Kinetics of aerosol formation. 1. Decay of metastable phase on several types of heterogeneous centers

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Abstract

A system of a metastable phase with several sorts of the heterogeneous centers is considered. An analytical theory for the process of decay in such a system has been constructed. The free energy of formation of the critical embryo is assumed to be known in the macroscopic approach as well as the energy of solvatation. The process is split into some periods and the analytical description of every period is given. The most difficult to describe is the period of the essential formation of the embryos of a new phase. At first some asymptotes are investigated and then a general solution is suggested. Several approximate transformations are accomplished with the corresponding numerical estimates and some analytical justifications.
1 Introduction

The case of condensation of the supersaturated vapor into the state of liquid droplets seems to be the simplest one among the first order phase transitions. Traditionally this case is treated as a model to introduce some new theoretical constructions in the description of the first order phase transitions. This leading role of the case of condensation was outlined by the creation of the classical theory of nucleation by Volmer [1], Becker and Doering [3], Zeldovich [4] and Frenkel [1] which gave for the first time a rather simple expression for the rate of nucleation (i.e. for the rate of the appearance of new droplets).

The careful analysis of the classical theory leads to the great number of the publications with the various reconsiderations of the classical expressions. Among them one has to notice the account of the internal degrees of freedom in the embryo made by Lothe and Pound [5], another modifications made by Reiss, Cohen and Katz [6], Reiss [7], Fisher [8]. The application of the density functional theory to the first order phase transition made by R.Evans and D.Oxtoby [10] and D.Oxtoby and D.Zeng [13] allowed to put the microscopic (mesoscopic) model for the condensing substance as the base for the expression for the free energy of the critical embryo and for the rate of nucleation. The latest reconsideration of the classical theory can be associated with the contributions of Reiss, Tabazadech and Talbot [9], Reiss, Ellerby and Weakliem [12] - [15], Oxtoby and Talanquer [14]. In these publications the role of the environment of the droplet is carefully analysed. The choice proposed in these publications is equivalent to some specific choice of the statistical ensemble.

Nevertheless one has to notice that there is no perfect coincidence between the concrete theoretical predictions and the experimental results. The macroscopic expression reproduces only the qualitative behavior of the experiment results. Meanwhile, the relative deviation between the rate of growth of the nucleation rate in the theoretical predictions and in the experimental results is rather small.

These efforts allowed to start the investigation of kinetics in the field of the first order phase transition. The qualitative description of the phase transition was started by Wakeshima [20] who considered some time lags for condensation. As far as the characteristic time of formation of the droplets spectrum was necessary to ensure the correct experimental definition of the stationary rate of nucleation namely this value was investigated in [20]. In [28] the picture of the more realistic phase transition under the smooth behavior of the external conditions (i.e. under the external conditions of the dynamic type) was given. The form of the spectrum in these publications was introduced by some artificial models. But the real problem is to determine the form of the spectrum.

The homogeneous decay of a metastable phase was investigated in [17] by Kuni, Grinin, Kabanov. The analogous consideration for the heterogeneous decay was fulfilled by Kuni in [18] where only two limit situations were considered. The consideration of the simultaneous heterogeneous and homogeneous decay was made in [19], [20] by the formal generalization of the procedure for the homogeneous decay [17].

The homogeneous condensation under the smooth behavior of the external conditions (i.e. under the dynamic conditions) was investigated in [20], [27]. The case of the heterogeneous condensation was analyzed in [28], [29] where the based qualitative descriptions of the phase transition were given.

The external conditions of the dynamic type and the decay type are the most natural external conditions and can be treated as some basic ones.

Practically in the condensing system there are several types of the heterogeneous centers of a different nature. Moreover in the process of condensation on the ions the free energy of the critical embryo depends on the sign of the electric charge. As it is shown in [20] the free energy $F$ of the near-critical embryo in the state of the internal equilibrium can be presented in the following manner:

$$F = -b\nu + a\nu^{2/3} + c_1\nu^{1/3} + (c_2 + c_3)\nu^{-1/3} + c_0\ln\nu - G$$

Here and in the further considerations all energy-like values are expressed in the units of the thermal energy $k_BT$ ($k_B$ is the Boltzmann constant, $T$ is absolute temperature); $a, b, c_0, c_1, c_2, c_3$ are some constants; $G$ is the energy of the nuclei solvatation. It necessary to notice that in contrast to $a, b, c_0, c_1, c_2$ which don’t depend on the sign of the charge $q$ the value of $c_3$ is proportional to $q$. The value of $G$ also depends on the sign of $q$. This dependence is similar to dependence (3) of $F$ (without $G$). The only specific feature we must fulfil is to substitute the number of the molecules $\nu_e$ of the solvated ion instead of $\nu$. As far as $\nu_e \neq \nu$, for the near-critical embryo the value of $\nu_e$ is (certainly, one can not check the general recipes as to calculate the objects like the statistical sums.
\[ F \text{ depends on the sign of } q. \] Hence, in the presence of the radiation we immediately have two sorts of the centers (positive and negative) with the different heights of the activation barrier, i.e. with the different activities of the heterogeneous centers.

When one has the spectrum of the sizes of the solid nucleus of condensation with the weak interaction one must immediately come to the spectrum of activities of the heterogeneous centers. Really, in the most simple model appears when the nuclei is essentially noninteractive and one has simply to add the surface term to the number of the molecules imaginary contained in the volume occupied by the nuclei. The free energy of the critical embryo is given by

\[ F = -b\nu + a\left(\nu + \frac{4\pi r^3}{3v_l}\right)^{2/3} - G \] where \( r \) is the radius of the nuclei, \( v_l \) is the volume occupied by a molecule of the condensed substance in the liquid phase. So, the spectrum of sizes of the heterogeneous centers immediately initiates the spectrum of the activities of the heterogeneous centers.²

Any spectrum of the activities of the heterogeneous centers can be split into several continuous parts (may be also like \( \delta \)-functions) which will be considered as the “types” of the heterogeneous centers. So, one can see four rather natural kinetic problems:

- The process of the decay of the metastable state on the several types of the heterogeneous centers.
- The process of the decay of the metastable state on the continuous spectrum of the heterogeneous centers.
- The process of condensation on the several types of the heterogeneous centers under the dynamic conditions.
- The process of condensation on the continuous spectrum of the heterogeneous centers under the dynamic conditions.

The set of these publications is based on the ideas proposed in [32] - [37]. Nevertheless the theory of the heterogeneous decay was constructed only for one type of the heterogeneous centers. The task to construct the kinetic theory for these situations is rather essential. It will be completely fulfilled here.

The equations of condensation are rather similar in these four situations. Unfortunately, the methods of their solution are absolutely different. This is caused by the specific nonlinear character of the condensation equations. Moreover, the analysis of any separate situation can not be spread on another one. That’s why the four separate publications are devoted to the kinetics in these situations.

One has to study only the periods of the intensive formation of the droplets. But in contrast to condensation on the one sort of the heterogeneous centers [28], [29] these periods aren’t very short³.

