Decay on several sorts of heterogeneous centers: Special monodisperse approximation in the situation of strong unsymmetry. 1. General results

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1 Introduction

Metastable phase decay on the several types of heterogeneous centers remains a rather actual problem for theoretical investigation. For the first time the theory for the kinetics description was constructed in [2]. This approach decomposes the general situation into characteristic situations which are rather simple. All limit situations characterized by small values of characteristic parameters can be solved by the slightly modified versions of the iteration method initially proposed in [1]. Only the intermediate situation requires a special method of consideration which is based on the special monodisperse approximation.

When the total number of the heterogeneous centers is one and the same for different types of centers then as it is shown in [3] there are only two characteristic situations: the intermediate situation and the situation of the strong unsymmetry.

The special monodisperse approximation is well based and can be spread on a more general situation. This generalization is important not only to present the description in a more compact form. The special monodisperse approximation allows to reduce the error appeared in the limit situations. Really, in the situation of the strong unsymmetry (this is a standard limit
situation) one has to use the monodisperse approximation. If we use the special monodisperse approximation instead of the already used one we shall reduce the error.

The universal character of obtained solution was shown in [4].

The general recipe to use the special monodisperse approximation was suggested in [5] in the abstract manner. So, now it rather natural to show how the special monodisperse approximation works in the limit situations concretely.

This publication is intended to show how to use the special monodisperse approximation in the limit situations. We shall use for example the situation of the strong unsymmetry which appeared when the number of the first type centers equals to the number of the second type centers (see [3]). This situation together with the intermediate situation completes the consideration of the general case [3].

2 Formulation of the problem

Consider the system with two sorts of heterogeneous centers (they are marked by subscripts 1 and 2). Suppose that the total numbers of heterogeneous centers \( \eta_{\text{tot}1} \) and \( \eta_{\text{tot}2} \) are equal

\[
\eta_{\text{tot}1} = \eta_{\text{tot}2} \quad (1)
\]

At the initial moment of time which is denoted by the subscript \( t^* \) there exists only heterogeneous centers. We shall call the period of intensive formation of the droplets on the heterogeneous centers of given type as the nucleation on the centers of given type.

We shall use in the estimates some characteristic values. Denote by \( \Delta_1 t \) the duration of the nucleation on the first type centers and by \( \Delta_2 t \) the duration of the nucleation on the second type centers.

Consider the situation when the rate of nucleation on the first type of heterogeneous centers strongly exceeds the rate of nucleation on the second type of heterogeneous centers. We shall choose the sorts of heterogeneous centers to have

\[
f_{*1} \gg f_{*2}
\]

where \( f_{*i} \) is the amplitude value of the stationary distribution function.
Due to (3) the last inequality is practically equivalent to

\[ \exp(-\Delta F_1) \gg \exp(-\Delta F_2) \]

where \( \Delta F \) is the height of the activation barrier.

The power of metastability is characterized by the supersaturation

\[ \zeta = (n - n_\infty)/n_\infty \]

where \( n \) is the molecules number density of the vapor, \( n_\infty \) is the molecule number density of the saturated vapor.

Then the balance of the substance in the closed substance requires

\[ \zeta^* = \zeta + G_1 + G_2 \]

where \( G_1 \) is the number of the molecules in the liquid phase around the first type centers (taken in units of \( n_\infty \)), \( G_2 \) is the number of molecules in the droplets formed on the second type centers.

We shall describe the droplet by the value of dimensionless radius \( \rho \) which equals to the cube root of the number \( \nu \) of the molecules inside the droplet

\[ \rho = \nu^{1/3} \]

This value is convenient because the rate of its growth is one and the same for all sizes

\[ \frac{d\rho}{dt} = \zeta/\tau \]

where the constant \( \tau \) is the characteristic time. The last equation is valid for the supercritical droplets under the free molecular regime of the substance exchange.

Then automatically one can see that the distribution \( f_i(\rho, t) \) of the droplets over \( \rho \) in the moment \( t \) depends only on the intensity of the droplets formation in the time when the droplet of given size were formed.

