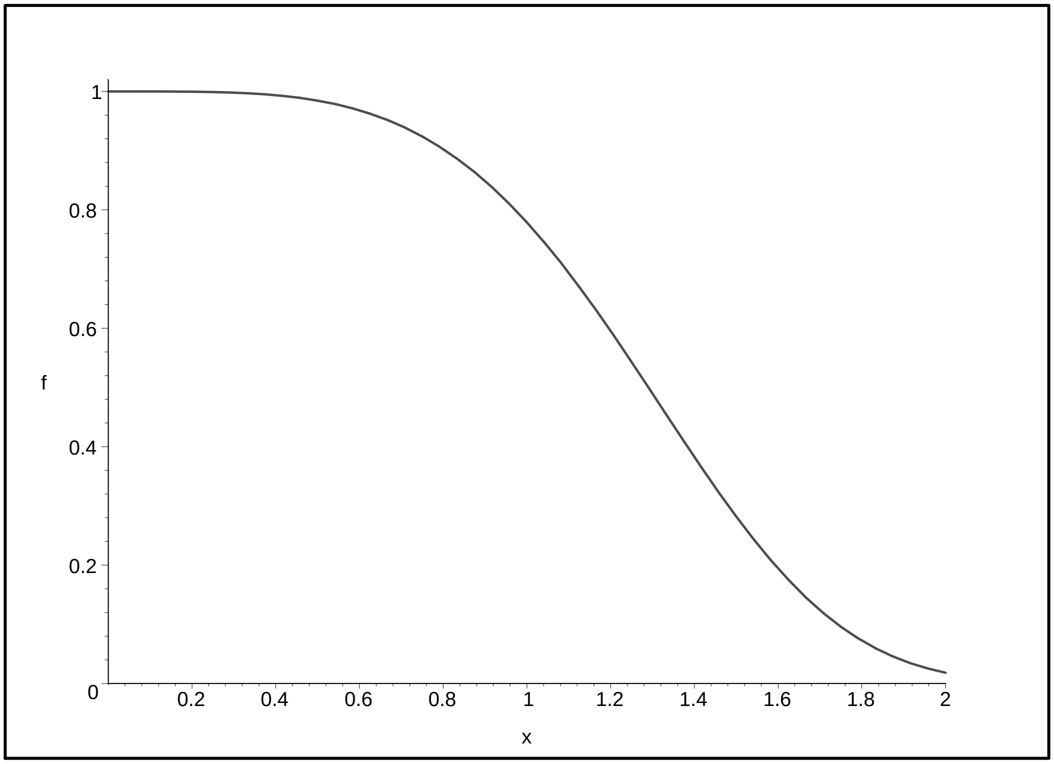

Figure 13: A form of approximation for size spectrum

the nucleation period stops.

Approximation (4) has rather high precision [2]. It is based on the following law of substance accumulation

$$G = z^4/4 = \int_0^z (z-x)^3 dx \equiv \int_0^z g(x)dx, \quad g = (z-x)^3 \equiv \rho^3$$

for the renormalized number $G$ of molecules in a new phase. For any moment $t$ or $z$ a function $g$ has one and the same form. We shall call this property as a "similarity of nucleation conditions". We see that every time the droplets formed at the last third of a period from beginning of nucleation until a current moment will accumulate a negligible quantity of substance. The relative quantity of the substance there has an order of ($\sim 1/27$) and is so small that even if there will be fluctuations the quantity will remain small.

From the form of $f_1$ it is seen that until $z_= \equiv 0.7 z_0$ all droplets deplete vapor rather weak. It will be important for future analysis.

Another important property is the possibility to describe kinetics in frames of TAC with the help of monodisperce approximation (see [2]). The mentioned property of $g$ allows to use a monodisperse approximation [2] not only at the end of nucleation but in every moment of the nucleation period [2]. Let $t(G)$ be the moment when there are $G$ molecules in droplets (in appropriate units). An application of the monodisperse approximation [2] leads to

$$G \approx N_m(z) z^3$$

where $N_m(z)$ is the number of droplets born until $z/4$

$$N_m(z) = N(z/4) \approx z/4$$

and

$$N_m(z) \approx \frac{N(z)}{4}$$

for $z$ which are essentially less than those corresponding the end of the nucleation period (in reality $z \leq z_=$.

## 4.2 Interaction of arbitrary stochastic fluctuations

The account of fluctuation interactions at every moment of time is important in justification of the smallness of stochastic corrections. Generally speaking, one can not take consideration only at the end of nucleation period without justifications that the characteristic features of nucleation kinetics remains the same at every moment of time.

The arbitrary value of $z$ in the period of nucleation corresponds to the arbitrary value of the number of droplets in a liquid phase $G$ (in renormalized units which will be used (see [3]) the value $G$ will belong to interval $(0, 1)$). Now it will be possible to repeat in some features the approach from [10] with arbitrary parameter $G$ instead of 1 (in renormalized units, before renormalization it would be $1/\Gamma$ (see [3])). The sense of a difference from [10] is consideration of an arbitrary moment $z$ instead of the end of nucleation. It is very important because allows to take into account all fluctuation effects during the nucleation period.

Let $t(z)$ be the current moment of time ($z$ is the coordinate of the spectrum front, actually $t$ is proportional $z$). We suppose that before $az$ ($a$ is some parameter) droplets are formed without mutual influence and one can write Poisson's distribution. This is the first group of droplets. The second group of droplets are all other droplets formed until the time moment $z$. A natural restriction on $a$ appeared, namely $a < 0.7$. We shall take $a > 1 - 0.7 = 0.3$ also for the purposes explained below. We suppose that the influence of other droplets on its own formation is negligible (this follows from $2 * 0.7 = 1.4 > 1.25$ and from notation made above about the last third of nucleation period). Then it is possible to write Poisson's distribution for the second group of droplets, but with parameters depended on stochastic values - characteristics of the droplets distribution from the first group. Rigorously speaking one has to use the first four moments of the droplets distribution in accordance with [3], but for simplicity we shall use here only the zero momentum. As a compensation for this simplicity we has to use here only $a = 1/4$ which corresponds to the applicability of monodisperse approximation. But due to the arbitrary value of $G$ this is quite sufficient for our goal.

Certainly, one can not state that precisely the first fourth of the spectrum plays the main role in vapor consumption. So, we have to consider interactions of stochastic fluctuations for all $a$ which aren't too small in comparison with $1/4$ as well as $1 - a$ isn't too small in comparison with the same $1/4$. This will be done below.

At the next step of consideration one has to come from Poisson distributions to Gauss distributions and integrate them with account of connection between stochastic parameters of embryos formation from the first group and parameters of distribution from the second group. The same was done in [10] but only for a leading term.

Why it is necessary to get all ascending terms in corrections? The existence of at least one coefficient with a big absolute value means (see the theory of Chebyshev polynomials) that there exist a size of a group where the interaction will lead to the big effect. Then it would lead that the interaction in these groups will be the real driving force of the process and these groups can be regarded as quasiparticles.

Contrary to [10] we shall take into account all correction terms which come from transition from Poisson's distributions to Gauss distributions and corrections for nonlinear connection between the group distributions. We shall take all terms which are growing when the total number of droplets grows.

We get the following result for droplets distribution

$$P = P_{\infty}(1+y)$$

where

$$P_{\infty} = (\frac{9a}{2\pi N(3a+1)})^{1/2} \exp(-\frac{9a}{3a+1}\frac{D_s^2}{2})$$

$$D_s = \frac{\hat{N} - N}{\sqrt{N}}$$

$\hat{N}$ - some stochastic value of the total number of droplets, $N$ - the mean value of droplets and $y$ is the correction for spectrum.

At $= 1/4$ we get

$$y = \frac{1}{74088} D_s (8087 D_s^2 - 10269) s + (-\frac{4}{9} + \frac{305}{1176} D_s^2$$
$$- \frac{85903}{12446784} D_s^4 + \frac{65399569}{10978063488} D_s^6) s^2$$

where

$$s \equiv 1/\sqrt{N}$$

is a small parameter of decomposition. To get all ascending (with $N$) corrections we must fulfill decomposition until $s^2$.

Why it was necessary to get all ascending terms in decomposition? The answer lies in specific sequential influence which can be observed in nucleation period. The droplet appeared in the first moment of time forms condition for the embryos appearance in the second moment, then the embryos appeared in the first and in the second moments form conditions for further appearance, etc. So, if there would be some $N$ at which corrections will be big then immediately namely this value will be the crucial value for all kinetics. Fortunately here there is no such effect and, thus, we can take the theory with the averaged characteristics as the base for further constructions.

At arbitrary $a$ we get for $P/P_\infty$ (here $P_\infty$ is the limit at $N = \infty$) the following expression

$$P/P_\infty = 1 + w_1 s + w_2 s^2$$

Here

$$w_1 = -\frac{1}{6}((486l^{12} + 486D_s^2 l^{12} - 972l^{11}D_s^2 + 324l^{10} - 648D_s^2 l^{10} + 756l^9$$

$$+810l^9 D_s^2 - 459l^8 + 297D_s^2 l^8 - 135l^7 D_s^2 -$$

$$387l^7 + 90l^6 D_s^2 - 153l^6 + 27l^5 D_s^2 - 213l^5 - 66l^4 D_s^2 - 3l^4 + 27l^3 - 3l^3 D_s^2 + 16l^2 D_s^2 - 3l^2 +$$

$$9l + lD_s^2 + D_s^2)D_s)/((1+3l^2)^3(l+1)(-1+l^2))$$

where

$$l = \sqrt{a}$$

and

$$w_2 = w_{02}/((l+1)^2(-1+l^2)(1+3l^2)^6 l^2)$$

$$w_{02} = \sum_{i=0}^{3} q_{2i} D_s^{2i}$$

$$q_0 = -\frac{1}{12} - \frac{1}{6}l + \frac{243}{4}l^{16} - \frac{135}{2}l^7 - 90l^8 - \frac{87}{2}l^6 + \frac{243}{2}l^{14} + \frac{81}{2}l^{12}$$

$$-\frac{153}{2}l^{10} - \frac{39}{2}l^5 - \frac{67}{6}l^4 - \frac{225}{2}l^9 - \frac{3}{2}l^2 - \frac{81}{2}l^{11} + \frac{243}{2}l^{13} - \frac{243}{2}l^{15} - \frac{17}{6}l^3$$

$$q_2 = \frac{5265}{4}l^{12} + \frac{51}{2}l^6 + 117l^{10} + \frac{333}{2}l^{11} + \frac{31}{8}l^4$$

$$+\frac{17}{2}l^5 + \frac{5049}{2}l^{14} - \frac{15309}{2}l^{19} + 2079l^{13}$$

$$+31l^8 - 8748l^{18} + 42l^9 + \frac{24057}{2}l^{21} + \frac{103}{2}l^7 + \frac{16767}{8}l^{20} + 6561l^{22}$$

$$+\frac{4617}{2}l^{15} - 3159l^{16} - 8262l^{17}$$

$$q_4 = -\frac{4413}{2}l^{13} - \frac{477}{2}l^{15} + 7047l^{21} - \frac{1161}{4}l^{18}$$

$$+\frac{361}{6}l^8 + \frac{105}{2}l^{11} - \frac{104247}{4}l^{22} - \frac{3}{4}l^4 + 17091l^{20}$$

$$-5103l^{23} + \frac{43}{6}l^5 - \frac{31185}{4}l^{19} + 7965l^{17} - \frac{3213}{4}l^{12} - \frac{475}{3}l^{10} + 510l^{14} - \frac{49}{6}l^7 + \frac{23}{4}l^6$$

$$+\frac{1}{12}l^3 + \frac{44469}{4}l^{24} - \frac{1}{12}l^2 - \frac{6903}{4}l^{16} + \frac{74}{3}l^9$$

$$q_6 = -13122l^{25} - \frac{40419}{8}l^{18} + \frac{17253}{2}l^{20} - \frac{24057}{2}l^{22} + 4374l^{24} + \frac{6561}{2}l^{26} -$$

$$\frac{48843}{2}l^{21} - \frac{623}{24}l^8 + \frac{59}{36}l^6 - \frac{3609}{4}l^{14}$$

$$-\frac{57}{8}l^{12} + \frac{411}{4}l^{10} + \frac{11}{24}l^4 + \frac{1}{72}l^2 - \frac{29}{12}l^7 - \frac{345}{4}l^{11} + \frac{1}{36}l^3 +$$

$$\frac{13}{36}l^5 + \frac{65}{4}l^9 + \frac{2421}{4}l^{13} - \frac{7857}{4}l^{15} +$$

$$\frac{8667}{4}l^{17} + 28431l^{23} + 7047l^{19} + \frac{24705}{8}l^{16}$$

Having integrated this expression we get corrections to droplets number. The term at $s$ gives zero after integration and the first non zero correction has an order of $\sim s^2$ and doesn't depend on the total number of droplets. A coefficient at $s^2$ has at $a = 1/4$ a value

$$d_0 = 311/3024 \ll 1$$

At arbitrary $a$ a coefficient at $s^2$ in correction for the total number of droplets will be

$$d_a = \frac{1}{72}[108a^6 + 540a^{11/2} - 72a^5 - 930a^{9/2} - 336a^4 +$$

$$713a^{7/2} + 158a^3 + 4a^2 - 203a^{5/2} - 6a + 39a^{3/2} - 3a^{1/2}]/[a^{3/2}(1-a)^2(1+3a)]$$

It will be interesting to compare results with and without corrections from transition from Poisson's distribution to Gauss distribution. So, we consider now this case. At the leading term there will be no change. At correction terms we have

$$y = -\frac{17}{74088}D_s(-2331 + 289D_s^2)s + (\frac{17}{196}D_s^2 +$$

$$\frac{732037}{12446784}D_s^4 + \frac{24137569}{10978063488}D_s^6 - \frac{13}{36})s^2$$

$$d_0 = -37/126$$

$$d_a = \frac{1}{72}(648a^{11/2} - 216a^5 - 1062a^{9/2} + 108a^4 + 753a^{7/2} -$$

$$30a^3 - 195a^{5/2} - 12a^2 + 19a^{3/2} + 6a - 7a^{1/2})/(a^{3/2}(1+3a)(1-a)^2)$$

It is seen that these corrections are small. At arbitrary $a$ except too small ones and those close to 1 (these values are unreal) we get values shown at fig.14

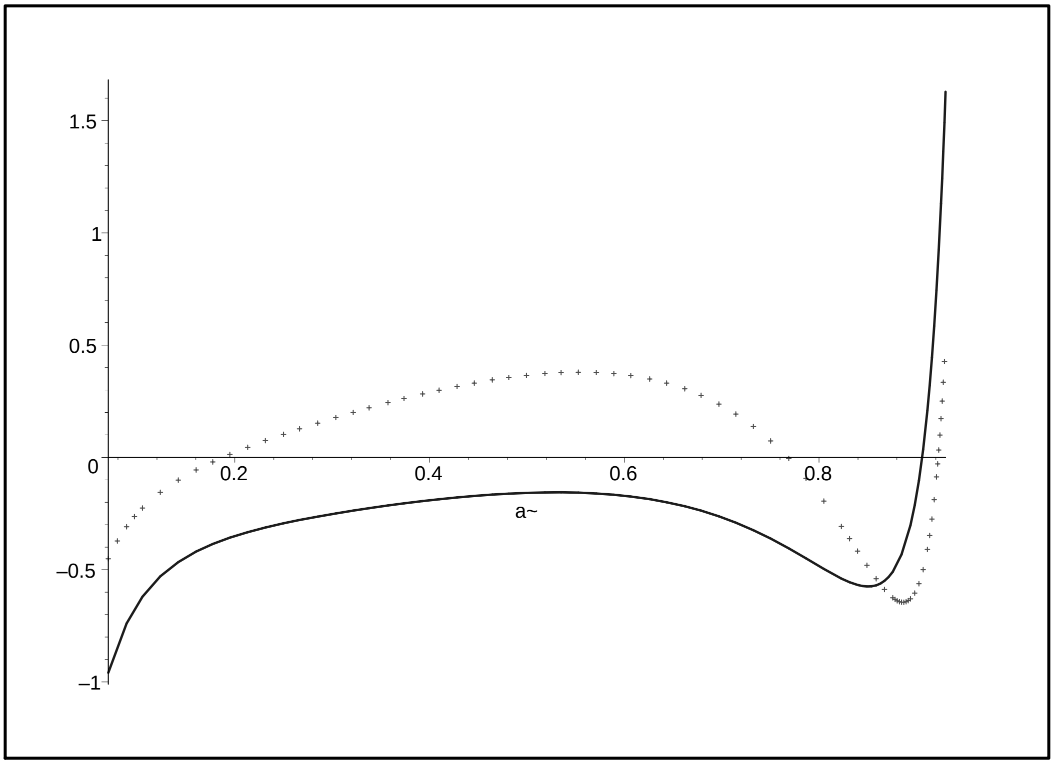

Figure 14: Dependence of corrections, i.e. of $d_a$ on $a$

A point curve shows corrections with transition from Poisson's distribution to Gauss distribution taken into account, a line shows corrections without transition from Poisson's distribution to Gauss distribution. Both corrections have one and the same order and they are small.

We see the plateau for all $a$ except $a \ll 1/4$ and $1-a \ll 1/4$. So, here the smallness of corrections due to the interactions of stochastic peaks is quite clear.

But still the small value of corrections can lead through sequential influence to essential change of the total droplets number. Conclusion about the smallness of correction in the total number of droplets can be made on the base of specific kinetic features of the process (see "the effect of the first droplet") which will be done later.

One has to note that we have not taken into account corrections from transition from summation to integration. This is definitely required by discrete character of droplets number. It is made due to reasons formulated below. Really, we have at transition from summation in formula

$$P(N) = \sum_{\hat{N}_1} P_1(\hat{N}_1, N_1) P_2(N - \hat{N}_1 - \hat{N}_2, N_2(\hat{N}_1))$$

to integration[5]

$$P(N) = \int d\hat{N}_1 P_1(\hat{N}_1, N_1) P_2(N - \hat{N}_1 - \hat{N}_2, N_2(\hat{N}_1))$$

to use the Euler-McLorrain's decomposition. It brings to asymptotic serial, which can be included into a final answer.

This is the formal solution of the problem. But discrete character in nucleation isn't so trivial. The process of vapor consumption can not begin without the first droplet. The system will wait for droplet as long as it will be necessary. It shows that discrete effects are complicate and require a separate publication. At least one has to put the initial moment at the moment of the first droplet appearance and then to consider condensation with the substance in the first droplet calculated explicitly as $\sim z^3$

This property will be called as "the effect of the first droplet". Here it leads only to the small effects, but in the situation of smooth variation of external conditions the effect can be greater.

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[5] Here $N$ is the total number of droplets, $\hat{N}_1$ is the stochastic number of droplets in the first group, $\hat{N}_2$ is the stochastic number of droplets in the second group, $N_1$ is the mean number of droplets in the first group, $N_2$ is the mean number of droplets in the first group, which is a function of $\hat{N}_1$. The value $N$ remains stochastic number.

## 4.3 Self similarity of Gaussians

To use Poisson's distribution for the first group of droplets one has to make the following notation. Really nucleation conditions for the first group don't differ from the whole group. So, for distribution for the first group one has to take distribution $P_1$ with reduced half-width. But one can not attribute a half-width to Poisson's distribution. That's why we considered effects with and without corrections from transition from Poisson's to Gauss distribution. So, we can use Gauss distributions as initial ones. For Gauss distribution one can easily reconsider the half-width. Then for $P_1$ one can take

$$P_1 \sim \exp(-(\hat{N}_1 - N_1)^2/(2bN_1))$$

where $b$ is a renormalization coefficient. Distribution $P_2$ remains previous

$$P_2 \sim \exp(-(\hat{N}_2 - N_2)^2/(2N_2))$$

where $N_2$ is given by

$$N_2 = (1 - \frac{1}{3}s + \frac{2}{9}s^2 - \frac{14}{81}s^3 + \frac{35}{243}s^4 - \frac{91}{729}s^5 - a)N$$

where $N$ is a mean total number of droplets,

$$s = \frac{\hat{N}_1 - aN}{aN}$$

is a small parameter of an order $N^{-1/2}$

After integration one comes to

$$P \sim \exp(-\frac{9a}{2(9a + b - 6ba + 9ba^2 - 9a^2)}d^2)$$

where

$$d = (\hat{N} - N)/\sqrt{N}$$

The half-width of the distribution $P_1$ must be equal to the half-width of $P$, which leads to

$$b = 9\frac{a(1-a)}{-9a^2 + 15a - 1} \qquad (5)$$

This value is drawn in fig. 15.