We shall use the following physical assumptions:

- 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 barrier⁴,
- the absence of the thermal effects.

²Later the value of the activity will be accurately defined
³Under the dynamic conditions
⁴The theory without the heterogeneous activation barrier is much more simple.
As far as according to \cite{32} the condensation equations in the general conditions of the condensation process are analogous to the case of the free molecular consumption of the vapor we shall study namely this case.

We assume the total number of the heterogeneous centers to be constant in time.

As far as the most interesting characteristics of this process are the numbers of the heterogeneously formed droplets of the different types we shall estimate the accuracy of the theory by noticing the error of the obtained solutions for these values. The whole process of the metastable phase decay can be split into two periods: the period of the essential formation of the droplets and the period of the essential consumption of a metastable phase. At first we shall investigate the period of formation of the droplets. The unit volume is considered.

The consideration of the further evolution is rather simple and can be reduced to the first order differential equation in the manner of \cite{25} for the situation of the decay and in the manner of \cite{28}, \cite{29} for the situation of the dynamic conditions. We needn’t to consider this period here.

In order to present the clear descriptions some common facts will be recalled at the beginning of every publication. It allows to consider the theories as the separate ones.

Below the situation of the decay of the metastable phase on the several sorts of the heterogeneous centers will be described.

We assume the total number of the heterogeneous centers to be constant in time.

\section{Kinetic equation}

Suppose that there are several sorts of the heterogeneous centers. We shall mark the total number of the heterogeneous centers by $\eta_{\text{tot} \, i}$ where $i$ corresponds to some sort of the heterogeneous centers. The real values of the free heterogeneous centers which may be solvated but aren’t occupied by the super-critical embryos are marked by the value of $\eta_i$. The index $i$ or $j$ below the value marks the sort of the heterogeneous centers.

The sort of the droplets means the sort of the heterogeneous centers. The absence of this index points that the formula is valid for an arbitrary sort of the heterogeneous centers. 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 the value $n$.

The power of the metastability will be characterized by the value of the supersaturation

\[ \zeta = \frac{n - n_\infty}{n_\infty} \]

We shall define the super-critical embryos as the ”droplets”. Every droplet is described by the molecule number $\nu$, or by the linear size $\rho = \nu^{1/3}$. Due to the free-molecular regime of the vapor consumption we have

\[ \frac{d\rho}{dt} = \zeta \alpha \tau^{-1} \]

where $\alpha$ is the condensation coefficient and $\tau$ is some characteristic collision time obtained from the gas kinetic theory.

The characteristic time $t_*$ will be the time of the beginning of the process of condensation. The values at the moment $t_*$ will be marked by the lower index $t_*$. The frontal type of the size spectrum allows to introduce the frontal size $z$ according to

\[ z = \int_0^t \zeta \alpha \tau^{-1} dt' \] \tag{3}

Until the coalescence \cite{22}, \cite{23} which isn’t considered here equation (3) ensures the growth of $z$ in time and can be inverted

\[ t(z) = \int_0^z \tau \alpha^{-1} \frac{dx}{\zeta(x)} \] \tag{4}

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 the value $t(x)$ as the moment when the droplet with the given $x$ has been formed (as a droplet) we can consider the 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 $\zeta(x)$. 

\pagebreak
3 Condensation equations system

We shall mark by the argument $\infty$ the total values of the characteristics formed during the whole condensation process.

Immediately after the creation the value of the supersaturation falls down to the value

$$\Phi_\ast = \zeta(0) - \sum_i \eta_{\text{tot } i} \nu_{e i} n_{\infty}$$  \hspace{1cm} (5)

where $\nu_{e i}$ is the number of the molecules of the condensed substance in the equilibrium heterogeneous embryo. During the period of the essential formation of the droplets one can assume that the value $\nu_{e i}$ is the constant one and take it at $\zeta = \Phi_\ast$. Ordinary $\nu_{e i}$ can be taken at $\zeta = \zeta(0)$.

The following statements can be analytically proved for the consideration of this process:

- (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.

The justification of the second statement uses the estimate for the times $t_s^i$ of the establishing of the stationary state in the near-critical region which can be found in [3], [24] (for the heterogeneous barrier the consideration is the same one). Here it is necessary to remark that, certainly, there may exists some rather huge times $t_s^i$. They correspond to some rather big values of the number of the molecules inside the critical embryos. The half-width of the near-critical region can be estimated by the homogeneous value at the supersaturation corresponding to the same value of the number of the molecules inside the critical embryo. It is proportional to $\nu_{e i}^{2/3}$. Here and in the further considerations the lower index "c" marks the values for the critical embryos. As far as the absorption ability is proportional to $\nu_{c i}^{2/3}$ and the size of the near-critical region is proportional to $\nu_{c i}^{2/3}$ then the value of $t_s^i$ is proportional to $\nu_{c i}^{2/3}$. The big value of the activation barrier $\Delta F_i = F_i(\nu_c)$ in the case when $\nu_c$ is greater than the characteristic length $\Delta x$ of the size spectrum means that these kinds of the heterogeneous centers are excluded from the kinetic process.

One can analytically prove that during the period of the intensive formation of the droplets of one sort or for all sorts

- the variation of the supersaturation allows the estimate

$$|\zeta - \zeta_\ast| \leq \frac{\Phi_\ast}{\Gamma}$$

where

$$\Gamma_i = -\Phi_\ast \frac{dF(\zeta)}{d\zeta} \bigg|_{\zeta = \Phi_\ast}$$  \hspace{1cm} (6)

For the majority of the types of the heterogeneous centers the following approximations of the nucleation rates $J_i$ are valid during the period of the essential formation of the droplets

$$J_i = J_i(\eta_{\text{tot } i}, \Phi_\ast) \exp(\Gamma_i \frac{(\zeta - \Phi_\ast)}{\Phi_\ast}) \frac{\eta_i}{\eta_{\text{tot } i}}$$  \hspace{1cm} (7)

The validity of these approximations is justified for the heterogeneous embryos with the monotonous interaction between the center and the molecules of the condensed substance weaker or equal than the interaction reciprocal to the space distance.

