Heterogeneous condensation on the centers with continuous activity in dynamic conditions

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Abstract

A system with a metastable phase and a pseudo continuous set of the heterogeneous centers is considered. An analytical theory for kinetics of the process of condensation in such a system is constructed. The free energy of formation of the critical embryo is assumed to be known in the capillary (macroscopic) approach as well as the solvation energy of the embryo. The theory is based on the quasistationary approximation for the nucleation rate which has been justified analytically. An effective iteration procedure is presented. The iterationa are calculated analytically. The approximate universal form of the spectrum is established.
1 Introduction

The theory considered here completes the program of construction of the theory of the aerosol formation announced in [14]. It will be based on the capillary approximation of the height of the activation barrier. This approximation lies in the base of the classical theory of the homogeneous nucleation. All necessary bibliographic remarks can be found in [14].

Speaking about the activity of the heterogeneous centers we mean that the different activity initiates the different height of the activation barrier $\Delta F$, i.e. the difference between the free energy of the critical embryo $F_c$ and the free energy of solvatation $G$. The set of the different activities of the heterogeneous centers can be so dense that we can regard it as the pseudo continuous one. In the case of the "solid nucleus of condensation with the weak interaction" the continuous size of the nucleus ensures the continuous set of $\Delta F$.

The ordinary external conditions for the phase transition have the smooth character in time. The external action on the system leads to formation of the droplets of the new phase. The process of condensation violates the thermodynamic parameters of the system. When the external action on these parameters has the smooth behavior in time we shall say that condensation occurs under the dynamic conditions.

Nevertheless the theory of the heterogeneous condensation in the dynamic conditions has been constructed only for one type of the heterogeneous centers. So, the task to construct the kinetic theory for the system with a continuous set of the heterogeneous centers is rather essential. It will be completely fulfilled here.

We shall use the physical assumptions analogous to [14] which are necessary to construct the mathematical model:

- the thermodynamic description of the critical embryo,
- the random homogeneous space distribution of the heterogeneous centers,
- the free-molecular regime of the droplets growth,
- the homogeneous external conditions for the temperature and for the pressure,
• rather a high activation barrier.

As far as the most interesting characteristics of this process are the numbers of the heterogeneously formed droplets on the centers with a different activity we shall estimate the accuracy of the theory by the error of the obtained solutions for these values. The unit volume is considered. All energy-like values are measured in the thermal units.

The publication has the following structure:

• In the first part the system of the equations of condensation is constructed.
• In the second part the explicit calculation of the iterations is presented.
• In the third part the conception of the universal spectrum is developed.
• In the last part some realistic spectrum of activities is considered and the principle of the self-consistency of the spectrum of the activities is presented.

We shall define the activity of the heterogeneous center as some parameter $w$ which is proportional to the height of the activation barrier

$$
\Delta F(w) = \Delta F \bigg|_{w=0} - \lambda w
$$

with some positive coefficient $\lambda$. Note that the choice of the initial point $w = 0$ is rather arbitrary now. We suppose $\Delta F(w) \gg 1$ for all essential types of the heterogeneous centers.

The total number of the heterogeneous centers with the given activity $w$ will be marked by $\eta_{\text{tot}}(w)$. Naturally $\eta_{\text{tot}}(w)$ is rather a smooth function of $w$. We shall suppose that $\eta_{\text{tot}}$ in the essential region is near some constant value or it can be well approximated by the polinom which power isn’t too high. This value is constant in time.

The density of the molecules in the equilibrium vapor is marked by $n_\infty$, the density of the molecules in the real vapor is marked by $n$. The power of the metastability will be characterized by the value of the supersaturation

$$
\zeta = \frac{n - n_\infty}{n_\infty}
$$

---

1But not for the total number of the droplets.

2When this condition is violated the kinetics of the process can be described by the trivial modification of the theory presented below.
We shall define the super-critical embryos as the "droplets". Every droplet is described by the number of the molecules $\nu$, or by the linear size $\rho = \nu^{1/3}$

Due to the free-molecular regime of the droplets growth we have

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

where $\alpha$ is the condensation coefficient and $\tau$ is some characteristic time between the collisions in the saturated vapor obtained from the gas kinetic theory.

Let us introduce the size $z$ according to

$$z = \int_{t_*}^{t} \zeta \alpha \tau^{-1} dt'$$

(2)

Here $t_*$ is some characteristic moment of time which belongs to the period of the intensive formation of the droplets. The choice of $t_*$ is rather arbitrary. One can use for example the choice described in [8]. Until the beginning of the coalescence [3],[4] which isn’t considered here equation (2) ensures the growth of $z$ in time and can be inverted

$$t(z) = \int_{0}^{z} \tau \alpha^{-1} \frac{dx}{\zeta(x)} + t_*$$

(3)

Hence, all values dependent on time become the values dependent on $z$ and the relative size

$$x = z - \rho$$

can be introduced. During the whole evolution the droplet has one and the same value of the variable $x$. Considering $t(x)$ as the moment when the droplet with the given $x$ has been formed (as a droplet) we can consider all functions of time as the functions of $x$. Hence, we can see that the kinetic equation is reduced to the fact that every droplet keeps the constant value of $x$. To reconstruct the picture of the evolution one must establish the dependencies $t(z)$ and $\zeta(x)$.

The values at the moment $t_*$ will be marked by the lower index "*". The positions of the region of the intensive formation of the droplets are essentially different. But one can introduce $t_*$ as the moment corresponding to the maximum of the supersaturation.
2 The system of the equations of condensation

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

Introduce the value of

$$\zeta_{\text{ideal}} = \frac{n_{\text{tot}}}{n_{\infty}} - 1$$

where $n_{\text{tot}}$ is the total number of the molecules in the system.

We must take into account the reduction of $\zeta_{\text{ideal}}$ to some value $\Phi$ due to the consumption of the vapor molecules in the process of solvation \[9\] \[10\] \[11\]. Moreover, according to \[11\] the ideal supersaturation can be changed by the external supersaturation. In any case we shall assume this value as the known one and mark it by $\Phi$. In some rough approximation $\zeta_{\text{ideal}} \approx \Phi$.

We shall mark by $\eta_{\text{tot}}$ the total number of the heterogeneous centers of all types:

$$\eta_{\text{tot}} = \int dw \eta_{\text{tot}}(w) \quad (4)$$

where $\eta_{\text{tot}}(w)$ is the total number of the heterogeneous centers of the given type (the density of the total value of the heterogeneous centers).

The following statements are valid in the further consideration:

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

- (2) The quasistationary approximation for the nucleation rate is valid during the period of the essential formation of the droplets for those sorts of the heterogeneous centers which aren’t completely exhausted in this process.

