Decay of metastable phase on heterogeneous centers with continuous activity

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Abstract

A system of a metastable phase with a pseudo continuous set of the heterogeneous centers is considered. An analytical theory for kinetics of decay of the metastable phase in such a system is constructed. The free energy of formation of a critical embryo is assumed to be known in the macroscopic approach as well as the solvation energy. The theory constructed below is based on the quasistationary approximation for the nucleation rate.
1 Introduction

The theory considered here will be based on the macroscopic approximation of the height of the activation barrier. This approximation lies in the base of the classical theory of nucleation. The theory presented below forms the part in the program announced in [6]. All bibliographical remarks can be found in [3].

The further investigation of the heterogeneous condensation requires to take into consideration the process of the heterogeneous decay on the band of centers with the different activity. 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 is so dense that we can regard it as a pseudo continuous one. In the atmosphere this fact is proved experimentally. In the case of the "solid nucleus of condensation with the weak interaction" the continuous size of the nucleus ensures the continuous set of $\Delta F$.

Nevertheless the theory of the heterogeneous decay was constructed only for one type of the heterogeneous centers. So, the task to construct the kinetic theory of the decay for the system with the continuous set of the heterogeneous centers is rather essential. It will be completely fulfilled here.

We shall use the ordinary physical assumptions formulated in [6] including the following ones:

- 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 for the nucleus which are really going to be the centers of the droplets and aren’t absolutely exhausted in the process.

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

The characteristic moment $t_*$ of the process of formation can be chosen as the initial moment. The values at the moment $t_*$ will be marked by the lower index "*".
We assume the total number of the heterogeneous centers to be constant in time.

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

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

with some positive parameter $\lambda$.

The total number of the heterogeneous centers with the given activity $w$ will be marked by $\eta_{tot}(w)$. Naturally $\eta_{tot}(w)$ is rather a smooth function of $w$.

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

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

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 vapor consumption we have

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

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

The frontal type of the size spectrum allows to introduce the frontal size $z$ according to

$$z = \int_0^t \zeta \alpha \tau^{-1} \, dt'$$

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

$$t(z) = \int_0^z \tau \alpha^{-1} \frac{dz}{\zeta(z)}$$

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 $x$. Consider $t(x)$ as the moment when the droplet with the given $x$ has been formed (as a droplet). We can see that the functions of time are the functions of $x$. Hence, we can see that the kinetic equation can be 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 Condensation equations system

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

We must take into account the reduction of $\zeta(0)$ to some value $\Phi^*$ due to the consumption of the vapor molecules in the process of solvatation. For $\Phi^*$ we have

$$\Phi^* = \zeta(0) - \int dw \eta_{tot}(w) \nu_e(w) n_\infty$$

(4)

where $\nu_e$ is the number of the molecules of the condensed substance in the equilibrium embryo. The discrepancy between $\Phi^*$ and $\zeta(0)$ for the monotonic interaction between the molecules in the liquid phase and the heterogeneous center can be estimated as

$$\Phi^* - \zeta(0) \geq \eta_{tot} \frac{\nu_{c, hom}}{n_\infty}$$

(5)

Here $\eta_{tot}$ is the total number of the heterogeneous centers of all types:

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

(6)

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.

They are proved analytically.

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 heterogeneous barrier the consideration is quite analogous).

Let $f_s$ be the stationary value of the size distribution for the heterogeneously formed droplets measured in the units of $n_\infty$. It can be presented in the following form

$$f_s = f_\zeta(\zeta(x), w) \eta(x, w)$$

(7)

where $\eta(x, w)$ is the number of the heterogeneous centers free from the super-critical embryos and $f_\zeta$ is given by the following formula [3]

$$f_\zeta = \frac{W^+ \exp(-DF(\zeta, w))}{\pi^{1/2} \Delta_e \nu_0 \Delta_e \nu_0^* n_\infty}$$

(8)

where $W^+$ is the number of the molecules interacting with the droplet in the unit of time, $\Delta_e \nu$ is the width of the equilibrium distribution

$$\Delta_e \nu = \sum_{\nu=1}^{\nu=\nu_e + \nu_c} \exp(-F(\nu) + G)$$
and $\Delta_c \nu$ is the halfwidth of the near-critical region

$$\Delta_c \nu = \frac{2^{1/2}}{|(\frac{\partial^2 F}{\partial \nu^2})_{\nu=\nu_c}|^{1/2}}$$

Index "c" marks the values for the critical embryo. Certainly, $W^+, \Delta_c \nu$ and $\Delta_e \nu$ are some smooth functions of $w$ and we neglect this dependence.

