Different approaches in the theory of the metastable phase decay on several types of heterogeneous centers

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The problem of the metastable phase decay remains one of the most actual questions in the field of kinetics of the first order phase transitions. The first theories \cite{2}, \cite{3} determined only the characteristic time lag of the nucleation process. The first well grounded theory which allows to describe the evolution of the system during the nucleation period and to find the form of the droplets size spectrum was presented in \cite{1} where the iteration procedure was formulated.

Now the theoretical description is going to be spread on the systems with the several types of heterogeneous centers. Unfortunately the direct generalization of the iteration method failed due to existence of the specific interaction between different sorts of heterogeneous centers through the vapor consumption.

The first attempt to solve this problem was done in \cite{4} where the structure of announced description was composed by many asymptotic cases including the intermediate case where the new special monodisperse approximation was suggested.

This monodisperse approximation was well grounded but there was no evident correspondence between the iteration procedure and the results presented in \cite{4}. Following the suggestion of F.M.Kuni to seek for this correspondence we shall present here the iteration solution of this problem.

We shall consider the physical situation from \cite{4} and use all definitions introduced there.

The structure of the publication will be the following:
• In the first part the iteration procedure will be presented.

• In the second part we shall calculate iterations on the base of the property of the "avalanche consumption" of the metastable phase.

• In the third part we shall calculate the iterations based on the special monodisperse approximation.

1 Iteration method

We shall present all formulas for the case of two sorts of heterogeneous centers. They will be marked by two subscripts $A$ and $B$. The generalization for the arbitrary number of heterogeneous centers types is evident. It is one of the real advantages of the presented theory.

The system of the condensation equations according to [4] can be presented as following

\[
G_A(z) = F_A \int_0^z (z - x)^3 \exp(\Gamma_A(\zeta(x) - \Phi))\theta_A(x)dx
\]

\[
G_B(z) = F_B \int_0^z (z - x)^3 \exp(\Gamma_B(\zeta(x) - \Phi))\theta_B(x)dx
\]

\[
\Phi = \zeta(z) + G_A(z) + G_B(z)
\]

\[
\theta_A(z) = \exp(-K_A \int_0^z \exp(\Gamma_A(\zeta(x) - \Phi))dx)
\]

\[
\theta_B(z) = \exp(-K_B \int_0^z \exp(\Gamma_B(\zeta(x) - \Phi))dx)
\]

with six parameters $F_A$, $F_B$, $K_A$, $K_B$, $\Gamma_A$, $\Gamma_B$. Note that the definition of $\Gamma_A, \Gamma_B$ slightly differs from the standard one - it is $\Phi$ times less.

The presented system can be directly seen from the condensation equations system for one type of heterogeneous centers and there is no need to discuss it more. The problem is how to solve it.

According to the scale invariance one can put $F_A = 1, \Gamma_A = 1$. According to the symmetry of the types one can choose them as to have $F_B < 1$. These simplifications will be interesting only in numerical modeling and here we shall keep all parameters.
We shall define the iteration procedure by the following relations

\[
G_{A_{i+1}}(z) = F_A \int_0^z (z - x)^3 \exp(\Gamma_A(\zeta_i(x) - \Phi))\theta_{A_i}(x) dx
\]

\[
G_{B_{i+1}}(z) = F_B \int_0^z (z - x)^3 \exp(\Gamma_B(\zeta_i(x) - \Phi))\theta_{B_i}(x) dx
\]

\[
\Phi = \zeta_i(z) + G_{A_i}(z) + G_{B_i}(z)
\]

\[
\theta_{A_{i+1}}(z) = \exp(-K_A \int_0^z \exp(\Gamma_A(\zeta_i(x) - \Phi)) dx)
\]

\[
\theta_{B_{i+1}}(z) = \exp(-K_B \int_0^z \exp(\Gamma_B(\zeta_i(x) - \Phi)) dx)
\]

The number of the iteration approximation is marked by the ordinary subscript instead of the capital letter which marks below the sort of the centers. The values without the number of iteration will mark the real solutions.

The initial approximations are the following

\[G_{A0} = 0, \quad G_{B0} = 0, \quad \theta_{A0} = 1, \quad \theta_{B0} = 1\]

Then one can note the following important chains

\[G_{A0} < G_{A2} < \ldots < G_{A2i} < \ldots < G_A < \ldots < G_{A2i+1} < \ldots < G_{A3} < G_{A1}\]

\[G_{B0} < G_{B2} < \ldots < G_{B2i} < \ldots < G_B < \ldots < G_{B2i+1} < \ldots < G_{B3} < G_{B1}\]

\[\theta_{A0} > \theta_{A2} > \ldots > \theta_{A2i} > \ldots > \theta_A > \ldots > \theta_{A2i+1} > \ldots > \theta_{A3} > \theta_{A1}\]

\[\theta_{B0} > \theta_{B2} > \ldots > \theta_{B2i} > \ldots > \theta_B > \ldots > \theta_{B2i+1} > \ldots > \theta_{B3} > \theta_{B1}\]

\[\zeta_0 > \zeta_2 > \ldots > \zeta_{2i} > \ldots > \zeta > \ldots > \zeta_{2i+1} > \ldots > \zeta_3 > \zeta_1\]

for all values of arguments.