The justification of the second statement uses the estimate for times $t_1^*$ of the relaxation to the stationary state in the near-critical region which can be found in \[1\], \[4\] (for the investigation of the heterogeneous barrier the consideration is the same one).

\[3\] The second statement isn’t valid for those sorts of the heterogeneous centers which are going to be completely exhausted. But there the result is obvious. Note that the periods of the intensive formation of the droplets on the centers with the different activities don’t coincide.
Let $f_s$ be the stationary value of the distribution of the sizes of the hetero-
geneously formed droplets measured in the units of $n_{\infty}$. It can be presented
in the following form

$$f_s = f_\zeta(\zeta(x), w)\eta(x, w)$$  \hspace{1cm} (5)

where $\eta(x, w)$ is the density on activities of the number of the heterogeneous
centers which are free from the super-critical embryos and $f_\zeta$ is given by the
following formula \[6\]

$$f_\zeta = \frac{W^+ \exp(-\Delta F(\zeta, w))\tau}{\pi^{1/2} \Delta_{e}\nu \Delta_{c}\nu \zeta n_{\infty}}$$  \hspace{1cm} (6)

where $W^+$ is the number of the molecules in the vapor which interact with the
droplet in the unit of time, $\Delta_{e}\nu$ is the width of the equilibrium distribution

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

and $\Delta_{c}\nu$ is the halfwidth of the near-critical region

$$\Delta_{c}\nu = 2^{1/2} \left| \left( \frac{\partial^2 F}{\partial \nu^2} \right)_{\nu=\nu_c} \right|^{1/2}$$

Index "c" marks the values for the critical embryo and "e" - the values for
the equilibrium embryo. Certainly, $\Delta_{c}\nu$ and $\Delta_{e}\nu$ are some smooth functions
of $w$ and we shall neglect this dependence.

We shall mark by $n_{\infty}g(w)$ the density of the distribution on activities
of the total number of the molecules of the condensed substance in the
heterogeneous droplets formed on the centers of the activity $w$. To simplify
the formulas we shall use

$$\theta(w) = \eta(w)/\eta_{tot}(w)$$

We obtain for $g_i, \theta_i$ the following equations

$$g(z, w) = \int_{-\infty}^{z} (z - x)^3 f_\zeta(\zeta(x), w)\eta(w)dx$$  \hspace{1cm} (7)

$$\theta(z, w) = \exp(-n_{\infty} \int_{-\infty}^{z} f_\zeta(\zeta(x), w)dx)$$  \hspace{1cm} (8)
As far as we measure the accuracy of the theory in the terms of the error in the droplets number we define these values as the following ones:

\[ N(z, w) = \eta_{tot}(w)(1 - \theta(z, w)) \]  \hfill (9)

The total number of the droplets is

\[ N^{tot} = \int \eta_{tot}(w)(1 - \theta(z, w))dw = \int N(z, w)dw \]  \hfill (10)

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

\[ f_\zeta(\zeta(x), w) = f_\zeta(\Phi_*, w) \mid_{w=0} \exp(\Gamma(\zeta - \Phi_*) \Phi_*) \exp(w\lambda) \equiv f_\zeta* \exp(\Gamma(\zeta - \Phi_*) \Phi_*) \exp(w\lambda) \]  \hfill (11)

where

\[ \Gamma = -\Phi_* \frac{d\Delta F(\zeta)}{d\zeta} \mid_{\zeta=\Phi_*} \mid_{w=0} \]  \hfill (12)

and \( \Delta F \) is the height of the heterogeneous activation barrier. The validity of these approximations can be justified for the heterogeneous embryos with the interaction between the center and the molecules of the condensed phase weaker or equal than the reciprocal to the space distance. So, we can imagine this as a hard sphere with a weak interaction on which the embryo is formed.

The dependence of \( \Gamma \) on \( w \) is rather weak. So we can put

\[ \Gamma(w) = \Gamma \mid_{w=0} \]  \hfill (13)

for any essential part of the spectrum of the activities. The applicability of the last approximation is based on the following qualitative model. It

\footnote{Note that the position of the regions of the intensive formation of the droplets on some sort essentially depends on the activity of the centers. the following approximation isn’t valid for the regions of the intensive formation on the active centers. But for these centers the result is evident - all centers are going to become the centers of the droplets.}

\footnote{The validity of these approximations may fail in the situations of the extremely long spectrums (see later). But the square form of the behavior of the supersaturation near the maximum will be attained earlier.}
is known that \( \Gamma \) is approximately \( \Phi_*(\nu_e - \nu_e)/(\Phi_* + 1) \). When the supersaturation is slightly changed then the value of \( \nu_e \) doesn’t undergo some big variations and the variation of \( \Gamma \) occurs mainly due to the variation of \( \nu_e \). The behavior of the value \( \nu_e \) resembles the analogous behavior in the homogeneous case. As a result we can justify not only the approximation concerning the dependence on the supersaturation, but also the dependence on the activity.

A natural question about the essential part of the spectrum appears here. The process of condensation on the centers with some relatively high activity occurs earlier than the supersaturation attains maximum. These centers form the droplets which can be included in the value of the external supersaturation in the manner of [11] [16]. For these centers the number of the formed droplets coincides approximately with the number of the heterogeneous centers - all centers are now the centers of the droplets.

The action of this part of the spectrum on the further evolution can be treated in the terms of the external supersaturation \( \Omega \) (see [11]). The non-trivial statement that the process of formation of the droplets on the centers with the intermediate activity occurs near the maximum of the supersaturation lies in the base of such a method of description. This fact can be analytically proved.

The centers with some relatively low activity remain practically unexhausted (when the spectrum \( \eta_{tot} \) has no singularities they can not play any important role in condensation). The singularities can be described in this region in a manner from [11] [16]. So only some centers with the intermediate activity are essential near the maximum of the supersaturation. In the scale of the activities this region corresponds to the variation of \( w \) by the value of the order of \( \lambda^{-1} \).

Now we shall formulate the system of the balance equations for the functions \( g(x, w) \), \( \theta(x, w) \) and

\[
G(x) = \int dw g(x, w)
\]

where the integral is taken over the whole spectrum of the heterogeneous centers. In principle we can write that the region of integration goes from \(-\infty \) up to \( \infty \) but in fact this integration must be carried out in the region which covers the essential region of the spectrum[1]. In this region it is necessary to

\[\text{[1]}\]

The extraction of this region is quite analogous to the case of the decay on the spectrum of activities.
have relatively smooth behavior of $\eta_{tot}$. This value must be approximately constant

$$\eta_{tot} \approx const$$

or must be well approximated by the polinom on the activities:

$$\eta_{tot} = P_n(w)$$

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

Using the conservation laws for the heterogeneous centers and for the molecules of the condensing substance we get for $g, \theta$ the following equations

$$g(z, w) = f_* \int_{-\infty}^{z} (z - x)^3 \exp(-\Gamma \frac{\zeta - \Phi_{*}}{\Phi_{*}}) \theta dx \exp(w\lambda)$$  \hspace{1cm} (14)$$

$$G(z) = \int dw g(z, w)$$  \hspace{1cm} (15)$$

$$\theta(z, w) = \exp\left(-\frac{f_* \exp(\lambda w) \eta_{tot}}{\eta_{tot}} \int_{-\infty}^{z} \exp(-\Gamma \frac{\zeta - \Phi_{*}}{\Phi_{*}}) dx\right)$$  \hspace{1cm} (16)$$

$$\Phi = \zeta + G(z)$$  \hspace{1cm} (17)$$

where $f_* = f_{\zeta} \cdot \eta_{tot}$

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

We shall consider this system of equations during the period when the centers with the intermediate activity are going to become the centers of the droplets. We shall call this period as the period of the intensive formation of the droplets (PIFD).