Let $f_{\ast i}$ be the amplitude value of the distribution of sizes of the heterogeneously formed droplets measured in units of $n_{\infty}$. The supersaturation $\Phi_\ast$ and the number of the heterogeneous centers $\eta_{\text{tot } i}$ are the already known values. Then the stationary distribution $f$ can be easily calculated by the following known formulas:

$$\frac{J_i}{\alpha \zeta n_{\infty}} = f = \frac{W^+_c \exp(-\Delta F)\tau}{n_{\infty} \pi^{1/2} \Delta e i \nu \Delta c i \nu \zeta \alpha \eta_i}$$  \hspace{1cm} (8)
where $W^+$ is the number of the molecules absorbed by the critical embryo in the unit of time, $\Delta \nu$ is the characteristic width of the equilibrium distribution

$$\Delta \nu = \sum_{\nu=1}^{\nu=(\nu_c+\nu_e)/2} \exp(-F(\nu))$$

and $\Delta \nu$ is the halfwidth of the near-critical region

$$\Delta \nu = \frac{2^{1/2}}{|\frac{\partial^2 F}{\partial \nu^2}|^{1/2} \nu = \nu_c}$$

We shall mark by $n_{\infty}g_i$ the total number of the vapor molecules in the droplets formed on the centers of the sort $"i"$. To simplify the formulas we shall use

$$\theta_i = \frac{\eta_i}{\eta_{\text{tot} i}}$$

Using the conservation laws for the heterogeneous centers and for the molecules of the substance we obtain for $g_i, \theta_i$ the following equations

$$g_i = f_i \int_0^{z} (z-x)^3 \exp(-\Gamma \frac{\sum_j g_j}{\Phi_i}) \theta_i dx \equiv G_i(\sum j g_j, \theta_i)$$

$$\theta_i = \exp(-f_i \frac{n_{\infty}}{\eta_{\text{tot} i}} \int_0^{z} \exp(-\Gamma \frac{\sum_j g_j}{\Phi_i}) dx) \equiv S_i(\sum j g_j)$$

where $f_i = J_i(\eta_{\text{tot} i}, \Phi_i), \Phi = \alpha n_{\infty}$.

These equations form the closed system of the condensation equations. This system will be the subject of our investigation. For simplicity we shall investigate it for $i = 1, 2$. 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:

$$N_i = \eta_{\text{tot} i} (1 - \theta_i(z)) \equiv Q_i(\theta_i)$$

The spectrum of sizes can be found as the following one

$$f_i = f_i \exp(-\Gamma \frac{\sum_j g_j}{\Phi_i}) \theta_i$$

4 Formal generalization of iteration method

The formal transformation of the iteration method for the process of condensation on the one sort of the heterogeneous centers leads to the following equations:

$$g_i(t+1) = G_i(\sum j g_j(t), \theta_i(t))$$

$$\theta_i(t+1) = S_i(\sum j g_j(t))$$

$$N_i(t) = Q_i(\theta_i(t))$$

$$g_i(0) = 0$$

$$\theta_i(0) = 1$$

$$g_i(1) = f_i \frac{z^4}{4}$$
\[
\theta_i(1) = \exp(-f_* i n_{i\infty} \eta_{i\text{tot}})
\]

\[
N_i(2)(\infty) = \eta_{i\text{tot}} [1 - \exp(-f_* i n_{i\infty} \sum_j \frac{\Gamma_i f_j}{4\Phi_j})^{-1/4} A)]
\]

where

\[
A = \int_0^\infty \exp(-x^4) dx \approx 0.9
\]

The third iteration cannot be calculated in the analytical form. Meanwhile one can prove the convergence of the iterations analytically.

Let us analyze the expression for \(N_i(2)(\infty)\). Assume for a moment that for some \(i\) and \(j\)

\[f_* i \gg f_* j\]

Let us decrease \(\eta_{i\text{tot}}\) keeping the constant value of \(f_* i\) which is proportional to \(\eta_i\) with the fixed dependence on \(\zeta\) by the increasing of the activity of the heterogeneous centers of the sort "i", i.e. by the decreasing of the height of the heterogeneous activation barrier. It is obvious that when \(\eta_{i\text{tot}}\) is small then the total number of the heterogeneously formed droplets coincides with the total quantity of the heterogeneous centers and goes to zero when \(\eta_{i\text{tot}}\) goes to zero. The value of \(g_i\) at the end of the period of formation of the droplets on the heterogeneous centers of the sort "j" can be estimated as

\[g_i \leq \frac{\eta_{i\text{tot}} (\hat{\Delta}x_j)^3}{n_{i\infty}}\]

where \(\hat{\Delta}x_j\) is the width of the size spectrum (the size distribution function) of the droplets of the sort "j". This value of \(\hat{\Delta}x_j\) is above restricted by the value \(\Delta x_j\) which is the width of the size spectrum without any influence of the droplets of the other sorts. Certainly, the value of \(\Delta x_j\) doesn't depend on \(\eta_{i\text{tot}}\) and on \(f_* i\) for all \(i\). Hence, the influence of the heterogeneous centers of the sort \(i\) on the process of condensation on the centers of the sort \(j\) becomes unessential (negligible) in the limit \(\eta_{i\text{tot}} \to 0\). At the same time the expression for \(N_j(2)(\infty)\) shows that in the limit \(\eta_{i\text{tot}} \to 0\), \(f_* i = const\) the influence of the heterogeneously formed droplets of a sort \(i\) doesn't become unessential. This leads to the enormous error in \(N_j(\infty)\). One cannot obtain the analytical expression in the third approximation for \(N_j\) in the frames of the standard iteration method and the second iteration gives the wrong qualitative results.

The reason for the deviation in the results from the pure heterogeneous consideration is the following one. In the case when the interruption of the embryos formation is caused by the exhaustion of the heterogeneous centers the error in the value of \(g\) is compensated by the squeezing force of the operator \(S_i\). The analogous property isn't valid for the operator \(Q_i\) due to the cross influence of the droplets formed on some different sorts.

Note that the procedure of this section can be successfully applied for the heterogeneous condensation on the centers of the one sort. Then one can analytically prove that the relative error of \(N(2)\) is less than 0.015.

## 5 Limit cases

The remarkable property of condensation in the situation considered here is that we can construct the theory by the simple investigation of all limit cases and cover practically all situations.

At first we shall extract the characteristic sizes in order to construct rather a simple solution.

### 5.1 Characteristic lengths

The direct generalization of the iteration method fails due to the unappropriated account of the cross influence of the heterogeneous droplets of some different sorts. Nevertheless it allows to define the spectrum of the droplets in a proper way when the cross influence is eliminated. Hence, we may use it to get the characteristics of the "self-formation" of the droplets of the various sorts.
On a base of the first iterations in the general procedure one can realize that for some process of a separate formation there are two characteristic lengths. The first one is the length of spectrum in the situation when there are no exhaustion of the heterogeneous centers (and no droplets of the other sort). One can say that condensation occurs in the pseudo-homogeneous way. For this characteristic value we have:

$$\Delta_i x = \left( \frac{4\Phi_*}{\Gamma_i f_* i} \right)^{1/4}$$  \hspace{1cm} (22)

This length is going from the first iteration for $g_i$ if the process is split into the separate processes of condensation.

The second length is the length of the spectrum when there is no vapor exhaustion but only the exhaustion of the heterogeneous centers. Then the width of the spectrum is:

$$\delta_i x = \frac{\eta_{tot \ i}}{f_* i n_{\infty}}$$  \hspace{1cm} (23)

This length is going from the first iteration for $\theta_i$.

