Heterogeneous condensation on several types of centers in dynamic conditions

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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 condensation in such a system is constructed in dynamic conditions. 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 recurrent procedure of the establishing of the characteristic times and lengths is presented. The semiempirical method of the description of the period of essential formation of new phase embryos on the heterogeneous centers of some sort is given.
1 Introduction

The theory considered here will be based on the capillary approximation of the height of the activation barrier. This publication can be regarded as the direct continuation of the publications [10], [11] and is going to fulfil the program announced in [10]. All necessary bibliographical cites can be found in [10].

It is necessary to stress that in the nature the more spread conditions are the external conditions of the dynamic type. In such conditions the external action on the volume of the system, the temperature and the pressure are changed in some continuous smooth way. The process of condensation violates these characteristics. But this process itself takes place under the action of external influence on the metastability of the system. These conditions were considered at first by Raiser [7]. The theory of the heterogeneous condensation on the centers of one sort was done in [6]. Practically in the condensing system there are several types of the heterogeneous centers of the different nature (see [10]).

The theory when the processes of the homogeneous and heterogeneous nucleation are taken into account in the dynamic conditions was constructed in [8]. The problem of construction of the theory for condensation on the heterogeneous centers of several sorts still remains actual. Here such a theory will be constructed.

Here and in the further considerations all energy-like values are expressed in the units of the thermal energy $k_bT$ ($k_b$ is Bolzman constant, $T$ is absolute temperature). The theory presented here will be valid also for the pure homogeneous process.

We shall use the following physical assumptions analogous to [10], [11]:

- 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 of condensation,
- the absence of the thermal effects.

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 the error of the obtained solutions for these values. The unit volume is considered.

We assume the total number of the heterogeneous centers to be constant in time.
The indexes "∗∗", "∗∗∗" below the values may refer to some characteristic times \( t_∗ \) and \( t_{∗∗} \), correspondingly.

The theory of the process appears to be rather long and complex. So we shall use some already known constructions [6], [8] as some blocks in this theory. Recall that the heterogeneous condensation under the action of the linear source of the metastability was considered in [6]. The same problem for the source of the "square" form was studied in [8].

Suppose that in the system there are several sorts of the heterogeneous centers distributed homogeneously in the space volume. We shall mark the total number of the heterogeneous centers by \( \eta_{\text{tot}} \) where \( i \) corresponds to some sort of heterogeneous centers. The real values of the free heterogeneous centers which may be solvatated but aren’t occupied by the super-critical embryos are marked by \( \eta_i \). The index \( i \) or \( j \) below the value marks the sort of the heterogeneous center. 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 \( n_∞ \), the density of the molecules in the real vapor in the system is marked by \( n \). The power of the metastability will be characterized by the value of the supersaturation

\[
ζ = \frac{n - n_∞}{n_∞}
\]

We shall define the super-critical embryos as the "droplets". Every droplet is described by the number of the molecules inside the droplet \( ν \), or by the linear size \( ρ = ν^{1/3} \). Due to the free-molecular regime of the vapor consumption we have

\[
\frac{dρ}{dt} = ζατ^{-1}
\]

where \( α \) is the condensation coefficient and \( τ \) is some characteristic time between collisions of the given molecule of the vapor with the molecules obtained from the gas kinetic theory.

Let us introduce some size \( z \) according to

\[
z = \int_{t_*}^{t} ζατ^{-1} dt'
\]

where \( t_* \) is some characteristic time. The choice of \( t_* \) is more complex than in [6]. For every sort of the heterogeneous centers there will be some special \( t_{*i} \). It is chosen as the moment until which the half of the droplets formed on the centers of the given sort is already appeared. In such a case the variable \( z \) will be marked as \( z_i \).

Until the coalescence [2], [3] which isn’t considered here equation (1) ensures the growth of \( z \) in time and can be inverted

\[
t(z) = α^{-1} \int_0^z \frac{τdz}{ζ(z)} + t_∗
\]
Hence, all values dependent on time become the values dependent on \( z \) and the relative size \( x = z - \rho \) can be introduced. For \( z_i \) the values \( x_i \) are introduced by the same procedure.

During the whole evolution the droplet has one and the same value of the variable \( x_i \). Considering \( t(x) \) (or \( t_i(x) \)) 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 \( \zeta(x) \).

2 The system of the equations of condensation

To describe the action of the external conditions we shall introduce the value of the ideal supersaturation

\[
\zeta_{id} = \frac{n_{tot}}{n_\infty} - 1
\]

Due to solvatation of the heterogeneous centers the ideal supersaturation falls to the value

\[
\Phi = \zeta_{id} - \sum_i \eta_{tot i} \nu_{e i} \frac{\nu_{e i}}{n_\infty}
\]

where \( \nu_{e i} \) is the number of the molecules of the condensed phase in the equilibrium heterogeneous embryo.

One can assume that \( \nu_{e i} \) can be taken at \( \zeta = \zeta_* \).

One can put approximately

\[
\Phi = \zeta_{id}
\]

with a small relative error. We shall call \( \Phi \) the ideal supersaturation also.

To construct the mathematical model we must formulate some statements:

- (1) The main role in the vapor consumption (when this consumption is really essential) during the evolution is played by the super-critical embryos, i.e. by the droplets.

- (2) The quasistationary approximation for the nucleation rate can be accepted during every period of the essential formation of the droplets on every sort of the heterogeneous centers (except the situations when the considered sort of the heterogeneous centers is exhausted). When this approximation is essential it is valid. Namely, it is not valid only in the situation when all the nucleus of the given sort become the centers of the droplets. We shall call this situation as the "exhausted centers situation" (ECS). In this very situation the quasistationary approximation isn’t necessary as far as the result of the process is obvious.
• (3) It is possible to change $t_*$ in the formalism of the iteration procedure in \[6\] to the choice of $t_{**}$ which corresponds to the maximum of the supersaturation. Really, the "correct" choice $t_*$ as the time when the half of the total number of the droplets is already formed begins to deviate essentially from the choice of $t_{**}$ only in ECS when the result is already known. Certainly, the parameter in the linearization must be reconsidered if it is necessary.¹

The justification of the second statement uses the estimate for the times $t^*_s$ of the establishing of the stationary state in the near-critical region which can be found in \[1\], \[4\] (for the heterogeneous barrier the consideration is quite the same). Here it is necessary to remark that, certainly, there may exist some rather huge times $t^*_s$. They correspond to rather big values of the number of the molecules in the critical embryos. The halfwidth of the near-critical region \[1\] can be estimated by the homogeneous value at the supersaturation corresponding to same value of the volume of the critical embryo. It is proportional to the value near $\nu_{c,i}^{2/3}$. 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 $\nu_{c,i}^{2/3}$ the value of $t^*_s$ is proportional to $\nu_{c,i}^{2/3}$. Practically, the big value of the activation barrier $\Delta F_i = F_i(\nu_{c,i})$ (in the case when $\nu_{c,i}$ 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.