We assume that the ordinary \[8\] linearization of the ideal supersaturation is valid during PIFD\[7\]

$$\Phi(x) = \Phi_{*} + \frac{\Phi_{*} \cdot \text{CE}}{\Gamma}$$  \hspace{1cm} (18)$$

\[7\] One can analytically show that the duration if PIFD is rather short. Namely

$$\frac{\Phi(z) - \Phi_{*}}{\Phi_{*}} \leq \frac{1}{\Gamma}$$
with some positive parameter $c$.

After the substitution of this linearization into the system of the condensation equations this system transfers to

$$g(z, w) = f_* \int_{-\infty}^{z} (z - x)^3 \exp(cx - \frac{\Gamma}{\Phi} G(x))\theta(x, w) dx \exp(w\lambda)$$  \hspace{1cm} (19)

$$G(z) = \int dw g(z, w)$$  \hspace{1cm} (20)

$$\theta(z, w) = \exp(-\frac{f_* \exp(\lambda w) n_{\infty}}{\eta_{tot}} \int_{-\infty}^{z} \exp(cx - \frac{\Gamma}{\Phi} G(x))dx)$$  \hspace{1cm} (21)

The spectrum of sizes can be found as the following one

$$f(x, w) = f_* \exp(\lambda w) \exp(-\Gamma \frac{\zeta - \Phi}{\Phi} x) \theta(x, w)$$  \hspace{1cm} (22)

and when the linearization is taken into account:

$$f(x, w) = f_* \exp(\lambda w) \exp(cx - \frac{\Gamma}{\Phi} G(x))\theta(x, w)$$  \hspace{1cm} (23)

### 3 Iteration procedure

Such systems as the already obtained one can be solved by the iteration procedure. It can be constructed by the following way: For the initial approximations we choose:

$$g_0(z, w) = 0 \quad \theta_0(z, w) = 1$$  \hspace{1cm} (24)

The recurrent procedure is defined according to

$$g_{i+1}(z, w) = f_* \int_{-\infty}^{z} (z - x)^3 \exp(cx - \frac{\Gamma}{\Phi} G_i(x))\theta_i(x, w) dx \exp(w\lambda)$$  \hspace{1cm} (25)

$$G_i(z) = \int dw g_i(z, w)$$  \hspace{1cm} (26)

$$\theta_{i+1}(z, w) = \exp(-\frac{f_* \exp(\lambda w) n_{\infty}}{\eta_{tot}} \int_{-\infty}^{z} \exp(cx - \frac{\Gamma}{\Phi} G_i(x))dx)$$  \hspace{1cm} (27)

The chains of inequalities analogous to [7] guarantees the convergence of the iterations and some estimates analogous to [7] can be established here.
The direct calculation of the iterations gives

\[ g_1(z, w) = f_\star \frac{6 \exp(cz)}{c_4} \exp(\lambda w) \] (28)
\[ \theta_1(x, w) = \exp(-f_\star \ast n_\infty \exp(\lambda w) \frac{\exp(cx)}{c}) \] (29)
\[ G_1(x) = f_\star \ast \frac{6 \exp(cx)}{c_4} \int dw \exp(\lambda w) \eta_{\text{tot}} \] (30)

The last integral causes some problems with convergence. When \( \eta_{\text{tot}} = \text{const} \) it can not be calculated. At least there are two possibilities to overcome this difficulty.

The first possibility is a more formal one. Certainly, in every system \( \eta_{\text{tot}}(w) = 0 \) when \( w \) is greater than some maximum value \( w_{\text{max}} \). So, formally the integral exists and it is equal to some constant. This constant is generally unknown, but one can act in the manner like it was done with the supersaturation in [8]. In [8] the value of \( \Phi_\star \) was not the matter of consideration in the iteration method, but was included in the set of the undefined parameters. After the final form of the size spectrum was established an equation on parameters was studied. The form of the spectrum can play a role of some ansatz with several parameters. The same procedure can be inserted here.

The reason is that we can observe the separation of the functions containing \( w \) from the terms containing the other parameters of the condensation process. This fact remains valid also in the second iteration which is rather a good approximation for the final solution as it can be analytically proved on the base of the analysis of the iteration procedure.

The second possibility seems to be more physical one because it allows to combine the current problem with the problem of the correct definition of the region of rather active and exhausted centers. Really we have not separated the region included into the external supersaturation from the region which isn’t included into the external supersaturation. Note, that in the dynamic conditions the spectrum of sizes of the droplets formed on some fixed sort of the heterogeneous centers has well defined boundaries. The sizes (and the times of formation) of the droplets which are essential in the vapor consumption can be also well localized. Namely, the spectrum is essentially situated in the region

\[-\frac{1}{c} \leq z \leq \frac{1}{c} \] (31)
and the region of the droplets essential for the vapor consumption during PIFD is essentially covered by the interval

$$-\frac{8}{c} \leq z \leq 0$$

(32)

As a result one can state that for $z \sim -a/c$ where $a \sim 8$ one can get the start of PIFD for the centers which are in the process of nucleation near the maximum of the supersaturation.

Note that the moment $t_\ast$ can be taken as a moment of the maximum of the supersaturation. Really, when the maximum of intensity of formation (or the moment of formation of the half of the droplets) lies far from maximum of the supersaturation, then the result of nucleation of this sort of centers is rather obvious: the supersaturation is equal to the ideal (or external) supersaturation

$$\zeta = \Phi$$

the total number of the droplets is equal to the total number of the heterogeneous centers

$$N_{tot} = \eta_{tot}$$

and the moment of formation of the spectrum on the centers of some fixed sort which can be considered as a monodisperse one can be found from

$$\theta(z, w) = 1/2$$

which is equivalent to

$$f_\zeta \ast \exp(\lambda w)n_\infty \exp(cz) = c \ln 2$$

where the first two terms can be changed by some slightly other amplitude of the spectrum and the parameter $c$ can be reconsidered as far as the derivative can vary.

The simplest regularization by the cut-off is the following one. We must substitute the value of $\eta_{tot}$ by the value $\eta_{init}$ calculated as

$$\eta_{init} = \eta_{tot}\theta(x = -a, w)$$

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8See the analysis of the second figure from [10].
after the calculation of \( \theta(-a, w) \) which can be calculated on the base of the ideal supersaturation, i.e. in the first iteration. As far as

\[
\theta_1(-a, w) = \exp(-f_\xi * n_{\infty} \exp(\lambda w) \frac{\exp(-ca)}{c})
\]

the value of \( f_* \) must be changed by

\[
f_* = f_\xi * \eta_{tot}(w) \exp(-f_\xi * n_{\infty} \exp(\lambda w) \frac{\exp(-ca)}{c})
\]

4 Calculation of the iterations

Let us calculate the iterations. Then the expression for \( G \) will be the following

\[
G_1 = f_\xi \int_{-\infty}^{\infty} \eta_{tot}(w) \exp(\lambda w) \exp(-A \exp(\lambda w)) dw \frac{6 \exp(cz)}{c^4}
\]

where

\[
A = f_\xi * n_{\infty} \frac{\exp(-ca)}{c}
\]

When \( \eta_{tot} = \text{const} \) the integral can be taken which leads to

\[
G_1 = f_\xi * \eta_{tot} \frac{1}{\lambda A} \frac{6 \exp(cz)}{c^4}
\]

Note that the integral can be taken in the final limits which allows to take into account only the finite region of activities as far as an approximation of the total number of heterogeneous centers by the composition of the Heavisaid’s functions.