The application of the ordinary monodisperse approximation ("total monodisperse approximation") is based on the following explanation:

- Suppose we can suggest an approximation

\[ G_1 \sim N_{1\text{tot}}\rho_0^3/n_\infty \]
where $N_{1\text{tot}}$ is the total number of the droplets formed on the first type centers during the condensation process.

The last approximation is good when $\rho_0$ is many times grater than the value of $\rho_0$ at the end of the period of intensive formation of the droplets on the first type centers, i.e. $\rho_0(\Delta_1 t)$:

$$\rho_0(t) \gg \rho_0(\Delta_1 t)$$

This approximation is important when $G_1$ stops the formation of the droplets on the second type centers, i.e. at $\Delta_2 t$. So, it is necessary to be

$$\rho_0(\Delta_1 t) \ll \rho_0(\Delta_2 t)$$

As far as $d\rho/dt$ is rather smooth function of time one can rewrite the last estimate as

$$\Delta_1 t \ll \Delta_2 t \quad (2)$$

One can estimate the number $N_{1\text{tot}}$ of the droplets formed on the centers of given sort as

$$N_{1\text{tot}} \sim J_{1*} \Delta_1 t$$

where

$$J_{1*} \equiv f_{1*} n_\infty \tau / \zeta$$

is the initial rate of nucleation$^1$. Then the violation of (2) means that

$$N_{1\text{tot}} \gg N_{2\text{tot}}$$

As the result the number of the droplets formed on the second type centers is negligible.

The negligible value of $N_{2\text{tot}}$ in the unique situation when the ordinary monodisperse approximation fails was the ground to apply this approximation in the situation of the strong unsymmetry$^2$. But we see that if we are interested in the value of $N_{2\text{tot}}$ without any respect to $N_{1\text{tot}}$ then the question is still open. Below we shall resolve this problem.

\[ f_{1*} \] is expressed in units of $n_\infty$
3 Special monodisperse approximation

For $G_i$ one can write the following relation

$$G_i = \int_0^\infty \rho^3 f_i(\rho, t) d\rho$$

Now one can analyze the subintegral function

$$g_i(\rho, t) = \rho^3 f_i(\rho, t)$$

which has the sense only for positive $\rho$.

One can see that

$$g_i(\rho, t) = 0$$

for

$$\rho > \rho_0(t) \equiv \int_0^t \frac{\zeta(t')}{\tau} dt'$$

One can see that

$$g_i(\rho, t) < \rho^3 f_{i*} \equiv g_{i\text{ appr}}$$

Consider now the pseudo homogeneous situation. It means that we neglect the exhaustion of the heterogeneous centers by the droplets. Here

$$g_i(\rho, t) \approx \rho^3 f_{i*}$$

for all $\rho$ from

$$\rho_0 - \rho < (0.7 \div 0.8) \zeta \Delta_i t/\tau$$

As far as $\rho^3 f_{i*}$ is the sharp function of $\rho$ we see that $g_i$ is even more sharp function of $\rho$. Then it is quite reasonable to suggest the monodisperse approximation for $g_i$.

To construct the monodisperse approximation for $g_i$ one has to solve how to cut the tail at small $\rho$. Despite the rapid decrease at small $\rho$ the tail can not be integrated at least on the base of approximation $g_{i\text{ appr}}$ (if we forget about the restriction $\rho > 0$). There are two ways to do it.

The first way is to cut off the spectrum on the halfwidth of $g_{i\text{ appr}}$. It gives the halfwidth

$$\Delta \rho = (1 - 2^{-1/3})\rho_0(t) = 0.21\rho_0(t) \equiv \Delta_{diff} \rho$$
which is small in comparison with $\rho_0(g)$. So, really, the approximation $g_i\text{ appr}$ can be used here.

The second way is more close to the iteration procedure from [1]. One can define $\Delta \rho$ by the integral way. One can integrate the approximation $g_i\text{ appr}$ from $\rho_0$ up to 0 taking into account that $g_i = 0$ for $\rho < 0$. Then

$$\Delta \rho = \rho_0(t)/4 \equiv \Delta_{\text{int}} \rho$$

As far as $\Delta_{\text{diff}} \rho \approx \Delta_{\text{int}} \rho$ one can use both these two ways. The integral way is more convenient as far as it gives precise asymptotes.