For the majority of the types of the heterogeneous centers the following approximations for the nucleation rate $J_i$ are valid during the period of the essential formation of the droplets on the centers of the given sort

$$J_i = J_i(\eta_{tot,i},\zeta_*) \exp(\Gamma_i \frac{(\zeta - \zeta_*)}{\zeta_*}) \frac{\eta_i}{\eta_{tot,i}}$$  \hspace{1cm} (4)

where

$$\Gamma_i = -\zeta_* \frac{d\Delta_i F(\zeta)}{d\zeta} \bigg|_{\zeta=\zeta_*}$$  \hspace{1cm} (5)

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

Let $f_{*,i}$ be the amplitude value of the size distribution of the homogeneously formed droplets measured in the units of $n_\infty$. As far as the supersaturation $\zeta_*$ and the number of the heterogeneous centers $\eta_{tot,i}$ are the already known values the stationary rate of nucleation $J$ and the stationary distribution $f$ can be easily

¹Here the simplest explanation is given. The precise analytical analysis which confirm this statement is also available.
calculated by some formulas derived in [3]:

$$J_i \tau = f = \frac{W_+^+ \exp(-\Delta_i F)\tau}{n_\infty \pi^{1/2} \Delta_c \nu \Delta_c \nu \alpha \eta_i}$$  \hspace{1cm} (6)$$

where $W_+^+$ is the number of the molecules absorbed by the embryo in the unit of time, $\Delta_c \nu$ is the width of the equilibrium distribution

$$\Delta_c \nu = \sum_{\nu=1}^{\nu=\nu_c} \exp(-F(\nu))$$

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

$$\Delta_c \nu = \frac{2^{1/2}}{\left| \frac{\partial^2 F}{\partial \nu^2} \right|^{1/2} \nu}$$

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

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

Let us choose for the simplicity the concrete conditions of the constant volume and pressure of the system. This allows to cancel some unimportant parameters and to exclude them from formulas.

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

$$g_i = f_{\ast - i} \int_{-\infty}^{z_i} (z_i - x_i)^3 \exp(\Gamma_i \Phi(x) - \zeta_{\ast i}) \exp(-\Gamma_i \sum_j g_j \zeta_{\ast j}) dx_i \equiv G_i(\sum_j g_j, \theta_i)$$

$$\theta_i = \exp(-f_{\ast - i} \frac{n_\infty}{n_\text{tot} i} \int_{-\infty}^{z_i} \exp(\Gamma_i \Phi(x) - \zeta_{\ast i}) \exp(-\Gamma_i \sum_j g_j \zeta_{\ast j}) dx_i) \equiv S_i(\sum_j g_j)$$

where $f_{\ast - i} = J_i(\eta_\text{tot} i, \zeta_{\ast i}) \tau / \zeta_{\ast i} \alpha n_\infty$.

These equations form the closed system of the equations of the condensation kinetics. This system will be the subject of our investigation.

As far as we measure the accuracy of the theory in the terms of the error in the number of the droplets we define these values as the following ones:

$$N_i = \eta_\text{tot} i (1 - \theta_i(z)) \equiv Q_i(\theta_i)$$  \hspace{1cm} (9)$$

The size spectrum can be found as the following one

$$f_i = f_{\ast - i} \exp(-\Gamma_i \sum_j g_j \zeta_{\ast j}) \exp(\Gamma_i \Phi(x) - \zeta_{\ast i}) \theta_i$$  \hspace{1cm} (10)
Note that system (7) - (8) is rather more complex than in the case of decay. The specific feature is not only the presence of the factor $\exp(\Gamma_i \frac{\Phi(x_i) - \zeta_{i*}}{\zeta_{i*}})$ but also the necessity of the introduction of the separate scales for $z$ and $x$. It means that the periods of the essential formation of the droplets on the centers of a different nature don’t coincide or have any common regions. Such a situation can be guaranteed by the following inequalities
\[
\frac{f_{s,i}}{f_{s,j}} \ll 1 \quad (11)
\]
or
\[
\frac{f_{s,i}}{f_{s,j}} \gg 1 \quad (12)
\]
for all arbitrary pairs of the sorts of the centers $i$ and $j$. The situation
\[
\frac{f_{s,i}}{f_{s,j}} \sim 1 \quad (13)
\]
will be at first excluded from consideration. Later the generalization will be presented.

Note that inequalities (11) - (13) are rather unsensitive to the change of the supersaturation. Note that
\[
f_s \sim \exp(-F_c + F_e) \sim \exp(-F_{c\text{ hom}} + F_e)
\]
where the free energy $F$ is counted in the "absolute" scale with the zero point of the energy corresponding to the standard homogeneous zero point $F_{\text{hom}}(\nu = 1) = 0$ and $F_{j \cdot e}$ are the energies of solvatation, So, we can write
\[
\frac{f_{s,i}}{f_{s,j}} \sim \frac{\eta_{i\text{ tot}} \exp(+F_{i e})}{\eta_{j\text{ tot}} \exp(+F_{j e})} \quad (14)
\]
Hence, we can see that when the free energy of solvatation is unsensitive to the supersaturation (as it occurs really in the nature) then the r.h.s. of the last equation doesn’t depend on the supersaturation.

So, the set of the heterogeneous centers $\{\eta_{i\text{ tot}}\}$ initiates the set of the characteristic times $\{t_{*i}\}$ and the characteristic supersaturations $\{\zeta_{*i}\}$. Suppose that $\zeta_{i*} > \zeta_{*j}$ if $i > j$.

3 External supersaturation

The analysis of the last section simplifies the treatment, but isn’t absolutely necessary. The more rigorous recipe is to solve the separate problems
\[
g_i = f_{s,i} \int_{-\infty}^{x_i} (z_i - x_i)^3 \exp(\Gamma_i \frac{\Phi(x) - \zeta_{i*}}{\zeta_{i*}} \theta_i dx_i \equiv G_i(g_i, \theta_i) \quad (15)
\]
\[ \theta_i = \exp(-f_i \int_{-\infty}^{\infty} \frac{\Phi(x) - \zeta i}{\zeta i} \exp(-\Gamma_i \frac{g_i}{\zeta i}) \theta_i dx_i) \equiv S_i(g_i) \quad (16) \]

This solution can be obtained by the methods from [6] and we needn't to describe it here. As a result we get the set \( \{\zeta i\} \). The solution is valid only for \( i = 1 \) \( (\zeta 1 < \zeta i \neq 1) \). All other solutions are got only to construct the set \( \{\zeta i\} \). Now they are useless.

The further condensation can’t be described by system (15) - (16) because the droplets formed on the centers of the first sort consumes the vapor. This system must be substituted by

\[ g_i = f_i \int_{-\infty}^{z_i} (z_i - x_i) \exp(\Gamma_i \frac{\Phi(x) - \zeta i}{\zeta i} \exp(-\Gamma_i \frac{g_i + g_1}{\zeta i}) \theta_i dx_i \]  

\[ \theta_i = \exp(-f_i \int_{-\infty}^{\infty} \frac{\Phi(x) - \zeta i}{\zeta i} \exp(-\Gamma_i \frac{g_i + g_1}{\zeta i}) \theta_i dx_i) \quad (17) \]

Here \( i \neq 1 \). In order to simplify this system it is necessary to take into account the following statement

- The size spectrum of the droplets of those sorts for which the formation of the droplets has been already described can be treated as the set of the monodisperse spectrums with some coordinates (depended on the sort of the centers).

The solution of the system of the condensation equations was necessary to get the number of the droplets and the coordinate of the spectrum.

Then the system of the condensation equations can be reformulated in the following way

\[ g_i = f_i \int_{-\infty}^{z_i} (z_i - x_i)^3 \exp(\Gamma_i \frac{\Phi(x) - \zeta i}{\zeta i} \exp(-\Gamma_i \frac{g_i + g_1}{\zeta i}) \theta_i dx_i \]  

\[ \theta_i = \exp(-f_i \int_{-\infty}^{\infty} (z_i - x_i)^3 \exp(\Gamma_i \frac{\Phi(x) - \zeta i}{\zeta i} \exp(-\Gamma_i \frac{g_i + g_1}{\zeta i}) \theta_i dx_i) \quad (19) \]

Here \( i \neq 1 \), \( N_{tot 1} \) is the total number of the droplets formed on the heterogeneous centers of the first sort and \( z_{1 i} \) is the coordinate of spectrum of the sizes of the droplets formed on the heterogeneous centers of the first sort.