When \( \eta_{tot} \) is approximated by the polinom it is easy to note that each monom in the integral leads to some elementary functions with some universal constants. This fact can be seen from the simple translation of the variable in

\[
\int_{-\infty}^{\infty} w^m \exp(\lambda w) \exp(-A \exp(\lambda w)) dw
\]

to the variable

\[
\lambda w + \ln(A)
\]

Here the integration must be fulfilled in the infinite limits. These integrals can be expressed through \( \Psi \)-function and its derivatives when the argument is put to 1.
The second approximation for $\theta$ leads to the following result:

$$
\theta_2(z, w) = \exp(-f_\zeta n_\infty \exp(\lambda w) \int_{-\infty}^{z} \exp(cx - B \exp(cx)) dx)
$$

where

$$
B = \frac{\Gamma}{\Phi_* f_\zeta} \frac{6 \eta_{tot}}{c^4} \frac{1}{\lambda A}
$$

Note that the integral can be taken here also in the finite limits. After the integration we get

$$
\theta_2(z, w) = \exp(-f_\zeta n_\infty \exp(\lambda w) \frac{1}{cB} (1 - \exp(-B \exp(cz))))
$$

Note that $\eta(w) = \eta_{init}(w) \theta(z, w)$.

Particularly, for the final values one can get

$$
\theta_2(\infty, w) = \exp(-f_\zeta n_\infty \exp(\lambda w) \frac{1}{cB})
$$

This value of $B$ is obtained in the approximation $\eta = const$. For the further consideration only the analytical structure of $B$ is important. Namely, in any case (and also in the case $\eta_{tot}(w) = P_n(w)$) we have for $G$ the expression with the following analytical structure

$$
G_1 \sim const(z, w) \exp(cz)
$$

So, $B$ is some constant and this fact ensures the possibility of the further calculation of the iterations.

The next step is the calculation of the total number of the droplets appeared in the considered period which can be done by the simple integration

$$
N^{tot} = \int_{-\infty}^{\infty} dw N_{tot}(w)
$$

Note that instead of

$$
N^{tot} = \int_{-\infty}^{\infty} dw \eta_{tot}(w)(1 - \theta_2(\infty, w))
$$

which can not be integrated we must take

$$
N^{tot} = \int_{-\infty}^{\infty} dw \eta_{init}(w)(1 - \theta_2(\infty, w))
$$
which gives the integral with no problems of convergence. To calculate the last integral note that

\[ \theta_2(-a, w) = \exp(-f_\zeta \exp(\lambda w) n_\infty \int_{-\infty}^{-a} \exp(cx - \frac{\Gamma}{\Phi_*} G) dx) \]

Consider now the case \( \eta_{tot} = const \). After the evident renormalization of the variables of integration the integral can be reduced to

\[ \int_{-\infty}^{\infty} \exp(-\exp(x))(1 - \exp(-H \exp(x))) dx = \]

\[ \int_{-\infty}^{\infty} \sum_{i=0}^{\infty} \frac{y^i H^{i+1}}{(i+1)!} \frac{1}{\sum_{i=0}^{\infty} \frac{y^i H^i}{i!}} dy \]

Note, that it is necessary to left the serial in the denominator.

The necessary accuracy will be ensured by the first three terms in the decompositions of

\[ \int_{0}^{\infty} \sum_{i=0}^{\infty} \frac{y^i H^{i+1}}{(i+1)!} \frac{1}{\sum_{i=0}^{\infty} \frac{y^i H^i}{i!}} dy \approx \int_{0}^{\infty} \sum_{i=0}^{2} \frac{y^i H^{i+1}}{(i+1)!} \frac{1}{\sum_{i=0}^{3} \frac{y^i H^i}{i!}} dy \]

Then an integral from the rational function can be simply calculated (also in the finite limits).

Now the integrals

\[ I_j \equiv \int_{0}^{\infty} \ln^j y \frac{\sum_{i=0}^{\infty} \frac{y^i H^{i+1}}{(i+1)!}}{\sum_{i=0}^{\infty} \frac{y^i H^i}{i!}} dy \approx \int_{0}^{\infty} \ln^j y \frac{\sum_{i=0}^{n-1} \frac{y^i H^{i+1}}{(i+1)!}}{\sum_{i=0}^{\infty} \frac{y^i H^i}{i!}} dy \]

will be calculated. These integrals appear when the polynomial approximation for \( \eta_{tot} \) is accepted.

Consider the function

\[ f(y) = \ln^{i+1} y \frac{\sum_{i=0}^{n-1} \frac{y^i H^{i+1}}{(i+1)!}}{\sum_{i=0}^{\infty} \frac{y^i H^i}{i!}} \]
as the function of a complex variable. Integrate this function along the closed path $\Omega$ constructed in the following manner: the big circumference with an infinite radius; two straight lines $|y + i0, \infty + i0|, |y - i0, \infty - i0|$; the little circumference with a zero radius. The integrals along the circumferences are going to the zero. The integrals along the straight lines give:

$$\int [\ln^{j+1}_{j+1} y - (\ln y + 2\pi i)^{j+1}] \sum_{i=0}^{n-1} \frac{\psi^{H+1}_{i+1}}{(i+1)!} \sum_{i=0}^{n} \frac{\psi^{H+i}_{i+1}}{i!} dy$$

which can be reduced to $I_j$ and $\sum_{k<j} c_k I_k$ with some known coefficients. On the other hand this integral can be reduced to

$$\sum \text{res} [\ln^{j+1}_{j+1} y \frac{\sum_{i=0}^{n-1} \psi^{H+1}_{i+1}}{(i+1)!} \sum_{i=0}^{n} \frac{\psi^{H+i}_{i+1}}{i!}]$$

inside $\Omega$. As the result we have the recurrent procedure which allows us to calculate all $I_j$.

Now let us see how the corrections due to the cut-off can be introduced in the value of $g(z, w)$. In the first approximation we have:

$$g_1(z, w) = \frac{6f_s}{c^4} \exp(\lambda w)(\exp(cz) - \exp(-ca))$$

The value of $G_1$ in the approximation $\eta_{tot} = \text{const}$ is given by

$$G_1 = f_\zeta, \frac{6\eta_{tot}}{c^4} \frac{1}{A\lambda}(\exp(cz) - \exp(-ca))$$

Note that it can be calculated for the finite band of the spectrum of the activities. The calculation under the polynomial approximation for $\eta_{tot}$ can be done in the same manner.

Instead of the pre-exponential factor one can put some other function. The separation of this expression into two factors depended on $w$ and on $z$ is obvious.