Now we can suggest approximation

$$G_1 = f_{1*} \Delta \rho \rho_0(t)^3$$

and rewrite it as

$$G_1 = N_1(t/4)\rho_0(t)^3$$

where $N_1(t/4)$ is the number of the droplets formed until the moment $t/4$ and the behavior of $G$ is analyzed in the current moment $t$.

When we consider the heterogeneous condensation with essential exhausting of centers one can easily note that the function $g_i$ becomes even more sharp. So, the previous derivation is suitable here. Certainly, the value of $N_1(t/4)$ has to be calculated with account of exhaustion of the heterogeneous centers as it was described in [2], [4].

Here we can present the last approximation as

$$G_1 \sim (\eta_{1\text{tot}} - \eta_1(t/4))\rho_0(t)^3$$

where $\eta_1$ is the number of the free heterogeneous centers of the first sort.

## 4 Floating monodisperse approximation

In [2] we were interested in the final parameters of the whole nucleation periods and used the monodisperse approximation at $t = \Delta_2 t$. It allowed to use for $N_1(\Delta_2 t/4)$ the following approximation

$$N_1(\Delta_2 t/4) = \eta_{1\text{tot}}(1 - \exp(-B\Delta_2 t/4))$$

where

$$B = f_{1*} n_\infty \zeta_*/\tau \eta_{1\text{tot}}$$
Now we don’t want to use the monodisperse approximation only at \( t = \Delta_2 t \). So, we shall act without the last approximation. But now we have to use the monodisperse approximation at the arbitrary moment of time \( t \).

We shall use the variables \( x, z \) (see [1], [2]) and shall investigate the system of equations

\[
\begin{align*}
\zeta_* &= \zeta + G_1 + G_2 \\
G_1 &= f_1 \star \int_0^z (z - x)^3 \exp(\Gamma_1(\zeta - \zeta_*)/\xi) dx \\
G_2 &= f_2 \star \int_0^z (z - x)^3 \exp(\Gamma_2(\zeta - \zeta_*)/\xi) dx \\
\theta_1 &= \exp(-\frac{f_1 \eta}{\eta_{1tot}} \int_0^z \exp(\Gamma_1(\zeta - \zeta_*)/\xi) dx) \\
\theta_2 &= \exp(-\frac{f_2 \eta}{\eta_{2tot}} \int_0^z \exp(\Gamma_2(\zeta - \zeta_*)/\xi) dx)
\end{align*}
\]

where \( \Gamma_i \) are some parameters (see [2]), \( \theta_i \) are the relative numbers of the free heterogeneous centers of the given sort.

In the situation of the strong unsymmetry we can rewrite this system in the following manner

\[
\begin{align*}
G_1 &= f_1 \star \int_0^z (z - x)^3 \exp(-\Gamma_1 G_1(x)/\xi) dx \\
G_2 &= f_2 \star \int_0^z (z - x)^3 \exp(-\Gamma_2 (G_1 + G_2)/\xi) dx \\
\theta_1 &= \exp(-\frac{f_1 \eta}{\eta_{1tot}} \int_0^z \exp(-\Gamma_1 G_1(x)/\xi) dx) \\
\theta_2 &= \exp(-\frac{f_2 \eta}{\eta_{2tot}} \int_0^z \exp(-\Gamma_2 (G_1 + G_2)/\xi) dx)
\end{align*}
\]

The first and the third equations of the previous system form the closed system which allows to consider \( G_1 \) in the second and the forth equations as some known value. According to the monodisperse approximation it can be presented as

\[
G_1(z) = \frac{f_1 E}{1 - \theta_1(z/4)} z^3
\]

where

\[
\theta_1(z/4) = \exp(-E \int_0^{z/4} \exp(-\Gamma_1 f_1 x^4/4\zeta) dx)
\]
\[ E = \frac{f_1 n_\infty}{\eta_{1\,tot}} \]