These chains prove the convergence of iterations and allow to estimate the accuracy at every step of the calculation.

The problem is to calculate the iterations. In the situation with one type of heterogeneous centers the system of condensation equations can be gotten if we chancel \(G_B\) and the index \(A\). The same thing we have to do with the iteration procedure and one can get the mentioned properties. In [1] only one iteration for \(G\) and two first iterations for \(\theta\) were calculated. The further
iterations can not be calculated analytically. In the situation of nucleation in the system with one type of heterogeneous centers it is sufficient. But in the situation with several types of heterogeneous centers it isn’t so. To show this we has to recall the physical sense of the first iterations.

The first iteration for $G$ is calculated on the base of unexhausted number of heterogeneous centers. So, the behavior of $\zeta$ is wrong when the power of exhaustion is essential. But when the centers are exhausted the number of droplets is known - it is equal to the initial number of centers. This primitive notation is the reason why the second iteration for $\theta$ gives already suitable result.

In the situation with the several types of heterogeneous centers the situation is different. Really, it is quite possible to have the exhaustion of the first type of heterogeneous centers and the moderate exhaustion of the second type centers. Then the exhaustion of the first type centers has to be taken into account in calculation of the supersaturation which is necessary to get the number of the droplet appeared on the second type centers. But as far as the power of exhaustion of the second type centers is moderate one can not say that the number of the droplets on the second type centers is equal to the total number of the second type centers. So, we have to know the behavior of supersaturation in all cases and it is impossible to do already in the first iterations. Then we have to calculate further iterations.

Unfortunately it is impossible to calculate the further iteration approximations without any simplifications. That’s why two ways of possible approximations are presented in the next sections.

2 Avalanche consumption of the metastable phase

The sequential calculation of iterations gives

$$G_{A1} = F_A \frac{z^4}{4}$$

$$\theta_{A1} = \exp(-K_A z)$$

$$G_{B1} = F_B \frac{z^4}{4}$$
\[ \theta_{B1} = \exp(-K_B z) \]

\[ G_{A2} = F_A \int_0^z (z - x)^3 \exp(-\Gamma_A (F_A + F_B) x^4 / 4) \exp(-K_A x) dx \]

\[ G_{B2} = F_B \int_0^z (z - x)^3 \exp(-\Gamma_B (F_A + F_B) x^4 / 4) \exp(-K_B x) dx \]

The problem is how to calculate the integrals for \( G_{A2}, G_{B2} \). To calculate these integrals we shall extract functions

\[ \varphi_A = \exp(-\Gamma_A (G_A + G_B)) \]

\[ \varphi_B = \exp(-\Gamma_B (G_A + G_B)) \]

These functions can be calculated in the iteration approximation as

\[ \varphi_{Ai} = \exp(-\Gamma_A (G_Ai + G_Bi)) \]

\[ \varphi_{Bi} = \exp(-\Gamma_B (G_Ai + G_Bi)) \]

One can see that \( \varphi_{A1}, \varphi_{B1} \) can be well approximated as the step functions. Really, \( \exp(-x^4) \) can be approximately interpreted as the step function on \( x^4 \).

Then

\[ G_{A2} = F_A \int_0^z (z - x)^3 \exp(-K_A x) \Theta(z_{1A} - x) dx \]

\[ G_{B2} = F_B \int_0^z (z - x)^3 \exp(-K_B x) \Theta(z_{1B} - x) dx \]

where

\[ z_{1A} \equiv \left( \frac{4}{\Gamma_A (F_A + F_B)} \right)^{1/4} \]

\[ z_{1B} \equiv \left( \frac{4}{\Gamma_B (F_A + F_B)} \right)^{1/4} \]

and these integrals can be easily calculated.

For \( z > z_{1A} \) we have

\[ G_{A2} = \sum_{i=0}^3 p_{Ai} z^i \]

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1. This was the reason why in experiments one can observe characteristic time lag and this characteristic was introduced in the theory of the metastable phase decay. Then the first theoretical descriptions adopted this fact as the given one without any justification.

2. More correctly one gas to multiply \( z_{1A} \) and \( z_{1B} \) on \( \ln^{1/4} \). This corresponds to the definition of the halfwidth at the halfheight.
where
\[ p_{Ai} = \frac{3!(-1)^i}{i!(3-i)!} F_A \int_0^{z_{1A}} x^{3-i} \exp(-K_A x) \, dx \]
are some constants which can be calculated analytically.