For $\theta_2$ we get:

$$\theta_2(z, w) = \exp(-f_\zeta, n_\infty \exp(\lambda w) \int_{-\infty}^{z} \exp(cx - B(\exp(cx) - \exp(-ca))) dx)$$
and after the simple calculation:

\[ \theta_2(z, w) = \exp\left(-f_\zeta n_\infty \exp(\lambda w) \exp(B \exp(-ca)) \frac{1}{cB} (1 - \exp(-B \exp(cz)))\right) \]

The final value is the following:

\[ \theta_2(z, \infty) = \exp\left(-f_\zeta n_\infty \exp(\lambda w) \exp(B \exp(-ca)) \frac{1}{cB} \right) \]

It differs from (33) only by the remormalisation of the amplitude thanks to \( \exp(B \exp(-ca)) \).

The value of \( N^{tot} \) is calculated in the same manner.

Note that one can change \( -\infty \) to \(-a\) and repeat all calculations in the same manner.

The analytical estimates show that the second iteration gives rather a good approximation for the process. The reason is quite similar to [8]. Really, one can simply integrate all estimates from [8] to justify the validity of the obtained expressions.

Another important remark must be given. One can see that all obtained values have the separation of the expressions (or arguments of exponents) in two terms: the first one depended on \( w \) and the second one depended on \( z \). This reduction can not be observed in all high iterations. It is responsible for the absence of the cross influence of exhaustion of the heterogeneous centers with the different activity in the first iterations. The similar property is absent in the situation of decay [14], [15]. Here such a cross influence can be neglected because the equation on the parameters of condensation balances the time of formation with the characteristic intensity of formation and leads to the fact that the characteristic width of the size spectrum is always approximately equal to \( \frac{1}{c} \). The probability to form the droplet on the center is always determined only by the supersaturation and by the value of activity (and not by the total number of centers of the given sort).

5 Universal solution

Now the problem of the construction of the universal solution will be considered. The idea of the universal solution [2] lies in the fact that after formation of the spectrum of the droplets the further evolution of the process
depends only from the first three (and zero) momentums of the distribution function. So if one can choose some variables in which the solution (the distribution function) is the universal function (undepended on the parameters of the problem) then the expressions for the momentums have rather a simple analytical structure combining some parameters of the problem with the universal constants.

For the process of the homogeneous condensation the universal solution was obtained in [2]. For the process of the heterogeneous condensation the universal solution is absent, but some pseudo universal solution can be considered as the base for the further iterations [7].

We shall rewrite the system of the condensation equations in the terms of \( \zeta \) and \( \Phi \)

\[
\Phi_\ast + \frac{\Phi_\ast}{\Gamma}cz = \zeta + G
\]

\[
G = \int dwg(w)
\]

\[
g(w) = f_\ast \int_{-\infty}^{z} (z - x)^3 \exp\left(\frac{\Gamma}{\Phi_\ast}(\zeta - \Phi_\ast)\right) \theta(w, x) dx \exp(\lambda w)
\]

\[
\theta(w) = \exp(-f_\ast \Phi_\ast n_\infty \exp(\lambda w) \int_{-\infty}^{z} \exp\left(\frac{\Gamma}{\Phi_\ast}(\zeta - \Phi_\ast)\right) dx)
\]

Introduce the function

\[
\delta = \frac{\Gamma}{\Phi_\ast}(\zeta - \Phi_\ast)
\]

Then after the substitutions

\[
\lambda w \rightarrow w
\]

\[
p x \rightarrow x
\]

\[
\frac{\Gamma}{\Phi_\ast} G \rightarrow G
\]

\[
\frac{\Gamma}{\Phi_\ast} \lambda g \rightarrow g
\]

one can get

\[
\frac{c}{\rho}z = \delta + G
\]

\[
G = \int dwg(w)
\]
\[ g(w) = \frac{f_* \Gamma}{\lambda \Phi_p} p^4 \int_{-\infty}^{z} (z - x)^3 \exp(\delta) \theta(w, x) dx \exp(w) \]

\[ \theta(w) = \exp(-f_* \frac{n_{\infty}}{p} \int_{-\infty}^{z} \exp(\delta) dx) \]

Let us choose \( p \) as
\[ \frac{f_* \Gamma}{\lambda \Phi_p} p^4 = 1 \]

and now there are no parameters in the expression for \( g \). If the moment of \( t_* \) is chosen as the moment when the supersaturation attains the maximum, then
\[ \frac{c}{p} = \int dw 3 \int_{-\infty}^{z} (z - x)^2 \exp(\delta) \theta(w, x) dx \exp(w) \]

Then
\[ f_* \frac{n_{\infty}}{p} = \frac{f_*^{3/4} \lambda^{1/4} \Phi_p^{1/4}}{n_{\text{tot}} \Gamma^{1/4}} \]

An ordinary and natural condition to establish the zero point of activity can be written as the following one:
\[ \theta(w = 0, z = \infty) = \frac{1}{2} \]

which gives
\[ f_* \frac{n_{\infty}}{p} = \frac{\ln 2}{\int_{-\infty}^{\infty} \exp(\delta(x)) dx} \]

and there are no parameters in the last equation.

As the result there are no parameters in the system of the condensation equations and the solution has the universal form. It can be analytically proved that it is a unique solution. All consequences now coincides with analogous conclusions from [2]

Note that there is a property of a very smooth dependence of the number of droplets on the \( f_* \). So we can get the equation on the parameters of the process in some rough approximation (see the iteration procedure) and then use the universal law.

The last model has the evident disadvantage. The equation for \( G \) demonstrates no convergence. Really, we can substitute the expression for \( g \) into the expression for \( G \) and fulfil the integration over \( w \). Then we come to
\[ G = A_{00} \int_{-\infty}^{z} (z - x)^3 \frac{\exp(\delta(x))}{\int_{-\infty}^{z} \exp(\delta(x')) dx'} dx \]
where
\[ A_{00} = \frac{f_s \Gamma}{\lambda \xi_*^p n_\infty f_\xi} \]

The evident necessary asymptote \( G \to 0 \) when \( z \to -\infty \) leads to \( \delta(z) \to \frac{c}{p} z \) when \( z \to -\infty \). Then the exponents can be cancelled and the subintegral expression has the asymptote \((z - x)^3\) which doesn’t ensure the convergence. Then we need some regularizations. The most evident one is to notice that after the process of any appearing of the droplets the constant value of \( \eta \) transforms into
\[ \eta_{\text{new}} = \eta_{\text{old}} \exp(-Q \exp(w)) \]

where \( Q \) is some constant.

We shall use this value as the initial one and after the analogous transformations we can come to
\[ G = \frac{f_s \Gamma}{\lambda \Phi_s p^t} \int_{-\infty}^{z} (z - x)^3 \exp(\delta(x)) \exp(\frac{L_{n_\infty}}{p} \int_{-\infty}^{x} \exp(\delta(x'))dx') dx \]

The coefficient \( \frac{L_{n_\infty}}{p} \) can be made equal to some constant (may be 1) due to the choice of the scale of activities. This choice states some concrete value of \( Q \) (which has the same dependence on the choice as \( \frac{L_{n_\infty}}{p} \) has). The limit \( Q \to 0 \) corresponds to the already observed situation. Now we have more general equation taking into account the power of the previous deformation of the activity spectrum. Evidently the solution depends on the parameter \( Q \) and isn’t universal. We see the further inclusion of the distribution into some more general set of the solutions for the various powers of the deformations of the spectrums by the previous nucleation.

Due to the problems of convergence for \( Q = 0 \) we must describe the form of the spectrum explicitly. We are going to show that the size spectrum has the universal character.