Practically the hierarchy between $\Delta_i x$, $\delta_j x$ is ensured by the hierarchy between $f_* i$, $\eta_* j$. The values of $\Gamma_i$ are rather (in comparison with $f_* i$) unsensible to the value of the supersaturation. Really:

$$-\frac{\Gamma_i}{\zeta} = \frac{d\Delta F}{d\zeta} \sim \frac{dF_c}{d\zeta} - \frac{dG}{d\zeta}$$  \hspace{1cm} (24)

In the frameworks of the barrier character of condensation ($\Delta F \gg 1$) we can give the above estimate for $(dF_c/d\zeta)$ for the force of the interaction between the heterogeneous center and the molecules of a liquid when this force decreases monotonously in space. The value of $(dF_c/d\zeta)$ can be above estimated by its value in the limit of the homogeneous condensation $(dF_c^{\text{hom}}/d\zeta)$. As far as the energy of solvatation depends on the supersaturation essentially weaker than $(dF_c/d\zeta)$ we can neglect the last term of the previous equation and obtain:

$$\frac{d\Delta F}{d\zeta} \sim \frac{dF_c^{\text{hom}}}{d\zeta}$$  \hspace{1cm} (25)

But this dependence is rather weak one in comparison with the very sharp $f_* i$ dependence on the supersaturation.

Another one important fact is the frontal character of the back side of the spectrum in the pseudo-homogeneous situation (when $\Gamma_i$ plays some role\[\text{5}]) The frontal character can be seen from

$$f_i = f_* i \exp\left(-\frac{\Gamma_i}{4\Phi_*} \sum_j f_* j z^4\right)$$  \hspace{1cm} (26)

Hence, the essential variation of the length $\Delta_i x$ can be caused only by the enormous variation of $f_* i$.

Instead of $\delta_i x$ we shall use the parameter

$$h_i = \frac{\delta_i x}{\Delta_i x}$$  \hspace{1cm} (27)

In the reasons of simplicity we shall restrict ourselves by two sorts of the heterogeneous centers.

### 5.2 The case $\Delta_1 x \sim \Delta_2 x$

#### 5.2.1 Situation $h_1 \ll 1$, $h_2 \geq 1$

In this situation the following fact can be noticed:

- The process of formation of the droplets on the heterogeneous centers of the first sort (the "first sort droplets") doesn’t depend on formation of the droplets of the second sort.

\[\text{5}]\text{The pseudo homogeneous situation can be treated as the situation when the centers of condensation remain practically unexhausted (in relative sense).}
It can be directly seen from the chain of inequalities
\[ \delta_1 x \ll \Delta_1 x \sim \Delta_2 x \leq \delta_2 x \] (28)

So we can describe the process of formation of the first sort droplets by the following equalities:
\[ g_1 = f_{*1} \int_0^z (z - x)^3 \exp\left(-\Gamma_1 \frac{g_1(x)}{\Phi_*}\right) \theta_1 dx \equiv G_1(g_1, \theta_1) \] (29)
\[ \theta_1 = \exp\left(-f_{*1} n_{\etatot1} \int_0^z \exp\left(-\Gamma_1 \frac{g_1(x)}{\Phi_*}\right) dx \right) \equiv S_1(g_1) \] (30)

This system can be solved by the following iterations
\[ g_{1(i+1)} = G_1(g_{1(i)}, \theta_{1(i)}) \] (31)
\[ \theta_{1(i+1)} = S_1(g_{1(i)}) \] (32)
\[ N_{1(i)} = Q_1(\theta_{1(i)}) \] (33)

The operators \( G_1, S_1 \) and \( Q_1 \) have some remarkable properties. When for all values of the arguments we have
\[ w_1 \leq w_2 \]
then
\[ S_1(w_1) \leq S_1(w_2) \]
is valid for all values of the arguments. When for all values of the arguments we have
\[ w_1 \leq w_2 \]
then
\[ Q_1(w_1) \geq Q_1(w_2) \]
is valid for all values of the arguments. When for all values of the arguments we have
\[ w_1 \leq w_2 \]
\[ v_1 \geq v_2 \]
then
\[ G_1(v_1, w_1) \leq G_1(v_2, w_2) \]
is valid for all values of the arguments. Let us choose the initial approximations as the following ones
\[ g_1(0) = 0 \] (34)
\[ \theta_1(0) = 1 \] (35)

We see that
\[ g_1(0) \leq g_1 \]
\[ g_1(0) \leq g_1(i) \]
for an arbitrary \( i \), and
\[ \theta_1(0) \geq \theta \]
\[ \theta_1(0) \geq \theta_1(i) \]
for an arbitrary \( i \). Particularly, the following estimate is valid
\[ N_1(2) \leq N_1 \leq N_1(3) \] (36)
These estimates allow to prove the convergence of the iterations. The calculation of the iterations gives

\[ g_1 (1) = f_\ast \frac{z^4}{4} \]

\[ \theta_1 (1) = \exp(-f_\ast \frac{n_{\infty}}{\eta_{\text{tot}} 1}z) \]

\[ N_1 (2)(\infty) = \eta_{\text{tot}} 1 (1 - \exp(-f_\ast \frac{n_{\infty}}{\eta_{\text{tot}} 1} (\frac{\Gamma_1}{4\Phi_\ast})^{-1/4} f_\ast^{-1/4} A)) \]

As far as one can prove that

\[ \frac{d}{dx} \mid N_1 (i) - N_1 (j) \mid \geq 0 \]

then by the simple numerical calculation of \( N_1(3)(\infty) \) one can easy obtain that

\[ \frac{|N_1 (2) - N_1 |}{N_1} \leq 0.015 \]

which completes the iteration procedure.

On the base of the iterations one can get some approximations for the supersaturation:

\[ \zeta_{(t+1)} = \Phi_\ast - f_\ast 1 \int_0^z (z - x)^3 \exp(-\Gamma_1 \frac{g_1 (i)}{\Phi_\ast}) \theta_1 (i) dx \]

The strong inequality allows to obtain the second approximation for \( \zeta \)

\[ \zeta (2) = \Phi_\ast - f_\ast 1 \int_0^z (z - x)^3 \exp(-Hx)dx \]

where

\[ H = \frac{f_\ast 1 n_{\infty}}{\eta_{\text{tot}} 1} \]

or after the calculation

\[ \zeta (2) = \Phi_\ast + f_\ast 1 [-\frac{z^3}{H} + \frac{3z^2}{H^2} - \frac{6z}{H^3} + \frac{6}{H^4} - \frac{6}{H^4} \exp(-Hz)] \]

This expression can be simplified. Let us notice that the supersaturation appears in the expression for the size spectrum \( f(x) \) in the following form

\[ \exp(-\Gamma_1 \frac{\zeta - \Phi_\ast}{\Phi_\ast}) \]

After the substitution of \( \zeta (2) \) into this expression we realize that in the case when \( \zeta \) deviates essentially from \( \Phi \) all the terms except the first two terms can be neglected:

\[ \zeta (2) = \Phi_\ast - z^3 \frac{\eta_{\text{tot}} 1}{n_{\infty}} \]