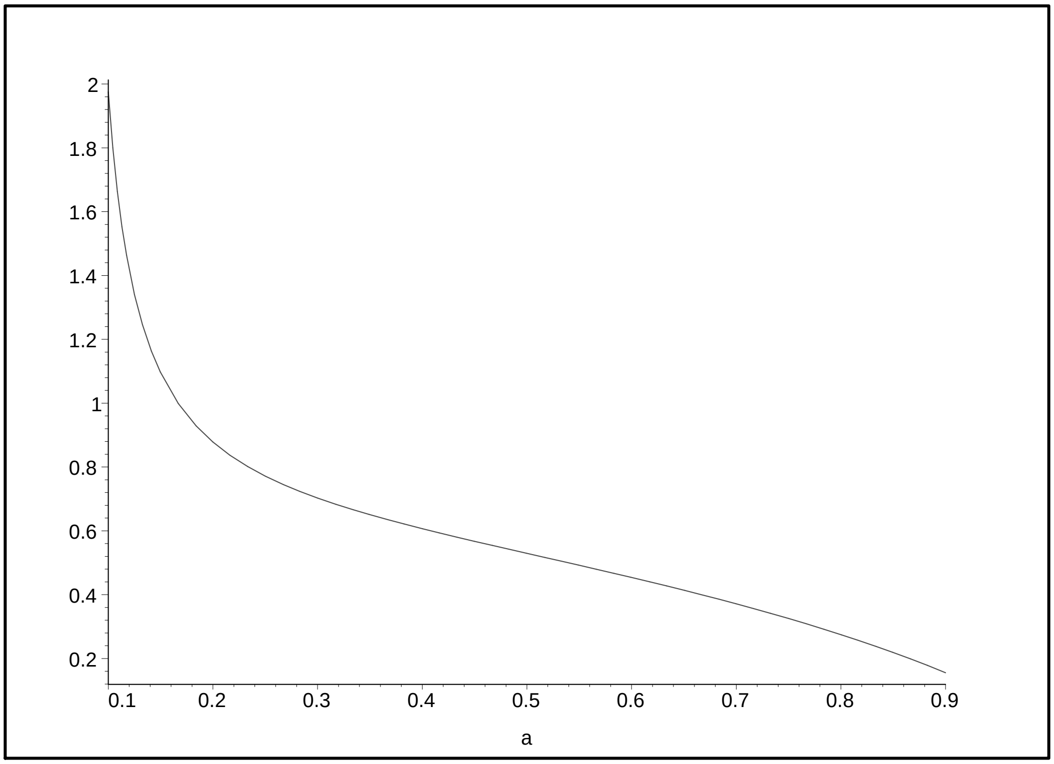

Figure 15: Function $b(a)$.

Now we shall consider effects of renormalization. The ratio of corrections with renormalization and without renormalizations is given by

$$r = \frac{1}{9} \frac{\sqrt{-9a^2 + 15a - 1}\sqrt{3a+1}}{a\sqrt{1-a}}$$

and it is shown at fig. 16

For all reasonable values of $a$ the last ratio is approximately 1. At $a = 1/4$ we get 1.0041 Here the effect of similarity of nucleation conditions doesn't lead to remarkable effects in the change of half-width. But here the smallness of change takes place only because of application of monodisperse approximation and later this change will be essential.

Instead of taking into account all moments of distribution we can directly calculate the effects on the base of explicit form of spectrum in frames of iteration procedure.

The result of the previous consideration is the following: we have proved

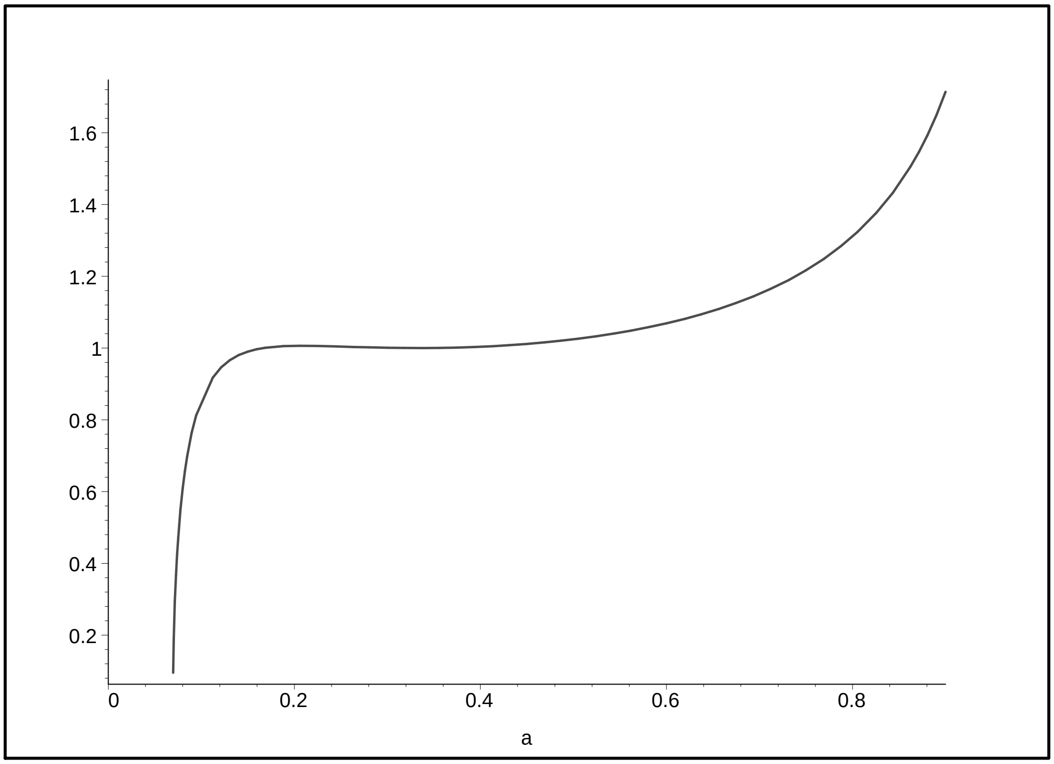

Figure 16: Ratio of halfwidths

that stochastic effects are small. Beside this we have demonstrated how to use the similarity of nucleation conditions. Here it doesn't lead to any remarkable effect, but later under the smooth external conditions this method will lead to some essential numerical corrections.

One has to stress that in [1] a linearization over deviation of the droplets number from the mean value was made. It was necessary to perform calculations. But in the linear theory one can not get the deviation of the mean value of result from the value calculated on the base of averaged characteristics. So, the attempt to get deviations in the mean value of droplets in [1] is senseless.

## 4.4 Calculation of dispersion

Since the mentioned combination of gaussians is also a gaussian characterized by a mean value and by a dispersion one has to determine these values for the distribution of the total number of droplets. As it was shown above the mean value of the droplets number is practically the same as it is prescribed by TAC and we are interested in dispersion. Now we shall calculate this value properly.

The most advanced approach to solve this problem[6] was suggested in [1]. But even this approach has many disadvantages and we need to reconsider it.

We shall characterize a droplet by a linear size $\rho$ which is the cubic root of its molecules number. Its velocity of growth at fixed supersaturation does not depend on $\rho$.

Decomposition of a whole interval of nucleation into elementary intervals is connected with some difficulties. An elementary length $\tilde{\Delta}$ according to [1] must satisfy two requirements:

1. A number of droplets formed during elementary length must be great.

2. An amplitude of a spectrum has to be approximately constant during an elementary interval.

It is clear that the second requirement can not be satisfied. Stochastic deviations of an amplitude leads to the violation of the second requirement.

We shall apply the second requirement not to the stochastic amplitude as it was stated in [1], but to the averaged amplitude. Then the second requirement is:

An averaged amplitude of a spectrum has to be approximately constant during an elementary interval.

Now we shall see the evident illegal consequences of the approach from [1]. "Stochastic" amplitudes $f_i$ are introduced in [1] as

$$f_i = \frac{N_i}{\tilde{\Delta}}$$

where $N_i$ is the number of droplets formed during $\tilde{\Delta}$. It isn't the height of spectrum but simply the renormalized value of the droplets number appeared during this interval. An expression for the number of molecules in droplets formed during interval number $i$ at a moment $t_k$ (or $z_k$) (it means that now we are at interval number $k$) with approximately constant rate of nucleation

---

[6] Certainly, already expression (5) gives the decrease of the Gaussian halfwidth and can lead directly to dispersion where $b$ is smaller than a standard one. But $b$ essentially depends on $a$. For $0.2 \leq a \leq 0.9$ one can see the approximate formula $b = 0.6 - (a - 0.5)\frac{0.7-0.2}{0.9-0.3}$ and the absence of concrete value for $a$ doesn't allow to get a concrete value for $b$.

$\bar{f}_i$ would be the following one

$$\int_{x_{k-i}}^{x_{k-i+1}} \bar{f}_i \rho^3 d\rho = \frac{1}{4} \bar{f}_i (x^4_{k-i+1} - x^4_{k-i})$$

Namely, this equation was derived in [1] and forms the base of further consideration. Here $x_{k-i}$ is the coordinate $\rho$ of the droplet which was born at $z_i$ at a moment $z_k$ (it corresponds to the definition $x = z - \rho$) The difference between forth powers corresponds to a constant amplitude of spectrum. It is wrong and then eq. (12) in [1] and all further equations are not correct.

But the is no necessity to use such a way to make an account of the number of molecules in a new phase. It is absolutely sufficient to take the following expression

$$\int_{x_{k-i}}^{x_{k-i+1}} \bar{f}_i \rho^3 d\rho = N_i x^3_{k-i} \approx N_i x^3_{k-i+1}$$

which is valid at $k - i \gg 1$. In a whole quantity of substance it is sufficient to take into account only droplets with $k - i \gg 1$. The relative weight of dismissed terms will be small.

Then for the total number of molecules in droplets at interval number $k$ we have the following expression

$$Q_k = \sum_{i=1}^{k} N_i x^3_{k-i}$$

where $x_{k-i}$ is a corresponding coordinate. This expression can be rewritten as

$$Q_k \sim \sum_{i=1}^{k} N_i \hat{\Delta}^3 (k-i)^3$$

This representation is important because now the note in [1] after eq. (15) isn't necessary. That note stated that the probability for $N_i$ to deviate from the number $\bar{N}_i$ of droplets calculated in TAC under the supersaturation formed by stochastically appeared droplets in previous intervals is very low. That note is doubtful because namely these deviations are the base for stochastic effects. Now there is no need in this note.

The next step is to build [1] a two cycle construction for nucleation period. During the first cycle the main consumers of vapor appeared in a system and during the second cycle they govern a process of formation of all other droplets. In [1] it is supposed that during the first cycle a vapor depletion is negligible and during the second cycle new droplets are absolutely governed by droplets from the first cycle. Now we shall analyze an effectiveness of such procedure.

In TAC the corresponding evolution equation will be

$$\psi(z) = \int_0^z (z-x)^3 \exp(-\psi(x))dx$$

The first iteration [3] is practically a precise solution and it gives the number of droplets

$$N_{tot} = \frac{1}{4}\frac{4^{1/4}\pi\sqrt{2}}{\Gamma(3/4)} = 1.2818$$

A model solution requires that until $z = p$ there will be no depletion of vapor and then only the droplets formed before $z = p$ will consume vapor. Then for a total number of droplets we have an expression

$$N_{tot\ appr} = p + \int_p^\infty \exp(-\frac{1}{4}x^4 + \frac{1}{4}(x-p)^4)dx$$

A ratio $q = N_{tot\ appr}/N_{tot}$ is given in fig. 17

Always $N_{tot\ appr}$ is greater than $N_{tot}$. The value of minimum corresponds to $p \sim 0.78$ which is 55 percent of the total length of spectrum. We can stress the smooth dependence $N_{tot\ appr}$ on $p$.

It is clear that in [1] the value of parameter of separation into two cycles was not chosen in a good style (at least from the point of view of TAC). It corresponds to $p = 0.64$.

Now we shall study the probability $P_k$ of formation of stochastic number $N_k$ of droplets at the first $k$ elementary intervals. Our constructions now resemble [1] but there is one essential difference. We have no necessity to linearize expression with respect to $(N_i - \bar{N}_i)/\bar{N}_i$, where $N_i$ is a stochastic number of droplets formed at interval $i$, $\bar{N}_i$ is a mean number of droplets formed at interval $i$ (it is a function of stochastic numbers of droplets at preceding intervals). This linearization can not take place because a ratio $(N_i - \bar{N}_i)/\bar{N}_i$ can be zero or can attain huge value (with a low probability). It is more simple and more justified to linearize expression on $\sum_i \rho_i^3 (N_i - \bar{N}_i)/\bar{N}_i$ where $\rho_i$ is a linear size of droplets formed at interval $i$ (all of them have approximately the same size). Really, due to summation the relative variations of $\sum_i \rho_i^3 (N_i - \bar{N}_i)/\bar{N}_i$ are much smaller than variations of $(N_i - \bar{N}_i)/\bar{N}_i$.

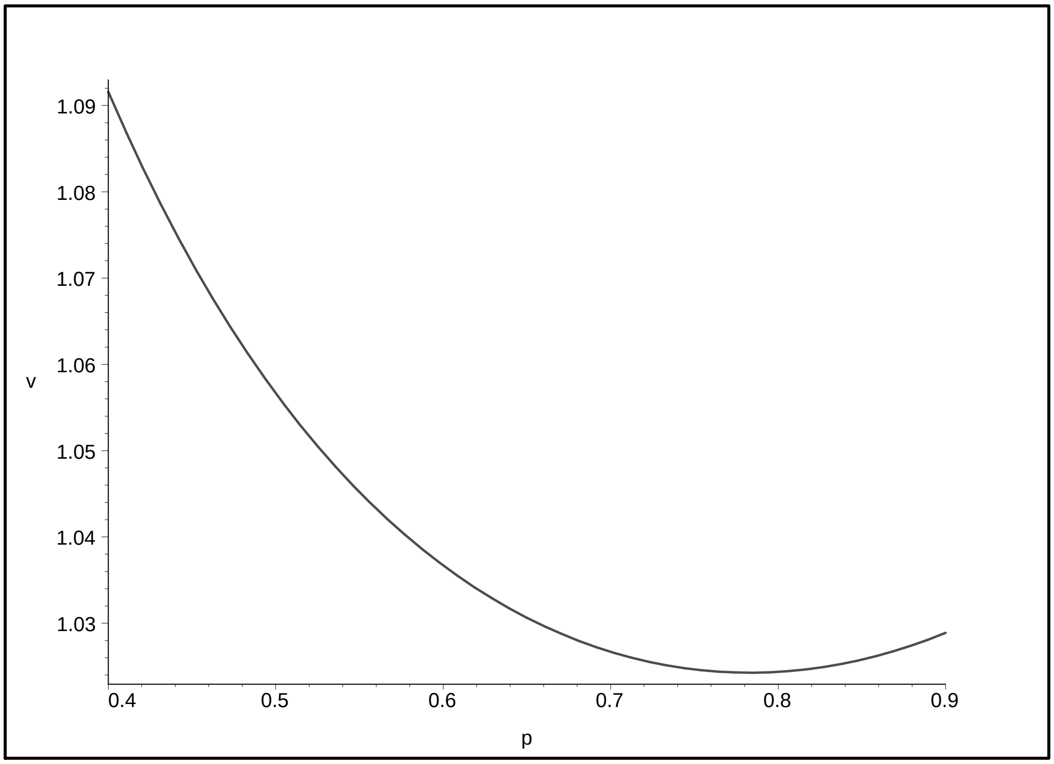

Figure 17: The ratio of mean numbers of droplets

Variations of $(N_i - \bar{N_i})/\bar{N_i}$ would be small only at very big numbers of droplets $N_{tot}$. One can get

$$(N_i - \bar{N_i})/\bar{N_i} \sim \bar{N_i}^{-1/2}$$

$$N_{tot} \sim M\bar{N_i}$$

$M$ is a number of elementary intervals. So, the theory with linearization proposed in [1] would be well justified only in a region where the result can be obtained on the base of averaged characteristics. The internal contradiction between the big number $M$ and the smallness of fluctuations in the elementary interval in [1] is obvious.

The linearization proposed here is much more weak than in [1]. But it leads to the analogous numerical expressions as in [1]. So, restrictions from [1] are not necessary.

For dispersion of the total distribution the result proposed in [1] was the following

$$D^{\infty} = \tilde{N^{\infty}}(1-\frac{\beta}{\alpha})$$

where

$$\beta = \beta_1 - \beta_2$$

$$\beta_1 = 8\int_{1/2}^{\infty} d\xi \int_0^{1/2} d\tau (\xi-\tau)^3 \exp(-\xi^4)$$

$$\beta_2 = 16\int_{1/2}^{\infty} d\xi \int_{1/2}^{\infty} d\eta \int_0^{1/2} d\tau (\tau-\xi)^3(\tau-\eta)^3 \exp(-\xi^4)\exp(-\eta^4)$$

$$\alpha = \int_0^{\infty} dx \exp(-x^4)$$

In the two-cycles construction the value of $\alpha$, which is proportional to the total number of droplets has to be reconsidered and recalculated on the base of two cycles. Then we have to use instead of previous $\alpha \equiv \alpha_0$ a new value

$$\alpha = \alpha_1 \equiv 1/2 + \int_{1/2}^{\infty} \exp(-x^4 + (x-1/2)^4)dx$$

In our approach we shall use parameter $k$ of separation[7] of two cycles and we shall calculate $\alpha_1$ as

$$\alpha_1 \equiv k + \int_{k}^{\infty} \exp(-x^4 + (x-k)^4)dx$$

Then according to fig. 17 we see that the ratio $\alpha_0/\alpha_1$ is greater than 1 and $\alpha_1$ is greater than $\alpha_0$. Here we see that two-cycles construction is approximate one. Then result for $D^{\infty}$ will differ from the number published in [1] and will be (here one has to put $k = 1/2$)

$$D_e^{\infty} = \tilde{N^{\infty}} 0.69$$

instead of

$$D_f^{\infty} = \tilde{N^{\infty}} 0.67$$

as it is written in [1].

Numerical simulations show that the value $D_e^{\infty}$ is one tenth more than a real result. So, the new theory is necessary.

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[7] Here for simplicity we use $k$ instead of $p/4^{1/4}$.

Now it is necessary to decide what $k$ shall we choose. At arbitrary $k$ the expression for $\beta$ will be the same but for $\beta_1$ $\beta_2$ we have

$$\beta_1 = 8 \int_k^\infty d\xi \int_0^k d\tau (\xi - \tau)^3 \exp(-\xi^4)$$

$$\beta_2 = 16 \int_k^\infty d\xi \int_k^\infty d\eta \int_0^k d\tau (\tau - \xi)^3 (\tau - \eta)^3 \exp(-\xi^4) \exp(-\eta^4)$$

We have also to reconsider expression for $\alpha$.