When \( Q \) is going to zero the region where \( Q \) is unessential starts at \( z_l \) corresponding to
\[ \int_{-\infty}^{z_l} \exp(\delta(x))dx \sim (p/c) \exp(cz_l/p) \approx Q \]

and becomes larger. The asymptote \((z - x)^3\) of the subintegral expression is attained from \( z_l \) till some \( z \) with no respect to \( Q \). So, the asymptotic region becomes larger. Certainly, we can integrate the asymptote explicitly
and come to \((z - z_l)^4/4\). Only due to the linear size this asymptote provides the main quantity of the substance in the droplets. As a result we have the following expression for the behavior of \(f_\zeta\)

\[
f_\zeta \sim \exp(z - \alpha(z - z_l)^4)
\]

where the scale of \(z\) is chosen to put \(c/p = 1\) and \(\alpha\) is some constant. The value of \(\alpha\) can be determined from the requirement that \(\max f_\zeta\) (the maximum of the supersaturation) is attained at \(z = 0\). Then

\[
\alpha = -z_l^{-3}/4
\]

The expression for \(f_\zeta\) can be presented in the following form

\[
f_\zeta \sim \exp(-\alpha z_l^4) \exp(-(z/\Delta)^2) \exp(-4\alpha z^3|z_l|) \exp(-\alpha z^4)
\]

where \(\Delta\) is the characteristic halfwidth

\[
\Delta = (2|z_l|/3)^{1/2}
\]

One can see that at the characteristic scale \(z \approx \Delta\) the arguments of the third and the forth exponents have the characteristic values \(z_l^{-1/2}\) and \(z_l^{-1}\) respectively. Thus, these terms can be neglected and the form of \(f_\zeta\) is the gaussian one:

\[
f_\zeta \sim \exp(-(z/\Delta)^2)
\]

and it has no parameters after the evident rescaling \(z \to z/\Delta\). So, we see that the universal gaussian form of \(\exp(\delta)\) ensures the universal expression for \(\theta\)

\[
\theta = \exp(-\exp(w)\ln 2 \int_{-\infty}^{z} \exp(-x^2)dx)
\]

This universal form will be attained earlier than \(Q = 0\) (where the property of convergence disappears) and has the true physical sense.

Figure 1 shows the forms of the size spectrums in some different situations presented in the normalized coordinates. The curves "a", "b", "c", "d" are the solutions of the following equation

\[
z = A_1 \int_{-\infty}^{z} (z - x)^3 \frac{\exp(\delta(x))}{Q + \int_{-\infty}^{x} \exp(\delta(x'))dx'}dx'
\]

\(^9\)This rescaling excludes the unphysical parameter \(z_l\).
for the different values of $Q$ ( "a" : $Q = 10$ "b" : $Q = 1$ "c" : $Q = 0.001$
"d" : $Q = 0.0001$ ). The curve "a" practically coincides with "b", the curve 
"c" practically coincides with "d" for all $x$. The curve "e" is the spectrum of
the gaussian type $\exp(-x^2)$. The curve "f" is the universal form of the first
iteration $\exp(x - \exp(x))$ after the renormalization in order to have the same
position of the maximum of the curve and to conserve the integral over the
spectrum. This curve practically coincides with "a", "b" but only for the
negative values of the argument.

One can prove that for all possible values of $Q$ the spectrum lies between
the first iteration and the Gaussian spectrum. It can be seen that the differ-
ence between the first iteration and the Gaussian curve is rather small (less
than 0.2) and lies in the frames of the accuracy of the modern experiment[10].

Note that the value of $A_1$ must be chosen to ensure the position of the max-
imum of the supersaturation near $max \delta = 0$. For $Q \to 0$ the quantity of
the substance in the droplets isn’t small due to the known power asymptote
and one have to remove the choice of $t_*$ from the previous condition that
the $max \delta$ is attained at $z = 0$ to the new condition $max \delta = 0$. In the
concrete calculations one needn’t to fulfil this condition precisely but only in
a very approximate way as far as the form of the spectrum doesn’t change
essentially for the different choice of the $max \delta$ near zero. This property can
be shown analytically and is illustrated by Figure 2.

Figure 2 demonstrates the weak dependence of the form of spectrum on
the choice of the base point for the linearizations, i.e. the choice of $t_*$. This
property is important for the justification of the conception of the universal
spectrum and can be proved analytically. This property is also necessary for
the simplification of the numerical calculations. For $Q = 10$ the two values
of $A_1$ have been chosen. This corresponds to the different manners of the
choice of $t_*$ or the choice of $max \delta$. Two curves for $\delta$ for different $A_1$ are
shown in the part "a" of this illustration. The upper curve corresponds to
$A_1 = 0.5$, the lower curve - to $A_1 = 1$. In the part "b" the size spectrums
for these situations are drawn in the normalized coordinates. They coincide
and one can see only one curve drawn in the part "b".

Note that the limit $Q \to 0$ is analogous to the situation of the "wide spec-
trum" considered in [13]. Here we have some additional difficulties. These

\footnote{This ensures the weak sensitivity to the choice of the parameter $a$. It is necessary to
the self-consistency of the presented theory.}
difficulties appear from the asymptote \((z - x)^3\) for the subintegral expression. As a result the relative quantity of the substance in the droplets is greater than \(\Gamma^{-1}\), the spectrum is going to be formed during the period with duration essentially longer than \(c^{-1}\tau/\zeta\), the quasistationary approximation isn’t valid during all the period of the droplets formation. So, one has to reconsider the approximations which form the base of the concrete constructions.

The simplification goes from the asymptote \((z - x)^3\). Really, this asymptote doesn’t depend on the concrete form of the free energy and the derivatives of the free energy. So, the quasistationarity and exponential approximation ([1]) aren’t so essential (they are going to fail namely at this asymptote). The big quantity of the substance in the droplets require to reconsider the condition of the choice of \(t_\ast\) as it is done above. The essential duration of the period of the droplets formation may lead to some new approximations and, thus, change the form of the asymptote \((z - x)^3\). But the consideration of the process remains quite analogous to the already fulfilled one. One of such examples is given in the next section.