One can simplify the last expression as

\[ \eta_1(z/4) = \eta_{tot} \exp(-Ez/4) \]  (3)

for

\[ z/4 < z_m \]

and

\[ \eta_1(z/4) = \eta_{tot} \exp(-E(\frac{4\zeta_*}{\Gamma_1 f_1^*})^{1/4} A) \]  (4)

for

\[ z/4 > z_m \]

where

\[ A = \int_0^\infty \exp(-x^4)dx = 0.905 \]

and

\[ z_m = (\frac{4\zeta_*}{\Gamma_1 f_1^*})^{1/4} A \]

Then the nucleation on the second sort centers can be described by the following equations

\[ G_2 = f_2^* \int_0^z (z-x)^3 \exp(-\Gamma_2(\frac{f_1^*}{E}(1-\theta_1(z/4))z^3 + G_2)/\zeta_*)\theta_2(x)dx \]

\[ \theta_2 = \exp(-\frac{f_2^* n_\infty}{\eta_{2\,tot}} \int_0^z \exp(-\Gamma_2(\frac{f_1^*}{E}(1-\theta_1(z/4))z^3 + G_2)/\zeta_*)dx) \]

We can adopt with a rather high accuracy the following expression for \( \theta_2 \) (the reasons are the same as in the section ”Final iterations” in [2])

\[ \theta_2 = \exp(-\frac{f_2^* n_\infty}{\eta_{2\,tot}} \int_0^z \exp(-\Gamma_2(\frac{f_1^*}{E}(1-\theta_1(x/4))x^3 + f_2^* x^4/4)/\zeta_*)dx) \]

or with the help of approximation (3), (4) it can be presented in more simple form.

If \( z/4 < z_m \) then

\[ \theta_2 = \exp(-\frac{f_2^* n_\infty}{\eta_{2\,tot}} \int_0^z \exp(-\Gamma_2(\frac{f_1^*}{E}(1-\exp(-Ex/4))x^3 + f_2^* x^4/4)/\zeta_*)dx) \]

(5)
If \( z/4 > z_m \) then

\[
\theta_2 = \exp\left(-\frac{f_{1s}E}{\eta_{2tot}} \int_0^{4z_m} \exp(-\Gamma_2\frac{f_{1s}E}{E}(1-\exp(-Ex/4))x^3 + f_{2s}x^4/4)/\zeta) dx + \int_{4z_m}^{z} \exp(-\Gamma_2\frac{f_{1s}E}{E}(1-\exp(-E(\frac{4\zeta}{\Gamma_1f_{1s}})^{1/4}A)x^3 + f_{2s}x^4/4)/\zeta) dx) \right)
\]

Now we have to calculate the integrals appeared in the last two expressions. We shall start from the first one.

Consider (5). One can see that function

\[
\phi \equiv \Gamma_2\frac{f_{1s}E}{E}(1-\exp(-Bx/4))x^3 + f_{2s}x^4/4)/\zeta
\]

is very sharp function. It is more sharp than

\[
\phi_0 \equiv const x^3 + const x^4
\]

The function \( (1 - \exp(-Bx/4)) \) is rather smooth in comparison with \( \phi \) and \( \phi_0 \).

One can note that integrals \( \int_0^\infty \exp(-x^3)dx = 0.89 \) and \( \int_0^\infty \exp(-x^4)dx = 0.90 \) are approximately equal. Both subintegral functions have very sharp back front and one can speak about the cut-off in both cases. The approximate equality of these integrals means that these cut-off have approximately same values.

We shall define the characteristic parameter \( z_q \) by equality

\[
\Gamma_2\frac{f_{1s}E}{E}(1-\exp(-EZ_q/4))z_q^3 + f_{2s}z_q^4/4)/\zeta = 1
\]

Then the integral in (5) can be rewritten as

\[
\int_0^{z} \exp(-\Gamma_2\frac{f_{1s}E}{E}(1-\exp(-Ex/4))x^3 + f_{2s}x^4/4)/\zeta) dx = \Theta(z - CZ_q)Cz_q + \Theta(Cz_q - z)z
\]

where

\[
C = \frac{1}{2}(\int_0^\infty \exp(-x^4)dx + \int_0^\infty \exp(-x^3)dx)
\]
This representation of the integral transfers (5) into

$$\theta_2 = \exp\left(-\frac{f_2 \eta_{\infty}}{\eta_{2\text{tot}}}(\Theta(z - Cz_q)Cz_q + \Theta(Cz_q - z))\right)$$