After calculations we have for dispersion as function of $k$ the following fig. 18

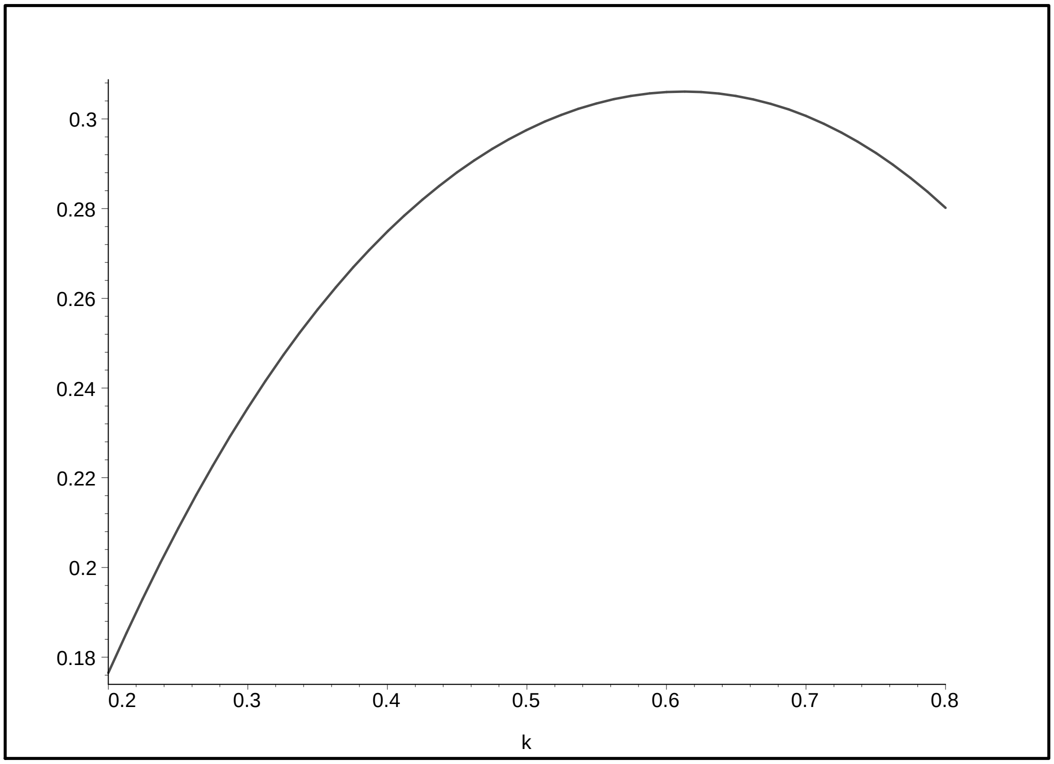

Figure 18: Relative deviation in dispersion as function of $k$

A minimal dispersion will be at $k = 0.6$. This value approximately equals to $k = 0.55$ which ensures minimum of $\alpha_1$ where the result is the most close to the real value in the number of droplets. One can also add that this is the true value of $k$ because namely this value corresponds to the sense of minimal work when we have the low dispersion. It corresponds to a minimal (in a certain sense) entropy and later we can get additional work from increase of entropy.

Dispersion at $k = 0.6$ will be

$$D^{\infty} = 2\tilde{N^{\infty}}0.66$$

Now we shall calculate the value of dispersion more accurate. Due to the similarity of nucleation the first cycle doesn't differ from the whole period. Function $\beta$ for the first cycle will be

$$\beta = \beta_1 - \beta_2$$

$$\beta_1 = 8 \int_{k_1}^{k} d\xi \int_{0}^{k_1} d\tau (\xi - \tau)^3 \exp(-\xi^4)$$

$$\beta_2 = 16 \int_{k_1}^{k} d\xi \int_{k_1}^{k} d\eta \int_{0}^{k_1} d\tau (\tau - \xi)^3 (\tau - \eta)^3 \exp(-\xi^4) \exp(-\eta^4)$$

Calculations for $k_1 = 0.6 * 0.6 = 0.36$ and $k = 0.6$ give $\beta = \beta' \equiv 0.0255$.

In the most rough approximation one has to add $\beta' = 0.0255$ to the previous value of $\beta = 0.305$ which leads to $\beta = 0.32 \div 0.33$. The smallness of $\beta'$ in comparison with $\beta$ allows to use this linear approximation. For this value of $\beta$ the value of dispersion will be

$$D^{\infty} = D_3^{\infty} \equiv 2\tilde{N^{\infty}}0.64$$

It is interesting that this result can be gotten by another (rather artificial) procedure:

We suppose that $\beta_1$ and $\beta_2$ are the first two terms of some series. We don't know other terms, but it is reasonable to suppose that the series resembles geometric progression with denominator $\beta_2/\beta_1$. This leads to dispersion

$$D^{\infty} = 2\tilde{N^{\infty}}0.64107$$

As it follows from fig.19 the value of extremum remains $k = 0.6$.

The absence of the shift of extremum is important and is necessary for this approach to be a self consistent.

Now we shall see whether some other approaches can lead to essential reconsideration of result for dispersion.

A way to make results more precise is take into account the shift of dispersion directly in initial formulas. Having written for the dispersion correction in the first cycle

$$D_3^{\infty} = 2\tilde{N^{\infty}}\gamma$$

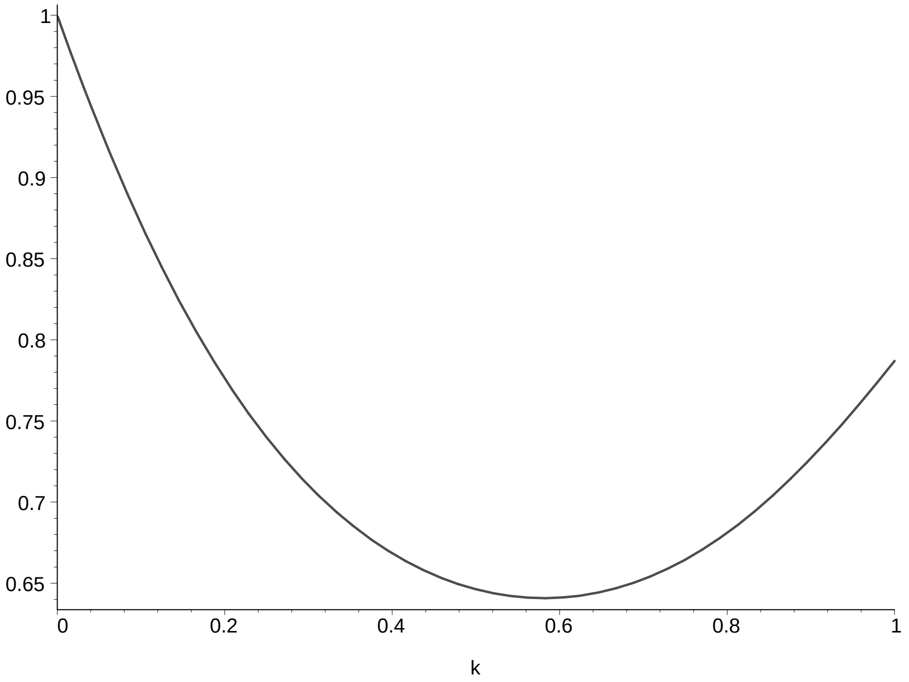

Figure 19: Dispersion.

with parameter $\gamma$, we get for the final distribution

$$P^{(k)} \sim \int_{-\infty}^{\infty} dN_1 dN_2 ... dN_P \prod_{i=1}^{P} \exp(-\frac{(N_i - \bar{N}_1)^2}{2\gamma \bar{N}_1})$$

$$\exp[\frac{[N^{(k)} - \tilde{N^{(k)}} - \sum_{j=1}^{P} a_j^{(k)} (N_j - \bar{N}_1)]^2}{2(\tilde{N^{(k)}} - P\bar{N}_1)}]$$

where $P$ is the number of elementary intervals until the argument $k$, $\tilde{N^{(k)}}$ is the number of droplets calculated on the base of the theory with averaged characteristics, $\bar{N}_i$ the mean number of droplets formed during interval number $i$ with account of fluctuations from previous intervals. The values $a_i^{(k)}$ are given by

$$a_i^{(k)} = 1 - \sum_{j=P+1}^{k} \frac{\exp(-j^4/M^4)}{M^4} 4(j-i)^3$$

and $M$ is the total number of intervals.

Having fulfilled integration $\int_{-\infty}^{\infty} dN_1 dN_2 ... dN_P$, we get for a limit value of dispersion

$$D^{\infty} = 2\tilde{N^{\infty}}(1 - \frac{k(1-\gamma)}{\alpha} - \frac{\gamma\beta}{\alpha})$$

The approximate similarity of spectrums leads to equation on $\gamma$, which can be easily solved

$$\gamma = \frac{1 - \frac{k}{\alpha}}{1 + \frac{\beta}{\alpha} - \frac{k}{\alpha}}$$

Calculations lead to

$$\gamma(k = 0.6) = 0.51$$

This result is very strange. It radically differs from the previous one. Certainly we made an error. The reason of the error in previous approach is that the duration of the first cycle is limited by $k$. So, we have to limit the duration of a whole period. The limit of the whole nucleation is, evidently, $\sim 1$.

The limit of integration corresponds to the current moment of time. It can not be greater than 1. So, we have to take it equal to 1. Then we have to recalculate $\beta$ as

$$\beta_{initial} = \beta_1 - \beta_2$$

$$\beta_1 = 8 \int_k^1 d\xi \int_0^k d\tau (\xi - \tau)^3 \exp(-\xi^4)$$

$$\beta_2 = 16 \int_k^1 d\xi \int_k^1 d\eta \int_0^k d\tau (\tau - \xi)^3 (\tau - \eta)^3 \exp(-\xi^4) \exp(-\eta^4)$$

To calculate the value of dispersion we can act in two manners. The first way is to calculate dispersion at the point of extremum of $\beta$. Now we shall show a dependence $\beta_{initial}$ on $k$ at fig. 20.

Calculations give $\beta_{initial} = 0.18$ and for the final dispersion

$$D_3^{\infty} = 2\tilde{N^{\infty}} 0.65$$

This value practically coincides with a previous approach.

It is necessary to stress that one can not directly use extremal properties of $\gamma$ to get $p$ which provides $\beta$ extremum. In reality the final characteristic is $\gamma$, but the calculations show that $\gamma$ has no extremum. Certainly, this is the weak point of approach based on extremal properties.

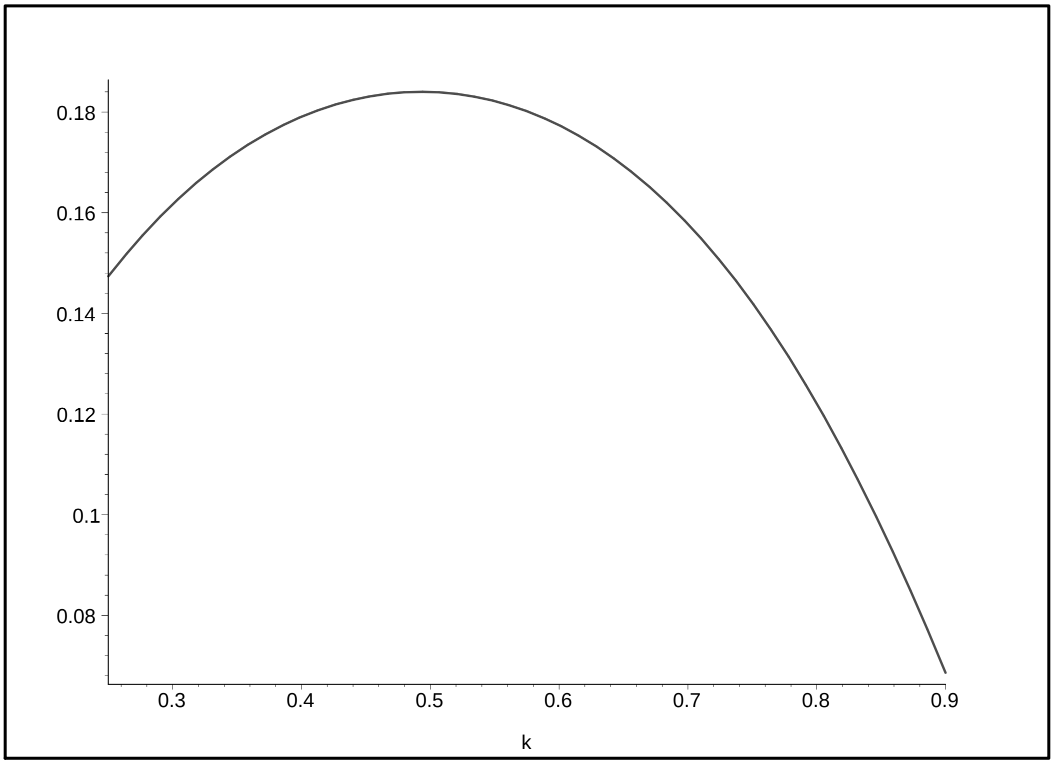

Figure 20: $\beta_{initial}$ as a function of $k$

Another way is to use $k$ which provides the most precise value for the total number of droplets in this model. Having compared the mean total number of droplets in TAC calculated in this model one can see that this number has minimum 0.927 which is greater than the precise value and the value 0.90 given in the first iteration. This extremum is attained at $k = 0.55$. Namely this value will be chosen as $k$ and this leads to

$$D_4^{\infty} = 0.62$$

which lies in frames of precision of numerical simulation.

One can add that there is no need to use $k$ corresponding to extremum of the number of droplets calculated up to 1 instead of $\infty$. Then the minimum is 0.852 and it is attained at $k = 0.45$. Actually there is no reasons to take this value because here the value of minimum is strongly less than the precise value and it corresponds to the maximum of deviation from the precise value. So, there are no reasons to take this value.

One has to stress that the procedure adopted here is really necessary. The two-period model with a fixed boundary in time scale used in [1] can not be the base of the correct calculation of dispersion. The reasons are the following

- The behavior of supersaturation here is the model behavior (MB) with parameters, which characterize the influence of the first part of spectrum. In investigation of stochastic effects the fluctuations of these parameters are the source of fluctuations of the total number of droplets. The fuctional form of MB is chosen to ensure the correct number of droplets in frames of TAC. The change of parameters in MB leads to the imaginary change of external conditions in TAC which corresponds to the MB with given parameters.

- The change of external parameters in TAC has to lead to the change of the boundary between parts. But this can not be done in the model with a fixed boundary.

In our approach the summation of geometric progression and all other approaches ensure the possibility to overcome the restrictions of the two parts approach with a fixed boundary. The summation of geometric progression describes the equivalence of all points which is prescribed by the property of similarity of spectrums.

The relative smallness of numerical errors in [1] is caused by the following reasons

- The moderate possibility of linearization (the non-linearity isn't too big) in kinetics of decay

- The weak dependence $N_{tot}$ on $p$ in frames of TAC

- The weak dependence of $N_{tot}$ on $N(p)$ in frames of TAC

- The effects of stabilization are very strong. Really, instead of addition 0.5 the benefit of the second part to dispersion is only $0.64 - 0.5 = 0.14$ (or even less if we use $p \sim 0.55$ instead of $p \sim 0.5$)

- The existence of the special buffer part of nucleation period which will be described later

## 4.5 Numerical results

Numerical simulation of nucleation can be done by the following method. We split the nucleation interval into many parts (steps). At every step a droplet will be formed or not. The probability to appear must be rather low, then we ensure the smallness of probability to have two droplets at the same interval. This means that the interval is "elementary".

The process of formation is simulated by a random generator in a range $[0,1]$. If a generated number is smaller than a threshold parameter $u$, then there will be no formation of a droplet. If it is greater than a threshold, we shall form a droplet. As a result we have spectrum $\hat{f}$ of droplets sizes. Now it is a chain of 0 and 1. The parameter $u$ descends according to macroscopic law [3]

$$u = u_0 \exp(-\Gamma G/\Phi)$$

from a theory with averaged characteristics (it is based only on a conservation law without any averaging and can be used). Here

$$\Gamma \sim \frac{dF_c}{d\Phi} \sim \nu_c \tag{6}$$

$\Phi$ is the initial supersaturation, $F_c$ is a free energy of critical embryos formation, $\nu_c$ is a number of molecules inside a critical embryo, $G$ is the number of molecules in a new phase taken in units of a molecules number density in a saturated vapor. By renormalization one can take away all parameters except $G$.

To simplify calculations radically one can use the following representation [3] for $G$:

$$G = z^3 G_0 - 3z^2 G_1 + 3z G_2 - G_3$$

where $z$ is a coordinate of a front of spectrum, and $G_i$ are given by

$$G_i = \int_0^z \hat{f}(x) x^i dx$$

We needn't to recalculate $G_i$, but can only ascend the region of integration, having added to integrals the functions $z^i \hat{f}(z) dx$ at every step.

Our results are given below. The interval is split into 30000 parts. Parameter $u_0$ have been varied from 0 up to 1 which leads to a different number of droplets. It is clear that the limit values are not good: at 0 there are no droplets in the system, at 1 our intervals are not elementary. At every $u_0$ results were averaged over 1000 attempts.

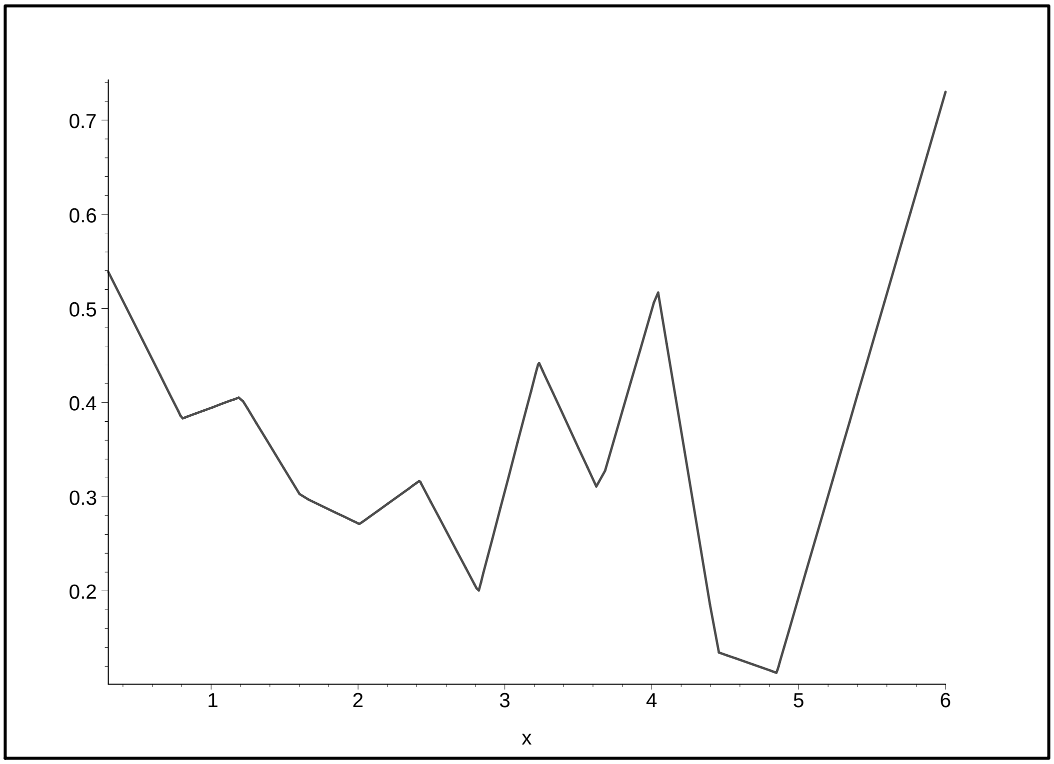

Figure 21: Shifts of droplets numbers as a function of $\ln N^{\tilde{(\infty)}}$

Shifts of droplets numbers are drawn at fig.21 as a function of $\ln N^{\tilde{(\infty)}}$

It is seen that an analytical result about negligible value of corrections is correct.

Dispersion as a function of $\ln N^{\tilde{(\infty)}}$ is shown in fig. 22.

It is seen that the analytical value of dispersion coincides with numerical simulation. The ends of the curve correspond to a zero number of droplets and to a giant number of droplets when the elementary intervals are not elementary and have to be thrown out.

Stochastic effects in dynamic conditions [3] can be analyzed by the same method. We needn't to describe it here. Numerical results are drawn below. Fig. 23 shows the shift in the number of droplets. It is small. Dispersion is drawn in fig. 24 (i.e. the value of $\gamma$). It is greater than in the case of decay.

The physical reasons for the smallness of the droplet number shift for decay and for dynamic conditions will be different.