We shall mark by $n_{\infty} g(w)$ the total number of the vapor molecules in the heterogeneously formed droplets on the centers of the activity $w$. To simplify the formulas we shall use

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

We obtain for $g, \theta$ the following equations

$$g(z, w) = \int_0^z (z-x)^3 f_\zeta(\zeta(x), w) \eta(x, w) dx$$

$$\theta(z, w) = \exp(-n_{\infty} \int_0^z f_\zeta(\zeta(x), w) dx)$$

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

$$N(z, w) = \eta_{tot}(w)(1 - \theta(z, w))$$

The total number of the droplets is

$$N_{tot} = \int n_{\infty} g(w)(1 - \theta(z, w)) dw = \int N(z, w) dw$$

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

$$f_\zeta(\zeta(x), w) = f_\zeta(\Phi, w) \bigg|_{w=0} \exp(\Gamma \frac{\zeta - \Phi}{\Phi}) \exp(w \lambda)$$

where

$$\Gamma = -\Phi \frac{d\Delta F(\zeta)}{d\zeta} \bigg|_{\zeta=\Phi}$$

and $\Delta F$ is the height of the heterogeneous activation barrier. The validity of these approximations can be analytically justified for the heterogeneous embryos with the interaction between the center and the molecules of the condensed phase weaker or equal than the function reciprocal to a space distance. Then we can imagine the center as the hard sphere with a weak interaction on which the embryo is formed.
The dependence of $\Gamma$ on $w$ is rather a weak one. So we can put

$$\Gamma(w) = \Gamma \mid_{w=0}$$

for some essential part of the activity spectrum.

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

$$g(z, w) = f_\ast \int_0^z (z-x)^3 \exp(-\Gamma \frac{g^{tot}}{\Phi_\ast}) dx \theta \eta_{tot}(w) \exp(w \lambda) \equiv G_w(g^{tot}, \theta)$$

$$g^{tot} = \int dw g(z, w)$$

$$\theta(z, w) = \exp(-f_\ast \exp(\lambda w) n_\infty \int_0^z \exp(-\Gamma \frac{g^{tot}}{\Phi_\ast}) dx) \equiv S_w(g^{tot})$$

where $f_\ast = f_\ast(\Phi_\ast, w = 0)$

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

The size spectrum can be found as the following one

$$f(x, w) = f_\ast \exp(\lambda w) \exp(-\Gamma \frac{\int dw g(x, w)}{\Phi_\ast}) \theta(x, w) \eta_{tot}(w)$$

### 3 Iteration procedure

The systems like (17)-(18) are the ordinary solved by the iteration procedure. It can be constructed by the following way: For the initial approximations we choose:

$$g_0(z, w) = 0 \quad \theta_0 = 1$$

Ordinary the recurrent procedure is defined according to

$$g_{i+1}(z, w) = G_w(g_i^{tot}, \theta_i(w))$$

$$g_i^{tot}(z) = \int dw g_i(z, w)$$

$$\theta_{i+1}(z, w) = S_w(g_i^{tot})$$

The remarkable monotonic properties of $G, \int dw$ and $S$ ensures the guaranties for the error of the approximation. In this situation they can be observed also in the manner analogous to the case of ordinary heterogeneous condensation. Certainly, for the calculation of the iterations we must use some expression for $\eta_{tot}(w)$. So at first we shall consider the limit cases and obtain some estimates.

An interesting fact goes from the absence of $\eta_{tot}$ in the r.h.s. of (23). So for some rather an arbitrary $\eta_{tot}$ the power of exhaustion will be determined...
only by \( w \). The centers with the high activity \( w \) are almost exhausted during the process of condensation. The centers with the relatively small activity \( w \) remain unexhausted. The intermediate region has rather a small size. To give the qualitative estimates let us notice that the supersaturation \( \zeta \) appears only in the function \( f_\zeta \). For the behavior of \( f_\zeta \) we can obtain the following estimate

\[
f_\zeta \sim f_* \exp(-\text{const} x^\epsilon) \quad 3 \leq \epsilon \leq 4 \tag{24}
\]

This estimate goes from the general obvious fact that the spectrum of the droplets must be wider than the monodisperse one and the intensity of formation must decrease in the \( x \) scale. So we see that the width \( \Delta x \) of the spectrum is a well defined value. We must stress that (24) is valid not only for the separate process of condensation on the centers with some separate activity but also for condensation on the centers with the set of all activities.

The most rough approximation for the exhaustion of the heterogeneous centers can be obtained from the first approximation in the iteration procedure. We have

\[
\theta = \exp[-f_* \exp(\lambda w) n_\infty z] \tag{25}
\]

and for the final value

\[
\theta_{\text{final}} = \exp[-f_* \exp(\lambda w) n_\infty \Delta x] \tag{26}
\]

Let us define \( w_\langle \) and \( w_\rangle \) according to the following expressions

\[
w_\langle = w_0 - \frac{\epsilon}{\lambda} \tag{27}
\]

\[
w_\rangle = w_0 + \frac{\epsilon}{\lambda} \tag{28}
\]

where

\[
w_0 = \frac{1}{\lambda} \ln\left( \frac{\ln 2}{f_* n_\infty \Delta x} \right) \tag{29}
\]

\( \epsilon \sim 1 \)

For \( w > w_\rangle \) almost all heterogeneous centers are exhausted. For \( w < w_\langle \) almost all heterogeneous centers remain free. This remark allows to rewrite the expression for \( g^{\text{tot}} \) in the following form

\[
g^{\text{tot}} = \int_{w_\langle}^{w_\rangle} dw g(z, w) + \int_{w_\rangle}^{\infty} \eta_{\text{tot}}(w) dw z^3 n_\infty \tag{30}
\]

The size of the intermediate region has in the scale of \( w \) of the order of \( 1/\lambda \). This size corresponds to the variation of \( \Delta F \) of the order of 1. As far as \( \Delta F \) has rather big values, the relative variation of \( \Delta F \) in the intermediate region is rather small. So we can put in this region

\[
\eta_{\text{tot}}(w) = \eta_* = \text{const} \tag{31}
\]
We can spread this approximation over the region $w > w_>$ because the real activity of these centers isn’t important. Certainly, we must obtain the boundary $w_{\text{max}}$ of this region from the following equation:

$$\int_{w>}^{w_{\text{max}}} \eta_\ast dw = \eta_\ast (w_{\text{max}} - w_>) = \int_{w_>}^{\infty} \eta_{\text{tot}}(w)dw$$  \hspace{1cm} (32)$$

For $w < w_<$ the accuracy of the approximation is not so essential because these centers remain free.