Hence, for the second sort we can obtain the following system of equations

\[ g_2 = f_\ast 2 \int_0^z (z - x)^3 \exp(-\Gamma_2 \frac{g_2 (x) + (\eta_{\text{tot}} 1/n_{\infty}) x^3\Phi_\ast}{\Phi_\ast}) \theta_2 dx \equiv G_2 (g_2 + (\eta_{\text{tot}} 1/n_{\infty}) x^3, \theta_2) \]

and

\[ \theta_2 = \exp(-f_\ast 2 \frac{n_{\infty}}{\eta_{\text{tot}} 2} \int_0^z \exp(-\Gamma_2 \frac{g_2 (x) + (\eta_{\text{tot}} 1/n_{\infty}) x^3\Phi_\ast}{\Phi_\ast}) dx) \equiv S_2 (g_2 + (\eta_{\text{tot}} 1/n_{\infty}) x^3) \]

Having introduced

\[ \lambda_2 = g_2 + (\eta_{\text{tot}} 1/n_{\infty}) x^3 \]
we can rewrite this system as

\[ \lambda_2 = G_2(\lambda_2, \theta_2) + (\eta_{tot \ 1}/n_{\infty})z^3 \equiv G_2^+(\lambda_2, \theta_2) \quad (49) \]

\[ \theta_2 = S_2(\lambda_2) \quad (50) \]

The operator \( G_2^+ \) has the same properties as \( G_1, G_2 \) have. All estimates (34)-(36) remain valid after the substitution of the index "2" instead of "1" and the operator \( G^+ \) instead of \( G \). Moreover one can see that

\[ \frac{d}{d(\eta_{tot \ 1}/n_{\infty})} | N_2 (i) - N_2 (j) | \leq 0 \quad (51) \]

which leads to the same estimate of the relative error (0.015) as in the pure heterogeneous condensation of a separate sort.

Actually we can avoid here the calculations according to such a complex procedure. Let us notice that the term \( \eta_{tot \ 1}z^3/n_{\infty} \) ensures the characteristic length

\[ D_1 = (\frac{\Phi_{*}n_{\infty}}{\Gamma_2\eta_{tot \ 1}})^{1/3} \quad (52) \]

Really

\[ D_1 \geq \epsilon \Delta_1x \sim \epsilon \Delta_2x \quad \epsilon \sim (3 \pm 1) \quad (53) \]

So, condensation on the centers of the second sort occurs in the separate way and we can use formulas (29)-(33), (37)-(40) with the substitution of the index "2" instead of the index "1".

5.2.2 Situation \( h_1 \geq 1, \ h_2 \ll 1 \)

As far as \( \Delta_1 \sim \Delta_2 \) we can change the numbers of sorts and reduce this situation to the previous one.

5.2.3 Situation \( h_1 \geq 1, \ h_2 \geq 1 \)

In order to analyze this situation we must realize why in the separate condensation of one sort the second iteration gives rather precise results. This fact is explained by the free molecular regime of the vapor consumption which leads to the power 3 in the expression for \( g \). Due to rather a great (in comparison with 1) value of this power the droplets of the big sizes situated near the front side of the spectrum are the main consumers of the vapor. These droplets have rather a small (in comparison with \( \Delta_i x \)) values of the variable \( x \). The exhaustion of the heterogeneous centers due to \( h_1 \geq 1, h_2 \geq 1 \) doesn’t affect in a strong manner on the process of their formation. Hence, the cross influence is rather weak and we can use the general iteration procedure. After the calculation of the iterations we have

\[ g_1 (1) = f_1 + z^4 \frac{1}{4} \quad (54) \]

\[ \theta_1 (1) = \exp(-f_1 n_{\infty}/\eta_{tot \ 1}) \quad (55) \]

\[ N_1 \ (2)(\infty) = \eta_{tot \ 1}[1 - \exp(-f_1 n_{\infty}/\eta_{tot \ 1}((\frac{\Gamma_1}{4\Phi_{*}})f_1 + (\frac{\Gamma_1}{4\Phi_{*}})^{-1/4}A))] \quad (56) \]

\[ g_2 (1) = f_2 + z^4 \frac{1}{4} \quad (57) \]

\[ \theta_2 (1) = \exp(-f_2 n_{\infty}/\eta_{tot \ 2}) \quad (58) \]

\[ N_2 \ (2)(\infty) = \eta_{tot \ 2}[1 - \exp(-f_2 n_{\infty}/\eta_{tot \ 2}((\frac{\Gamma_2}{4\Phi_{*}})f_2 + (\frac{\Gamma_2}{4\Phi_{*}})^{-1/4}A))] \quad (59) \]
5.2.4 Situation $h_1 \ll 1, h_2 \ll 1$

As far as
\[ \delta_1 x \ll \Delta_1 x \sim \Delta_2 x \]
the droplets formed on the heterogeneous centers of the second sort don’t act on the process of formation of the droplets on the heterogeneous centers of the first sort. Due to
\[ \delta_2 \ll \Delta_2 x \sim \Delta_1 x \]
the same fact is valid for the droplets formed on the other sort of the heterogeneous centers. Hence, the system is split into some parts corresponding to the separate processes of condensation on the different sorts.

Constructions (29)-(33) can be reproduced here. But in the case $h_i \ll 1$ for all $i$ the vapor exhaustion can be neglected in comparison with the exhaustion of the heterogeneous centers. In this situation we can obtain some precise explicit results for the values of $f_i(x), \zeta(x), \theta_i(x)$:

\[ \theta_1(x) = \exp(-f_1 x n_\infty/z) \]
\[ \theta_2(x) = \exp(-f_2 x n_\infty/z) \]
\[ f_1(x) = f_* \exp(-f_1 x n_\infty/z) \]
\[ f_2(x) = f_* \exp(-f_2 x n_\infty/z) \]
\[ \zeta = \Phi_* - (\eta_\text{tot} 1 n_\infty + \eta_\text{tot} 2 n_\infty)z^3 \]

This expression for $\zeta$ is obtained by the same procedure as that which led to (45).

5.3 Case $\Delta_1 x \ll \Delta_2 x$

The case $\Delta_2 x \gg \Delta_1 x$ is symmetrical to this case and can be considered by the simple change of the indexes.

Due to $\Delta_1 x \ll \Delta_2 x$ the droplets of the second sort don’t act on the process of formation of the droplets of the first sort. Hence, the process of formation of the droplets of the first sort can be described by the iteration procedure from the section 5.2.1 (eq.(29)-(40)).

5.3.1 Situation $h_1 \ll 1, h_2 \geq 1$

Due to $h_1 \ll 1$ the equation for the first sort can be simplified and we have the following equations

\[ g_1 = f_* 1 \int_0^z (z-x)^3 \exp(-H x) dx \sim \frac{\eta_\text{tot} 1 n_\infty}{z^3} \]

The value of $\theta_1$ is given by (62), the value of $f_1$ is given by (64).