The opposite situation corresponds to the validity of the iteration procedure with the ideal supersaturation taken as the external one.\(^{11}\) Note that the final results for \(\theta\) and for the spectrum are obtained (in the second approximation) on the base of the supersaturation calculated without the appropriate account of the exhaustion of the centers, i.e. in the pseudohomogeneous situation. The same situation occurs when we study the condensation on the separate sort of the heterogeneous centers [8], [7]. This analogy leads to the three important consequences. To establish the first one note that the ”pseudohomogeneous” base for the final results evidently has some universality. In [7] the universality can be broken by the change of the regime of the consumption of the vapor by the droplets. The result of [8] is more approximate, but it is based on the form of the first iteration which can not be depended on the regime of the vapor consumption. So, the universality here is more general. The analogy of the forms of the ”pseudohomogeneous” spectrums allows to give the definition of the relative activity also to the centers in the the process of condensation on the centers of the separate sort. The point \(w = 0\) corresponds to \(\theta_{final} = 1/2\). The value of \(w\)

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\(^{11}\)Certainly, with the corresponding choice of the renormalization of \(\theta_{init}\) and the choice of the ”external” supersaturation the iteration procedure remains valid in all cases with the linear ”external” supersaturation.
can be reconstructed from $\theta_{\text{final}}$ as

$$w = \ln \left( \frac{\ln \theta_{\text{final}}}{\ln(1/2)} \right)$$

The invariant $\ln \theta/\exp(w)$ can be also observed for an arbitrary $z$. Hence, the condensation occurs in a hierarchical manner\footnote{Certainly, the shift and the zero roint $w = 0$ depend on the parameters of the process including $\eta_{\text{tot}}$.}. Then one can consider the distribution $f(x, w)$ over the two variables $x$ and $w$ obtained in the process of condensation on the heterogeneous centers with the spectrum of activities as the formal generalization of the distribution in the process of condensation on the heterogeneous centers of the separate sort. Now the distribution has the universal functions as the base. This base doesn’t depend on the process of the exhaustion of the heterogeneous centers. The dependence on $w$ is rather explicit

$$f(x, w) \sim \exp(\delta(x)) \exp(-w \int_{-\infty}^{\infty} \exp(\delta(x'))dx' \frac{\ln 2}{\int_{-\infty}^{\infty} \exp(\delta(x'))dx'})$$

The factor $\exp(\delta)$ is the universal base for this distribution. That’s why we prefer to present it in Figure 1 and to call it simply the spectrum. The last expression is precisely valid for $\delta$ calculated on the base of the precise solution. As for approximations for $\delta$ one can take $\delta$ from the pseudohomogeneous situation in two manners (from \footnotemark[3] and from [7]). The first one corresponds to the first iteration and doesn’t depend on the regime of the vapor consumption. The second one is more precise but depends on the regime of the vapor consumption. Note that the last expression contains an unessential approximation because it is based on the pseudohomogeneous situation. The negligible character of correction can be seen simple from the result of the iteration procedure in the situation with one sort of the heterogeneous centers. Hence, one can state the natural inclusion of the specific condensation on a sort of the heterogeneous centers into the practically universal distribution appeared from the process of the condensation on the heterogeneous centers with the spectrum of activities.

The second consequence is connected with the fact that now we know the ansatz necessary for the realization of the first opportunity (alternative to
the regularization of $\theta$). One can use the form of $\delta$ obtained in the pseudohomogeneous situation in the first iteration or from the universal homogeneous precise solution.

The third consequence can be noticed in frames of the modified method of the steepens descent \[16\]. Really, the form of the external supersaturation can be essentially nonlinear\[13\]. Then we have to use the modified method of the steepens descent. The generalization is evident. Due to the negligible effect of the account of the exhaustion of the heterogeneous centers in all steps except the final formulas which can be seen from the iteration method (in the nonlinear case all analogous estimates can be given) we can simply integrate (summarize) the amplitudes of the distribution\[14\] over the activity, then get the result for the pseudohomogeneous situation and then apply the final formulas for the number of the heterogeneous centers on the base of the supersaturation.

One can analytically show for $Q \geq 1$ that the differences in the forms of the spectrums between the real solution and the first iteration, between the real solution and the pseudohomogeneous universal precise solution decrease when $Q$ increases. Also one can prove that for $Q \geq 1$ the difference between the external supersaturation and the real supersaturation at some arbitrary moment of time decreases\[15\] when $Q$ increases. So, the results of Figure 1 show that the required limit corresponding to the practically universal spectrum is attained already when $Q \geq 1$.

One can analytically show that the form of the spectrum lies between the gaussian iteration and the first iteration (or between the gaussian form and the universal precise pseudohomogeneous solution). We can see from Figure 1 that the difference in the form of the spectrum is rather small for all situations. This can lead us toward the general approximate universality. So, the analogy with the ideas of the universality in the previous considerations is now stated.

Certainly, in the case of the condensation on the separate sort of the heterogeneous centers the spectrum (as $\theta \exp(\delta)$) isn’t universal. But the

---

\[13\] In a very specific global form of the activity spectrum $\eta_{tot}$. One can prove that in any case one can restrict the expression for the external supersaturation during the period of the intensive formation of the droplets on the centers with the intermediate activity by the constant, linear and square terms.

\[14\] The characteristic values of the distribution at $t_*$.

\[15\] And also at $t_*$. 

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25
difference between the forms of the spectrum isn’t so important. One can show analytically that the form of the spectrum changes continiously from the case of the relatively small number of the heterogeneous centers up to the pseudohomogeneous case and lies between these two limit cases. Really, when the relative number of the heterogeneous centers is small the first iteration \(e^{x} - e^{x}\) gives the precise expression for the spectrum. In the pseudohomogeneous case the same first iteration is the base for the result which lies practically near the precise solution (this is the base point for the effectiveness of the iteration method [8]). So, the form of the spectrum doesn’t essentially variate. It can be also treated as as some universal form. Hence, this case also allows the universal description. Namely this is the base for the applicability of the iteration procedures from [3], [4].

6 Advantages of the model

The results of the iteration procedure can give not only the description of the process of the heterogeneous condensation but also the information about the form of the activity spectrum. From the first point of view this question appears to be an external one to the process of condensation.

Experimental results [13] show that the spectrums of the activities are rather smooth and have the form

\[ \phi(v) \sim v^{-(1+s)} \]

where \(s\) is some small positive parameter. Here \(v\) has the sense of the activity introduced in a slightly another manner. Namely, the free energy can be approximately written as the function of \(v\) in the leading term as

\[ F = -\ln(\zeta + 1)\rho^3 + \text{const}\rho^2 + \text{const}v \ln v + \text{const} \]

which leads to the approximate applicability of the linearization of \(\Delta F = F_c - G = F(\rho_c) - F(\rho_e)\) as function of \(w\) together with the identification of \(v\) as \(w - w_0\) with some characteristic value of the parameter \(w_0\). Then \(\eta_{tot}\) can be presented as

\[ \eta_{tot}(w) = \eta_{tot}(w_0)(w - w_0)^{-(1+s)} \]  

\[ (35) \]

After renormalization and as the function of a rescaled variable.
The positive value of \( s \) ensures the convergence of the total number of the heterogeneous centers:

\[
\eta_{tot} = \int_{w}^{\infty} \eta_{tot}(w)dw
\]

Define the class of the "long tail spectrums" (LTS) as the spectrums with extremely long tails in the active region. This spectrum shows an example of such a spectrum. Here we shall develop the theory for condensation on such spectrums.