For decay the reason is the following. The system wait the first droplet

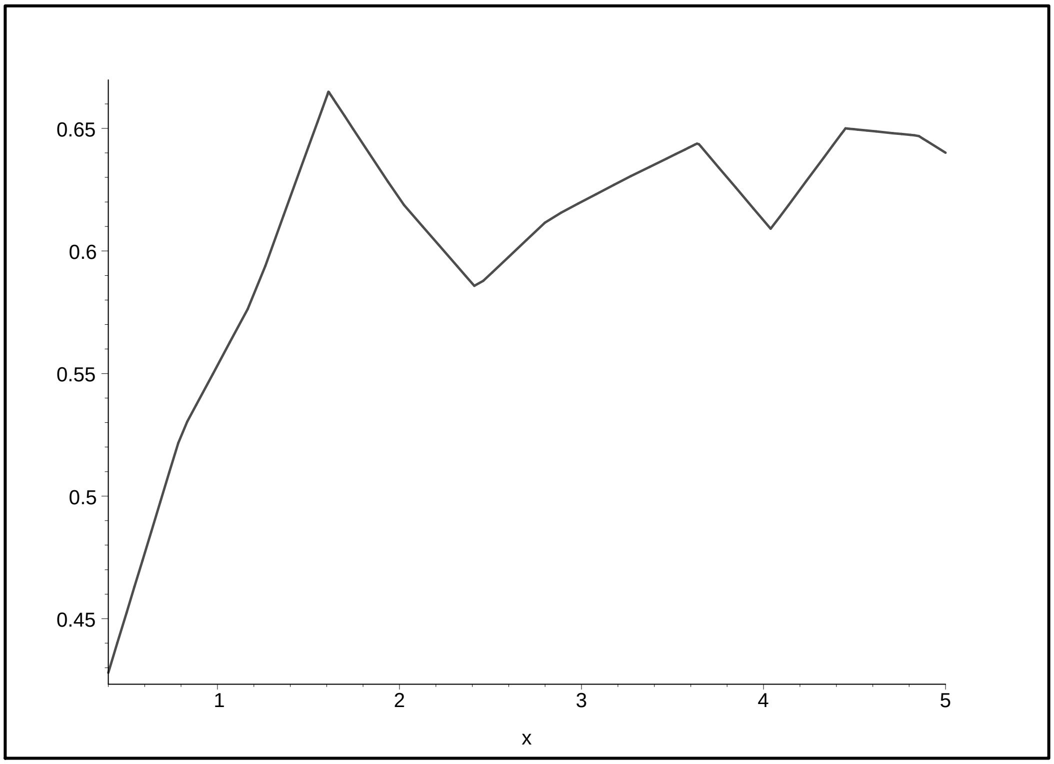

Figure 22: Relative dispersion $\gamma$ as a function of $\ln N^{\tilde{(\infty)}}$

as long as necessary. Actually the time for kinetics of this system is $t(G)$ with no connection with real time (certainly, the rate of nucleation has such connection). This phenomena is the reason for a smallness.

In dynamic conditions there is a time dependent parameter - the intensity of external source. So, there is no such a reason.

But here in the theory with averaged characteristics there is a property of a weak dependence of the total number of droplets on microscopic corrections for a free energy [3]. The same is valid also for fluctuation deviations. So there will be a weak effect of stochastic nucleation.

Because the reasons for smallness of effect in decay and dynamic conditions are different it is interesting to see whether they continue to act when the supersaturation is stabilized at some moment. Analytical results shows that the will be an overlapping of two reasons.

Really, if stabilization takes place at the period where the main consumers of vapor are going to appear then the majority of droplets appear in the

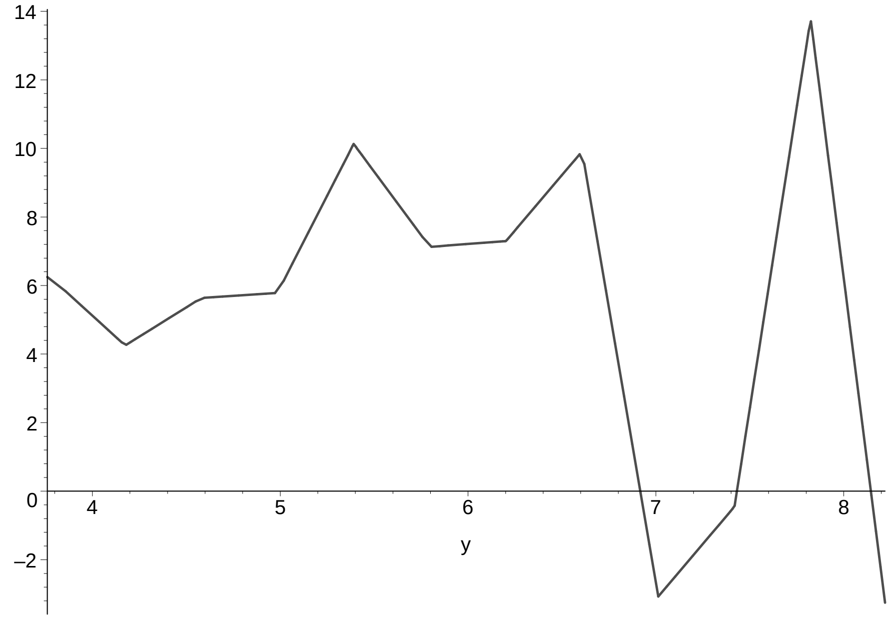

Figure 23: Shift in a droplets number as a function of $\ln \tilde{N^{(\infty)}}$ for dynamic conditions

situation when there is no influence on the system. Then the situation for these droplets resembles decay conditions (and may be even better because the external supersaturation [12] is going to decrease). So the reason for the decay situation works here.

If stabilization takes place at the second cycle, then the behavior of supersaturation is governed by droplets formed in dynamic conditions and we have here the reason for smallness in dynamic conditions. In both situations the effect is small. Numerical results confirm this conclusion.

## 4.6 Conclusions

The main result of this publication is a correct definition of all main characteristics of stochastic nucleation. It is shown that the main role in stochastic effects belongs to all droplets, but not to the main consumers of vapor. Only

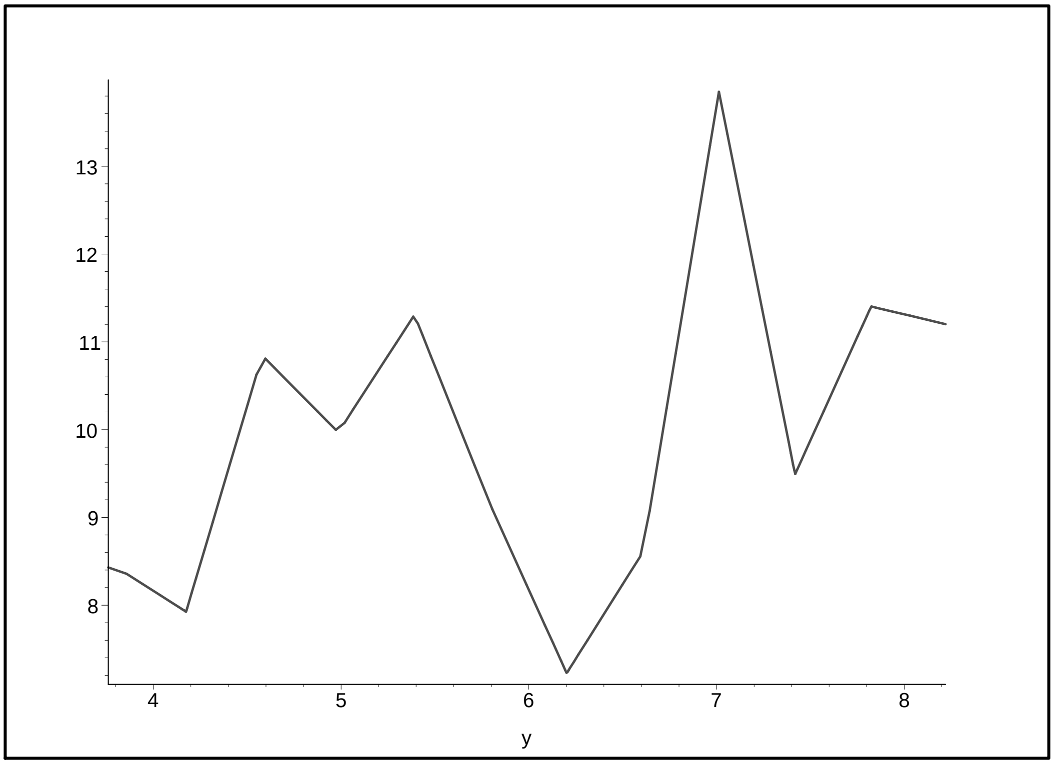

Figure 24: Relative dispersion $\gamma$ as a function of $\ln N^{\widetilde{(\infty)}}$ for dynamic conditions

the property of the nucleation conditions similarity allows us to solve the problem of account of all influences during the nucleation period.

When all disadvantages of [1], [10] are shown it is clear that these publications can not be considered as a solid base for nucleation investigation.

But why results obtained in [1], [10] are so close numerically to real values? The reason is that on a level of averaged characteristics there is a universality of nucleation process. So, the errors of [1], [10] cannot lead to a qualitatively wrong results.

One has to stress that all corrections obtained in this paper are also universal ones. Certainly, they are some coefficients in decompositions and the functional form of decomposition is prescribed now.

There is also a second specific reason for the smallness of an error in numerical values presented in [1]. The reason is the following

- The process of nucleation can be split in three sequential parts.

- The first part is the part where the main consumers of vapor were appeared. Here the vapor depletion is small
- The second (buffer) part is the part where conditions are ideal, the vapor depletion is small, but the droplets formed in this part can not attain big sizes even at the end of the whole nucleation period and, thus, can not consume enough vapor and they are not the main consumers of vapor
- The third part is the part where the depletion isn't small and droplets appeared in this part aren't the main consumers of vapor in the nucleation period.
- All parts have the lengths of one and the same scale.

Certainly this structure was not declared in [1] which made the derivation in [1] illegal.

The existence of the buffer part is necessary to balance the errors appeared from the fact that the fluctuations leads to to the absence of applicability of functional approximations for the nucleation kinetics. More correctly is to use the property of the "internal time of decay" which will be done separately.

It seems that all effects considered here are negligible. For simple systems it is really true. But for systems with more complex kinetic behavior these effects can be giant. One of such systems is already described theoretically and this description will be presented soon in a separate publication.

To compare results given here with the previous approach one can simply recall that the real error is the error in the relative deviation of dispersion from the standard value. In [1] this error is more than one quarter. Here the error is practically absent.

In diffusion regime of droplets growth one has to use another approach based on [4], [14]. In [14] an explicit description of nucleation with account of stochastic effects was constructed.

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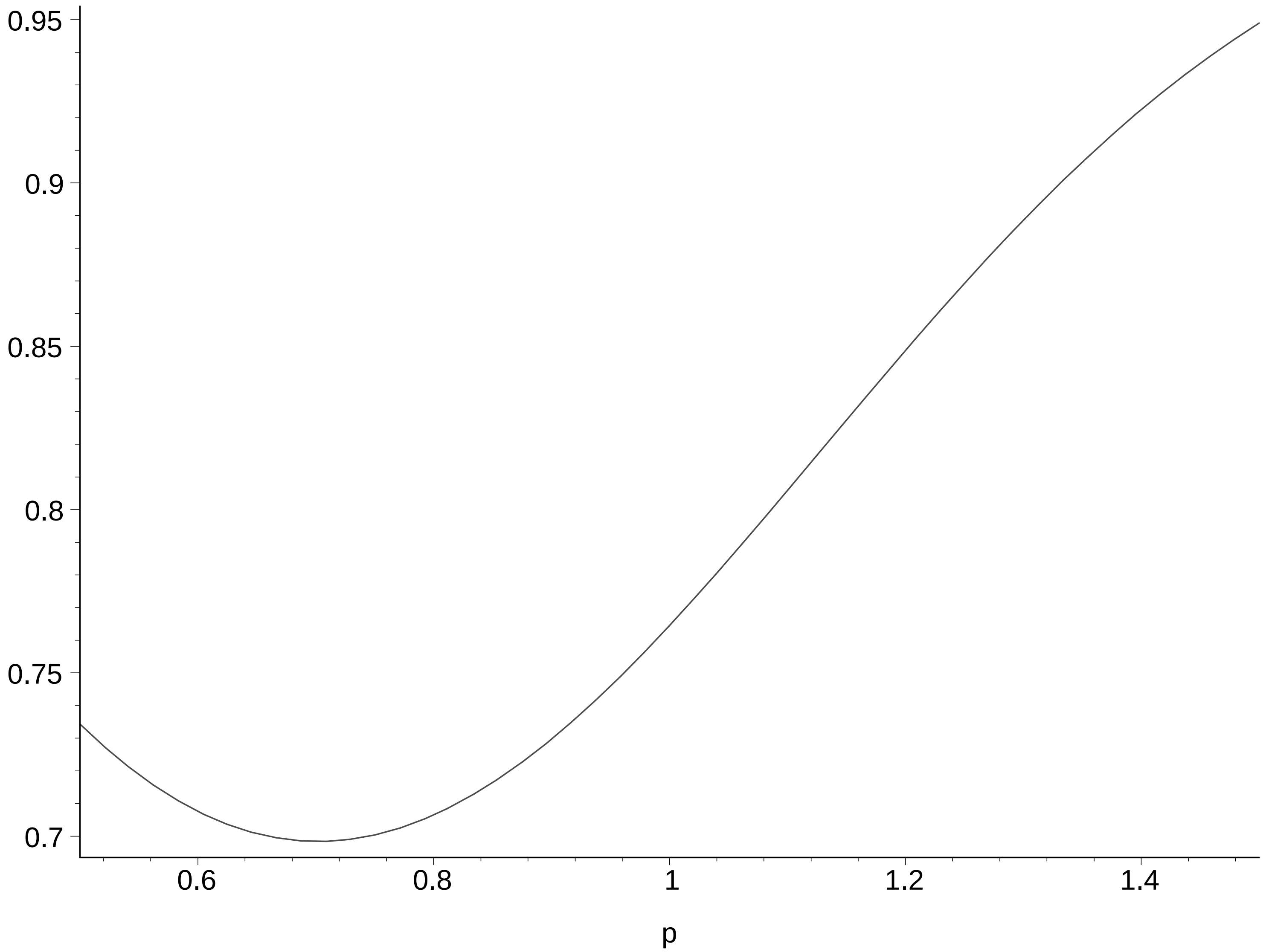
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# Late periods of the condensation process

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**Abstract**

The full evolution during the late periods of the condensation process is described in the analytical form. The process is split into several periods and for every period the simple approximate solution is given.

## 1 Introduction

The first order phase transition is characterized by the temporal duration - the process of the condensation lasts in time and consists of several characteristic periods. The kinetics of the first order phase transition is one of the actual problems in the phase transformations.

Ordinary it is supposed that the final stage (period) of the phase transition is the stage of coalescence. This name goes from the theory given by Lifshic and Slezov [1]. This terminology is not absolutely correct - formally the coalescence means the adhesion of the embryos. But the Lifshic-Slezov (LS) consideration does not take into account the adhesion, the evolution in the LS picture is the competition between the embryos through the exhaustion of the vapor environment. One has to clarify this difference. In the case of adhesion we shall speak about the coagulation and when the Lifshic-Slezov mechanism takes place we shall speak about the over-condensation.

The over-condensation means the competition between the already formed embryos when the embryos of the relatively big sizes eat the embryos of the relatively small sizes not directly but through the exhaustion of the

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metastable old phase until such a degree that the mentioned small embryos become the pre-critical ones and begin to eject the molecules in the vapor. These embryos begin, thus, to disappear.

Beside this opportunity it is possible to see in the open systems the situation when all embryos continue to grow until all volume of the system will be transformed into a new phase. Certainly this situation takes place when there is an effective source of the substance in the old phase. This is also an alternative possibility for the final of the phase transition. So, we see that the final stages of the phase transformation can be very different.

Here we shall speak about the over-condensation and consider the closed system. The effect of coagulation is not taken here into account. The temperature of the system is supposed to be fixed. The mentioned restrictions are not the crucial ones.

The methodology of analysis of such systems is given by Lifshic and Slezov in [1]. Strictly speaking the results of Lifshic and Slezov can not be directly applied for the systems with the diffusion regime of the substance exchange (as it was done in [1]) because in this case around every embryo there will be a profile of the metastable (old) phase substance. The profiles around different embryos overlap. This changes the rates of growth. Then one has to consider an interaction between the density profiles. So, one can not directly take the integral form of the balance equation as it is done in the theory of Lifshic-Slezov. The last task to describe the interaction of profiles is extremely difficult and the precise analytical solution of this problem is hardly possible.

The ignorance of the diffusion profiles leads to the necessity to consider the situation with the free molecular regime of interaction when there is no profiles. This was done by Wagner [2] and we shall follow this regime of the substance exchange below.

The fundamental fact is that the LS asymptotics was confirmed experimentally (see [3], [4], [5]). Here one has to stress that according to the notation made in [6] the accuracy is not very high - one can speak only about the qualitative confirmation of the form of the spectrum and about the precise confirmation of the power-like law of evolution of parameters of the spectrum (in some sense the power-like law is rather evident and it can be derived from some simple qualitative remarks). Also it is necessary to stress that according to the references from [6] the form of the size spectrum is more sharp than it follows from the leading term of the LS theory.

The next step in modification of the LS approach was done by Osipov and

Kukushkin in [6] where the "regular asymptotic" was constructed. Since the first two terms in asymptotic decomposition in the LS theory are universal (independent from the initial size spectrum) it is possible to introduce such variables (coordinates) where already the initial approximation is equivalent to the first two terms of the LS decomposition. So, the modification of Osipov and Kukushkin seems to be natural. But this modification is important because it allows to speak on the level of the regular asymptotics already from the very beginning.

The LS asymptotics has an amazing feature - it allows to establish the universal form of the size spectrum. One can admit that the power of metastability has some universal asymptotics, but one can hardly believe that the spectrum of the embryos sizes is universal. This will be the matter of discussion is this paper. Below it will be shown how the real spectrum of sizes approaches the form given by LS theory.

## 2 Some remarks initiated by technique of Lifshic and Slezov

Now we shall consider the simplest model leading to the over-condensation. At first we shall consider the embryos with linear sizes which strongly exceed the critical size. We shall call them as the supercritical embryos. The growth of the supercritical embryo in time $t$ is given by the following equation

$$\frac{d\rho}{dt} = \frac{\zeta}{t_1}$$

Here $\rho$ is the cubic root of the number of molecules inside the embryo (it plays the role of the linear size), $\zeta$ is the supersaturation of the metastable phase, $t_1$ is some characteristic time (this is simply the constant coefficient). The supersaturation is defined as the ratio of the surplus density of the metastable phase (with respect to the saturated phase) to the density of the saturated phase or the ratio of the real density of metastable phase to the density of the saturated phase minus one.

The simplest asymptotic correction to the asymptotic law of growth will be the following

$$\frac{d\rho}{dt} = \frac{\zeta}{t_1}(1 - u^{-1})$$

Here

$$u = \frac{\rho}{\rho_c}$$

is the ratio of $\rho$ to the critical size $\rho_c$ to have the zero rate of growth for the critical embryo. It is quite possible that this ratio has been changed by an analogous ratio in some power but this does not lead to the essential reconsideration of this approach.

One can give the interpretation of the last correction term as the leading term in the asymptotic expansion in inverse powers of the linear size. It is possible that this decomposition starts from the non-integer power as it takes place in construction of series for solutions of the linear second order differential equations. It is also possible that the law of growth for the supercritical embryos has some power of the linear size which grows with a constant velocity. Namely this situation takes place in the diffusion regime of the metastable phase exchange. In both cases the technique described below can be applied.

So, since one can see that

$$\frac{(d\rho/dt)}{(d\rho/dt)_{asymp}} = (1 - 1/u)$$

or there is some function of $u$ in the rhs it is convenient to consider $du/dt$ instead of $d\rho/dt$. For the derivative $du/dt$ we get an additional term

$$\frac{d\rho}{dt} = \rho_c \frac{du}{dt} + u\frac{d\rho_c}{dt}$$

which is linear on $u$. So,

$$\frac{du}{dt} = \frac{\zeta}{t_1}(1 - u^{-1}) - u\frac{d\rho_c}{dt}$$

In the LS theory there exists a hidden supposition that $\rho_c$ depends on time droningly. This supposition was reexamined in approach which predicts the periodic formation of the tail of the size spectrum and then the consumption of this tail. But nevertheless this supposition is rather natural at least at the asymptotics. If we adopt this supposition then all values depending on time are the values depending on the critical size. At least one can consider the intervals of the monotonous dependence.

The generalization of this law on other regimes of growth leads to

$$\frac{du}{dt} = \phi_1(t)u^{\alpha}(1 - u^{-1}) - u\phi_2(t)$$

The functions $\phi_1$, $\phi_2$ are the functions of time. The function $\phi_1$ can be excluded by transition to the rescaled time $\tau$. The same can be done with $u^{\alpha}$.

The right hand side of the last equation (let it be $\Gamma$) can not attain asymptotically the positive value at some argument - then the substance balance will be violated. The balance equation will be violated also when the rhs is negative at all values of argument $u$. Hence, the unique possibility is to touch the zero level at the main maximum. Then it is necessary that the rhs as a function of $u$ has a maximum and then by the correct choice of $\varphi$ one can put the maximum to the zero level. The class of functional dependencies which allow this operation forms the class of dependencies where the LS technique can be applied at least formally. The fine unjustified supposition here is the monotonous approach (in time) of the maximum to the zero level. It is quite possible that this maximum oscillates near zero - at some moments is it greater than zero, at some times it is less than zero. This possibility is considered in [8]. Here we do not consider the oscillating scenarios.