After the scale transformations $\Gamma g_{\text{tot}}/\Phi_\ast \rightarrow G; \quad \Gamma g/\Phi_\ast \rightarrow g$ we have

$$g = \frac{\Gamma f_\ast \eta_\ast}{\Phi_\ast} \exp(\lambda w) \int_0^z (z - x)^3 \exp(-G)\theta dx$$  \hspace{1cm} (33)$$

$$G = \int_{-\infty}^{w_{\text{max}}} dwg$$  \hspace{1cm} (34)$$

$$\theta = \exp[-f_\ast n_\infty \exp(\lambda w) \int_0^z \exp(-G)dx]$$  \hspace{1cm} (35)$$

By the appropriate shift of $w$ one can put $w_{\text{max}}$ to the zero. By the appropriate scale of $w$ one can put $\lambda = 1$. By the appropriate choice of $z$ we put the coefficient in (33) to unity. As a result we have only one parameter - the coefficient in the last equation. We shall mark it by ”$A$”.

The final form of the system of the balance equations is the following one

$$g = \exp(w) \int_0^z (z - x)^3 \exp(-G)\theta dx$$  \hspace{1cm} (36)$$

$$G = \int_{-\infty}^{0} dwg$$  \hspace{1cm} (37)$$

$$\theta = \exp[-A \exp(w) \int_0^z \exp(-G)dx]$$  \hspace{1cm} (38)$$

An iteration procedure can be constructed by the following way

$$g_{i+1} = \exp(w) \int_0^z (z - x)^3 \exp(-G_i)\theta_i dx$$  \hspace{1cm} (39)$$

$$G_i = \int_{-\infty}^{0} dwg_i$$  \hspace{1cm} (40)$$

$$\theta_{i+1} = \exp(-A \exp(w) \int_0^z \exp(-G_i)dx)$$  \hspace{1cm} (41)$$

$$g_0 = 0 \quad \theta_0 = 1$$  \hspace{1cm} (42)$$
So, we have in the first iteration
\[ g_1 = \exp(w) \frac{z^4}{4} \] (43)
\[ G_1 = \int_{-\infty}^{0} dw g_1 = \frac{z^4}{4} \] (44)
\[ \theta_1 = \exp(-A \exp(w)z) \] (45)
The second approximation gives for \( \theta \) the following result
\[ \theta_2 = \exp[-A \exp(w) \int_{0}^{z} \exp(-\frac{z^4}{4})dz] \] (46)
and for the final value
\[ \theta_{\text{final}} = \exp[-A \exp(w)1.28^{1/4}] \] (47)
Then for \( N_{\text{tot}} \) we have
\[ N_{\text{tot}} = \int_{-\infty}^{0} [1 - \exp(-A \exp(w)1.28^{1/4})]dw \eta_* \] (48)
For \( g \) in the second approximation we have
\[ g_2 = \exp(w) \int_{0}^{z} (z - x)^3 \exp(-A \exp(w)x) \exp(-x^4/4)dx \] (49)
The analytical expression for these and the further iterations can not be obtained. So we shall investigate the reduced iterations. In this procedure \( \theta_i \) is substituted by \( \theta_{i+1} \) in the expression for \( g_{i+1} \). So, we have
\[ \theta_1 = \exp[-A \exp(w)z] \] (50)
\[ g_1 = \exp(w) \int_{0}^{z} (z - x)^3 \exp(-A \exp(w)x)dx \] (51)
\[ g_1 = \frac{1}{A} z^3 - \frac{3}{A^2} z^2 \exp(-w) + \frac{6}{A^3} z \exp(-2w) - \frac{6}{A^4} \exp(-3w) + \exp(-3w)6A^{-4} \exp(-A \exp(w)z) \] (52)
\[ G_1 = \int_{0}^{z} (z - x)^3 \int_{-\infty}^{0} \exp(w) \exp(-A \exp(w)x)dx dw \] (53)
\[ G_1 = \int_{0}^{z} (z - x)^3 \frac{1}{Ax} [1 - \exp(-Ax)]dx \] (54)
After the decomposition of the last subintegral expression we have
\[ G_1 = z^3 I_0 - 3z^2 I_1 + 3z I_2 - I_3 \] (55)
where

\[ I_0 = \int_0^z \frac{1}{Ax} [1 - \exp(-Ax)] dx \]  \hspace{1cm} \text{(56)}

\[ I_1 = z - \frac{1 - \exp(-Az)}{A} \]  \hspace{1cm} \text{(57)}

\[ I_2 = \frac{z^2}{2} + \frac{1}{A^2} Az \exp(-Az) - \frac{1}{A^2} (1 - \exp(-Az)) \]  \hspace{1cm} \text{(58)}

\[ I_3 = \frac{z^3}{3} + \frac{1}{A^3} (Az)^2 \exp(-Az) + \frac{2}{A^3} Az \exp(-Az) - \frac{2}{A^3} (1 - \exp(-Az)) \]  \hspace{1cm} \text{(59)}