Actually

\[ N_{i tot} \sim \eta_i \]

If the last equality isn’t valid it means that the supersaturation is going to attain soon the maximum and then to fall. So, no other formation of the droplets can be observed.
One must solve the last system for all sorts of the heterogeneous centers and construct the sequence \( \{\zeta_i\}_{i \geq 2} \). Ordinary the sequence will be the old one, but the concrete values are changed.

Again we can use only the lowest \( \zeta_i \), i.e. the second sort. Then we must repeat this procedure again and again. The question how to solve these systems will be discussed later.

After condensation on \( i_0 \) sorts of the heterogeneous centers has been already described and we are going to describe condensation on the centers of the sort \( i \) the following system must be solved

\[
g_i = f_i \int_{-\infty}^{z_i} (z_i - x_i)^3 \exp(\Gamma_i \frac{\Phi(x) - \zeta_i}{\zeta_i}) \exp(-\Gamma_i g_i + \sum_{j \leq i_0} \frac{N_j}{n_i} \frac{z_j^3}{\zeta_i}) \theta_i dx_i
\]

\[
\theta_i = \exp\left(-f_i \frac{n_i}{\eta_{i,\text{tot}}} \int_{-\infty}^{z_i} \exp(\Gamma_i \frac{\Phi(x) - \zeta_i}{\zeta_i}) \exp(-\Gamma_i g_i + \sum_{j \leq i_0} \frac{N_j}{n_i} \frac{z_j^3}{\zeta_i}) dx_i\right)
\]

Here \( i > i_0 \), \( N_{j,\text{tot}} \) is the total number of the droplets formed on the centers of the sort \( j \) (it is near to \( n_j \)), \( z_j \) is the coordinate of these droplets.

System (21) - (22) is rather complex because the values \( z_j \) are unknown ones. The next statement simplifies the problem and reduces it to the two more simple problems:

- System (21) - (22) can be with a high accuracy reduced to the following system

\[
g_i = f_i \int_{-\infty}^{z_i} (z_i - x_i)^3 \exp(\Gamma_i \frac{\Omega(x) - \Omega_i}{\Omega_i}) \exp(-\Gamma_i g_i + \sum_{j \leq i_0} \frac{N_j}{n_i} \frac{z_j^3}{\zeta_i}) \theta_i dx_i
\]

\[
\theta_i = \exp\left(-f_i \frac{n_i}{\eta_{i,\text{tot}}} \int_{-\infty}^{z_i} \exp(\Gamma_i \frac{\Omega(x) - \Omega_i}{\Omega_i}) \exp(-\Gamma_i g_i + \sum_{j \leq i_0} \frac{N_j}{n_i} \frac{z_j^3}{\zeta_i}) dx_i\right)
\]

where the function \( \Omega \) satisfies the following equation

\[
\Phi = \Omega + \sum_{j \leq i_0} \frac{N_j}{n_i} (z + \delta z_j)^3
\]

\[
\Omega = \frac{\tau}{\alpha} \frac{dz}{dt}
\]

and \( \delta z_j \) are some fixed and already known distances between the monodisperse spectrums.

Here the following statement is also taken into account
The following approximation during the period of the intensive formation of the droplets on the heterogeneous centers of the given sort (PIFDGS) is valid for the nucleation rates \( J_i \)

\[
J_i = J_i(\eta_{tot i}, \Omega_*) \exp(\Gamma_i(\zeta - \Omega_*) \eta_{tot i})
\]

(27)

where

\[
\Gamma_i = -\Omega_* \frac{d\Delta_i F(\zeta)}{d\zeta} \bigg|_{\zeta=\Omega_*}
\]

(28)

and the index "*" corresponds to \( t_{* i} \).

The validity of the last system of equations is based on the simple fact that the rate of the vapor consumption is violated by the relatively essential deviation of the supersaturation and the rate of nucleation is violated by the relatively small violation of the supersaturation corresponding to the violation of \( \Gamma_i \).

We shall call \( \Omega \) the external supersaturation. Our next task is to determine it.

4 Iterations for the external supersaturation

System (25) - (26) forms the ordinary differential equation (of the Abel’s type) and doesn’t allow the analytical solution. The initial condition is the following

\[
z \bigg|_{t=t_{init}} = 0
\]

where \( t_{init} \) is the time of formation of the last known peak of the droplets distribution.

Meanwhile one can construct the iterations on the base of the small parameter

\[
\delta = \frac{\sum_{j \leq i_0} N_j \eta_{tot n}(z + \delta z_j)^3}{\Phi_n \infty}
\]

(29)

We suppose that

\[
\frac{d^2 \Phi}{dt^2} \leq 0
\]

and can announce the following statements

- The iterations defined according to

\[
\Phi = \frac{\tau}{\alpha} \frac{dz(k+1)}{dt} + \sum_{j \leq i_0} N_j \eta_{tot n}(z(k) + \delta z_j)^3
\]

(30)

converge to a unique solution (an ordinary property of a differential equation).\(^2\)

\( ^2\)We shall put for simplicity \( z(0) = 0 \).
• We need to investigate the region where

\[ \frac{d\Omega}{dt} \geq 0 \]

When \( \frac{d\Omega}{dt} = 0 \) at the final of the period under the consideration we have

\[ \frac{d|\max \Omega(k) - \max \Omega(k+1)|}{d(\frac{d^2\Phi}{dt^2})} \geq 0 \]

Actually we can remove \( t_{\text{init}} \) to the time of formation of the first peak and consider all \( \delta z_j \) as the positive values. Then

\[ \frac{d|\max \Omega(k) - \max \Omega(k+1)|}{d\delta z_j} \leq 0 \]

The previous inequality in such a reformulation can be also justified. Another inequality can be also taken into account

\[ \frac{d|\max \Omega(k) - \max \Omega(k+1)|}{dt_{\text{init}}} \geq 0 \]

Certainly, \( t_{\text{init}} \) can not be put earlier than the moment when \( \Phi = 0 \).

So in the worst situation the form of the differential equation is the following:

\[ At = \frac{\tau d\zeta}{\alpha dt} + \frac{N_{\text{tot}}}{n_\infty} z^3 \]

(30)

where \( A \) is some constant and \( N_{\text{tot}} \) is some value.

If \( \Phi \) is the polinom then all iterations are calculated analytically and have the form of polinoms. Their convergence is rather high. The value of a relative error in the maximum of \( \Omega \)

\[ \Delta_i \leq \frac{|\max_z \Omega(i) - \max_z \Omega|}{\max_z \Omega} \]

is less than

\[ \Delta_{i+1} \sim \frac{|\max_z \Omega(i) - \max_z \Omega(i+1)|}{\max_z \Omega(i+1)} \]

and can be easily calculated on the base of (30). As a result one can get \( \Delta_2 < 4.2 \times 10^{-2}, \Delta_3 < 8.68 \times 10^{-3} \).

Note that the requirement for the choice of the number of iterations is the following

\[ \Delta_k \leq \frac{1}{\Gamma_i} \]
Really, $\Gamma_i$ is the big parameter of the theory and goes to infinity, but actually $\Gamma_i \sim 50$ which is necessary for the intensive formation of the droplets ($f_* \sim \exp(-\text{const} R_i^{2/3})$). So, we need to calculate only the few first iterations.

Figure 1 shows the form of the iterations. Note that the evident renormalization can lead to the differential equation without parameters

$$t = \frac{dz}{dt} + z^3$$

with the previous initial condition.

The forms of the iterations $f_1 - f_4$ are drawn in Figure 1 where the index points the number of the iteration. Note, that only the behavior until the maximum is interesting for us. It can be seen that $f_3$ can not already be separated from $f_4$.