For the function $\varphi$ we get

$$\varphi = \gamma_0$$

where $\gamma_0$ is some constant. Even when this supposition is adopted the velocity at the maximum is zero and the balance equation is violated. Then it is necessary to be:

$$\varphi = \gamma_0(1 + \varepsilon^2(\tau))$$

with $\varepsilon \to 0$ at $\tau \to \infty$.

The reason that $\gamma_0$ is a constant lies in the form of equation for $du/d\tau$. It would be interesting to consider equations which do not belong to the established form and to get the evolution analogous to the over-condensation.

Let the argument of the main maximum be $u_m$. One can see that at $\varphi = \gamma_0$ the embryos with $u > u_m$ can be dissolved only at the infinite time (the diffusion is not considered here).

Now we shall establish the function $\varepsilon(\tau)$. To find this function one has to analyze the solution near the maximum of $\Gamma$. We introduce the variable

$$z = (u - u_m)/\varepsilon$$

Then we see that

$$du/d\tau = d(u - u_m)/d\tau = dz\varepsilon/d\tau = \varepsilon dz/d\tau + zd\varepsilon/d\tau$$

and

$$\varepsilon \frac{dz}{d\tau} = \Gamma(\gamma_0(1+\varepsilon^2)) - zk_1$$

where $k_1$ is the coefficient equal to $d\varepsilon/d\tau$. In the last equation it is necessary to express $u$ in the function $\Gamma$ through $z$ and $\varepsilon$. Then we rescale the time to exclude the coefficient in the rhs and then we get an equation which allows (or does not allow according to the reasons mentioned above) the analysis analogous to the already made one. If equation allows such analysis one can get the correction term of the asymptotic.

One has to get the equation binding $d\varepsilon/d\tau$ and $\varepsilon$. In the power-like laws of growth this equation is trivial and has the form $f(\varepsilon)d\varepsilon/d\tau = const$ with some known function $f$. It is interesting whether one can get any more complex form of this equation. It is quite possible that some more complex form can lead to some new physical effects. Here we do not consider this question and assume that the dependence $\varepsilon$ on $\tau$ for the correction term is established.

Having calculated one correction term after another we establish all asymptotic series until the step when we can not perform the procedure described above because the obtained equation does not allow to put maximum to the zero level. In the natural physical situations only the initial and the first correction term can be established. It is worth seeking the situations where one can make more steps.

In the Osipov-Kukushkin approach we get the correction term already as the initial approximation since one can choose such variables where the correction term can be treated as the initial one. Certainly, it is possible to continue this procedure but it appears that under the natural regimes of the substance exchange it is impossible to choose parameters in equations for correction terms that the main maximum will touch the zero level. It is interesting to find situations where all corrections are the universal ones.

One can see that the account of the diffusional term in the evolution equation can not lead to another asymptotics because the diffusion process along $u$ becomes negligible at the infinitely big time. In correction terms it is necessary to check that the diffusion process is really negligible in account of corrections. It would be interesting to seek the situations where the account of the diffusion process changes the correction terms.

The unpleasant fact for the LS theory is the following one. In the zero approximation the time of the dissolution of the embryo with $u > u_m$ is infinite and has to be refined. But in the first approximation the time of dissolution of every finite embryo is the finite one and it means that every finite size spectrum will be dissolved (dissolved at the finite time). After the spectrum is dissolved the balance equation will be certainly violated.

The mentioned difficulty has a fundamental character which is confirmed by further constructions in frames of the LS theory. It is reasonable to connect the finite time of dissolution with the possibility to find the universal form of the size spectrum. The authors of the LS approach treat the universal distribution as the distribution which is the limit of the relaxation process. But it evident that namely the initial form of the size spectrum determines the whole further evolution. Under the regular and only under the regular law of growth we have

$$p(\rho, t)d\rho = f(\rho', t')d\rho'$$

where $p$ and $f$ are the old spectrum and the new spectrum of sizes and $\rho$ at the moment $t$ has to come by the regular growth into $\rho'$ at $t'$. Then

$$p(\rho, t)\frac{d\rho}{dt} = f(\rho', t')\frac{d\rho}{dt}|_{t=t', \rho=\rho'}$$

Since for $d\rho/dt$ we have the concrete given expression it is hardly possible to change the form of the size spectrum to come to the universal form of the LS theory. If one determines the velocity of growth from comparison of the initial form of spectrum and the final universal form of spectrum it leads to the unpleasant contradiction.

The alternative is the following: to have the size spectrum prescribed by the initial distribution or to see the leading role of diffusion (at least at some time).

It appears that the universal form of the size spectrum has absolutely another sense - this form of spectrum is such a form which corresponds to the already established asymptotics for the critical size precisely or at least ensures the optimal relaxation to the established asymptotics for the velocity of growth. With the real form of the size spectrum this asymptotic form of the size spectrum has no direct connection. Then the asymptotic for the velocity of growth corresponding to the ideal size spectrum will be never attained at finite time.

# 3 Asymptotic form of the size spectrum

One can get the universal form of the size spectrum in the LS formalism rather simply. In the LS approach it is supposed that the main quantity of the substance is in the region $u < u_m$. Then the balance of the substance leads to

$$\int_0^{u_m \rho_c} \rho^3 f(\rho, t) d\rho = const$$

where $f(\rho, t)$ is the distribution function. From this function we come to the distribution over $u$, namely to $\phi(u, \tau)$. Then

$$\phi(u, \tau) du = f(\rho, t) d\rho$$

The substance balance can be rewritten as

$$\rho_c^3 \int_0^{u_m} u^3 \phi(u, \tau) du = const$$

The form of the function $\phi$ can be determined from the continuity equation

$$\frac{\partial \phi}{\partial \tau} = - \frac{\partial \phi v_u}{\partial u}$$

where $v_u$ is the velocity of the growth for $u$. The solution of this equation is rather simple

$$\phi(u, \tau) = \theta(\tau - \tau(u))/v_u$$

where $\tau(u)$ is the time for the embryos to attain $u$. Instead of the last function one can write the function of $u - u(\tau)$, where $u(\tau)$ is the size attained at the given time. The sense of solution is that the dependence over two variables is performed through the dependence over one variable. The concrete form of this dependence is determined by initial conditions (in the LS approach it is detemined by asymptotic relations).

The transformation to the variable $u$ is made to ensure the constant value of the upper limit of integration.

Ordinary the concrete form of the functional dependence of $\theta$ has to be determined from the initial conditions. But in the LS formalism this form is determined from the asymptotic balance equation which can be written as

$$\rho_c^3 \int_0^{u_m} u^3 \theta(\tau - \tau(u))/v_u du = const$$

The function $v_u$ depends only on $u$, but not on $\tau$. This is the consequence of the fact that in the zero approximation for $du/d\tau$ one can take $\gamma_0$ which excludes the dependence on time.

The function $\rho_c^3$ at the already established asymptotic is the known function of time. This dependence has to be cancelled by the true choice of the functional dependence for $\theta$. Namely this cancellation is the recipe to choose the true form of the function $\theta$.

The simple dependence (but may be not the unique one) is the following one

$$\theta(\tau - \tau(u)) = g(\exp(\tau - \tau(u)))$$

where the function $g$ satisfies the relation

$$g(ab) = g_1(a)g_2(b)$$

for any $a$ $b$. As this function one can take the power function. Since we have to cancel only the leading term in asymptotic the choice of the power-like function is quite satisfactory.

So, the solution is announced. But is it well justified?

Really, the ordinary solution of the problem (not the asymptotic one) is very simple it is already presented in the form of the function $\theta$, i.e. in the fact that $\theta$ is the function of only one variable. Certainly, this function has to coincide with the initial spectrum of sizes at the initial moment of time. It is sufficient to calculate the origin of the given embryo taking into account the known supersaturation, then to take the initial distribution and divide it on the velocity of growth in the given point (or on the ratio of the velocities of growth in corresponding points).

We shall speak here about the evolution scenario. This scenario is in contradiction with the LS scenario. It conserves the explicit dependence on the initial distribution. It is clear that the evolution scenario is more correct in comparison with the LS scenario. The LS scenario has at least two disadvantages

- -The absence of the spectrum at $u > u_m$
- -The spectrum is determined to ensure the asymptotic, but it is more reasonable to get the asymptotic on the base of spectrum.

The first disadvantage can be ignored by notation that every finite spectrum sooner or later will leave the region $u > u_m$.

The second disadvantage is more serious because it destroys the methodology of the LS approach. It seems that it is the crucial point and the real size spectrum will differ from the result of the LS theory.

But one can see the amazing fact - the similarity between the form of the LS spectrum and the results of experiment. We shall explain this similarity below.

## 4 Approximate similarity between the real size spectrum and the results of the LS approach

We start to consider the strange fact - why the form of the size spectrum prescribed by initial conditions will resemble the universal result of the LS theory?

At first one has to stress the low accuracy in the experimental determination of the size spectrum form. As an example one can consider the style of discussion in [6]. In [6] one can see not only the account of the initial approximation but already of the first correction in the form of the size spectrum. The form of the size spectrum with the first correction essentially differs from the form in the zero approximation. This fact is very important and leads at least to two essential conclusions

- - the correction term in the asymptotic expansion is not small at least for the size spectrum - one can not see the parameter with a property: the small value of this parameter leads to the size spectrum in the zero approximation. Moreover, one can state that there is no such parameter because the size spectrum in the first approximation is universal one. This shows that there is no reliable way to determine the size spectrum because the next correction can change the form of the size spectrum radically.

  One can also give an interpretation which is not favorable for the LS approach - the modified zero (Osipov-Kukushkin) approximation is only the starting point and all further terms of decomposition depend on the initial size spectrum. So, there is no reason to speak about the universality.

- \- the accuracy of the experimental results is rather low. Really, the difference between the size spectrum in the zero (LS theory) and in the first approximation is very essential. Earlier the experimental results confirmed the LS spectrum in the zero approximation. Now experiments confirm the Osipov-Kukushkin result. It can be only when the accuracy is low. So, one can speak only about the experimental observation of some tendencies in the form of the size spectrum.

  In the analysis of experimental results one has to note that some authors speak about the diffusional blurring of the size spectrum which corresponds to experiment.

  But one can show analytically that it is possible to neglect the diffusional term in the LS technique. It does not mean that in the evolution scenario one can neglect the diffusion - at least there are some periods when the diffusion is the driving force of evolution. Also one can see that in the case of the finite size spectrum one has to include diffusion.

As the result of these facts one has to conclude that there exists a tail of the size spectrum (it is the exponential one - this is explained by the diffusion process) at $u > u_m$ (in any other region it can not be noticed). This tail is observed experimentally. What is the reason for this tail? The LS formalism can not give an answer. Below this answer will be given.

Kinetics of the new phase embryos formation has some characteristic features which help to determine the characteristic features of the over-condensation. Roughly speaking, the "initial" size spectrum belongs to a narrow class of functional dependencies. So, we use the evolution approach and construct the sequence of stages for the process of condensation and over-condensation.

The process of condensation (the periods before the over-condensation) is investigated in [7]. This investigation gave the total number of the embryos and the form of the size spectrum. For the further regular evolution it is necessary to know the first three (and the zero) momenta of the size spectrum

$$\mu_i = \int_{-\infty}^{\infty} f(x) x^i dx$$

or of the distribution function $f(x)$ of the variable $x$, defined as the deviation of the coordinate $\rho$ from the size $z$ of the maximal value of this variable corresponding to the embryo formed at the very beginning of the condensation process.

## 4.1 The period of the initial relaxation

The relatively intensive formation of droplets stops at the relative decrease of the supersaturation equal to the value reciprocal to the quantity of the molecules in the critical embryo.

The number of molecules in the critical value is a big value. The relatively small decrease of the supersaturation stops the nucleation (formation of new embryos) and later the size spectrum moves along the $\rho$-axis without any change of the form. To ensure the essential exhaustion of the metastable phase the spectrum has to move along $\rho$-axis for a rather long distance. So, at the end of this evolution the spectrum of sizes can be considered as the monodisperse one.

The balance equation can be written in the following form

$$\Phi = \zeta + \sum_{j=0}^{3} \frac{3!|}{i!(3-i)!} z^{(3-i)} \mu_i$$

or

$$\Phi = t_1 \frac{dz}{dt} + \sum_{j=0}^{3} \frac{3!|}{i!(3-i)!} z^{(3-i)} \mu_i$$

which is the ordinary first order differential equation without the explicit dependence on the argument. So, it can be easily integrated. The result is the monodisperse spectrum and the relaxation of the spectrum coordinate to the critical size (or more correct the relaxation of the critical size to the coordinate of the spectrum).

Here we use the law of growth for the supercritical embryos. It can be replaced by the precise law of embryos growth. Really, in the law

$$\frac{dz}{dt} = \frac{\zeta}{t_1}(1 - \frac{z3\zeta}{2a})$$

we replace $\zeta$ by $\Phi - \sum_{j=0}^{3} \frac{3!|}{i!(3-i)!} z^{(3-i)} \mu_i$ and get equation

$$\frac{dz}{dt} = \frac{\Phi - \sum_{j=0}^{3} \frac{3!|}{i!(3-i)!} z^{(3-i)} \mu_i}{t_1} (1 - \frac{z3(\Phi - \sum_{j=0}^{3} \frac{3!|}{i!(3-i)!} z^{(3-i)} \mu_i)}{2a})$$

which can be easily integrated. Here it is ignored that during the evolution the momenta $\mu_i$ will be changed which is considered as a correction. In any case we need only the initial approach to the critical size where the rough monodisperse approximation is sufficient. Then there will be no problem with changing momenta.

One can show that the account of the diffusional term will be essential only when the coordinate of the size spectrum is rather close to the critical size. This is the end of the relaxation stage and the beginning of the new period.

## 4.2 The period of the diffusional blurring of the size spectrum

The result of the previous period is the relaxation of the spectrum coordinate to the critical size. The spectrum resembles the delta-like function, The spectrum width $\delta\rho$ is many times less than the coordinate $\rho$ or $\rho_c$ which is the spectrum coordinate.

If there would be no diffusion then the spectrum will remain near the critical coordinate until the end of the whole evolution. But after the time of relaxation at the previous period the diffusion becomes the main driving force of the process.

Kinetics of the diffusion blurring is rather simple and it is described in [8]. It is possible to approximate evolution by diffusion blurring without any regular growth with a boundary condition

$$f(\rho = 0) = 0$$

and the initial condition

$$f(t = t_{initial}) \sim \delta(\rho - \rho_c)$$

The method to solve this problem is the combination of the Green functions at the infinite interval. The method of images allows to construct solution by addition of the negative gaussian in the symmetrical point.

So, we write the diffusional equation in the following form

$$\frac{\partial f}{\partial t} = W_c \frac{\partial^2 f}{\partial \rho^2}$$

Here $W = W^+ + W^-$ is the generalized kinetic coefficient equal to the weighted sum of the adsorption coefficient $W^+$ and the ejection coefficient $W^-$. One can take these coefficients in the critical point marked by the index

$c$. Then one can assume that $W_c = 2W_c^+$. Taking into account the evident relation

$$W^+ = Sv_t/4 = 3\rho^2(\zeta + 1)/t_1$$

where $v_t$ is the mean thermal velocity, $S$ is the surface square of the embryo one can determine the dependence of $W_c$ on $\rho$. Then it is necessary to go from $\rho$ to a new variable $r$ which is $\rho$ in some constant power, i.e. $\rho^{const}$. This transition excludes the dependence of the diffusion coefficient on the size at least asymptotically. It occurs at $\rho d\rho \sim ds = d\rho^2$.

The Green function at the infinite interval is written in the following form

$$G(s,t|s_0,t_0) \sim \exp(-\frac{(s-s_0)^2}{4D(t-t_0)})$$

where $D$ is the diffusion coefficient (this is the known constant value), $s_0$ is the point of appearance of elementary disturbance at the moment $t_0$, $s$ is the point of observation at the moment $t$.

Here one can take as $s_0$ the critical size and the time $t_0$ has to correspond to the time of the end of relaxation (actually it is the time of relaxation).

To observe the boundary condition $f(s=0) = 0$ it is necessary to take the combination

$$f_0 = f_+ + f_-, \quad f_+ = G(s,t|s_0,t_0), \quad f_- = G(s,t|-s_0,t_0)$$

This gives the solution of this problem.

Consider the behavior of the critical size $\rho_c$. It is important to know $\rho_c$ because $u = \rho/\rho_c$. One can propose the equilibrium critical size $\rho_{ce}$ which can be determined on the base of the size spectrum as

$$\int_{-\infty}^{\infty} f(\rho,t)3\rho^2(1-\frac{\rho_c}{\rho})d\rho = 0$$

This corresponds the stationary value of the critical size, i.e. $d\rho_c/dt = 0$.

It is clear that never $\rho_c$ equals $\rho_{ce}$ because this means the stationary value of $\rho_c$ and of the supersaturation $\zeta$. But approximation $\rho_c \approx \rho_{ce}$ is rather good. Namely, at the beginning of the diffusion blurring this equality takes place. So, the critical radius $\rho_c$ (we shall mark it $\rho_{c0}$ for initial time) is given by condition

$$\int_0^{\infty} f_0(\rho)v_\rho(\rho_{c0})dr = 0$$

Here $v_\rho$ is the velocity of growth of the variable $\rho$. It is supposed that the size spectrum is relatively narrow. Another variant taking into account the different volumes of embryos is the following

$$\int_0^\infty f_0(\rho)\rho^2 v_\rho(\rho_{c0}) dr = 0$$

Also one can propose to extract the deviation of $\rho_c$ from $\rho_{ce}$

$$y = (\rho_c - \rho_{ce})/\rho_{ce}$$

and see that ordinary $y$ is small. Then one can analyze the evolution of the system through decomposition on $y$.

When $y$ is big it means that the size spectrum is essentially greater than $\rho_c$. But this corresponds to the evolution via supercritical embryos where we have extremely simple law of growth $d\rho/dt = \zeta/t_1$. So, the combination of the consideration of supercritical embryos and decompositions on $y$ with restriction in the first several terms (actually the first non-zero term) can be very effective.

Now we return to the diffusion blurring. The result of the diffusion blurring is very optimistic for the final conclusions. It sounds as following: The distribution function is the universal one and does not undergo the change of the form any more. So, one can see that the asymptotic solution is found. But the situation is not so simple.

Really the function $f_0$ after scaling in units of $\rho_{ce}$ will be the universal function without any parameters.

On the base of distribution we can calculate the behavior of the critical radius. Note that it is impossible to find the critical size directly from the balance equation $2a/3\rho_c + \int_0^\infty \rho^3 f(\rho, t) d\rho = const$ because here $\int_0^\infty \rho^3 f(\rho, t) d\rho \approx const$ and the error radically increases. Instead of the direct balance equation one can use the differentiated variant $2(a/3\rho_c^2)(d\rho_c/dt) = 3\int_0^\infty \rho^2 f(\rho, t) d\rho$ which allows to find $\rho_c$

If the size spectrum will be the universal function then the critical size will be also the universal function.

The special question is the correct boundary condition at small sizes. The velocity of the dissolution of the small embryos is a rather complex function of size and the regular dissolution exists. One can not neglect this regular dissolution. But fortunately the small embryos are dissolved very quickly with the growing velocity. So, one can suppose that they disappear immediately at $\rho = \rho_f = (0.6 \div 0.8)\rho_c$. So, the zero boundary condition has to be put at $\rho_f$ and all further considerations remain without reconsideration. Certainly, to keep the boundary condition we have to put the negative Green function symmetrical to $s$ with respect to $s_f$.

In the situation with $s_f$ we have also the universal spectrum and the universal behavior of the critical size.

But this universal asymptotics is only the intermediate asymptotics.

Now we shall introduce the regular growth and destroy this universality.

It is necessary to put some boundary of the type

$$\rho_r = (2 \div 3)\rho_c$$

and for the sizes greater than $\rho_r$ one has to consider the regular motion with the asymptotic velocity. The choice of $\rho_r$ can be made also on the base of the LS analysis.

It is trivial to refine the solution by investigation of the transition zone explicitly.