For \( I_0 \) we have the following result

\[ \int_0^z \frac{1 - \exp(-y)}{y} \, dy = E_1(z) + \gamma + \ln(z) \]  \hspace{1cm} \text{(60)}

where

\[ \gamma = 0.57721 \quad E_1(z) = -Ei(z) \]  \hspace{1cm} \text{(61)}

and \( Ei \) is the exponential integral function. We can present this result in the following approximate form

\[ \int_0^z \frac{1 - \exp(-y)}{y} \, dy \approx \frac{z}{z^3 + 17z^2 + 60z + 480} \]  \hspace{1cm} \text{(62)}

The final approximation for \( \theta \) has the following form

\[ \theta_2 = \exp\{ -A \exp(u) \int_0^z \exp(-G_1) \, dx \} \]  \hspace{1cm} \text{(63)}

This expression can be calculated only approximately. Notice that \( G \) increases faster than \( x^3 \). The action of the subintegral factors like the functions \( \exp(-const x^n) \) approximately leads simply to the cut-off of the region of integration when \( n \geq 3 \)

\[ \exp(-const x^n) \approx \Theta(const^{-1/n} - x) \]  \hspace{1cm} \text{(64)}

In order to obtain the position of the end of the process of formation we must solve the algebraic equation

\[ G_1 = 1 \]  \hspace{1cm} \text{(65)}

We can also use the other method. From (64) after the decomposition of the exponent one can get the series containing some non-negative powers of \( A \). So, for small \( A \) one can restrict the series by several first terms and promote the calculations by the following method. All integrals with the combination of \( \exp(-const x) \) and \( \exp(-const x^2) \) can be calculated with the help of the Boyd’s approximation

\[ \frac{\pi/2}{(z^2 + \pi)^{1/2} + (\pi - 1)z} \leq \exp(z^2) \int_z^\infty \exp(-t^2) \, dt \leq \frac{\pi/2}{((\pi - 2)z^2 + \pi)^{1/2} + 2z} \]  \hspace{1cm} \text{(66)}
All terms like $\exp(-\text{const}x^n)$  $n = 3, 4, ...$ can be treated as some functions like the Heavisaid’s one.

The value of $\theta_2$ is the base for the final approximation $N_{\text{tot}}(w)$. The total number of the droplets can be found directly from (63) after the integration

\[ N_{\text{tot}} = \eta_0 \int_{-\infty}^{0} [1 - \theta(z, w)] \, dw \]  \hspace{1cm} (67)

In the second approximation we have

\[ N_{\text{tot}} = \eta_0 \int_{-\infty}^{0} [1 - \exp(-B \exp(-w))] \, dw \]  \hspace{1cm} (68)

where

\[ B = A \int_{0}^{z} \exp(-G_1) \, dx \]  \hspace{1cm} (69)

is calculated earlier. Hence, for the final expression we obtain the integral which is already calculated in (60), (62).

The alternative method is the following one. At least after the remark that in the essential region there is $\exp(-G_1) \leq 1$ we can decompose this exponent as a function of $G_1$ and get the answer for $\int_{0}^{z} \exp(-G_1) \, dx$ in the polynomial form.

4 Universal solution method

System of equations (36) - (38) doesn’t allow the universal solution as in the case of the homogeneous condensation. Equation (36) hasn’t $\theta$ in the r.s.h.. But the operator in the r.h.s. of (36) ensures rather a rapid convergence of the iterations. The worst situation for the iteration procedure is when $A = 0$. In this situation we have the universal system

\[ g = \exp(w) \int_{0}^{z} (z - x)^3 \exp(-G) \, dx \]  \hspace{1cm} (70)

\[ G = \int_{-\infty}^{0} g \, dw \]  \hspace{1cm} (71)

This system has the universal solution which will be marked by $G_0$.

This universal form of the size spectrum is shown by Figure 1.

The condensation process is determined by the first three momentums of the distribution function

\[ \mu_i(z) = \int_{0}^{z} x^i \exp(-G) \, dx \]  \hspace{1cm} (72)
and by the zero momentum

\[ \mu_+(z) = \int_0^z \exp(-G) \theta dx \]  \hspace{1cm} (73)

In the pseudo homogeneous case it is determined by

\[ \mu_i(z) = \int_0^z x^i \exp(-G) dx \] \hspace{1cm} (74)

\[ \mu_+(z) = \int_0^z \exp(-G) dx \] \hspace{1cm} (75)

After the end of rather a short period of the intensive formation we can substitute in (72) and (73) \( \infty \) instead of \( z \) in the region of the integration. So the further evolution will be determined by the first four momentums \( \mu_1(\infty) \).