To present the most simple variant we shall assume that for \( f_{\zeta} \) an approximation of the known form is adopted

\[
f_{\zeta} = f_{\zeta*} \exp\left(\frac{\Gamma}{\zeta_{**}}(\zeta - \zeta_{**})\right) (36)
\]

with some constant value of the known parameter \( \Gamma \). Here \( \zeta_{*} \) can be treated as a value corresponding to the moment when some sort of the heterogeneous centers is exhausted and \( \zeta_{**} \) is the base for approximations. Require that

\[
\theta(z = 0, w) = 1/2
\]

which leads to

\[
\frac{\Gamma}{\zeta_{**}}(\zeta_{*} - \zeta_{**}) + \lambda w = -\ln\left[\frac{f_{\zeta*} n_{\infty}}{c \ln 2}\right]
\]

The last approximation is valid when the relative variation of \( \zeta \) is small. In such a region we can put \( c \) in the r.h.s. of the last equation to some constant value and get for the size spectrum

\[
| f(z) | = | \eta_{tot}(w | w = \text{const} - cz) | \frac{c}{\lambda}
\]

where the dependence \( \ln c \) is assumed to be unessential. Then one can see that in the case of (36) the convergence of the integral for \( G \) can be attained only if \( s > 3 \) (note that \( c \to \text{const} \sim \frac{d\Phi}{dx} \) when \( w \to \infty \)). This result shows that LTS can not be effectively spread. More rigorously speaking, the contradiction can be overcome by noticing that this effect is only due to approximation (36). Certainly, \( G \) is restricted by the value \( \eta_{tot} z_{max}^{3} \) where

\footnote{The infinite tail must be cut off at the centers which must be already exhausted in the previous processes.}
$z_{\text{max}}$ is the coordinate of the droplets which are imaginary formed when the supersaturation attains some slightly positive value. Nevertheless in such a situation all global features of the free energy appear which doesn’t allow to get any effective method to all types of the heterogeneous centers. The leading idea will be that some of heterogeneous centers had been exhausted in the previous processes of condensation occurred earlier. Then the balance equation will be the following

$$
\frac{d\Phi}{dx} = c\frac{\Phi}{\Gamma} + 3 \int_{-d}^{z} (z-x)^2 f(x) dx
$$

where $d$ is some boundary parameter of size spectrum initiated by boundary of activity spectrum. This equation can be solved. In the case of $\eta_{\text{tot}} \sim \text{const}$ we have

$$
\frac{d\Phi}{dx} = c\frac{\zeta^{**}}{\Gamma} + 3 \int_{-d}^{z} (z-x)^2 c(x) dx \frac{\text{const}}{\lambda}
$$

(37)

Note that here $c\frac{\zeta^{**}}{\Gamma}$ is the derivative of the real (not the ideal) supersaturation on $x$. Having differentiated this equation three times\footnote{Now we are going to get the equation for the unknown function $c(x)$ so we have to keep the derivatives of $c(x)$} we get the ordinary linear differential equation with some constant coefficients, which has the known solution.

Now a new principle of the self-consistency of the activity spectrum will be elaborated. We have noticed that active centers have been exhausted in the previous processes of condensation. But the description of the previous processes of condensation is quite analogous to the description of the given process. As the result we have for spectrum of the heterogeneous centers

$$
\theta = \exp(-\text{const} \exp(\lambda w) \int_{-\infty}^{z} \exp(-\Gamma \frac{\zeta - \Phi_x}{\Phi_x}) dx)
$$

with the analytical structure

$$
\theta(z \to \infty) = \exp(-\text{const} \exp(\lambda w))
$$

(38)

But this structure is already known - it is the structure of the final and the start results for $\theta$ in the already investigated process. So, our start form was absolutely correct\footnote{One can repeat all calculations with the new value of parameters initiated by the previous process of consumption of the heterogeneous centers.}. Also it is very important that the structures before and...
after the process coincide in their analytical form. This statement will be called as the principle of the self-consistency of the spectrum of the activities.

Hence, our initial conditions satisfies this principle. The process of condensation conserves the analytical form of the spectrum of the activities and the result of the process can be regarded as some shift in the scale of activities. Only some parameters are changed. We needn’t to repeat the calculations as far as they are absolutely the same ones.

However, in \((37)\) when \(d \gg 1\) we needn’t to know the details of the cut-off of the spectrum and can use the cut-off by the Heavisaid’s function.

The last point of discussion is the possibility of the linearization of the external supersaturation. One can analytically prove the following statement:

- In the description of condensation on the centers of the intermediate activity the two manners of description cover all possible situations\(^\text{20}\). These manners of description are the following:
  1. The supersaturation is absolutely determined by the consumption of the vapor by the droplets formed on the centers with high activity.
  2. The linearization of the external supersaturation is possible during the period of formation of the droplets on the centers with the intermediate activity.

The first manner of description is obviously trivial. The second is completely described here. Note that in the case when the spectrum has some pseudo singularities the last statement isn’t valid and the special description is necessary. This description can be attained by the combination of the methods presented in [16] with this theory.

7 Concluding remarks

Now the theory of aerosol formation is completed. As a base for some concrete results the classical theory of nucleation was chosen. Meanwhile the validity of this theory remains the matter of discussion\(^\text{21}\). Note that this theory is

\(^\text{20}\)The natural requirement for the activity spectrum is that the activity spectrum must be a smooth function with the cut-off (or without the cut-off) like (38).

\(^\text{21}\)Note that formally we can put the discrepancy between the predictions of the classical theory and the real rate of nucleation into the values of the microscopic corrections.
necessary only to calculate the amplitude of the distribution. In the situation of the dynamic conditions the manner of the choice of \( t_* \) leads to the algebraic equation of the following form:

\[
f_* = \text{Smooth known function}(\Phi_*; \text{explicit external parameters})
\]

So, the microscopic corrections to the free energy aren't important for the process of condensation under the dynamic conditions. In the situation of the metastable phase decay the amplitude value of the spectrum is rather artificial. It is given explicitly by the initial supersaturation and one can not exclude the sharp dependence on the microscopic corrections to the free energy. Here any other concrete formula can be used instead of the expression from the classical theory for the nucleation rate in the stationary approximation. Note that the form of the spectrum doesn’t essentially depends on the value of the amplitude. That’s why we don’t pay any serious attention to the solution of the algebraic equations on the parametrs of the process and to the calculation of the concrete numerical results. We have concentrated our attention on the universal dependencies which form the base for the common knowledge in the field of the first order phase transitions. Namely the universality is the main result of our investigation. Note that the universality also takes place in the process of the condensation under the dynamic conditions.

The theory presented in these four publications can be easily reformulated when we assume that the rate of appearance of the critical embryos is proportional to

\[
F_1 \exp(F_2)
\]

where \( F_1 \) and \( F_2 \) are the smooth functions of the supersaturation and \( F_2 \) has the big absolute values. Evidently all reasonable recipes for the rate of nucleation satisfies the last ansatz. We kept the classical stationary flow only due to the tradition. The range of applicability of the presented theory is wider than the case of condensation. The possibility of the linearization of the ideal power of metastability during the period of the intensive formation of the super-critical embryos seems to be quite natural. The sharp increasing of the intensity of the metastable phase consumption by the separate super-critical embryo is also a natural requirement. This theory is based only upon these assumptions. All positions used in the construction of the mathematical model (except the absence of coalescence) can be missed\(^22\) by the obvious

\(^{22}\text{The thermal effects can be taken into account in the manner analogous to\([8]\).}\)
generalization conserving the mathematical structure. The requirement of the homogeneous character of the external action and of the nucleus distribution can be attained by the consideration of an arbitrary hydrodynamic element. As the result one can conclude that the general theory for the kinetics of formation of the dispersed embryos of a new phase on the dispersed impurities in a metastable phase is constructed.

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Figure 1

Form of spectrum under the different powers of deformation.
Weak dependence of the spectrum on the base of approximations.