One can also introduce another approximation which is more accurate. This is the approximation of the ideal surface. In this approximation the term $z^3$ is split between the surface term $z^2$ and the linear term $z$. Return to the previous scales of the variables. The iterations are constructed by the following way

$$\Phi = \frac{\tau}{\alpha} \frac{dz(k+1)}{dt} + \sum_{j \leq k_0} \frac{N_j \text{tot}}{n_\infty} (z(k) + \delta z_j)^2 (z(k+1) + \delta z_j)$$

The rate of convergence of such iterations is higher than of the old ones, but there is no opportunity to calculate iterations analytically. Hence, this way of the approximation can be effectively used only at the last step.

Now we are going to solve system (23) - (24). This system is more complex than the system already considered in [6] because the behavior of $\Omega$ during PIFDGS is essentially nonlinear. One can not linearize $\Omega$ as the function of time and $x$ during PIFDGS. But some important conclusions about the behavior of $\Omega$ can be made. Consider an arbitrary sort of the heterogeneous centers $i$ on which the droplets have been already formed. Introduce the characteristic width $\Delta x$ of the peak which is going to be formed. Certainly,

$$\Delta x \ll z_i$$

The value of $g_i$ near $z \sim 0$ allows to give the estimate

$$g_i \sim \frac{N_i \text{tot}}{n_\infty} z_i^3$$

We can also give the analogous estimates for the derivatives

$$\frac{dg_i}{dz} \sim \frac{N_i \text{tot}}{n_\infty} z_i^2$$

$$\frac{d^2g_i}{dz^2} \sim \frac{N_i \text{tot}}{n_\infty} z_i$$
The actions of this terms on Ω are given by the following terms (i.e. the corresponding terms in the Tailor’s series)

\[
\begin{align*}
\frac{d^3g_i}{dz^3} & \sim \frac{Ni_{tot}}{n_\infty} \\
\frac{dg_i}{dz} & \rightarrow \frac{Ni_{tot}}{n_\infty} z_i \Delta x \\
\frac{d^2g_i}{dz^2} & \rightarrow \frac{Ni_{tot}}{n_\infty} z_i (\Delta x)^2 \\
\frac{d^3g_i}{dz^3} & \rightarrow \frac{Ni_{tot}}{n_\infty} (\Delta x)^3
\end{align*}
\]

Due to (32) one can see that

\[
\frac{N_i \Delta x}{n_\infty} z_i \gg \frac{N_i \Delta x}{n_\infty} z_i (\Delta x)^2 \gg \frac{N_i \Delta x}{n_\infty} (\Delta x)^3
\]

The action of \( \frac{dp}{dt} \) can be cancelled by \( \frac{dp}{dt} \) because they have the different signs. So the action of \( \frac{d^2p}{dt^2} \) must be taken into account. The action of \( \frac{d^3p}{dt^3} \) can be neglected.

As the result we justify the following approximation for the behavior of Ω during PIFDGS:

\[
\frac{\Gamma}{\Phi_*} \Omega = cx + lx^2 + \text{const}
\]

with the two known constants.

The characteristic length of formation of the spectrum by means of the vapor consumption by the droplets in this very peak is given by the following formula

\[
\Delta x \sim \left( \frac{\Omega_*}{\Gamma_{f_*}} \right)^{1/4}
\]

The halfwidth of the spectrum initiated by the external supersaturation is given by

\[
x_p = \left( \frac{2\Omega_{max}}{\Gamma_{f_*} |d\Omega|_{\Omega=\Omega_{max}}} \right)^{1/2}
\]

when formation of the droplets occurs near the maximum of Ω.

When \( \Delta x \ll x_p \) we can use the standard iteration procedure described in [6]. When \( \Delta x \gg x_p \) or \( \Delta x \sim x_p \) we must use the modified method of the steepens descent [8] which is described in the next section (it covers all situations). The case \( \Delta x \gg x_p \) is extremely simple (ζ coincides with Ω).
5 Modified method of the steepens descent

In this section we shall forget about the several types of the heterogeneous centers and about the several peaks in the spectrum of the droplets sizes. We shall consider the model situation when we have the nonlinear external source of the supersaturation of the square form and the process of the homogeneous (or the heterogeneous) condensation. We shall start with the homogeneous condensation and then the generalization on the heterogeneous case will be given. According to the results of the previous section this model covers all possible situations.

5.1 Homogeneous condensation

In order to obtain the form of the function $\zeta(x)$ the balance equation must be introduced. For the homogeneous condensation one can obtain the following balance equation

$$\Phi = \zeta + g$$

$$g(z) = \frac{n_{\infty} V}{n_{\infty} V} \int_{-\infty}^{z} dx (z - x)^3 f(x)$$

(34)

The value of $t_*$ can be chosen as the moment of the maximum of the supersaturation.

The term $\frac{n_{\infty} V}{n_{\infty} V}$ is approximately equal to 1 and can be missed.

The value of the ideal supersaturation can be presented in the following form

$$\Phi = \Phi_* + \Phi_* (c x + l x^2)/\Gamma$$

(35)

with the two parameters

$$c = \frac{\Gamma}{\Phi_*} \frac{d\Phi}{dx} |_{x=0}$$

$$l = \frac{\Gamma}{2\Phi_*} \frac{d^2\Phi}{dx^2} |_{x=0}$$

(36)

as it was done in [9]. The negative value of $l$ corresponds to the nonlinear character of the external conditions. The form of the ideal supersaturation can be treated as the Tailor’s series cut off on the second term. The result of [9] states the validity of (35) in the case when the nonlinearity of the external source is induced by the vapor consumption of the already formed spectrums.

The two assumptions justified analytically can be introduced. The first one establishes that

- the leading role in the vapor consumption belongs to the super-critical embryos, i.e. to the droplets.

The second assumption states

- the quasistationary state of the embryos in the near-critical region.
It must be valid during the period of the essential formation of the 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 the relaxation to the stationary state in the near-critical region. Then the required assumption can be written as the following one

\[
t_\zeta \gg t_s
\]  

These assumptions will be valid in all situations of the homogeneous case and in the heterogeneous case except the situation when almost all heterogeneous centers are exhausted at the final of the period of the essential formation. In this situation the result of the period of the essential formation of the droplets is obvious: the number of the droplets coincides with the total number of the heterogeneous centers. The form of the spectrum is unessential during the period of the essential formation of the droplets and the spectrum is the monodisperse one after the supersaturation begins to fall.

Note that the second statement may be not valid in some situations when the supersaturation doesn’t depend of the process of the vapor consumption by the droplets (it is negligible). As it can be shown in these situations the effects of the nonstationarity aren’t important for the results of the process.

Now let us analyze the behavior of \( g(z) \). At first we shall analyze it only qualitatively. We shall extract the three regions. Let us put \( l \sim 0 \). At first we shall define the period of the creation of the main consumers of the vapor during the period of the essential formation of the droplets. Then the behavior of \( g \) in the first iteration can be seen from

\[
g(z) \sim \exp(z) \int_{0}^{\infty} y^3 \exp(-y)dy
\]  

One can note the following important fact:

- The subintegral function in (38) is sufficient only when

\[
1 \sim y_{min} \leq y \leq y_{max} \sim 8 \quad y = \rho
\]  

This region is the region of the creation of the main consumers of the vapor during the period of the essential formation of the droplets. It is moving in time along the \( \rho \)-axis (and the \( t \)-axis) with the velocity of the droplets growth. When the last inequalities aren’t valid the subintegral function is negligible. The period which corresponds to (39) plays the main role in formation of the spectrum.

Now we shall extract the other regions

---

3 This case requires the special consideration which can be done and shows that the effects of the nonstationarity are cancelled.

4 Only until the end of the process of the creation of the droplets because the deviation of the supersaturation from the ideal one essentially transforms the definitions of the boundaries of this region.
During the period of the essential formation of the droplets one can extract the "initial" region according to
\[-9 \leq cz \leq cz_b\]  
(40)

The value of \(z_b\) must be established with the help of the additional condition
\[\frac{f(x) - f_1(x)}{f_1(x)} \ll 1\]  
(41)

where \(f\) is the size distribution of the droplets and \(f_1\) is the imaginary distribution formed at the supersaturation \(\Phi\) instead of \(\zeta\). The values corresponding to this region will be marked by the subscript "in".