As far as for \( G \) we substitute the universal solution \( G_0 \) (when \( \lambda = 0 \)), the values of \( \mu_i \) are the universal constants which can be obtained by the unique numerical solution of the last system.

Now we return to the previous iteration procedure (with the new initial approximation). We can use \( G_0 \) as the initial approximation in the iteration procedure. So we have

\[ \theta_1 = \exp[-A \exp(w) \int_0^z \exp(-G_0) dx] \] \hspace{1cm} (76)

\[ g_2 = \exp(w) \int_0^z (z - x)^3 \exp(-G_0) \exp(-A \exp(w) \int_0^x \exp(-G_0) dx') dx \] \hspace{1cm} (77)

\[ G_2 = \int_{-\infty}^0 \exp(w) \int_0^x (z - x)^3 \exp(-G_0) \exp(-A \exp(w) \int_0^x \exp(-G_0) dx') dx' dw \] \hspace{1cm} (78)

The decomposition of the exponents gives

\[ G_2 = \sum_{i=0}^{\infty} \frac{(-A)^i}{(i+1)!} P_i(z) \] \hspace{1cm} (79)

where

\[ P_i = \int_0^z (z - x)^3 \exp(-G_0) I_{i0}^i(x) dx \] \hspace{1cm} (80)

\[ I_{00}(x) = \int_0^x \exp(-G_0) dx \] \hspace{1cm} (81)

\(^1\) The main role is played by \( \mu_+ \).
Then the expression for the function $B(z = \infty)$ will be the following one

$$B(z = \infty) = A \int_0^\infty \exp(-G_2)dx = A \int_0^\infty \exp(-P_0(z)) \exp\left(-\sum_{i=1}^{\infty} \frac{(-A)^i}{(i+1)!} P_i(z)\right)dz$$

(82)

The decomposition of the last exponent leads to

$$B(z = \infty) = \prod_{i=1}^{\infty} \sum_{j=0}^{\infty} (-1)^j \frac{(A)^{ij}}{j! (i+1)!} C_{ij}$$

(83)

where

$$C_{ij} = \int_0^\infty \exp(-P_0(x)) P_i^j dx$$

(84)

are the universal constants. For the total number of the droplets with the given activity we have

$$N_{tot}(w) = \eta_\ast (1 - \exp(-B(z = \infty) \exp(w)))$$

(85)

For $N_{tot}$ we repeat expressions (67), (68), (60) with the new value of $B$ and obtain the final result.

In the same manner one can take into account the deviation of $\eta_\ast$ from the constant value. After the decomposition of $\eta_\ast$ into the Tailor’s series we substitute the initial approximation $g_0$ and act in the manner similar to (76) - (85). As a result we have some expansions in the powers of the parameter $A$, the derivatives of $\eta_{tot}$ and the universal constants.

There is another possibility to observe the universal solution in the wide class of the possible situations. We shall speak about the case of the "developed spectrum of activities" in the following situation. Earlier we extracted in the spectrum of activities the three regions: the region of rather active centers (they are almost exhausted), the region of the centers with the small activity (they remain practically free during the whole process) and the intermediate region. We have noticed that in the majority of the situations the intermediate region has a relatively small size in comparison with the active region (the unactive region has no size - it can be spread till infinity). In this case one can fulfill some further simplifications.

Let us transmit the point $w = 0$ to the special activity for which

$$\theta |_{w=0} (\infty) = \frac{1}{2}$$

e.g. the half of the centers became the centers of droplets. Then the system of the condensation equations after the rescaling of $w$ can be written as the following one

$$g = a_0 \exp(w) \int_0^z (z-x)^3 \exp(-G)\theta dx$$

(86)
\[ G = \int_{-\infty}^{w_+} g(w) dw \]  
\[ \theta = \exp(-a_1 \exp(w) \int_0^z \exp(-G) dx) \]

where \( w_+ \) is the upper boundary of the spectrum and \( a_0, a_1 \) are some constants. After the rescaling of \( z, x \) one can put \( a_0 = 1 \). The condition of the choice of \( w = 0 \) gives for \( a_1 \):
\[ a_1 = \frac{\ln 2}{\int_0^\infty \exp(-G) dx} \]

So, there remains only one parameter \( w_+ \).

Note that the result of the process of condensation will lead to the following functional form for the number of the heterogeneous centers
\[ \eta = \eta_{tot} \exp(-const \ \exp(w) \int_0^\infty \exp(-G) dx) \]
after the process of decay or
\[ \eta = \eta_{tot} \exp(-const \ \exp(w) \int_{-\infty}^\infty \exp(x - G) dx) \]
after condensation under the dynamic conditions where \( \eta_{tot} \) is the real initial (approximately constant) value of the number of the heterogeneous centers. The value of \( \eta \) must be now substituted by \( \eta_{tot} \). In any case as far as the integral gives some constant value the functional form is the following one
\[ \eta = \eta_{tot} \exp(-const \ \exp(w)) \]
or
\[ \theta_{init} = \exp(-const \ \exp(w)) \]

After the observed process of condensation the cut-off of the spectrum \( w_+ \) will be unessential when \( \theta_{init}(w_+) \to 0 \). This initiates the more natural definition \( w_+ \to \infty \) of the activity spectrum without rather an artificial parameter \( w_+ \).