For condensation on the centers of the second sort we have some equations analogous to (46),(47). So we can adopt here equations (48)-(51). But in this situation inequality (53) isn’t valid and we must calculate the iterations. We can choose $\lambda_2 (0) = 0$ and get

\[ \lambda_2 (1) = f_* 2 \int_0^z (z-x)^4 \exp(-H x/n_\infty)^2 + \frac{\eta_\text{tot} 1 n_\infty}{z^3} \]

\[ \theta_2 (2) = \exp(-f_* 2 \int_0^z \exp(-\frac{x}{\Delta_\infty 2x})^4 - (\frac{x}{\Delta h_1 x})^3) dx \]

where

\[ \Delta_\infty 2x = \left( \frac{4 \Phi_*}{\Gamma_2 f_*} \right)^{1/4} \equiv \Delta_2 x \]
and

$$\Delta_{h_1x} = \left(\frac{\Phi_s n_{\infty}}{\Gamma_2 \eta_{\text{tot}} 1}\right)^{1/3} \equiv D_1$$

The value of $\Delta_{\infty 2x}$ has the sense of the spectrum width when the cross influence and the exhaustion of the heterogeneous centers of this very sort are neglected. The value of $\Delta_{h_1x}$ has the sense of the spectrum width when the vapor consumption by the droplets is neglected.

In addition one can easily prove that

$$\frac{d}{dx} | N_2 (i) - N_2 (j) | \geq 0$$

and

$$\frac{d}{d\eta_{\text{tot}} 1} | N_2 (i) - N_2 (j) | \leq 0$$

for $i, j \geq 2$. Hence, it is easy to show that

$$\frac{| N_2 (2) - N_2 |}{N_2} \leq 0.015$$

by the calculation of $N_2 (2) (\infty)$ and $N_2 (3) (\infty)$ at $\eta_{\text{tot}} 1 = 0$. The analytical approximation valid for the clear interpretation can be obtained if we notice that

$$\theta_2 (2) (\infty) = \exp[-f_{s 2} x \Delta_{\infty 2x} n_{\infty} \frac{\eta_{\text{tot}} 2}{\Phi_s} \left(\frac{\Delta_{\infty 2x}}{\Delta_{h_1x} 2x}\right)^4 - 1/4 + \frac{B}{2} (1 + \left(\frac{\Delta_{\infty 2x}}{\Delta_{h_1x} 2x}\right)^3 - 1/3)] \quad (70)$$

where

$$B = \int_0^\infty \exp(-x^3) dy$$

with the relative error less than 0.02.

The spectrum of sizes of the droplets formed on the centers of the second sort is the following one

$$f_2 = f_{s 2} \exp\left(-\frac{\Gamma_2 f_{s 2} z^4}{4 \Phi_s}\right) \exp\left(-\frac{\Gamma_2 \eta_{\text{tot}} 1 z^3}{\Phi_s n_{\infty} x}\right) \exp\left(-f_{s 2} \frac{n_{\infty}}{\eta_{\text{tot}} 2} \int_0^z \exp(-\frac{x}{\Delta_{\infty 2x}} x^4 - \frac{x}{\Delta_{h_1x} 2x}) dx\right) \quad (71)$$

5.3.2 Situation $h_1 \geq 1, h_2 \ll 1$

The description of the process of formation of the droplets on the centers of the first sort can’t be simplified. It has been already fulfilled in the previous sections. But the process of formation of the droplets on the centers of the second sort is rather simple to describe. The supersaturation is absolutely determined by the vapor consumption by the droplets formed on the centers of the first sort. Hence, we have the following expressions

$$\theta_2 = \exp[-f_{s 2} n_{\infty} \frac{\eta_{\text{tot}} 2}{\Phi_s} \int_0^z \exp(-\Gamma_2 \frac{g_1}{\Phi_s}) dx] \quad (72)$$

$$g_2 = f_{s 2} \int_0^z (z - x)^3 \exp(-\Gamma_2 \frac{g_1}{\Phi_s}) \theta_2 dx \quad (73)$$

The value of $g_2$ during the period of nucleation on the centers of the second sort can be estimated in the following way

$$g_2 \ll \frac{\Phi_s}{\Gamma_2}$$

which is presented on the base of

$$\delta_{2x} \ll \Delta_{2x}$$

It is necessary to calculate only $\theta_2$. To calculate $\theta_2$ one can get into account that the value of $g_1$ grows so rapidly that for the value $\int_0^z \exp(-\Gamma_2 \frac{g_1}{\Phi_s}) dx$ one can show the following approximation

$$\int_0^z \exp(-\Gamma_2 \frac{g_1}{\Phi_s}) dx \approx z \Theta(1 - \frac{\Gamma_2 g_1}{\Phi_s}) + \int_0^\infty \exp(-\Gamma_2 \frac{g_1}{\Phi_s}) dx \Theta\left(\frac{\Gamma_2 g_1}{\Phi_s} - 1\right)$$
\[
\int_0^z \exp(-\Gamma g_1 \Phi) dx \approx z \Theta(1 - \frac{\Gamma g_1}{\Phi}) + z_b \Theta(\frac{\Gamma g_1}{\Phi} - 1)
\]
where \( z_b \) is extracted by the condition
\[
g_1(z_b) = \frac{\Phi}{\Gamma_2}
\]
and \( \Theta \) is the Heaviside’s function. The last approximation solves the problem of the analytical calculation of \( \theta_2 \).

5.3.3 Situation \( h_1 \geq 1, h_2 \geq 1 \)

Actually, the situation \( h_1 \geq 1, h_2 \geq 1 \) has been already described in the previous subsection. Due to \( \Delta_1x \ll \Delta_2x \) one can’t assume here that the inequality \( h_2 \ll 1 \) ensures the pure exhaustion of the heterogeneous centers without any vapor exhaustion and the consideration made in the previous section can’t be simplified.

5.3.4 Situation \( h_1 \ll 1, h_2 \ll 1 \)

From the first point of view it seems that the situation \( h_1 \ll 1, h_2 \ll 1 \) has been already described in the section 5.2.4. We have to stress that the equation \( h \ll 1 \) doesn’t allow to state that the process of condensation is going at the constant value of the supersaturation. For the process of condensation on the centers of the first sort we have previous expressions (62), (64). Analogous expressions (63), (65) for condensation on the centers of the second sort can be violated. So, the process of condensation on the centers of the second sort can not be described on the base of the unexhausted value of the vapor supersaturation.

The calculation of \( g_2 \) isn’t necessary and only the calculation of \( \theta_2 \) is essential. We have
\[
\theta_2(2) = \exp(-f^* 2 \frac{n_\infty}{\eta_{tot}} \int_0^z \exp(-\frac{x}{\Delta h 1x}) dx)
\]
and the final value for \( \theta_2 \) can be given by
\[
\theta_2(2)(\infty) = \exp[-f^* 2 \Delta h 1x \frac{n_\infty}{\eta_{tot}} B]
\]

The monodisperse approximation is based on the evident chain of the inequalities
\[
\hat{\Delta}x_1 \sim \delta_1x \ll \Delta_1x \leq \hat{\Delta}x_2
\]
or the monodisperse term isn’t essential.