The estimates for \(g(z)\) give the above estimate for the duration of the period of the essential formation of the droplets. The period of the intensive formation of the droplets finishes when \(cz \sim 1\). It starts when \(cz \sim -1\). One can define the peak of the period of the intensive formation of the droplets according to
\[-c^{-1} \leq z \leq c^{-1}\]  
(42)

The successful solution of the system of the condensation equations on the second step of iterations shows that the subintegral function lies essentially inside the initial period during the intensive formation of the droplets. Then one can conclude that\[\frac{\zeta - \zeta^*}{\Phi^*} \gg 1\]

If \(l \leq 0\) (namely this case must be considered), then the hierarchy becomes even more strong.

So, the region of the creation of the main consumers of the vapor during the period of the essential formation of the droplets belongs to the initial region.

5.2 Approximation of the spectrum

One need to construct some approximation for \(f(x)\) at the period of the essential formation of the droplets. The problem can be reduced to the suitable expression for \(\zeta - \zeta_*\) in the standard exponential approximation
\[f(x) = f_* \exp\left(\frac{\Gamma(\zeta - \zeta_*)}{\Phi_*}\right) \exp\left(\frac{\Gamma(\zeta_* - \Phi_*)}{\Phi_*}\right)\]  
(44)

\(^5\) and even
\[-y_{min} + 1 \sim cz_b\]
One can decompose $\zeta - \zeta^*$ into the Tailor’s series in the neighborhood of $z = 0$. The expressions for the derivatives are the following ones:

$$\frac{d\zeta}{dz} = \frac{d\Phi}{dz} - 3 \int_{-\infty}^{z} f(x)(z - x)^2 dx \quad (45)$$

$$\frac{d^2\zeta}{dz^2} = \frac{d^2\Phi}{dz^2} - 6 \int_{-\infty}^{z} f(x)(z - x) dx \quad (46)$$

$$\frac{d^3\zeta}{dz^3} = \frac{d^3\Phi}{dz^3} - 6 \int_{-\infty}^{z} f(x) dx \quad (47)$$

$$\frac{d^n\zeta}{dz^n} = \frac{d^n\Phi}{dz^n} - 6 \frac{d^{n-4}f(z)}{dz^{n-4}} \quad n \geq 4 \quad (48)$$

The value $d^3g/dz^3$ is proportional to the number of the already formed droplets. This value is the main result of the process of condensation and the subject of interest of the theoretical description. According to the iteration procedure one can note that

- 1). At the first step of the iteration procedure the expression for the total number of the droplets isn’t correct at all. The relative error goes to $\infty$.
- 2). The second step of the iteration procedure is the final one and it gives the almost precise expressions for all main parameters of the process of condensation.

Hence, one can introduce the procedure without the account of (47), (48). Then one can can restrict the Tailor’s series by the first two terms. This restriction leads to the following approximation

$$f(x) = f_* \exp(\Gamma \frac{\zeta}{2dz^2} |_{z=0} \frac{x^2}{\Phi_*}) \exp(\Gamma (\zeta - \Phi_*)) = f_m \exp(\Gamma \frac{\zeta}{2dz^2} |_{z=0} \frac{x^2}{\Phi_*}) \quad (49)$$

This approximation is valid only inside the peak of the period of the essential formation of the droplets. It fails outside this region. The standard method of the steepens descent spreads approximation on the whole period of the essential formation of the droplets (including the "initial" region and the region of the creation of the main consumers of the vapor during the period of the essential formation of the droplets) which leads to the essential relative error. Moreover, approximation (49) isn’t necessary because in the initial region the correct expression for the spectrum has been already established

$$f(x) = f_* \exp(\frac{\Phi(x) - \Phi_*}{\Phi_*}) \quad (50)$$
5.3 Equations on spectrum parameters

To obtain the system of equations on the parameters of the spectrum one can differentiate the balance equation for the condensed substance at \( z = 0 \). Then the following equations appear:

\[
\Phi(0) = g_{in}(0) + g_{ex}(0) + \zeta(0) \tag{51}
\]

\[
\frac{d\Phi}{dz} \bigg|_{z=0} = \left\{ \frac{dg_{in}}{dz} + \frac{dg_{ex}}{dz} + \frac{d\zeta}{dz} \right\} \bigg|_{z=0} \tag{52}
\]

\[
\frac{d^2\Phi}{dz^2} \bigg|_{z=0} = \left\{ \frac{d^2g_{in}}{dz^2} + \frac{d^2g_{ex}}{dz^2} + \frac{d^2\zeta}{dz^2} \right\} \bigg|_{z=0} \tag{53}
\]

The subscripts "\( in \)" and "\( ex \)" mark the part of \( g \) referred to the droplets formed inside the "initial" region and outside it. Equations (50) and (53) lead to

\[
g_{in} = \sum_{i=0}^{3} z^{3-i} \alpha_i \tag{54}
\]

\[
\frac{dg_{in}}{dz} = \sum_{i=0}^{2} z^{2-i}(3-i)\alpha_i \tag{55}
\]

\[
\frac{d^2g_{in}}{dz^2} = \sum_{i=0}^{1} z^{1-i}(3-i)(2-i)\alpha_i \tag{56}
\]

In these equations the values \( \alpha_i \) are defined according to

\[
\alpha_i = (-1)^i \frac{3!}{i!(3-i)!} f_x \int_{-\infty}^{z_b} x^i \exp(\lambda x^2) dx \tag{57}
\]

To obtain the algebraic system of equations one can substitute the integral term in the last expression by the one of the Boyd’s estimates

\[
\frac{\pi/2}{\sqrt{z^2 + \pi + (\pi - 1)z}} \leq \exp(z^2) \int_{-\infty}^{\infty} \exp(-t^2) dt \leq \frac{\pi/2}{\sqrt{\pi - 2)z^2 + \pi + 2z}} \quad z > 0 \tag{58}
\]

Analogous procedure can be proposed for the values \( g_{ex}, \frac{dg_{ex}}{dz} |_{z=0}, \frac{d^2g_{ex}}{dz^2} |_{z=0} \). According to (49) the expressions for \( g_{ex}(0), \frac{dg_{ex}}{dz} |_{z=0} \) have the following system

\[
g_{ex}(0) = f_m \int_{z_b}^{0} \exp\left(-\left(\frac{x}{x_p}\right)^2\right)x^3 dx = f_m x_p^4 \lambda_3 \tag{59}
\]

\[
\frac{dg_{ex}}{dz} \bigg|_{z=0} = 3f_m \int_{z_b}^{0} \exp\left(-\left(\frac{x}{x_p}\right)^2\right)x^2 dx = 3f_m x_p^3 \lambda_2 \tag{60}
\]

18
\[
\frac{d^2 g_{ex}}{dz^2} |_{z=0} = 6f_m \int_{z_0}^{0} \exp \left( -\frac{x}{x_p} \right) x dx = 6f_m x_p^2 \lambda_1
\]

where

\[
\lambda_i = \int_{\xi_0}^{0} \xi^i \exp(-\xi^2) d\xi \quad \xi_0 = \frac{z_b}{x_p}
\]

and \(x_p\) is some parameter like the characteristic halfwidth.

As the result one can see the system of the three algebraic equations which can be solved by the standard numerical methods. The solution of this equation gives all main characteristics of the process.