The growth of the supercritical tail leads to the growth of the size $\rho_c$ which can be calculated in approximation of the following iteration procedure: On the base of initial $\rho_{c0}$ we find the tail $f_{tail}$ of the size spectrum

$$f_{tail}(\rho, t) = f_0(\rho_r, t')v_\rho(\rho_r)/v_\rho(\rho)$$

where

$$t - t' = \int_{\rho_r}^{\rho} \frac{1}{v_\rho(\rho')} d\rho'$$

(the explicit dependence of $v_\rho$ on $t$ is weak or it can be expressed via $t$ iteratively).

The new distribution function $f_1$ will be the superposition of the initial part $f_0$ and the tail. Then from the balance equation

$$\int_0^\infty f_1(\rho)\rho^2 v_\rho(\rho|\rho_{c1}) d\rho = 0$$

we find $\rho_{ce1}$. This will be the new equilibrium critical size. It will be near the real critical size unless the tail begins to play the main role in the metastable phase consumption.

The period of the diffusion blurring come to the end when the velocity of the growth for the critical embryo becomes to be comparable with the velocity of the growth for the tail.

One has to analyze an attractive possibility to consider the process of diffusion in the region $s < s_r$ with the linear on $s - s_c$ rate of growth. Here $s_r$ has to be determined as the boundary between the linear and the asymptotic rates of the embryos growth. It seems from the first point of view that the linear rate of growth in the near critical region is preferable instead of the absence of the regular growth considered above.

The Fokker-Planck equation under the linear rate of growth has the following form

$$\frac{\partial p}{\partial t} = \gamma \frac{\partial y p}{\partial y} + D \frac{\partial^2 p}{\partial y^2}$$

Here the zero value of the coordinate as the critical size is taken, $\gamma$ and $D$ are some constants. Here $\gamma$ is negative. The Green function for the positive $\gamma$ at the infinite interval is well known and has the following form

$$G(x, t | x', t') = \sqrt{\frac{\gamma}{2\pi D(1 - e^{-2\gamma(t-t')})}} \exp(-\frac{\gamma(x - e^{-\gamma(t-t')}x')^2}{2D(1 - e^{-2\gamma(t-t')})})$$

Now it is necessary to take the combination of two Green functions and the answer is ready. The further analysis is absolutely the same.

This approach seems to be more precise than the previous one but it has many disadvantages. The first disadvantage is the following: one can see that here $\gamma$ has to be negative and then at some time the half width of the gaussian goes to infinity. So, the solution becomes illegal.

The second disadvantage is how to take into account the drift of the critical size. Now it appears in the rate of growth and then in the final formulas. The solution with a moving critical size is illegal also.

But the idea to consider the law of growth as a combination of the linear dependence at $\rho < \rho_r$ and the asymptotic law at $\rho_> \rho_r$ is very attractive. Really the term $1 - u^{-1}$ in the traditional law of growth can be treated as a correction term in the asymptotic decomposition. Here this asymptotic is taken over the positive powers of $\rho_r$. The decomposition on the positive powers is not less justified in comparison with the decomposition on inverse powers. But the last approximate rate of growth allows an explicit integration and then the LS technique can be analyzed explicitly.

One can try to construct the approximate Green function for the case of the presence of the regular growth in the following manner. We construct this function for initial perturbation at $x_0 = 0$ which is an equilibrium value for the regular growth $v_x(x = 0) = 0$. We suppose that there are no other points where $v_x = 0$ and $v_x(x) = -v_x(-x)$. Then we seek the Green function in the ordinary form

$$G(x,t|t_0) = A(t,t_0)\exp(-\frac{x^2}{\Delta(t,t_0)^2})$$

where the amplitude $A$ can be reconstructed on the base of normalizing equation $\int G dx = 1$ and the width $\Delta$ is found by relation

$$\Delta = \sqrt{4D(t-t_0)} + \int_{t_0}^{t} v_x(\Delta(t'))dt'$$

or

$$\Delta = \sqrt{4\int_{t_0}^{t} D(\Delta(t'))dt'} + \int_{t_0}^{t} v_x(\Delta(t'))dt'$$

for varying $D$. The last equation can be easily solved iteratively

$$\Delta_{i+1} = \sqrt{4\int_{t_0}^{t} D(\Delta_i(t'))dt'} + \int_{t_0}^{t} v_x(\Delta_i(t'))dt'$$

$$\Delta_0 = \Delta(t_0)$$

To ensure the correct boundary condition it is necessary to add the symmetrical negative Green function.

To refine the solution one can also use here the values of effective diffusion coefficient and effective law of the regular growth velocity from consideration made in [9].

## 4.3 The period of the dissolution of the head of the size spectrum

The tail of the size spectrum grows and earlier or later the main role of the metastable phase consumption will belong to the tail. This opens the period of dissolution of the head of the spectrum.

This period allows a rather trivial description since the high accuracy is not important here. Inevitably the head of the spectrum will be dissolved and this marks the end of this period.

The most primitive description is the following. We split the substance between the tail $G_{tail}$ and the head $G_{head}$. The spectrum in the head is described by $f_0$. The spectrum in the tail $f_{tail}$ is the direct translation of the blurring part of the head which comes to the zone $\rho > \rho_r$ by the regular growth with the known supersaturation. The supersaturation corresponds in the first iteration loop to the stationary position of the critical size. Then we can calculate the dissolution of the head, the growth of the tail and replace the critical size on the base of the balance equation. We know a new value of supersaturation. This closes the iteration loop.

Here it is impossible to use the model of the growth with a zero value of growth for $\rho > \rho_f$ and the zero value of $\rho$ for all $\rho < \rho_f$ (otherwise it produces the jumps in the supersaturation value). One has to use the explicit law $d\rho/dt = (2a/3\rho_c)(1 - (\rho_c/\rho))$.

Another style of description is to use the methods from description of the dissolution of the tail of the size spectrum which is analyzed below. Since the method is the same we do not consider it here explicitly. Certainly, the exponential tail like $\exp(-const\ \rho)$ has to be changed to the head of the size spectrum $f_0$.

This period is rather short and it is not very important for the further evolution. Details of this period description can be found in [8]. But one can see that in the theory presented here the new head at the tail is not formed. Here lies the main difference between this theory and the theory from [8]. The question whether the new head is formed is rather complex. This is the question of applicability of the gaussian tails of the Green function of diffusion equation. If we adopt the model with a finite upper limit of the size spectrum then we have a new head at the tail and have to use scenarios proposed in [8]. If we believe in long gaussian tails we come to the theory presented here. To solve this question we must go ahead of the level of description taken in the diffusion approximation. Otherwise there is no sufficient statistics to solve this question. We prefer to stop here at the statement that there is no sufficient statistics. It means that concrete details will determine the scenario. For example, we adopt that the act of the molecule consumption by the embryo requires a certain elementary time and we come to the finite upper limit of the spectrum. In the opposite situation we come to the gaussian tail. Certainly this question is out of the level of consideration adopted in the nucleation theory.

## 4.4 The period of the gradual consumption of the tail

Now we come to the period which in some sense resembles the LS results.

The result of the previous period is the formation of the exponential tail at $\rho > \rho_r$. Now we consider the process of the tail dissolution. Here one can see the true competition between the embryos with different sizes. So, here it is convenient to go to the LS coordinates.

To investigate this period we simplify the rate of the embryos growth. We assume the following rate of growth

$$\frac{du}{d\tau} \sim (1 - u^{-1}) - \gamma u$$

If there is a sufficient tail and the heat is already dissolved then at the moment of the end of the previous period

$$max\{\frac{du}{d\tau}\} \equiv v_m < 0$$

So, we assume that $v_m$ is negative.

We split the whole region of $u$ into three small regions. In the region of big $u$ we suppose

$$\frac{du}{d\tau} \sim (1 - 0) - \gamma u$$

This law allows integration even under the variation of $\gamma$.

The next region is the region of the intermediate $u$. Here we assume

$$\frac{du}{d\tau} = v_m$$

In the region of small $u$ we neglect $\gamma u$ and get

$$\frac{du}{d\tau} \sim (1 - u^{-1})$$

This law does not contain parameters and can be easily integrated. It means that the dissolution here is so fast that we can neglect the change of the critical size.

The boundaries $u_1$ and $u_2$ between these regions can be established from the continuity of the rate of growth.

One can also put an effective boundary of the total dissolution instead of the zero size.

It is possibly to refine the law of growth having introduced instead of $v_m$ some other effective value of the flat region.

When the size spectrum is known then the balance of the substance becomes the transcendental equation on $\gamma$. After we found $\gamma$ we can get $\rho_c$ by integration.

One can easily follow the dissolution of the spectrum on the base of the approximate rate of growth.

We accumulate the approximate law of growth in the following formula

$$du/d\tau \approx (du/d\tau)_{appr}$$

This law of of growth allows to know $u(\tau)$ on the base of some $u_0(\tau_0)$ for every arbitrary curve $\gamma(\tau')$

$$u(\tau) = u_0(\tau_0) + \int_{\tau_0}^{\tau} (du/d\tau)_{appr} \equiv F_{appr}(\tau|u_0, \tau_0; \gamma(\tau'))$$

For the law of growth we write

$$du/d\tau = \varphi(u, \gamma(\tau))$$

Here we can take both approximate or precise law of growth.

The substance balance equation

$$\frac{d\rho_c}{d\tau}\frac{2a}{3\rho_c^2(\tau)} = \rho_c^3(\tau)\int_0^\infty 3F_{appr}^2(\tau|u_0, \tau_0; d\ln\rho_c(\tau')/d\tau')$$
$$\varphi(F_{appr}(\tau|u_0, \tau_0; d\ln\rho_c(\tau')/d\tau'), d\ln\rho_c/d\tau) f_0(u_0, \tau_0) du_0$$
$$+3\rho_c^2(\tau)\frac{d\rho_c}{d\tau}\int_0^\infty F_{appr}^3(\tau|u_0, \tau_0; d\ln\rho_c(\tau')/d\tau') f_0(u_0, \tau_0) du_0$$

is now the closed equation on $\rho_c(\tau)$. Here instead of $a$ one can put the appropriate constant in accordance of normalization of the size spectrum.

It is necessary to stress that all functional dependencies here are explicit ones and except $\rho_c(\tau)$ all other dependencies are known. The best way to solve this equation is to use the steepest descent method. The methods to solve this equation will be discussed below.

This equation can be approximately simplified. Since the last term of the rhs is many times greater than the lhs one can approximately write

$$\rho_c(\tau)\int_0^\infty 3F_{appr}^2(\tau|u_0, \tau_0; d\ln\rho_c(\tau')/d\tau')$$
$$\varphi(F_{appr}(\tau|u_0, \tau_0; d\ln\rho_c(\tau')/d\tau'), d\ln\rho_c/d\tau) f_0(u_0, \tau_0) du_0 =$$
$$-3\frac{d\rho_c}{d\tau}\int_0^\infty F_{appr}^3(\tau|u_0, \tau_0; d\ln\rho_c(\tau')/d\tau') f_0(u_0, \tau_0) du_0$$

or

$$\frac{\int_0^\infty 3F^2_{appr}(\tau|u_0,\tau_0;d\ln\rho_c(\tau')/d\tau')\varphi(F_{appr}(\tau|u_0,\tau_0;d\ln\rho_c(\tau')/d\tau'),d\ln\rho_c/d\tau)f_0(u_0,\tau_0)du_0}{3\int_0^\infty F^3_{appr}(\tau|u_0,\tau_0;d\ln\rho_c(\tau')/d\tau')f_0(u_0,\tau_0)du_0}$$

$$= -\frac{d\ln\rho_c}{d\tau} \equiv -\gamma$$

This equation can be solved by the same methods but it is more simple than the previous one. We outline again that except $\gamma(\tau)$ all other dependencies here are known.

Another possible approximate variant of the balance equation is the following

$$\rho_c^{-3} = const^{-1}\int_0^\infty F^3_{appr}(\tau|u_0,\tau_0;d\ln\rho_c(\tau')/d\tau')f_0(u_0,\tau_0)du_0$$

It seems to be the most simple variant of the balance equation.

Now we shall discuss the asymptotic properties of the balance equation.

Generally speaking the problem is solved since we know the good approximation

$$d\ln\rho_c/dt = \gamma_0 + some \ \ positive \ \ small \ \ value.$$

We can solve this equation by decomposition in series or by some effective linearizations.

But below we shall analyze the properties of solution in order to see that the size spectrum here resembles the LS theory for the size distribution.

First of all we have to note that the tail has the exponential character. Really, the translation of the gaussian at some shift from the maximum leads to

$$f_{tail} \sim \exp(-const/t)$$

which can be easily approximated by the standard exponent of the argument linear on the size. Here the *const* is some fixed value proportional to $(s_r - s_c)^2$.

Here we have to recall that in the original paper by Lifshic and Slezov there is a reference on the exponential tail of the size spectrum. It is quite natural to check the theory on example of the exponential tail.

The exponential on $r$ spectrum is exponential on $u$ also in the asymptotic limit.

In frame of the steepest descent methods the utilization of the exponential tails is quite justified. One can simply refer to the steepest descent method instead of the explicit consideration made above. But one has to stress that we follow the explicit determination of the size spectrum instead of the formal methods. Explicit decompositions also give the exponential tail of the spectrum.

If the characteristic width of the tail is many times greater than the critical size then $v_m$ is far from zero and there appears the rapid dissolution of the size spectrum. If the width of the spectrum is many times less than the critical size then $v_m$ is close to zero. It is evident that earlier or later the last situation will take place. One can give the qualitative picture of the process - The evolution at the big finite time is the slow monotonous increase of $v_m$ up to zero.

The situation of the wide tail can be investigated rather elementary. The behavior of supersaturation is governed by the consumption of the substance by the wide tail. To see this consumption one can use the regular growth. This is described in [8] under the investigation of the oscillating regime. Evidently, the consumption of the substance leads to the growth of the critical embryo and the dissolution of the tail. This process will take place until the tail (or the rest of the tail) can be considered as the wide one.

The rest of the tail earlier or later will become the narrow tail and then we can use the theory of the narrow tail.

Now we consider the situation of the narrow tail.

We consider the form of the size spectrum. We use the known formula

$$f(u,\tau) \sim -\frac{\xi(\tau - \tau(u))}{v_u}$$

where $v_u$ is the velocity in $u$-axis, $\tau(u)$ is the time for the embryo to attain $u$.

One can note that

$$\tau(u) = \int_0^u \frac{du}{v_u} \to \ln(u)$$

This asymptotics makes the size $u$ inconvenient for analysis. It is more convenient to act in the $\rho$-scale where the asymptotic rate of growth is the constant one. In experiment under the instantaneous observation the variable $u$ is proportional to $\rho$ and there is practically no difference between them.

So, it is preferable to consider at big $u$ the $\rho$-scale. In the variable $\rho$ the picture is rather simple - the exponential tail begins to be transformed according to the variation in the velocity of growth

$$f(\rho) \sim \frac{\exp(-const \rho)}{(1 - \rho_c/\rho)}$$

The amplitude of the spectrum and the width are determined from the behavior of $\rho_c(t)$. Because of the asymptotic neighborhood of the behavior of the critical size to its behavior is the LS model these characteristics are close to the results of the LS technique.

Now we turn to the justification of the similarity of the form of the size spectrum in the LS technique and the spectrum established in this theory. Until $u \approx u_m$ or $\rho_0 \approx u_m \rho_c$ there is no spectrum in the LS theory. In the current theory the situation is analogous - the tail is very short.

Now we investigate the region $u \approx u_m$. Since $u_m$ is big the rate of growth $d\rho/dt$ is close to the asymptotic value, i.e. to the constant velocity and the tail in the current model will be close to the exponential one. But what will be in the LS theory? We turn to the formula

$$\theta(\tau - \tau(u)) = g(\exp(\tau - \tau(u)))$$

which can be rewritten with account of an initial form of the size spectrum as

$$\theta(\tau - \tau(u)) = \exp(const(\tau - \tau(u)))$$

Having recall that

$$\tau(u) = -\int_0^u \frac{du}{v_u} + const$$

which gives under the constant value of $v_u$ the evident relation near the maximum

$$\tau(u) \sim u + const$$

we see that the dependence of $\theta$ on $u$ ($\tau$ is fixed but it is excluded) becomes the exponential one.

Certainly here the derivation differs from the LS analysis and we ignore the change of $v_m$ in time which can be very essential. But qualitatively we come to the same results.

The distributions in the region with small $u$ are formed both in the LS theory and here by the dissolution of the exponential spectrum. They are, hence, similar.

When one neglects $\gamma u$ in comparison with $(1 - u^{-1})$ it means that we neglect the change of the height of the original spectrum because the time of the dissolution of the given embryo from the size $u \sim u_m$ is small and the change of the critical size during this time is small. This simplification is quite possible.

So, both distributions (in the LS theory and the derived here) are similar in their dorm. The similarity is ensured by the narrowness of the tail of the size spectrum. Namely the situation of the narrow tail is the dominating one in the evolution scenario. So, the similarity is the occasional coincidence corresponding to the initial exponential form of the size spectrum tail. But namely this coincidence leads to the experimental confirmation of the LS technique.

Later we return to the situation of the wide tail. Every wide tail as the narrow tail is also local in the size axis and, hence, there is the backlash in dependence of $v_u$ on time. The tail can be approximated in frames of the steepest descent method by an exponent. So, the style to construct the solution will remain the same. Hence, everything is reduced to the already analyzed situation.

One can see the following stabilizing property - the wider is the tail, the wider is the backlash and the local character is approximately conserved. This property is very important - it is responsible for the observation of the LS-like spectrum already at the moderate time.

Here the free molecular regime is adopted, this allows to write the balance equation in the integral form. The opposite case is the case of the profiles of metastability around the embryos. In this case one has to take into account the interactions between these profiles. The task seems to be extremely complex. Nevertheless the answer for the form of the size distribution is very simple. Certainly this answer is rather approximate.

Really, one can propose the following model. Since the profiles are sharp functions of the space coordinate one can imagine only the pair interactions. Such a pair battle will end by defeat on one of partners. The winner will continue to be the embryo of a new phase, the looser disappears. At the asymptotics of evolution the remaining embryo had to win many battles. With probability $p_1$ it wins the first battle, with probability $p_i$ it wins the $i$-th battle. The total probability $P_{tot}$ to win all battles is the product $\Pi_i p_i$ of all probabilities. Since $p_i$ are independent stochastic values we have for $P_{tot}$ the log-normal distribution.

Certainly this approach can be spread to the group interactions (triple, etc.) which will give the same final result.

# 5 Development of the model

Now we can note several important properties of the size spectrum. The first property concerns the influence of the boundary condition on the tail of the size spectrum. Consider

$$f = -f_- + f_+$$

$$f_- \sim \exp(-(x+x_0)^2/4Dt)$$

$$f_+ \sim \exp(-(x-x_0)^2/4Dt)$$

Then

$$f_- \sim \exp(-x^2/4Dt)\exp(-2xx_0/4Dt)\exp(-x_0^2/4Dt)$$

$$f_+ \sim \exp(-x^2/4Dt)\exp(2xx_0/4Dt)\exp(-x_0^2/4Dt)$$

$$f_+/f_- \sim \exp(4xx_0/4Dt)$$

and one can take into account in the tail only the term $f_+$.

One can add that the regular growth can not destroy the tail - one can speak only about the shift of the tail and the sequential cut-off of the regions preceding the tail.

The second property is the possibility to sweep out the boundaries between stages in the sequential description of the evolution. Really, does the diffusion stop after the end of diffusional blurring? Certainly, it continues and the time of diffusional blurring depends on the amplitude of the spectrum, i.e. of the rest of the tail.

One can note the following important feature - The tail blurring is so fast that it can not be overcome by the regular growth. So, the time of diffusion blurring is important and the diffusion process occurs during the whole time of evolution.

Now we specify the recipe of calculations for concrete case. We shall explicitly see what effect has the relatively small backlash in the law of growth.