Now we substitute this functional dependence into the system of the condensation equations. Then we fulfill the integration over \( w \) and come to
\[ G \sim \int_0^z \frac{(z - x)^3 \exp(-G)}{a + \ln 2 \int_0^\infty \exp(-G(x')) dx' \int_0^\infty \exp(-G(x')) dx'} dx \]

where the coefficient \( a \) is initiated by the new form of the activity spectrum.

For simplicity one can cancel the coefficient
\[ \frac{\ln 2}{\int_0^\infty \exp(-G(x')) dx'} \]
As far as one can see that $\int_0^\infty \exp(-G(x'))dx'$ has the values which are situated not so far from 1 the cancellation of this coefficient leads only to some unsufficient shift of the zero point in the scale of the activities.

Then we come to

$$G \sim \int_0^z \frac{(z - x)^3 \exp(-G)}{a + \int_0^1 \exp(-G(x'))dx'}dx$$

(95)

The main essential problem is to establish the form of the size spectrum. Then the system of the condensation equations can be reduced to the algebraic system.

Now we are going to show that the form of the spectrum has the weak dependence on the value of the parameter $a$. In the case $a \to 0$ the last equation can be reduced to

$$G \sim \int_0^z \frac{(z - x)^3 \exp(-G)}{\int_0^z \exp(-G(x'))dx'}dx$$

(96)

which resembles the homogeneous case but with the increasing function $\int_0^z \exp(-G(x'))dx'$ in the denominator.

When $a \to \infty$ we have the pure homogeneous case:

$$G \sim \int_0^z (z - x)^3 \exp(-G)dx$$

(97)

Recall that in the absence of this function the spectrum $\exp(-G)$ has rather a simple approximate qualitative behavior:

$$\exp(-G) \sim 1 \quad z < z_{\text{bound}}$$

$$\exp(-G) \sim 0 \quad z > z_{\text{bound}}$$

where the parameter $z_{\text{bound}}$ corresponds to $G(z_{\text{bound}}) = 1$.

Note that this function isn’t so sharp function of $z$ as $(z - x)^3$ is. The behavior of this function is the following

$$\int_0^z \exp(-G(x'))dx' \sim z \quad z < z_{\text{bound}}$$

$$\int_0^z \exp(-G(x'))dx' \sim \text{const} \quad z > z_{\text{bound}}$$

So the qualitative behavior of $G$ will be the same, only the value of the characteristic length of the spectrum $z_{\text{bound}}$ will be another.

In order to get the same length of the spectrum we rescale $z$ in such a manner that the parameter $a + c$ appears in front of the external integral.

Then we come to the following equation

$$G = \int_0^z \frac{(z - x)^3 \exp(-G)}{a + c \int_0^1 \exp(-G(x'))dx'}dx$$

(98)
This equation has the following asymptotes:

\[
G = \int_0^z \frac{(z-x)^3 \exp(-G)}{1+0} \, dx
\]  
when \(a \to \infty\) and

\[
G = \int_0^z \frac{(z-x)^3 \exp(-G)}{\frac{1}{c} \int_0^{x'} \exp(-G(x')) \, dx'} \, dx
\]  
when \(a = 0\).

The value of \(c = 0.08\) is determined in order to have the approximate coincidence of the characteristic lengths of the spectrums in these two limit cases. Our qualitative analysis shows that the form of the spectrum \(f \sim \exp(-G)\) will be approximately one and the same for all values of the parameter \(a\). The numerical results shown in the upper part of Figure 2 confirm this conclusion. We see that the curves \(f_{(a=0)}\) and \(f_{(a=\infty)}\) practically coincide.

Certainly, the integral in the denominator can influence on the process in another manner. It can attain some value and violates the correct rescaling of the spectrum to the standard length. The maximum of such an influence will be attained at \(a \sim c\). This case is drawn also and one can see that in this situation the flat region of the spectrum has the length of the flat region of the spectrum in the situation \(a = \infty\) and the inclined region has the slope as the inclined region in the situation \(a = 0\) has. This doesn’t lead as it is seen from this Figure to any essential deviation of the form of the spectrum.

In the lower part of this Figure the boundaries for the spectrum from below \(f_{bel}\) and from above \(f_{ab}\) for \(c = 0.08\) and arbitrary values of \(a\) are drawn. One can see that the form of the spectrum is the approximate universal function.

One can investigate now the situation with some finite value of \(w_{+}\). The analogous transformations lead to the following equation

\[
G = \int_0^z \frac{(z-x)^3 \exp(-G)}{\frac{a}{a+c} + \frac{1}{c} \int_0^{x'} \exp(-G(x')) \, dx'} \left[1 - \exp\left(-a+const \int_0^x \exp(-G(x')) \, dx'\right) \exp(w_+)\right] \, dx
\]  
(101)

For \(w_+ = -\infty\) one has the homogeneous situation. For \(w_+ = \infty\) one has the already analyzed situation which as it has been proved lies not far from the homogeneous one. So, we have the same limits as the boundaries and can assume that here the spectrum is also near the universal one.

Note that the physical reason of this universality is the sharp form of the function \((z-x)^3\) which induces the approximate rectangular form of the spectrum.