### 5.4 Linear source

In the case \( l = 0 \) the final expressions become more simple. For \( z_b \) one can take here the value \(-x_p\). Then one can obtain

\[
\alpha_i = f_x \frac{3!(-1)^i}{i!(3-i)!} e^{-i-1} \sum_{j=0}^{i} \frac{i!}{(i-j)!} (-1)^j (-cx_p)^{i-j} \exp(-cx_p)
\]

This induces the following expressions

\[
\begin{align*}
g_{in}(0) &= \alpha_3 = -f_x c^{-4} \sum_{j=0}^{3} \frac{3!}{(3-j)!} (-1)^j (-cx_p)^{3-j} \exp(-cx_p) \quad (64) \\
\frac{dg_{in}}{dz} |_{z=0} &= \alpha_2 = f_x c^{-3} \sum_{j=0}^{2} (-1)^j \frac{2!}{(2-j)!} (-cx_p)^{2-j} \exp(-cx_p) \quad (65) \\
\frac{d^2 g_{in}}{dz^2} |_{z=0} &= 2\alpha_1 = -f_x c^{-2} \sum_{j=0}^{1} (-1)^j (-cx_p)^{1-j} \exp(-cx_p) \quad (66)
\end{align*}
\]

The values of \( \lambda_i \) become the universal constants

\[
\lambda_i = \int_{-1}^{0} \exp(-x^2) x^i dx
\]

Introduction of the connection between \( \frac{d^2 \zeta}{dz^2} \) and \( x_p \)

\[
\left| \frac{d^2 \zeta}{dz^2} \right| = \frac{2\zeta_e}{\Gamma x_p^2} \approx \frac{2\Phi_s}{\Gamma x_p^2}
\]

leads to the transformation from (63) - (66) to the following form

\[19\]
\[ \Phi_* = \zeta_* - f_* e^{-4 \sum_{j=0}^{3} \frac{3!}{(3-j)!} (-1)^j (-cx_p)^{3-j} \exp(-cx_p) + f_m x_p^4 \lambda_3 } \quad (69) \]

\[ \Phi_* \frac{c}{\Gamma} = f_* e^{-3 \sum_{j=0}^{2} \frac{2!}{(2-j)!} (-1)^j (-cx_p)^{2-j} \exp(-cx_p) + 3 f_m x_p^3 \lambda_2 } \quad (70) \]

\[ 0 = -f_* e^{-2 \sum_{j=0}^{1} (-1)^j (-cx_p)^{1-j} \exp(-cx_p) + 6 f_m x_p^2 \lambda_1 - \frac{2 \Phi_*}{\Gamma x_p^2} } \quad (71) \]

From (70) it follows that

\[ f_* = \frac{\Phi_* c}{\Gamma} \left[ e^{-3 \sum_{j=0}^{2} \frac{2!}{(2-j)!} (-1)^j (-cx_p)^{2-j} \exp(-cx_p) + 3 \Psi x_p^3 \lambda_2 } \right]^{-1} \quad (72) \]

where

\[ \Psi = \frac{f_m}{f_*} \]

and (71) transforms to

\[ -\frac{\Phi_* c \left[ e^{-2 \sum_{j=0}^{1} (-1)^j (-cx_p)^{1-j} \exp(-cx_p) + 6 x_p^2 \lambda_1 \Psi } \right]}{\Gamma \left[ e^{-3 \sum_{j=0}^{2} \frac{2!}{(2-j)!} (-1)^j (-cx_p)^{2-j} \exp(-cx_p) + 3 \Psi x_p^3 \lambda_2 } \right]} = \frac{2 \Phi_*}{\Gamma x_p^2} \quad (73) \]

To solve the last equation one can simplify it by the following transformation: Consider \( \Psi \) as some known value. It can be found from (69). In (69), (70) in some rough approximation the last term is negligible in comparison with the second term and one can spread the approximation of the "ideal" supersaturation for all this region. Then we immediately get

\[ \Psi = \exp(-1) \]

Another simplification is to notice that at the characteristic scale \( cx_p \sim 1 \) the value of \( \exp(-cx_p) \) is near to \( \exp(-1) \) and can be linearized. When \( \Phi_* \) and \( \Gamma \) are the given values then equation (73) for \( x_p \) is the ordinary algebraic equation of the power 4 and can be analytically solved. Then (72) gives the value for \( f_m \) and, hence, for \( \Phi_* \) and \( \Gamma \). This completes the current step of the iteration procedure for \( \Phi_* \). The structure of solution in the nonlinear case is the same one.

System (69)-(71) allows some modifications which are available for the nonlinear case also. Note that the subintegral function \( f(x) \) in the expression for
$d^2g/dt^2$ is essential only in the finite region of the period of the essential formation of the droplets. The known approximation (49) also leads to the same conclusion. Then approximation (49) can be formally spread on the whole region of the essential values of the function $f(x)x$. Then equation (71) leads to the following expression for $x_p$

$$x_p = \left( \frac{2\Phi_*}{3f_m} \right)^{1/4}$$

(74)

In the nonlinear case equation (71) has the following form

$$\frac{d^2\Phi}{dz^2} = 3x_p^2f_m - 2\frac{\Phi_*}{\Gamma x_p}$$

(75)

This bisquare equation gives $x_p$ dependence on $f_m$. Then the second equation of system (69) - (71) becomes the close equation on the supersaturation and can be solved by iterations. These iterations can utilize the sharp dependence of $\exp(-F_c)$ on the supersaturation. The zero approximation can be chosen as $\Gamma = 1, \Phi_* = 1$. Then the second approximation gives rather a precise result for all parameters of the spectrum. Certainly, the amplitude $f_m$ must be obtained by (71) instead of the explicit expression from the classical theory of nucleation on the base of the supersaturation.

The system of the condensation equations can be even more simplified if one notices that approximation (50) can be spread over the whole region of integration in the first and in the second equations of the system. This simplification is valid as far as the subintegral functions in the first and in the second equations are essential only in the "initial" region of the period of the essential formation of droplets. Finally, the system of the condensation equations has the following form

$$\frac{d\Phi}{dz} \bigg|_{z=0} = 3f_* \int_{-\infty}^{0} x^2 \exp(cx + lx^2) dx$$

(76)

$$\frac{d^2\Phi}{dz^2} = 6\hat{\lambda}_1 x_p^2 f_m - 2\frac{\Phi_*}{\Gamma x_p^2} \hat{\lambda}_1 = \int_{-\infty}^{0} y \exp(-y^2) dy = 0.5$$

(77)

One must take into account the difference between $f_m$ and $f_*$ which is given by

$$\frac{f_m}{f_*} = \exp\left( -\frac{\Gamma d\Phi}{3\Phi_* dz} \right) \bigg|_{z=0} \int_{-\infty}^{0} x^3 \exp(cx+lx^2) dx / \int_{-\infty}^{0} x^2 \exp(cx+lx^2) dx$$

(78)

It is essential that equations (74) and (77) are the separate ones. Equation (76) can be solved by iterations. The total number of droplets can be obtained as

6 The integral can be calculated explicitly and we have the ordinary algebraic equation.

7 As the algebraic equation due to the sharp dependence of $f_*$ on the supersaturation
\[ N = f_m \sqrt{\frac{\pi}{2}} x_p n_{\infty} \]  

(79)

The value of parameter \( l \) is negative. But one can prove that the relative error of the last expression \( \delta \) increases when \( l \) decreases in the absolute value

\[ \frac{d | \delta |}{dl} > 0 \]  

(80)

In the linear case

\[ g(0) = \frac{\Phi_*}{\Gamma} \]  

(81)

\[ x_p = e^{-1}(4 \exp(1))^{1/4} \]  

(82)

\[ N = \frac{\Phi_* e^{3}(4 \exp(1))^{1/4} \sqrt{\pi}}{6 \Gamma \exp(1)} n_{\infty} \]  

(83)

Then \( N \) is 1.19 times greater than the result of iteration procedure at the second step and 1.03 times greater than the result at the third step. It can be regarded as the practically precise result. All mentioned above estimates obtained for \( l = 0 \) remain valid in the nonlinear case.