## 5.1 Explicit calculations

We start from the law of growth

$$\frac{d\rho}{dt} = \frac{\zeta}{t_1}(1-u^{-1})$$

for $u = \rho/\rho_c$. Since

$$\frac{d\rho}{dt} = \frac{d\rho_c u}{dt} = \rho_c \frac{du}{dt} + u\frac{d\rho_c}{dt}$$

we see that

$$\frac{du}{dt} = \frac{1}{\rho_c}\frac{\zeta}{t_1}(1-u^{-1}) - \frac{u}{\rho_c}\frac{d\rho_c}{dt}$$

Since

$$\zeta = \frac{2a}{3\rho_c}$$

we come to

$$\frac{du}{dt} = \frac{2a}{3\rho_c^2 t_1}(1-u^{-1}) - \frac{u}{\rho_c}\frac{d\rho_c}{dt}$$

or

$$\frac{3\rho_c^2 t_1}{2a}\frac{du}{dt} = (1-u^{-1}) - \frac{3\rho_c t_1}{2a}\frac{d\rho_c}{dt}u$$

We introduce $\tau$ to have

$$\frac{2a}{3\rho_c^2(t)t_1}dt = d\tau$$

and then

$$\frac{du}{d\tau} = (1-u^{-1}) - \frac{1}{\rho_c}\frac{d\rho_c}{d\tau}u$$

or

$$\frac{du}{d\tau} = (1-u^{-1}) - \frac{d\ln\rho_c}{d\tau}u$$

So,

$$\gamma = \frac{d\ln\rho_c}{d\tau}$$

Now we find the argument $u_m$ which provides maximum for the rate of growth $du/d\tau$, i.e. the maximum of the curve $(1-u^{-1}) - \gamma u$. Having differentiated $du/d\tau$ on $u$ we have

$$\frac{d}{du}[(1-u^{-1}) - \gamma u] = u^{-2} - \gamma$$

Then

$$u_m = \gamma^{-1/2}$$

The height of the curve $(1-u^{-1}) - \gamma u$ will be

$$\frac{du}{d\tau}|_{max} = 1 - 2u_m^{-1}$$

It has to be zero or some small negative value $-\delta$. Namely $\delta$ is the backlash. Then

$$1 - 2u_m^{-1} = -\delta$$

and

$$u_m = \frac{2}{1+\delta}$$

$$\gamma = \frac{(1+\delta)^2}{4}$$

Now we reconstruct the dependence of $\rho_c$ on $t$ based on the known value of $\gamma$. We have

$$\frac{(1+\delta)^2}{4} = \frac{d\ln\rho_c}{d\tau}$$

or

$$\frac{3t_1}{4a}\frac{d\rho^2}{dt} = \frac{(1+\delta)^2}{4}$$

Then

$$\rho_c^2 \sim \frac{a}{3t_1}(1+\delta)^2 t$$

or

$$(\frac{2a}{3\zeta})^2 \sim \frac{a}{3t_1}(1+\delta)^2 t$$

Then the supersaturation satisfies the asymptotic behavior

$$\zeta \approx \sqrt{\frac{4at_1}{3(1+\delta)^2 t}}$$

## 5.2 Contradiction in asymptotics

Now we can see the concrete picture for the approximate law of growth.

The asymptotics $1 - \gamma u$ at big $u$ crosses the axis $du/d\tau = 0$ at

$$u = \gamma^{-1} = \frac{4}{(1+\delta)^2}$$

The level of the backlash $-\delta$ it crosses at

$$u_r = (1+\delta)\gamma^{-1} = \frac{4}{(1+\delta)}$$

The asymptotics $1-u^{-1}$ for the rate of $u$ growth at small $u$ crosses the axis at

$$u = 1$$

and crosses the level of the backlash at

$$u_l = (1+\delta)^{-1}$$

So, the approximate rate of growth is constructed. One has to take into account that the backlash $-\delta$ can be also the function of time $t$ or $\tau$.

Now we analyze the asymptotic behavior of big $u$ We have

$$\frac{du}{d\tau} \sim 1 - \gamma u \sim -\gamma u$$

Then

$$\ln u \sim -\gamma\tau \qquad\qquad u \sim \exp(-\gamma\tau)$$

Now we can explicitly express $\tau$ on $t$ based on the known asymptotics $\rho_c$. Really,

$$\frac{2a}{3\rho_c^2 t_1} dt = d\tau$$

or

$$\frac{2a}{3(\frac{at}{3t_1})t_1} dt = d\tau$$

Then

$$\frac{2}{t} dt = d\tau$$

and

$$2\ln t \sim \tau$$

Then the asymptotics for $u$ in $t-$scale will be

$$u \sim \exp(-\gamma\tau) \sim t^{-2\gamma} \sim t^{-1/2}$$

Now we can see what will be the diffusional blurring $\exp(-const\ \ s^2/t)$. We see that

$$\exp(-const\ \ s^2/t) \sim \exp(-const\ \ \rho_c^2 u^2/t) \sim \exp(-const\ \ \frac{a}{3t_1} t t^{-1}/t)$$

and it seems that the diffusion blurring is the main effect. It is no more than an error. The reason is that $s$ does not grow here. Really, $\rho = \rho_c u \sim$

$t^{1/2}t^{-1/2} = const$ does not grow. This occurs because we throw away the negligible constant in the law $du/d\tau = 1 - \gamma u$. But the effect of non-zero growth of $\rho$ manifests in the constant 1 in this law. Certainly, it will be lost in comparison with the leading term. So, we see that the variables in LS theory are very dangerous. It is forbidden to choose new irregular variables and then fulfill the asymptotic analysis.

As for the smallness of diffusional blurring one can easily see it directly. Since $d\rho/dt = \zeta/t_1$ and we already know that $\zeta \sim t^{-1/2}$ then the integration gives $\rho \sim t^{1/2}$ and $s^2 \sim t^2 \gg t$. This shows the smallness of diffusional blurring.

One can take into account the modifications of the model

- At the tail of the diffusion gaussian the regular shift is not very important.
- The initial diffusional blurring does not stop at the beginning of the regular dissolution of the tail but takes place all time long.

In the LS approach it is used that all substance is in the region less than $u_m$ without justifications. Here we shall show the analogous fact (all substance is near $u_m$) explicitly. This fact has to correspond to the smallness of the diffusion blurring. We have to show this smallness. Really, the width $s^2 \sim t$ of the diffusion blurring is many times less than the critical size $\rho_c \sim t^{1/2}$ since $s \sim \rho^2$.

## 5.3 Modifications of the model

The balance equation is the main instrument to determine the evolution of the system. It can be written in the following form

$$\rho_c^3 \int_0^\infty u^3 \phi(u,\tau) du = const$$

Precisely speaking one has to add the the supersaturation as $2a/3\rho_c$ and get

$$\frac{2a}{3\rho_c} + \rho_c^3 \int_0^\infty u^3 \phi(u,\tau) du = const$$

but the first term goes to zero. In any case it is impossible to determine the critical size from the last equation having calculated the integral term in some approximation.

We see that in analysis of the balance equation lies a dangerous possibility to get wrong results. This possibility is extremely high in the LS analysis where the size spectrum has to cancel divergence of the critical size asymptotic behavior.

To see the behavior of $\rho_c$ we have to establish the form of $\phi$ at least in the asymptotics. We write

$$\phi(u,\tau) \to \phi_{as}(u,t)$$

where $\phi_{as}$ is defined at big $u$ from the gaussian (one can show that the back side gaussian is not important here). Namely, we have the following chain of equalities

$$\phi_{as}(u,\tau)du = f(\rho,\tau)d\rho$$

$$f(\rho,\tau)d\rho = \Psi(s,\tau)ds$$

$$\Psi(s,\tau) \sim \exp(-\frac{s^2}{4D_s t(\tau)})$$

where $s$ is $\rho^2$, $D_s$ is the diffusion coefficient over $s$ (known value).

Roughly speaking the problem is solved. But we can not combine the values of $u$, $\rho_c$ and $\tau$ until we integrate the law $du/d\tau = (1-u^{-1}) - \gamma u$ of growth. Fortunately we can not do this with $\gamma$ varying in time. So, it is necessary to introduce approximations for this law of growth. This has been done above. Actually we are interested now in the size spectrum for the values $u > u_r$. Then we have

$$u = \tilde{u} + \int_{\tau(t_0)}^{\tau(t)} (\frac{du}{d\tau}) d\tau = \tilde{u} + \int_{\tau(t_0)}^{\tau(t)} (1-\gamma u) d\tau$$

where $\tilde{u}$ is the size of $u$ at $t_0$. Here $t_0$ is the time when the diffusion transforms into the regular motion and $\tilde{u}$ is the corresponding size. The value of $\tilde{u}$ can be found on the base of $u, \tau$ and the initial value, then we take the initial size spectrum at $\tilde{u}$ and get the size spectrum for $u$ at $\tau$.

Very approximately we can substitute the law

$$\frac{du}{d\tau} = 1 - \gamma u$$

by

$$\frac{du}{d\tau} = -\gamma u$$

This gives

$$u = \tilde{u} \exp(-\int_{\tau(t_0)}^{\tau(t)} \gamma(\tau) d\tau)$$

or

$$\tilde{u} = u \exp(\int_{\tau(t_0)}^{\tau(t)} \gamma(\tau) d\tau)$$

But as we have seen earlier this leads to an error. Fortunately we can integrate already $du/d\tau = 1 - \gamma(\tau)u$ explicitly without simplification (formulas will be long).

On the base of $\tilde{u}$ one can find

$$\tilde{\rho} = \tilde{u}\rho_c(t_0)$$

and then $\tilde{s}$ equal to $\tilde{\rho}^2$.

For the distribution in $\tilde{\rho}$-scale it is very easy to write the gaussian

$$G \sim \exp(-\frac{\tilde{\rho}^4}{D_s t(\tau)})\frac{d\rho}{ds} \approx \exp(-\frac{\tilde{\rho}^4}{D_s t(\tau)})$$

Here we ignore the jacobians arrived from transition from $s$ to $\rho$ scale because $\exp(-const x^4)$ at the tail is a very sharp function. We shall ignore them below also.

We are interested now in behavior at $u \approx u_r$. Here the true approximation will be

$$\frac{du}{dt} = c_1 - \gamma u$$

$$c_1 = 1 - u_r^{-1}$$

Let us take $\gamma \approx \gamma_B = \gamma(t_B)$ ($t_B$ is the time when $u_r$ is attained).

Then

$$\ln[\frac{u - c_1/\gamma_B}{\tilde{u} - c_1/\gamma_B}] = -[\tau(t) - \tau]\gamma_B$$

So,

$$u - c_1/\gamma_B = (\tilde{u} - c_1/\gamma_B) \exp(-\gamma_B(\tau(t) - \tau(t_0)))$$

and $\tilde{u}$ is $u$ at $t_0$. As the result we know $\tilde{u}$ as a function of $u$, i.e. $\tilde{u} = F(u)$.

In any case we can integrate the equation with $\gamma = \gamma(\tau)$ since we have the first order linear differential equation. This will give the real true result with rather long formulas. So, we use the previous formulas keeping in mind the necessity to apply the formulas with varying $\gamma$.

Now we can see the asymptotics for the distribution function

$$\phi(u,\tau) \sim \exp(-\frac{\tilde{u}(u)^4\rho_c^4}{D_s t})\frac{c_1-\gamma_B\tilde{u}(u)}{c_1-\gamma_B u}$$

This result is for $u \geq u_r$.

One of important properties of this solution is the weak dependence of the form (after scaling) of the size spectrum on $\tau$. The quantity of substance in the region $[u_r,\infty)$ can be found as

$$G_> = \rho_c^3 \int_{u_r}^{\infty} u^3 \phi(u,\tau) du$$

Now we shall analyze the region $[u_l, u_r]$. The values at this region are marked by the subscript $=$. Here

$$\frac{du}{d\tau} = -\delta$$

Then

$$\phi(u,\tau) = \phi_=(u,\tau) = \phi(u_r,\hat{\tau})\frac{\frac{du_r(\hat{\tau})}{d\tau}}{\frac{du(\tau)}{d\tau}}$$

where $\hat{\tau}$ is defined as

$$u = \hat{u} - \int_{\hat{\tau}}^{\tau} \delta(\tau')d\tau'$$

which is a rather complex closure. The previous equation can be rewritten as

$$\phi(u,\tau) = \phi_=(u,\tau) = \phi(u_r,\hat{\tau})\frac{\delta(\hat{\tau})}{\delta(\tau)}$$

More rigorous is to make a shift of $u_r$ to exclude a slow evolution right of $u_r$. But this does not change the qualitative behavior.

The quantity of substance $G_=$ in this region is given by

$$G_= = \rho_c^3 \int_{u_l}^{u_r} u^3 \phi_=(u,\tau) du = \rho_c^3 \int_{u_l}^{u_r} u^3 \phi(u_r,\tau_r)\frac{\delta(\tau_r)}{\delta(\tau)} du$$

Here

$$u_r = u + \int_{\tau_r}^{\tau} \delta(\tau")d\tau"$$

Now we investigate the region $[0, u_l]$. The values at this region will be marked by the subscript $<$. Here the size spectrum can be given by

$$\phi(u, \tau) = \phi(u_l, \tau') \frac{\delta(\tau')}{1 - u^{-1}}$$

The quantity of substance is given by

$$G_< = \rho_c^3 \int_0^{u_l} u^3 \phi(u_l, \tau') \frac{\delta(\tau')}{1 - u^{-1}} du$$

Here

$$\tau - \tau' = \int_u^{u_l} \frac{du}{1 - u^{-1}}$$

The unknown function is $\delta(t)$.

All quantities of substance $G_<$, $G_=$, $G_>$ have to be substituted into the balance equation which gives the equation on $\delta(t)$ with the known coefficients.

## 5.4 Steepest descent procedure

Now we shall discuss the ways to solve this equation. At first we have to get a true algebraic equation. We differentiate the balance equation on time and get

$$\frac{d(G_< + G_= + G_>)}{d\tau} = 0$$

Then we use concrete approximations to get $dG_>/d\tau$, $dG_</d\tau$, $dG_=/d\tau$.

For $dG_>/d\tau$ we see that the subintegral function is the product of the three functions:

1. the moderate function $3u^2$,
2. the rapidly growing function for the absolute value of the rate of growth $du/d\tau$. This function becomes very small at $u_r$ (practically it is zero).
3. the rapidly decreasing function for the initial size spectrum. This function decreases in the main term even faster than $\exp(-x^4)$ and even being multiplied by the accelerating rate of growth and by $u^2$ the product goes to zero at big $u$.

So, one can effectively use the steepest descent method.

For $dG_{=}/d\tau$ we have a simple expression which is approximately proportional to the size spectrum multiplied on $3u^2\delta$ and due to the rapid decrease of the size spectrum we see that the subintegral function is the rapidly decreasing function of $u$. This is the ideal situation for the application of the steepest descent method with the maximum at the boundary point (here it is $u_l$).

For $dG_{<}/d\tau$ we have the integral with the subintegral function at the interval $]0, u_l]$, which is the product of three rapidly varying functions:

1. The function $3u^2$ which goes to zero at $u = 0$,
2. The function $du/d\tau \sim 1 - u^{-1}$ which goes to infinity at $u = 0$ while $u^2(du/d\tau)$ goes to zero at $u = 0$,
3. the rapidly decreasing size spectrum.

This provides good conditions for the application of the mentioned steepest descent method with the point of decomposition inside the interval.

The problem which can appear here is a too sharp form of the size spectrum which can cause the maximum of the subintegral function at $\rho = u\rho_c$ which is too small. Fortunately when such sharp size spectrum will come to the region $[0, u_l]$ the decrease of the substance in embryos will cause the decrease of $\rho_c$. It means that until the diffusion blurring the spectrum will not be dissolved. This situation is typical for the formation of the new head which has been discussed in [8].

The mentioned approximations lead to the algebraic equation on $\delta$. This equation allows the further simplification if we decompose $\delta(\tau)$ in Taylor's series on inverse time $\xi = \tau^{-1}$

$$\gamma(\xi) = \gamma_0 + \sum_j a_j \xi^j$$

with coefficients $a_j$. The choice of $\xi$ as a variable is recommended by the structure of the correction term in the LS procedure. Also one can use decomposition near some value $\xi_0$

$$\gamma(\xi) = \gamma(\xi_0) + \sum_j a_j (\xi - \xi_0)^j$$

The last modifications make the analysis of the evolution a technical task.

# 6 Situation of wide tails

Now we shall analyze the situation of the wide tails of the size spectrum. It means that the half-width of the size spectrum in the region $\rho > \rho_r$ is many times greater than $\rho_c$. It is clear that the approximate law of growth $du/d\tau = 1 - \gamma u$ corresponds to the law of growth $d\rho/dt = \zeta/t_1$ and the distribution function moves as a whole along $\rho$-axis. The critical size $\rho$ moves faster (but with the same time dependence $t^{1/2}$) and eats the spectrum sequentially. For all distribution tails (here we take the tail multiplied by the number of molecules in the droplet $\rho^3$) which decrease like $1/\rho^i$ with $i$ greater than 1 the relative half-width will decrease. But the situation with $i < 1$ do not ensure the finite substance, it is forbidden situation. So, earlier or later the tail will be narrow. One can speak, thus, only about the intermediate asymptotics.

Since here the width remains greater than the critical radius one can speak about another asymptotic behavior, at least the intermediate asymptotic corresponding to the wide spectrum can be observed.

Kinetics of the process here will differ from the LS case. All the time the main consumers of the metastable phase substance will be the big embryos and the backlash here is very wide. The asymptotic

$$\tau(u) = \gamma \ln u$$

ensures the infinite time of the embryos dissolution for the infinitely big embryos. Then the main supposition in the LS theory fails. This argument states that to keep the balance of the substance it is impossible that some relative size will only grow and it is impossible that all relative sizes will decrease. But now it is possible to see here the situation where all sizes decrease rather intensively but the main consumers of the vapor are the big embryos with $u$ many times greater than $u_m$. In the zero approximation the evolution is very simple - the size spectrum is cut-off by the critical size (for the sizes less than the critical one the dissolution is so rapid that we can speak about the instantaneous dissolution and neglect this region). This cut off corresponds to the conservation of the substance in the system.

Define that here the size spectrum $f_{long}(\rho)$ has the characteristic width $\Delta(f_{long})$ determined in the integral way as

$$\int_0^\infty f_{long}(\rho) d\rho = f_{long}^{max} \Delta(f_{long})$$

where $f_{long}^{max}$ is the amplitude of the size spectrum, or in the differential way as

$$f_{long}^{max}(\rho_m + \Delta(f_{long})) = f_{long}^{max} / \exp(1)$$

where $\rho_m$ is the argument for the amplitude value of spectrum. This width satisfies the strong inequality

$$\Delta(f_{long}) \gg \rho_c$$

The substance balance here is written as

$$\Phi = \zeta + q_+$$

where $\Phi$ is the supersaturation without the embryos formation, $q_+$ is the substance in the tail which can be calculated as

$$q_+ = \int_{\rho_c}^{\infty} f_{long}(\rho)\rho^3 d\rho \approx \int_{(2\div 3)\rho_c}^{\infty} f_{long}(\rho)\rho^3 d\rho$$

Then in the last integral we can take for $f_{long}$ the size spectrum fully determined by the supercritical law of growth from the "initial" spectrum $f_0$ (at the time $t_{init}$):

$$f_{long}(\rho, t) = (\zeta(t_{init})/\zeta(t)) f_0(\hat{\rho}(t, t_{init}))$$

where $\hat{\rho}(t, t_{init})$ is determined from

$$\rho = \int_{t_{init}}^{t} \zeta(t')/t_1 dt' + \hat{\rho}(t, t_{init})$$

It is more convenient to study the initial spectrum and to see how much this spectrum is cut off. So, we introduce the initial $\rho$-size variable $s$ and write a balance equation

$$\Phi = \zeta(t) + \int_{s_c}^{\infty} \varphi(s)^3 f_0(s) ds$$

Here $s_c$ is the initial size of the variable $s$ which attains at $t$ the size $(2\div 3)\rho_c$, $\varphi(s)$ is the size which will be attained at $t$ by the embryo with initial size $s$

$$\varphi(s) = s + \int_{t_{init}}^{t} \frac{\zeta(t')}{t_1} dt'$$

The balance equation can be rewritten as

$$\Phi = \zeta(t) + \int_{s + \int_{t_{init}}^{t} \frac{\zeta(t')}{t_1} dt' > (2\div 3)\frac{2a}{3\zeta(t)}} \varphi(s)^3 f(s) ds$$

or since $(2 \div 3)\frac{2a}{3\zeta(t)}$ has to be many times smaller than the width of the spectrum then

$$\Phi = \zeta(t) + \int_{s+\int_{t_{init}}^{t} \frac{\zeta(t')}{t_1} dt' > 0} \varphi(s)^3 f_0(s) ds$$

Having noticed that $s$ has to be at least positive we get the following modification of the balance equation

$$\Phi = \zeta(t) + \int_{s>0} \varphi(s)^3 f_0(s) ds$$

This equation can be easily solved. Having introduced the explicit equation for $\varphi$ we come to

$$\Phi = \zeta(t) + \int_{s>0} (s + \int_{t_{init}}^{t} \frac{\zeta(t')}{t_1} dt')^3 f_0(s) ds$$

One can see that the integral term is the polynomial on

$$\rho_m = \int_{t_{init}}^{t} \frac{\zeta(t')}{t_1} dt'$$

Then

$$\Phi = \zeta(t) + \sum_{i=0}^{3} \frac{3!}{i!(3-i)!} a_i \rho_m^{3-i}$$

with known constants

$$a_i = \int_0^\infty s^i f_0(s) ds$$

It can be rewritten as

$$\Phi = t_1 \frac{d\rho_m}{dt} + \sum_{i=0}^{3} \frac{3!}{i!(3-i)!} a_i \rho_m^{3-i}$$

The last equation is the differential Abel equation - the ordinary first oder differential equation. Since there is no explicit dependence on the argument this equation can easily integrated. This gives the solution of the problem.