(9)

Now we shall analyze the integral in (6). The reasons are the same. We shall introduce parameter \(z_l\) by the following relation

$$\Gamma_2\left(\frac{f_{1s}}{E}(1 - \exp(-E(\frac{4\zeta_+}{\Gamma_1 f_{1s}})^{1/4}A))z_l^3 + f_{2s}z_l^4/4\right)/\zeta_+ = 1$$

Note that we need only one parameter as far as

$$1 - \exp(-Ex/4) \leq 1 - \exp\left(-E\left(\frac{4\zeta_+}{\Gamma_1 f_{1s}}\right)^{1/4}A\right)$$

for \(x < z_m\) and

$$1 - \exp(-Ex/4)|_{x/4=z_m} \approx 1 - \exp\left(-E\left(\frac{4\zeta_+}{\Gamma_1 f_{1s}}\right)^{1/4}A\right)$$

If \(z_l < 4z_m\) then

$$\int_0^{4z_m} \exp(-\Gamma_2\left(\frac{f_{1s}}{E}(1 - \exp(-Ex/4))x^3 + f_{2s}x^4/4\right)/\zeta_+)dx \gg$$

$$\int_{4z_m}^{z} \exp(-\Gamma_2\left(\frac{f_{1s}}{E}(1 - \exp(-E(\frac{4\zeta_+}{\Gamma_1 f_{1s}})^{1/4}A))x^3 + f_{2s}x^4/4\right)/\zeta_+)dx$$

(10)

and one can analyze only

$$I_1 = \int_0^{4z_m} \exp(-\Gamma_2\left(\frac{f_{1s}}{E}(1 - \exp(-Ex/4))x^3 + f_{2s}x^4/4\right)/\zeta_+)dx$$

It was already done in consideration of (5).

If \(z_l > 4z_m\) then both

$$I_1 = \int_0^{4z_m} \exp(-\Gamma_2\left(\frac{f_{1s}}{E}(1 - \exp(-Ex/4))x^3 + f_{2s}x^4/4\right)/\zeta_+)dx$$

and

$$I_2 = \int_{4z_m}^{z} \exp(-\Gamma_2\left(\frac{f_{1s}}{E}(1 - \exp(-E(\frac{4\zeta_+}{\Gamma_1 f_{1s}})^{1/4}A))x^3 + f_{2s}x^4/4\right)/\zeta_+)dx$$
are essential.

Then

\[ I_1 = 4z_m \]

and \( I_2 \) can be analyzed quite analogously. Namely, we shall introduce \( z_t \) from equality\[\footnote{Certainly \( z_t = z_l \)}\]

\[ \Gamma_2 \left( \frac{f_{1*}}{E} (1 - \exp(-E(\frac{4\zeta}{\Gamma_1 f_{1*}})^{1/4}A))z_t^3 + f_{2*}z_t^4/4)/\zeta = 1 \]

If \( z_t \) is near \( 4z_m \) then \( I_2 \) is small in comparison with \( I_1 \) and there is no need to analyze \( I_2 \). If \( I_2 \) is essential in comparison with \( I_1 \) one can use the following approximation:

\[ I_2 = (z - 4z_m) \quad \text{for} \quad z < Cz_t \]

\[ I_2 = Cz_t - 4z_m \quad \text{for} \quad z > Cz_t. \]

This completes the approximate analysis of the expression for \( \theta_2 \).

Some parameters \( z_t \), \( z_m \), \( z_q \), \( z_t \) may coincide but they are conserved in order to avoid misunderstanding.

The main interesting value is \( \theta_2(\infty) \). The final expressions for this value are more simple. They can be directly obtained from the already presented ones.

On the base of \( \theta_i(z) \) one can easily find the number of droplets \( N_i \) as

\[ N_i = \eta_{tot} i(1 - \theta_i) \]

To find the total number of the droplets one has to put the arguments to \( \infty \).

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