Now we return to the previous definitions of the parameters made before the integration over \(w\). Let us explicitly extract the intermediate and the active regions. One can see that for the two different activities \(w_1\) and \(w_2\) the following equation is valid

\[\frac{\ln(\theta(w_1, x))}{\exp(w_1)} = \frac{\ln(\theta(w_2, x))}{\exp(w_2)}\]  
(102)
The same is valid for the final values. The value of \( \frac{\ln \theta}{\exp(w)} \) is invariant for the different activities acting in one and the same process. So, one can put \( w = w_{++} \) as the boundary between these two regions, where \( w_{++} \) is equal to 2 or 3. In the same manner we can separate the region of the inactive centers by the boundary \( w_- = -w_{++} \). One can neglect the substance in the droplets on the inactive centers and get

\[
G = \int_{w_-}^{w_+} g(w) dw
\] (103)

We denote by \( n_\infty G_+ \) the number of the condensing substance molecules in the droplets formed on the active centers. The system of the condensation equations can be rewritten as

\[
g = a_0 \exp(w) \int_0^z (z-x)^3 \exp(-G) dx
\]

\[
G = \int_{-\infty}^{w_{++}} g(w) dw + G_+
\]

\[
\theta = \exp(-a_1 \exp(w) \int_0^z \exp(-G) dx)
\]

Now one can write some expression for \( G_+ \)

\[
G_+ = \frac{n_\infty}{n_\infty}(w_+ - w_{++}) z^3
\] (104)

The system of the condensation equations is the following one

\[
g = a_0 \exp(w) \int_0^z (z-x)^3 \exp(-G) dx
\]

\[
G = \int_{-\infty}^{w_{++}} g(w) dw + \frac{n_\infty}{n_\infty}(w_+ - w_{++}) z^3
\]

\[
\theta = \exp(-a_1 \exp(w) \int_0^z \exp(-G) dx)
\]

The value of \( w_{++} \) is universal, but the coefficient in the term \( \frac{n_\infty}{n_\infty}(w_+ - w_{++}) z^3 \) depends on parameters.

Defining

\[
G_- = \int_{-\infty}^{w_{++}} g(w) dw
\] (105)

\(^2\)The absence of the active and intermediate regions \( (w_+ < w_-) \) means that condensation occurs in the pseudo homogeneous way.

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one can propose the following estimate

\[ G_\leq (w_{++} - w_{--}) \frac{\eta_s}{n_\infty} z^3 \quad (106) \]

When

\[ w_+ - w_{++} \gg w_{++} - w_{--} \]

one can approximately get

\[ G = \frac{\eta_s}{n_\infty} (w_+ - w_{++}) z^3 \]

Then the first equation isn’t necessary at all and one needn’t to consider it. So we needn’t to put \( a_0 \) to 1 and can use an arbitrary scale to cancel another constant. The system looks like

\[ \theta = \exp(-a_1 \exp(w) \int_0^z \exp(-G) dx) \]

\[ G = \frac{\eta_s}{n_\infty} (w_+ - w_{++}) z^3 \]

After the rescaling of \( x, z \) one can put \( \frac{\eta_s}{n_\infty} (w_+ - w_{++}) = 1 \) and the system looks like the universal expression:

\[ \theta = \exp(-\ln 2 \int_0^\infty \exp(-z^3) dx \exp(w) \int_0^z \exp(-z^3) dx) \]

Note that this law takes place only in the case of the “wide spectrum”.

The behavior of \( \theta \) as a function of \( z \) for the different values of \( w \) are shown by Figure 3.

Despite the accurate character of the methods discussed above these methods don’t allow the clear interpretation. That’s why we pay attention to the simple method presented below. It can be applied for rather an arbitrary conduction of \( \eta_s \) as the function of \( w \).

5 Monodisperse approximation

The level of the supersaturation leading to the cut-off of the spectrum by the exhaustion of the substance is practically one and the same for all sorts of the droplets (all sort of the centers). Let us see the droplets of what sizes play the leading role in this cut-off. Analyzing the subintegral expression in the equation for \( g \) we realize that this subintegral expression is the very sharp function of \( x \). It is less than the function

\[ s_{bel} = \Theta(z - x)(z - x)^3 \quad (107) \]
and greater than the function
\[ s_{ab} = \Theta(z-x)(z-x)^3 \exp\left(-\frac{\Gamma \int f_\ast \eta_{tot}(w) \exp(\lambda w) dw z^4}{4} \right) \exp(-f_\ast \exp(\lambda w) n_\infty z) \] (108)