Certainly, the last solution is not accurate because there all embryos remain in the integral term - they remain supercritical ones. This leads to the qualitatively wrong behavior. It is clear that the error will be essential namely when the tail stops to be really the wide tail. But nevertheless it is possible to take into account the dissolution of the embryos. The balance equation has to be written as

$$\Phi = \zeta(t) + \int_{s>(2\div 3)2a/3\zeta} (s + \int_{t_{init}}^{t} \frac{\zeta(t')}{t_1} dt')^3 f_0(s) ds$$

and conserves the polynomial structure on $\rho_m$.

$$\Phi = \zeta(t) + \int_{s>(2\div 3)2a/3\zeta} (s + \rho_m)^3 f_0(s) ds$$

or

$$\Phi = \zeta(t) + \sum_j \rho_m^j \frac{3!}{j!(3-j)!} \int_{s>(2\div 3)2a/3\zeta} s^{3-j} f_0(s) ds$$

Now the coefficients

$$a_j = \frac{3!}{j!(3-j)!} \int_{s>(2\div 3)2a/3\zeta} s^{3-j} f_0(s) ds$$

are known (since the initial size spectrum is known) functions of $\zeta$. But it is possible to solve this equation on $\rho_m$ as the third power algebraic equation

$$\rho_m = F(\zeta)$$

or

$$\rho_m = F(t_1 \frac{d\rho_m}{dt})$$

with a known function $F$ With the help of the inverse function $F^{-1}$ we can write

$$\frac{d\rho_m}{dt} = t_1^{-1} F^{-1}(\rho_m)$$

The last equation can easily solved.

Now we take into account the growth of the embryos. The balance equation has to be written as

$$\Phi = \zeta(t) + \int_{s+\rho_m>(2\div 3)2a/3\zeta} (s + \int_{t_{init}}^{t} \frac{\zeta(t')}{t_1} dt')^3 f_0(s) ds$$

and does not conserve the polynomial structure on $\rho_m$. It can be written analogously

$$\Phi = \zeta(t) + \sum_j \rho_m^j \frac{3!}{j!(3-j)!} \int_{s+\rho_m>(2\div 3)2a/3\zeta} s^{3-j} f_0(s) ds$$

or in the standard form but with the coefficients

$$a_j = \frac{3!}{j!(3-j)!} \int_{s+\rho_m > (2\div 3)2a/3\zeta} s^{3-j} f_0(s) ds$$

depended (since the initial size spectrum is known) on $\rho_m$ and $\zeta = t_1 d\rho_m/dt$. So, we have the first order differential equation without explicit dependence on the argument $t$

$$\Psi(\rho_m, d\rho_m/dt) = 0$$

This equation can be integrated when we can express $d\rho_m/dt$ via $\rho_m$. This is an algebraic problem which can be solved at least locally in a good approximation.

# 7 Approximations in the explicit construction the size spectrum

The first task in construction of the size spectrum is the construction of initial distribution which will be later gradually dissolved during the overcondensation. This task is very complex. Even the elementary approximate blocks for solution do not allow the solution. We do not know the solution of the diffusion equation for the diffusion blurring of the spectrum even with the stationary value of the supersaturation. As the result of such difficulties only very approximate methods can be formulated.

To see the initial distribution it is more easy to use the $\rho$-scale because in this scale the asymptotic law of growth is rather simple and the velocity of growth contrary to the $u$-scale does not go to infinity.

The first approximate model, which allows solution is "the model of sequential evolution". We consider the period of the initial diffusion blurring. Here we have the stationary supersaturation (and the critical radius).

Consider the value of distribution at some $\rho_f$, time being fixed. Let the initial distribution be $\delta$-function at $\rho = \rho_c$. The route from $\rho_c$ to $\rho_f$ will be split between the diffusion blurring and the regular growth. In this model the blurring occurs up to $\rho$ equal to some parameter $\rho_b$. Later there will be the pure regular growth. Parameter $\rho_b$ is reasonable to put equal to $2\rho_c$.

The time of the regular growth up to $\rho_f$ will be $(\rho_f - \rho_b)t_1/\zeta$ or $(\rho_f - \rho_b)t_1 3\rho_c/2a$. Then the time to quit the diffusion blurring will be

$$t_q = t - (\rho_f - \rho_b)t_1 3\rho_c/2a$$

The supercritical regular growth is the simple translation of the size spectrum, then we have to calculate the spectrum at $\rho_b$ and $t_q$ after the pure diffusion blurring (here for simplicity we do not consider the back side input $f_-$)

$$\vartheta(\rho_f, t) \sim \frac{2\rho_b}{\sqrt{4D_s t}} \exp(-\frac{\rho_b^4}{4D_s t_q}) = \frac{2\rho_b}{\sqrt{4D_s t}} \exp(-\frac{\rho_b^4}{4D_s(t-(\rho_f-\rho_b)t_1 3\rho_c/2a)})$$

The function $\vartheta$ can be considered as the initial size spectrum. The problem is, thus, solved.

But the function $\vartheta$ has a certain disadvantage - the size spectrum is finite. Really, for $\rho_f$ greater than $\rho_{lim}$

$$\rho_{lim} = \rho_b + 2at/t_1 3\rho_c$$

the spectrum is zero.

Actually the values of $\rho$ near $\rho_{lim}$ begin to dissolve (i.e. $\rho_{lim}$ is near $\rho_r$) when the amplitude of the rest of the spectrum is extremely small. So, the relative quantity of droplets in negligibly small. It will be big only in the systems of cosmological sizes.

Nevertheless one can refine this solution. Fortunately, the diffusion process can be easily estimated even with the varying $\rho_c$ because here $\zeta$ is very small and the average number of collisions in the time unit will be $(2/t_1)(3\rho^2(t))$. Here we can take $\rho$ on the base of the regular growth and get the total number of collisions

$$n_{tot} = \int_0^t 6\rho^2(t')dt'/t_1$$

The characteristic width $\Delta_{tot}$ can be estimated as $\Delta_{tot} = \sqrt{2n_{tot}}$ with a sufficient accuracy.

Then the resulting distribution will be proportional to

$$\hat{\vartheta} = \int_{-\infty}^{\infty} \exp(-\frac{(\rho-\rho_f)^2}{2n_{tot}})\vartheta(\rho_f, t)d\rho_f$$

or

$$\hat{\vartheta} = \frac{2\rho_b}{\sqrt{4D_s t}} \int_{-\infty}^{\infty} \exp(-\frac{(\rho-\rho_f)^2}{2n_{tot}}) \exp(-\frac{\rho_b^4}{4D_s(t-(\rho_f-\rho_b)t_1 3\rho_c/2a)})d\rho_f$$

It is quite satisfactory here to consider only the right hand wing of the distribution, i.e. to put $\rho > \rho_f$. Since the subintegral function is the product of exponents it is reasonable to use the steepest descent method.

The required result is attained by a simple combination of the regular growth and the pure diffusion. The cross effects when, for example, the stochastic increase of the embryos size leads to increase of the regular rate of growth are missed here. They can be included into consideration by consideration of the effective half-width of the diffusion blurring and the shift in regular growth proposed in [9]. Certainly, they have to be slightly reconsidered since now we start not from the very beginning of the size axis.

Now we shall show the primitive approximate way to construct the explicit form of the size spectrum for the narrow tail.

The initial distribution is supposed to be known.

We approximate the rate of growth for $u$ in rescaled time $\tau$ by the following approximation

$$\frac{du}{d\tau} \approx v_m \equiv max\{\frac{du}{d\tau}\} = -\delta(\tau)$$

for $u \in [u_l, u_r]$

$$\frac{du}{d\tau} \approx 1 - \gamma u$$

for $u > u_r$,

$$\frac{du}{d\tau} \approx 1 - u^{-1}$$

for $u < u_l$.

Parameters $u_l$ and $u_r$ have to be chosen to ensure the continuity of the whole approximation.

Consider $u > u_r$. The law of growth for $\rho$ corresponding to $du/d\tau \sim (1-\gamma u)$ is $d\rho/dt = \zeta/t_1$ (the r.h.s. is precisely taken into account by transition from $t$ to $\tau$). So, the distribution in $\rho$-scale is moving as a whole without changing of the form. We know this form - it is exponential form

$$f(\rho) \sim \exp(-\alpha\rho)$$

with some parameter $\alpha$.

Then the distribution $\varphi$ over $u$ is connected with $f$ by the following relation

$$\varphi(u) = f(\rho)\frac{\frac{d\rho}{dt}}{\frac{du}{dt}}$$

Having inserted the explicit relations for the derivatives we come to

$$\varphi(u) = f(\rho)\frac{1-u^{-1}}{(1-u^{-1})-\gamma u}$$

or in the supercritical limit

$$\varphi(u) = f(\rho)\frac{1}{1-\gamma u}$$

Here the distribution function is even sharper than the distribution over $\rho$.

Now at first we shall assume that the backlash is changing in time slowly in comparison with the time of dissolution of an embryo from $u_r$ to $u_l$. This case will be at least the base approximation for iteration procedures to refine the solution.

The known solution in the region $u > u_r$ leads to the known rate of appearance $\Psi_b(\tau)$ at $u = u_r$. This value is given by

$$\Psi_b(\tau) = \varphi(u)|_{u=u_r}(\frac{du}{d\tau}|_{u=u_r}) = \varphi(u)|_{u=u_r}v_m$$

Here $\varphi$ is the distribution over $u$. Now it can be established. One can easily show that $\Psi_b(\tau)$ at $u = u_r$ is sharp decreasing function of $\tau$.

The last function is the source at the left side of the central interval $[u_l, u_r]$. Now it is possible to solution at this interval. This solution is very simple and it is given by

$$\varphi(u,\tau) = \Psi_b(\tilde{\tau})/\frac{du}{d\tau}|_{u=u_r}$$

or

$$\varphi(u,\tau) = \Psi_b(\tilde{\tau})/v_m$$

The time $\tilde{\tau}$ satisfies relation

$$u - u_r = \int_{\tilde{\tau}}^{\tau} v_m(t')dt' \approx v_m(\tau - \tilde{\tau})$$

Hence, the solution in the central region is constructed.

Generalization for the varying $\delta$ is rather simple. The rate of appearance $\Psi_b(\tilde{\tau})$ at $u = u_r$ is given by

$$\Psi_b(\tilde{\tau}) = \varphi(u|\tilde{\tau})|_{u=u_r}v_m(\tilde{\tau})$$

Here $\varphi$ is the distribution over $u$. Now it can be established.

The last function is the source at the left side of the central interval $[u_l, u_r]$. Now it is possible to solution at this interval. This solution is very simple and it is given by

$$\varphi(u,\tau) = \Psi_b(\tilde{\tau})/v_m(\tau)$$

and

$$\tilde{\varphi}(u,\tau) = \varphi(u|\tilde{\tau})|_{u=u_r(\tilde{\tau})} v_m(\tilde{\tau})/v_m(\tau)$$

The time $\tilde{\tau}$ satisfies relation

$$u - u_r = \int_{\tilde{\tau}}^{\tau} v_m(\tau')d\tau' \neq v_m(\tau - \tilde{\tau})$$

Now only the last region - the region of small $u < u_l$, has to be investigated. Here the solution is also rather simple - it is the simple translation of the source from $u_r$ under the law of growth independent on $\gamma$. Here all constructions are analogous to the previous case but the transition over the central region has to be taken into account.

The distribution $\varphi$ is given by

$$\varphi(u,t) \sim \Psi_a(\hat{\tau})/(du/d\tau) \sim \Psi_a(\hat{\tau})/(1-u^{-1})$$

where

$$\Psi_a(\hat{\tau}) = \tilde{\varphi}(u_l(\hat{\tau}),\hat{\tau})v_m(\hat{\tau})$$

Here $\hat{t}$ is determined by the following way

$$\hat{\tau} - \tilde{\tau} = \int_{u_l}^{u_r} \frac{1}{v_m} du$$

and

$$\tau - \hat{\tau} = \int_{u}^{u_l} \frac{1}{du/d\tau} du$$

For $\delta = const$ one can simplify the last relation

$$\tau - \tilde{\tau} = \int_{u}^{u_l} \frac{1}{du/d\tau} du + (u_l - u_r)/v_m$$

or

$$\tau - \tilde{\tau} = \int_{u}^{u_l} \frac{1}{1-u^{-1}} du + (u_l - u_r)/v_m$$

The integral can be easily taken analytically and we get the explicit expression for $\tilde{t}$.

If $v_m$ does not essentially depend on time one can simply solve all these equations. The form of the size spectrum is determined, only parameter $v_m$ ($\gamma$, $u_r$, $u_l$ depend on $v_m$) is unknown. The balance equation will be algebraic equation on $v_m$ and can be easily solved since we know at least the zero approximation (for example, one can take LS asymptotic).

It is clear that the backlash is not a constant value, it changes in time. The effective way to investigate the situation of the varying backlash is to consider this variation small, then to decompose $v_m(\tau)$ in Taylor's series, to take few first derivatives and to fulfill the same program as was done above in the case of the constant value $v_m$.

# 8 Finite number of embryos

Under the finite spectrum of sizes the LS asymptotic will be also destroyed. After the size of the greatest embryo attains the critical value and $\gamma$ goes to zero the diffusion blurring begins and we return to the section about the diffusion blurring and the evolution will be described by the same formulas as mentioned above. Here it is important that the diffusion term plays the main role in evolution. Certainly, diffusion begins to play essential role earlier than the biggest embryo attains the critical size.

We see that the further scenario is built on the doubtful alternative whether the size spectrum finite or not. The diffusion process through the formula for the Green function gives the infinite size spectrum. But is every concrete system the spectrum is the finite one. The answer on this question also determines the asymptotic. The type of asymptotic is determined by the time of observation and the sizes of the system under the observation. Fortunately this question is artificial because other effects (the change of the regime of growth, the thermal effects, etc.) lead to the end of applicability of the chosen physical model.

In every system the finite spectrum is the direct consequence of the finite number of embryos. So, we have to develop methods to describe the evolution with the finite number of embryos.

Suppose we have few embryos in the system. Then the evolution is determined by the laws of their regular growth (diffusion has also to be taken into account but in the manner of some stochastic adsorption and ejection of the molecules by the embryo). The balance equation links these laws of growth in the closed system of equations. The number of these equations equals the number of embryos. When the number of embryos is less or equal to few hundreds it is preferable to solve these equations by computers explicitly.

We rewrite the law of growth for a chosen embryo in the following form

$$\frac{d\rho_i}{dt} = \frac{\zeta}{t_1}(1 - \frac{\rho_c}{\rho_i})$$

$$\rho_c \equiv \frac{2a}{3\ln(\zeta + 1)}$$

(index $i$ marks embryos), where $a$ is the rescaled surface tension (it is a constant) and $\zeta$ is the supersaturation. Namely through the supersaturation one can link the laws of growth having written the balance equation

$$\zeta = \Phi - \sum_i \rho_i^3$$

Here $\Phi$ is the initial value of supersaturation.

One can easily solve the system of these equations at least approximately. The first method is very simple. At given initial sizes of embryos we find the value of the supersaturation. Then we reconsider the sizes having moved them according to the law of growth at the given supersaturation. The time interval has to be small. Then we recalculate the supersaturation having made one step of evolution. This method is the step by step procedure.

The stochastic adsorption and ejection of the molecules by the embryo can be taken into account by the following simple procedure. We keep in the memory of computer all coordinates of embryos $\rho_i$ and for every embryo at the given supersaturation we determine the rate of adsorption as

$$R_+ = 3\rho^2(\zeta + 1)\Delta t/t_1$$

Here $\Delta t$ is an elementary time step. The rate of ejection will be

$$R_- = R_+ - (d\rho/dt)\Delta t$$

$$\frac{d\rho}{dt} = \frac{\zeta}{t_1}(1 - \frac{2a}{3\zeta\rho})$$

The rate of staying still will be

$$R_0 = 1 - R_- - R_+$$

We must choose $\Delta t$ enough small to have $R_0 > 0$ even for the greatest embryo.

Having put the point at the interval $[0, 1]$ stochastically we determine what action we have to do. If this point belong to interval $[0, R_-]$ we eject the molecule, i.e. we make a transition $\rho_i \to \rho_i - 1$. If this point belong to interval $[R_-, R_- + R_+]$ we accumulate the molecule, i.e. we make a transition $\rho_i \to \rho_i + 1$. If this point belong to interval $[R_- + R_+, 1]$ we keep the coordinate still, i.e. we make a transition $\rho_i \to \rho_i$.

We have to repeat this action for every embryo. Then we recalculate the supersaturation

$$\zeta = \Phi - \sum_i \rho_i$$

and fulfill the step in time.

We see that these procedures can not give the analytical properties of evolution with the finite number of embryos. Hence, the problem of the system of several embryos exists and the effective solution is absent.

Now we turn to the simplest case - the case of small quantity of embryos. The asymptotic of the process is the evident there will be the greatest embryo which will be the critical one. This embryo is in the effective potential well. Description here is analogous to the case of the several identical embryos.

Really, the law of growth

$$\frac{d\rho}{dt} = \frac{\Phi - \rho^3}{t_1}(1 - \frac{2a}{3\ln(\Phi - \rho^3 + 1)\rho})$$

corresponds to the regular motion in the potential

$$U = \int_0^\rho \frac{\Phi - \rho^3}{t_1}(1 - \frac{2a}{3\ln(\Phi - \rho^3 + 1)\rho})d\rho$$

which is very deep and only in the region of small $\rho$ it has a barrier and begins to decrease when $\rho$ decreases.

If we ignore the fluctuational formation of the new embryos then the evolution leads to the fluctuational disappearance of the last embryo. It requires absolutely giant times and at these times new supercritical embryos have to appear. So, the ignorance of the fluctuational formation of new embryos (with extremely slow rate) is illegal.

The flow of disappearance of the last embryo is many times less than the flow of appearance (formation) of the new embryo even in the system with the practically consumed metastable phase by the giant embryo. So, one can see the formation of the second embryo. Later one can observe the competition between these embryos. Practically inevitably the second (new) embryo will be dissolved but with a small probability $\pi$ which can be estimated (very roughly because we keep the old potential $U$ appropriate only for one embryo) as

$$\pi \sim \exp(U(\rho = \rho_{min}/2^{1/3}) - U(\rho_{min}))$$

(here $\rho_{min}$ is the argument of the minimum of potential) the first embryo becomes the second one and it will be dissolved. Certainly, the above presented picture is only the rough estimate.

# 9 Conclusions

In the theoretical constructions presented above we came to the following results

- In Sections 2,3 we pointed out the weak features of the LS approach. In section 2 the features concerning the behavior of the supersaturation were outlined. In section 3 the weak features in construction of the size spectrum were presented.
- In section 4 the sequential analysis of the evolution was given and it is shown why the form of the size spectrum resembles the form given in the LS approach
- In section 5 the details of the most difficult and the most important period of the tail dissolution are given
- In section 6 the approximate way to construct the initial size spectrum for the period of the tail dissolution is given. This point is very important for qualitative results.
- In section 7 the situation of the wide tail which allows essential simplification is presented
- Section 8 is devoted to the specifics of the case when only few embryos remain in the system.

Sections 7 and 8 are supplementary ones, the complete theory is given in sections 4 - 6. This theory gives an answer on two important questions - why LS spectrum of sizes can be really seen in nature and what is the difference between the real situation and the LS approach.

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