We have investigated all possible situations.\[6\]

6 General approximate solution

The reason why the general iteration procedure fails lies in the fact that we don’t know the true expression for \( g_i(z) \). In the case of condensation on the centers of the separate sort we don’t know this expression only when the spectrum is cut off by the exhaustion of the heterogeneous centers. So we don’t know it in the situation then the converging force of the operator in the expression for \( \theta \) is very strong. In the case of the several components the situation is different. We don’t know every term in \( \sum_j g_j(z) \). Hence, we may come to the situation when according to the first iteration the spectrum is cut off by the exhaustion of the supersaturation initiated by the other component but in reality the heterogeneous centers of the other component are exhausted and and the droplets formed on these centers consume the vapor much more weaker (simply due to their quantity). So, it is necessary to invent the new more precise expression for \( g_i \) which allows to calculate the next iteration in \( \theta \).

\[6\]It doesn’t follow that all of them can be really reproduced in the nature.
6.1 Monodisperse approximation

As it is stated in section 5.1 the length corresponding to the cut-off of the supersaturation which leads to the cut-off of the spectrum by the exhaustion of the substance is practically one and the same for all sorts of the droplets (all $\Gamma_i$ have approximately one and the same order). Let us see the droplets of what sizes play the leading role in this cut-off. Analyzing the subintegral expression in the equation for $g_i$ we realize that the subintegral expression connected with the variation of the supersaturation is a very sharp function of $x$. It is less than the function

$$s_{bel} = \Theta(z - x)(z - x)^3$$

and greater than the function

$$s_{ab} = \Theta(z - x)(z - x)^3 \exp\left(-\frac{\Gamma_i \sum_j f_{*j} x^4}{\Phi_*}\right)$$

Let us introduce the approximation for this function. We must extract the region of the sizes of the droplets which are essential in the vapor consumption. This consumption is essential when

$$x \approx \Delta x$$

where $\Delta x$ is the length of the cut-off by the supersaturation. Certainly, the region of the sizes of the droplets which are essential in the vapor consumption must have the sizes rather small in comparison with $\Delta x$ because the successful iteration procedure in the homogeneous decay is based on the fact that the droplets formed at the almost ideal supersaturation determine the process of formation of the spectrum. For the differential halfwidth $\delta_{1/2}$ we have the following expression

$$\delta_{1/2} x = (1 - \frac{1}{2^{1/3}}) x$$

The integral halfwidth $\Delta_{1/2} x$ can be obtained from the corresponding equation

$$N_{ess} x^3 = f_* \frac{x^4}{4} n_\infty$$

where $N_{ess}$ is the characteristic number of the droplets obtained as $N_{ess} = f_* \Delta_{1/2} x n_\infty$ which gives

$$\Delta_{1/2} x = \frac{1}{4} x$$

and it practically coincides with $\delta_{1/2} x$.

Figure 1 illustrates the behavior of the values $s_{ab}$ and $s_{bel}$ as the functions of $x$. It can be seen that they practically coincide. This lies in the base of the applicability of the first iteration as a good approximation for the precise solution.

So, the subintegral function $s$ is now decomposed into the essential part where

$$x \leq \frac{\Delta x}{4}$$

and the tail where

$$x \geq \frac{\Delta x}{4}$$

We shall neglect the tail and due to rather a small size of the essential region we shall use the monodisperse approximation for the droplets formed in this region. As the result we obtain the approximation for $g(x)$

$$g(z) = \frac{N(z/4)}{n_\infty} z^3$$

where $N(z/4)$ is the number of the droplets appeared from $x = 0$ till $x = z/4$. 

15
As far as the spectrum is cut off by the exhaustion of the supersaturation in a frontal (sharp) manner the value of \( g_i \) is unessential before \( z = \Delta_i x \) as a small one and after the moment of the cut-off it is unessential also as there is no formation of the droplets.

So instead of the previous approximation we can use

\[
    g_i(z) = \frac{N_i(\Delta_i x/4)}{n_\infty} z^3
\]

The process of the exhaustion of the heterogeneous centers makes the subintegral function more sharp and the monodisperse approximation becomes at \( \Delta_i x \) even better than in the pseudo homogeneous situation. But the exhaustion of the heterogeneous centers makes the coordinate of the cut-off of the supersaturation greater than \( \Delta_i x \) and the monodisperse approximation becomes even more better at the moment of the cut off of the imaginary supersaturation. Certainly, we must use \( N(\Delta_i x/4) \) calculated with account of the exhaustion of the heterogeneous centers (but at the coordinate, obtained without any account of the exhaustion of the heterogeneous centers).

Figure 2 illustrates the form of the spectrum in the "monodisperse approximation". The case of the pseudo homogeneous condensation is considered. Here two curves are drawn: the spectrum in the monodisperse approximation \( f_{\text{appr}} \) and the spectrum in the first iteration \( f_1 \) which can be considered as a very precise approximation. The first iteration has the more sharp back side (the front side in \( z \) scale) than the "monodisperse approximation. Nevertheless the deviation isn't so essential. It can be eliminated by the perturbation theory.

The concluding remarks concern the fact that we can obtain \( N(\Delta_i x/4) \) by the solution of the equations for the separate condensation process because we need the lowest length of the cut-off. This length is given without any cross influence taking into account due to the frontal character of the back side of the spectrum.

### 6.2 Final iterations

The solution of the system of the condensation equations is given by the following procedure.

At first we must solve the equations for the separate processes

\[
    g_i = f_{\ast i} \int_0^z (z - x)^3 \exp(-\Gamma_i g_i/\Phi_\ast) dx \equiv G_i(g_i, \theta_i) \tag{84}
\]

\[
    \theta_i = \exp(-f_{\ast i} n_\infty \eta_{\text{tot} i} \int_0^z \exp(-\Gamma_i g_i/\Phi_\ast) dx) \equiv S_i(g_i) \tag{85}
\]

for every \( i \).

This solution can be obtained by the iteration procedure described in section 4. The remarkable fact is that in the second approximation we can calculate the value of \( \theta(2)(\Delta_i x/4) \)

\[
    \theta_i(2)(\Delta_i x/4) = \exp(-f_{\ast i} n_\infty \frac{\eta_{\text{tot} i}}{1/4} \int_0^{\Delta_i x/4} \exp(-\Gamma_i f_{\ast i} z^4) dx)
\]

\[
    \theta_i(2)(\Delta_i x/4) = \exp(-f_{\ast i} n_\infty \frac{\Gamma_i f_{\ast i} (\eta_{\text{tot} i})^{-1/4} C}{4 \Phi_\ast}) \tag{87}
\]

where

\[
    C = \int_0^{1/4} \exp(-z^4) dx \approx 0.25 \tag{88}
\]

and \( N_i(2)(\Delta_i x/4) \) has the following value

\[
    N_i(2)(\Delta_i x/4) = \eta_{\text{tot} i} (1 - \theta_i(2)(\Delta_i x/4)) \tag{89}
\]

So the approximations for \( g_i \) are obtained now. We must fulfill these calculations for every sort of the heterogeneous centers. Considering these approximations as the initial ones it is necessary to do only one step of the iteration procedure to get the suitable results. They will be marked as the "final" ones.
Now we remove to the general iteration procedure. The only thing we have to do is to calculate $\theta_{i \text{ final}}(\infty)$ and $N_{i \text{ final}}(\infty)$. We have to obtain these values due to the iterations

$$
\theta_{i \text{ final}}(z) = \exp[-f_s \cdot \sum \frac{\Gamma_j N_j (\Delta_j z / 4)}{\eta_{\text{tot}} i} \int_0^z \exp(-\sum \frac{\Gamma_j N_j (\Delta_j z / 4)}{\Phi_n i}) dx]
$$

$$
N_{i \text{ final}}(\infty) = \eta_{\text{tot}} i [1 - \exp(-f_s \cdot \sum \frac{\Gamma_j N_j (\Delta_j z / 4)}{\Phi_n i})]^{-1/3} B
$$

All these equations are valid under the reasonable separation of the heterogeneous centers into the sorts when the centers with one and the same height of the activation barrier are considered as one sort. Meanwhile it is obvious that if we split one sort into very many subsorts then we can formally attain a wrong result.