As far as the interruption of the process of the droplets formation by the fall of the supersaturation is investigated we shall describe the pseudohomogeneous situation. Later the generalization will be presented. Let us extract the approximation for this function. In other words we must extract the region of the droplets of the sizes essential in the vapor consumption. This consumption in its turn is essential when
\[ x \approx \Delta x \] (109)
where \( \Delta x \) is the characteristic size of the cut-off. This value can be introduced due to the frontal character of the back side of the spectrum. Certainly, this region must have the sizes rather small in comparison with \( \Delta x \) because all iteration procedures in the homogeneous decay are based on the fact that the droplets formed at the almost ideal supersaturation determine the process of the spectrum formation. As for the differential halfwidth \( \delta_{1/2} \) we have the following expression
\[ \delta_{1/2} = (1 - \frac{1}{2^{1/3}})x \] (110)
As for the integral halfwidth \( \Delta_{1/2}x \), it is obtained from the following equation
\[ N_{ess} x^3 = f_\ast \frac{x^4}{4} \exp(\lambda w) n_\infty \] (111)
where \( N_{ess} \) is the number of the essential droplets obtained as \( N_{ess} = f_\ast \exp(\lambda w) \Delta_{1/2}x n_\infty \) which gives
\[ \Delta_{1/2}x = \frac{1}{4}x \] (112)
and practically coincides with \( \delta_{1/2} \). So, the subintegral function \( s \) is now split into the essential part where \( x \leq \frac{\Delta x}{4} \) and the tail where \( x \geq \frac{\Delta x}{4} \). We shall neglect the tail and use due to rather a small size of the essential region the monodisperse approximation for droplets formed in this region. As the result we obtain the approximation for \( g(x) \)
\[ g(z) = \frac{N(z/4)}{n_\infty} z^3 \] (113)
where \( N(z/4) \) is the number of droplets appeared from \( x = 0 \) till \( x = z/4 \). As far as spectrum is cut off by the supersaturation exhaustion in the frontal (sharp) manner the value of \( g \) is unessential before \( z = \Delta x \) as a small one. After the moment of the cut-off it is also unessential as there is no formation of the droplets. So instead of the previous approximation we can use
\[ g(z) = \frac{N(\Delta x/4)}{n_\infty} z^3 \] (114)
exhaustion of the heterogeneous centers makes the subintegral function more sharp and the monodisperse approximation becomes at $\Delta x$ even better than in the pseudo homogeneous situation. But the exhaustion of the heterogeneous centers makes the coordinate of the supersaturation cut-off greater than $\Delta x$ and the monodisperse approximation becomes even more better at the moment of the supersaturation cut-off. Certainly, we must use $N(\Delta x/4)$ calculated with the account of the exhaustion of the heterogeneous centers.

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

6 Equation on the parameters

We shall return to the initial system and introduce there a new approximation. The system of the condensation equations will be the following one

$$g = \exp(w) \int_{0}^{z} (z - x)^3 \exp\left(-\frac{\Gamma N_{tot}(\Delta x/4)}{n_\infty}z^3\right)dx$$  \hspace{1cm} (115)

$$G = \int_{-\infty}^{0} gdw$$  \hspace{1cm} (116)

$$\theta = \exp[-A \exp(w) \int_{0}^{z} \exp\left(-\frac{\Gamma N_{tot}(\Delta x/4)}{n_\infty}z^3\right)dx]$$  \hspace{1cm} (117)

where

$$N_{tot}(\Delta x/4) = \int_{-\infty}^{0} N_{tot}(\Delta x/4)dw \quad N_{tot}(\Delta x/4) = \eta_{tot}(1 - \theta(\Delta x/4))$$  \hspace{1cm} (118)

As far as we use the monodisperse approximation we have derived the behavior of the supersaturation and need only the parameters of such a behavior. So we can leave integral system (115) - (118) and reformulate it in the terms of $N_{tot}(\Delta x/4)$, i.e. use only (117) - (118). As we have seen the value of $\Delta x$ is defined only by the supersaturation cut-off. Hence, we have

$$\int_{0}^{\Delta x/4} \exp\left(-\frac{\Gamma N_{tot}(\Delta x/4)}{n_\infty}z^3\right)dz = \left(\frac{\Phi_\infty}{\Gamma N_{tot}(\Delta x/4)}\right)^{1/3}E$$  \hspace{1cm} (119)

where

$$E = \int_{0}^{1/4} \exp(-z^3)dz \approx 0.24$$  \hspace{1cm} (120)

We obtain the following system

$$\theta(\Delta x/4) = \exp[-A \exp(w)(\frac{\Phi_\infty}{\Gamma N_{tot}(\Delta x/4)})^{1/3}E]$$  \hspace{1cm} (121)
\[ N_{\text{tot}}(\Delta x/4) = \int_{-\infty}^{0} dw \left( 1 - \exp\left[-A \exp(w)\left(\frac{\Phi_\ast}{\Gamma N_{\text{tot}}(\Delta x/4)}\right)^{1/3} E\right]\right) \eta_\ast \quad (122) \]

The last equation is the ordinary algebraic equation with the well known methods of the solution. The integral can be taken according to the procedure after (67).

When \( \eta_{\text{tot}} \) is some function equation (122) remains the algebraic one. The number of the heterogeneous centers is obtained on the base of \( N_{\text{tot}}(\Delta x/4) \) and the value of \( g \) is obtained due to (115).

### 7 Concluding remarks

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

\[ \frac{\tau}{\alpha} \frac{dz}{dt} = \zeta = \Phi_\ast - N_{\text{tot}}^r \frac{z^3}{n_\infty} \quad (123) \]

where \( N_{\text{tot}}^r \) is the total number of droplets. The last equation can be easily integrated as far as the r.h.s. doesn’t depend on time. So there are no problems in the process description until the coalescence.

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Figure 1

Form of the spectrum of the universal solution.
Figure 2

Approximate universiality of the spectrum.
universal dependence in the case of the "wide spectrum".

Figure 3