Figure 2 illustrates these constructions in the linear case. This picture shows the contributions of the various forms of the spectrums into the values of \( g \), \( dg/dz \), \( d^2g/dz^2 \), \( d^3g/dz^3 \) (from upper till lower axes of the coordinates) at \( t = t_* \). Here the subintegral expressions obtained in the various approaches are drawn. The upper picture shows the subintegral functions in the expression for \( g \) at \( z = 0 \), i.e. \( x^3 f(x) \). The second picture shows the subintegral function in the expression for \( dg/3dz \) at \( z = 0 \), i.e. \( x^2 f(x) \). The third picture shows the behavior of the subintegral expression for \( d^2g/6dz^2 \) at \( z = 0 \), i.e. \( x f(x) \). The lower picture shows the subintegral expression for the number of the droplets or for \( d^3g/6dz^3 \), i.e. \( f(x) \). For \( f(x) \) several different approaches are accepted. The curve "a" corresponds to the precise universal solution, the curve "b" corresponds to the spectrum calculated on the base of the ideal supersaturation (i.e. the first iteration), the curve "c" corresponds to the gaussian form of the spectrum and the curve "d" can be drawn on the base of the spectrum of the gaussian type with the cube correction term (see later).

It can be seen that for \( g \) the suitable approximations can be given by the first iteration. For \( dg/dz \) the suitable approximations can be given by the first iteration and the gaussian spectrum with a correction term (with the appropriate cut-off). For \( d^2g/dz^2 \) and for \( d^3g/dz^3 \) the suitable results can be obtained from all approximations except the first iteration.

8In the homogeneous condensation the choice of \( t_* \) corresponds to the maximum of the supersaturation.
The adopted approximation has some resources of the modification inside itself. Namely, it can give the value of the correction term and the value of the boundary of the region of the applicability of this approximation. Really, let us add the next term to the square approximation. Then we have

\[ f(x) \sim f_m \exp\left(-\left(\frac{x}{x_p}\right)^2 - \left(\frac{x}{x_l}\right)^3\right) \]

with some parameter \(x_l\). The value of \(x_l\) will be established from the fact that the model curve for the supersaturation

\[ \zeta_{\text{appr}} = \zeta_s - \frac{\zeta_s}{1}\left(-\left(\frac{x}{x_p}\right)^2 - \left(\frac{x}{x_l}\right)^3\right) \]

must only touch the line of the ideal supersaturation at some point, which will mark the boundary between the initial region and the region of the applicability of above given approximation.

Figure 3 illustrates this construction. Figure 3 demonstrates the form of the modified spectrum with the cubic term taken into account. The upper picture shows the behavior of the normalized deviation of the supersaturation as function of \(z\) for the different models. The value \(\delta_{id}\) corresponds to the ideal supersaturation, the value \(\delta_{sq}\) corresponds to the gaussian approximation, the value \(\delta_{mod}\) comes from the consideration of the gaussian with a correction term. The curve \(\delta_{mod}\) touches the straight line \(\delta_{id}\). In the lower picture the gaussian spectrum \(f_{gauss}\) and the modified spectrum \(f_{mod}\) are drawn. The scale of \(x\) is chosen to have \(c = 1\). It is seen that the difference between these two spectrums is rather small.

In the case of the linear source it follows from the condition of equality of the derivatives of \(\zeta_{\text{appr}}\) and \(\Phi\) that

\[ x_l = \left(-\frac{2}{3}x_p^{-2}x_b^{-1} - \frac{1}{3}x_b^{-2}\right)^{-1/3} \]

After the substitution of \(x_l\) into the condition \[\zeta_{\text{appr}}(x_b) = \Phi(x_b)\] we shall come to

\[ x_b = \frac{-2 + (4 - 12x_p^{-2})^{1/2}}{2x_p^{-2}} \]

for the boundary between the initial and the central regions.

By the same way one can get the number of the molecules in the droplets by the separate integration and, thus, fulfil the next step of the iteration approximation.

\[ \text{We assume that approximately } \Psi = \exp(-1). \]
5.5 Heterogeneous condensation

In the case of the heterogeneous condensation one can obtain the following system at the period of the essential formation of the droplets:

\[ \Phi = \zeta + g \quad g(z) = \int_{-\infty}^{z} dx(z-x)^{3} f_{s} \theta \exp\left(\frac{-\Gamma(\Phi_{s} - \zeta)}{\Phi_{s}}\right) \]  \hspace{1cm} (84)

\[ \theta = \exp\left(-\frac{n_{\infty}}{\eta_{\text{tot}}} \int_{-\infty}^{z} dx f_{s} \exp\left(\frac{-\Gamma(\Phi_{*} - \zeta)}{\Phi_{s}}\right)\right) \]  \hspace{1cm} (85)

The straight development of the method utilized in the homogeneous case leads to the construction of the square approximation for the function

\[ \psi = f_{s} \exp\left(-\frac{n_{\infty}}{\eta_{\text{tot}}} \int_{-\infty}^{z} dx f_{s} \exp\left(\frac{-\Gamma(\Phi_{*} - \zeta(x))}{\Phi_{s}}\right)\right) \exp\left(-\frac{-\Gamma(\Phi_{*} - \zeta(z))}{\Phi_{s}}\right) \]  \hspace{1cm} (86)

which comes from the substitution of the second equation into the first one.

The square approximation for \( \psi \) isn’t suitable because the factor

\[ \exp\left(-\frac{n_{\infty}}{\eta_{\text{tot}}} \int_{-\infty}^{z} dx f_{s} \exp\left(\frac{-\Gamma(\Phi_{*} - \zeta)}{\Phi_{s}}\right)\right) \]

in the last expression has a very complex behavior. This term goes from the expression for \( \theta \). This allows to introduce the following method. Notice that the iteration procedure in the investigation of the heterogeneous condensation gives the appropriate result on the second step \[6\]. The second approximation is obtained on the base of approximation which doesn’t contain any functional dependence of \( \theta \) upon \( z \). Then one can solve the pseudo homogeneous equation, i.e. equation \[54\] with \( \theta \equiv 1 \) and then calculate \( \theta \) according to the final step of the iteration procedure \[54\]. The pseudo homogeneous equation will be solved by the method of the previous subsections. This solution will give the main parameters \( f_{m}, x_{p} \). The function \( \theta \) is approximately given by the following expression

\[ \theta = \exp(-\Theta(z_{b} - z)\phi' - \Theta(z - z_{b})\phi'') \]  \hspace{1cm} (87)

where

\[ \phi' = f_{s} \frac{n_{\infty}}{\eta_{\text{tot}}} \int_{-\infty}^{z} \exp(cx + lx^{2})dx \]  \hspace{1cm} (88)

\[ \phi'' = f_{s} \frac{n_{\infty}}{\eta_{\text{tot}}} \int_{-\infty}^{z_{b}} \exp(cx + lx^{2})dx + f_{m} \frac{n_{\infty}}{\eta_{\text{tot}}} \int_{z_{b}}^{z} \exp\left(-\left(\frac{x}{x_{p}}\right)^{2}\right)dx \]  \hspace{1cm} (89)

This expression can be taken in the elementary functions due to \[58\].

The number of the droplets which appears from \( \theta \) in a very simple form

\[ N(z) = \eta_{\text{tot}}(1 - \theta(z)) \]  \hspace{1cm} (90)
based on the conservation law for the heterogeneous centers.