Let us suppose that the number of the heterogeneous centers is so great that $h_i \gg 1$, i.e. the fall of the supersaturation leads to the interruption of formation of the droplets. We shall split this sort into so many subsorts that for every subsort $h_{ij} \ll 1$, i.e. we can see the exhaustion of the subsort in the separate process of condensation. Moreover, we can assume that this exhaustion finishes before $z$ attains the quarter of the length of the spectrum initiated by the fall of the supersaturation. Really, as far as $\Delta_j x$ is proportional to $\eta_{ij \text{ tot}}^{-1/4}$ (where $\eta_{ij \text{ tot}}$ is the total number of the centers of the given subsort) and $\delta_{ij} x$ doesn’t depend on this quantity the required property is obvious. Then after the summation over all subsorts we come to the conclusion that the total number of the droplets formed up to $\Delta_j x / 4$ coincides with the total number of the heterogeneous centers. This conclusion isn’t valid.

The reason of the error is that the width of the spectrum is much more small than the width in the process of the separate formation. Evidently, the monodisperse approximation doesn’t work at such distances. Ordinary, under the reasonable definition of the heterogeneous sorts all characteristic lengths are different. So, ordinary, there is no such effect in this situation.

Now we shall correct the theory. Note that the monodisperse approximation leads to some already defined functional form for $g$ and for the supersaturation. We already know this form and now we need only to establish the parameters in these functional dependencies.

We shall choose the unique length of the spectrum $\Delta x$. At this very moment this value is unknown, but $\Delta x$ satisfies the following inequality:

$$
\Delta x \leq \Delta_i x
$$

for every sort of the heterogeneous centers. Then for $g$ we have

$$
g_i(z) = \frac{N_i (\Delta x / 4)}{n_{\infty}} z^3
$$

which leads to

$$
N_i (\Delta x / 4) = \eta_{i \text{ tot}} (1 - \theta_i (\Delta x / 4))
$$

$$
\theta_i (\Delta x / 4) = \exp[-f_s \cdot \sum \frac{\Gamma_j N_j (\Delta_j x / 4)}{\eta_{\text{tot}} i} \int_0^z \exp(-\sum \frac{\Gamma_j N_j (\Delta_j x / 4)}{\Phi_n i}) dx]
$$

We neglect here for simplicity the weak dependence $\Gamma_i = \Gamma$ on the sort of the centers, while the strong dependence $f_s x, \eta_{ij \text{ tot}}$ on the sort of centers is taken into consideration. After the substitution we get the system of the algebraic equations for $N_i (\Delta x / 4)$

$$
N_i (\Delta x / 4) = \eta_{i \text{ tot}} (1 - \exp(-f_s \cdot \sum \frac{\Gamma_j N_j (\Delta_j x / 4)}{\Phi_n i} \int_0^{\Delta x / 4} \exp(-\sum \frac{\Gamma_j N_j (\Delta_j x / 4)}{\Phi_n i}) dx))
$$

Let us simplify the last system. To calculate the integral one can note that

$$
\int_0^x \exp(-x^3) dx \approx x \quad x \leq 1/4
$$
So the trivial dependence of the r.h.s. on \( N_j \) disappears. We come to

\[
N_i(\Delta x/4) = \eta_i \text{tot}(1 - \exp(-f_* \frac{n_\infty \Delta x}{\eta \text{tot}_i \Delta x/4}))
\]  

(97)

On the other hand we can utilize the sense of \( \Delta x \) as the halfwidth of the spectrum due to the fall of the supersaturation:

\[
\frac{\Delta x^3}{n_\infty} \sum_j N_i(\Delta x/4) \frac{\Gamma}{\Phi_*} = 1
\]  

(98)

After the substitution we can get the equation for \( \Delta x \)

\[
\frac{\Delta x^3}{n_\infty} \sum_j \eta_j \text{tot}(1 - \exp(-f_* \frac{n_\infty \Delta x}{\eta \text{tot}_j \Delta x/4})) \frac{\Gamma}{\Phi_*} = 1
\]  

(99)

Equation (97) expresses \( N_i(\Delta x/4) \) through \( \Delta x \) and solves the problem.

Equation (92) gives the expression for \( g \) and, thus, for the supersaturation as the function of time. The number of the heterogeneous centers can be found by (94). The final values can be found by the corresponding previous formulas.

We can estimate the relative error by the pseudo homogeneous case. Then we shall obtain that the relative error can be roughly estimated as

\[
\frac{| N_i(\infty) - N_{\text{final} i}(\infty) |}{N_i(\infty)} \leq \frac{| A - B |}{A} \sim 0.02
\]  

(100)

The investigation of the process of the essential formation of the droplets is completed.

7 Concluding remarks

As the result of the previous sections we know the behavior of the supersaturation and the behavior of the number of the free heterogeneous centers during the period of the intensive formation of the droplets. It allows to get the main characteristic of the process of condensation - the total number of the droplets formed on the heterogeneous centers of the different nature. The final formulas allow the interesting quantitative physical analysis which is missed only due to the lack of the volume. The evolution of the already formed spectrum is much more simple. The high accuracy in the determination of the supersaturation isn’t necessary now. Due to the proportionality of the velocity of growth to the supersaturation only the high relative accuracy is necessary. The description of the further evolution is analogous to the investigation of the homogeneous decay made in [17].

The description of the further periods can be given with the help of the direct application of the monodisperse approximation as in the case of the homogeneous decay of the metastable phase. We have the simple differential equation for some isolated hydrodynamic element

\[
\frac{\tau}{\alpha} \frac{dz}{dt} = \zeta = \Phi_* - \sum_i N_{\text{final} i}(\infty) \frac{z^3}{n_\infty}
\]  

(101)

which can be easily integrated as far as the r.h.s. doesn’t depend on time. All terms in this equation are known from the previous analysis. So there are no problems in the description of the process until the coalescence [22] [23].

\textsuperscript{7}Precise calculations for condensation of the separate sort give the relative error of the monodisperse approximation as 0.022 in the total number of the droplets. The summation over all sorts can not increase the relative error.
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Figure 1

Behavior of functions $s_{bcl}$ and $s_{ab}$. 
Figure 2

Form of the spectrum in the "monodisperse approximation".