One can introduce another approximation. In the final formulas one can spread approximation (49) over the whole period of the essential formation of the droplets. Then the value of $\theta_{\text{final}}$ can be presented in the following form

$$
\theta_{\text{final}} = \exp\left[-\frac{n_{\infty}}{\eta_{\text{tot}}} f_m \sqrt{\pi x_p}\right]
$$

and the total number of droplets is given by

$$
N_{\text{tot}} = \eta_{\text{tot}}(1 - \exp\left[-\frac{n_{\infty}}{\eta_{\text{tot}}} f_m \sqrt{\pi x_p}\right])
$$

The error of the above presented method is rather small, the accuracy is practically the same as the accuracy of the iteration procedure [6]. The advantage of this method lies in the fact that the iterations can’t be calculated in the case of the nonlinear external conditions.

Note that in the above presented procedure the cross influence of the exhaustion of the heterogeneous centers can not be observed. Really, suppose that there are many heterogeneous centers of the first sort and a few centers of the other sort. Certainly, the second sort can not act upon condensation on the first sort in reality. But in final formulas the second sort acts as there is no exhaustion of the second sort centers. The values $\Phi'$ and $\Phi''$ are based on some model for supersaturation. Only the parameter $x_p$ is determined by the consumption of the vapor by the droplets. But it is calculated on the base of the total values of the heterogeneous centers. So, we must reconsider this procedure.

The process of exhaustion of the heterogeneous centers makes the inequalities for the hierarchy of the regions even more strong. So, we can repeat the above presented procedure with the account of the exhaustion of the heterogeneous centers.

For the approximation of $\theta_j$ ($j$ marks the sort of the centers) in the ”initial” period one has

$$
\theta_j = \exp\left[-\frac{f_s_j}{c} \frac{n_{\infty}}{\eta_{\text{tot}, j}} \exp(cx)\right]
$$

Then this expression must be introduced into all expressions for $\alpha_i$. These expressions now are the following ones

$$
\alpha_{i,j} = (-1)^i \frac{3!}{i!(3-i)!} f_s j \int_{-\infty}^{z_b} x^i \exp(cx + lx^2) \exp\left[-\frac{f_s j}{c} \frac{n_{\infty}}{\eta_{\text{tot}, j}} \exp(cx)\right] dx
$$

When the last expression is going to be calculated we shall also use the steepens descent method and decompose $\theta$ into the Tailor’s series near $x = z_b$.

In the zero approximation

$$
\alpha_{i,j} = (-1)^i \frac{3!}{i!(3-i)!} f_s j \int_{-\infty}^{z_b} x^i \exp(cx + lx^2) dx \exp\left[-\frac{f_s j}{c} \frac{n_{\infty}}{\eta_{\text{tot}, j}} \exp(cz_b)\right]
$$
has the same analytical structure as the previous one. Also one can decompose exp(cx) near exp(cz_b) and restrict this decomposition by the zero and the first two terms of the Tailor’s serials.

The further generalization is rather simple. We must include $\sum_j$ all times when $f_j$ appeared.

In the case of the continuous spectrum we must substitute $\sum_j$ by $\int dw$ where $w$ is the activity of the heterogeneous center.

Note that the effect of the cross influence of the exhaustion of the heterogeneous centers doesn’t play any essential role in the dynamic conditions. This effect isn’t specific for dynamic conditions but takes place in the situation of the decay type. The reason is that in the situation of the decay there are many characteristic widths at one and the same (initial) moment of time for the given initial value of supersaturation. In dynamic conditions all halfwidths are approximately equal to $c^{-1}$.

The alternative opportunity is to consider $\exp(lx^2)$ as the correction term and to keep $\exp(-\frac{f}{c}\exp(cx))$ under the sign of integral.

One can say that in the situation of the dynamic conditions the process of the exhaustion (the probability to be exhausted) occurs only due to the activity of this very sort of the nucleus (at the given supersaturation).

6 Concluding remarks

The applicability of the quasistationary distribution as the boundary condition for the kinetic equation is based on the fact that the characteristic time of the establishing of the stationary distribution in the region $\nu^{1/3} \leq 3\nu^{1/3}/c$ is negligible in comparison with the characteristic time of the variation of the supersaturation up to the value $\zeta/\Gamma_i$. This statement is valid in all situations except the situations where there occurs the total exhaustion of the free heterogeneous centers and the result is obvious - all centers of the given sort became the centers of the droplets. This fact can be proved analytically. Also one can prove that the main consumers of the vapor are the super-critical embryos, i.e. the droplets.

The quasistationarity may not be valid when $\Delta x \gg x_p$. One can show that in this case the effects of nonstationarity are cancelled.

Consider how to include situation (13) in the general consideration. Note that in the iteration procedure [6] as far as in the modified method of the steepens descent the structure of the calculations has one remarkable feature: the final expressions for $\theta$ and $N$ are given on the base of the approximation obtained with the help of the ”ideal” laws. In these ”ideal” laws the analytical structure of the expressions for the different sorts is one and the same. It turns to manifest some features specific to the sort of the heterogeneous centers (due to their number) only at the final iterations. So, the generalization is rather formal and simple. It is necessary to have one common system of the coordinates $x$, $z$ and to calculate directly the iterations (or to use the modified method of the
steepens descent). For $\theta_{(2)}^i$ we get the separate expressions:

$$
\theta_{(2)}^i = \exp(-f_i^* \frac{n_{\infty}}{\eta_{i\text{tot}}} \frac{c^3 \Omega_i}{6 \Gamma_i (f_i^* + f_j^*)} (1 - \exp(-\frac{6 \Gamma_i (f_i^* + f_j^*)}{c^4 \Omega_i} \exp(cz))))
$$

Here no cross influence of the exhaustion of the heterogeneous centers of the different sorts can be observed. One must use the modified method of the steepens descent with the cross influence of the exhaustion of the heterogeneous centers as had been made for the case of the decay. The result of condensation on the spectrum of activities will show that the form of the spectrum is near the universal one. So, one can use it as some ansatz and formulate the algebraic equations on the parameters.

The account of the nonisothermal effects is rather simple. The intensity of the droplets formation is changed in $\frac{\zeta + 1}{\zeta} \ln(\zeta + 1)$ times (i.e. in the approximately constant number of times during the period of the intensive formation of the droplets). So, the description of the process can be attained if we assume that the consumption of one molecule effectively leads to the consumption of $(k_2 + 1)$ molecules, where $k_2$ is some known parameter [6]. So the description is reduced to the obvious renormalizations.

The global description of the evolution is more complex. One can show that the already known procedure of the iteration approximations for the external supersaturation (where $z$ in all terms except $\frac{dz}{dt}$ is supposed to be known) is successful in this case also. The application of this iteration procedure allows to cancel the restriction $k_2 \gg 1$ used in [6].

Practically one needn’t to fulfill such a complex procedure as to solve many system of the integral equations many times. Ordinary the following procedure must by accepted:

- Put $\zeta = \Phi$ and determine the moment $t_i$ of the exhaustion of the different sorts of the heterogeneous centers.
- Establish the maximum of $\Omega$ under the monodisperse approximation with the already defined coordinates of the peaks and $N_i = \eta_{i\text{tot}}$.
- Reconsider formation of the droplets of that sorts of the heterogeneous centers for which $z(t_i) \geq z(t(\text{max } \Omega)) - \Delta x$ by the modified steepens descent method.

\[\text{Here the initial approximation corresponds to the ideal law of evolution}\]

\[\text{Note that formation of the droplets on the sorts for which}\]

\[z(t_i) \geq z(t(\text{max } \Omega)) + \Delta x\]

\[\text{can be treated in the pseudo homogeneous manner}\]

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As far as the moments of formation of the droplets of these sorts are near \( t(\text{max} \Omega) \) the action of formation can be presented by the direct summation of all \( f_{*, i} \) for these sorts in the expression for \( g \) and its derivatives. The last step solves the problem.

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Figure 1

*Iterations for Ω.*
Figure 2

Subintegral functions in different approximations.
\[ \delta = \frac{\Gamma(z - \Phi)}{\Phi} \]

Figure 3

*Modified spectrum with cubic term.*