For \( z > z_{1B} \) we have
\[ G_{B2} = \sum_{i=0}^{3} p_{Bi} z^i \]
where
\[ p_{Bi} = \frac{3!(-1)^i}{i!(3-i)!} F_B \int_0^{z_{1B}} x^{3-i} \exp(-K_B x) \, dx \]
are some constants calculated analytically.

For \( z < z_{1A} \) we have
\[ G_{A2} = F_A \exp(-K_A z) \frac{1}{K_A^4} [(zK_A)^3 \exp(zK_A) - 3(zK_A)^2 \exp(zK_A) + 6zK_A \exp(zK_A) - 6(\exp(K_A z) - 1)] \]

For \( z < z_{1B} \) we have
\[ G_{B2} = F_B \exp(-K_B z) \frac{1}{K_B^4} [(zK_B)^3 \exp(zK_B) - 3(zK_B)^2 \exp(zK_B) + 6zK_B \exp(zK_B) - 6(\exp(K_B z) - 1)] \]

The calculation of \( \theta_{A2}, \theta_{A2} \) can be done in the same way
\[ \theta_{A2} = \exp(-K_A \int_0^{z} \exp(-\Gamma_A(F_A + F_B)\frac{x^4}{4}) \, dx) \]
\[ \theta_{B2} = \exp(-K_B \int_0^{z} \exp(-\Gamma_B(F_A + F_B)\frac{x^4}{4}) \, dx) \]

Then
\[ \theta_{A2} = \exp(-K_A[\Theta(z_{1A} - z) + \Theta(z - z_{1A})z_{1A}]) \]
\[ \theta_{B2} = \exp(-K_B[\Theta(z_{1B} - z) + \Theta(z - z_{1B})z_{1B}]) \]
Now we have to calculate $\theta_{A3}, \theta_{B3}$. One can note that functions $\varphi_{A2}, \varphi_{B2}$ can be also presented as the step functions. Namely, all functions

$$
\exp(-\Gamma_A(F_A \exp(-K_A z) \frac{1}{K_A^4} ((zK_A)^3 \exp(zK_A) - 3(zK_A)^2 \exp(zK_A) + 6zK_A \exp(zK_A) - 6(\exp(K_A z) - 1)) + F_B \exp(-K_B z) \frac{1}{K_B^4} [(zK_B)^3 \exp(zK_B) - 3(zK_B)^2 \exp(zK_B) + 6zK_B \exp(zK_B) - 6(\exp(K_B z) - 1)]) + 3(zK_A)^3 \exp(zK_A) - 3(zK_A)^2 \exp(zK_A) + 6zK_A \exp(zK_A) - 6(\exp(K_A z) - 1)] + \sum_{i=0}^{3} p_B i z^i))
$$

$$
\exp(-\Gamma_A(\sum_{i=0}^{3} p_A i z^i + \sum_{i=0}^{3} p_B i z^i))
$$

$$
\exp(-\Gamma_B(F_A \exp(-K_A z) \frac{1}{K_A^4} ((zK_A)^3 \exp(zK_A) - 3(zK_A)^2 \exp(zK_A) + 6zK_A \exp(zK_A) - 6(\exp(K_A z) - 1)) + F_B \exp(-K_B z) \frac{1}{K_B^4} [(zK_B)^3 \exp(zK_B) - 3(zK_B)^2 \exp(zK_B) + 6zK_B \exp(zK_B) - 6(\exp(K_B z) - 1)]) + 3(zK_B)^3 \exp(zK_B) - 3(zK_B)^2 \exp(zK_B) + 6zK_B \exp(zK_B) - 6(\exp(K_B z) - 1)) + \sum_{i=0}^{3} p_B i z^i)
$$

$$
\exp(-\Gamma_B(F_A \exp(-K_A z) \frac{1}{K_A^4} ((zK_A)^3 \exp(zK_A) - 3(zK_A)^2 \exp(zK_A) + 6zK_A \exp(zK_A) - 6(\exp(K_A z) - 1)) + F_B \exp(-K_B z) \frac{1}{K_B^4} [(zK_B)^3 \exp(zK_B) - 3(zK_B)^2 \exp(zK_B) + 6zK_B \exp(zK_B) - 6(\exp(K_B z) - 1)]) + \sum_{i=0}^{3} p_B i z^i))
$$
$$\exp(-\Gamma_B(\sum_{i=0}^{3} p_{Ai}z^i + \sum_{i=0}^{3} p_{Bi}z^i))$$

$$\exp(-\Gamma_B(\sum_{i=0}^{3} p_{Ai}z^i + F_B \exp(-K_B z) \frac{1}{K_B} [(zK_B)^3 \exp(zK_B) - 3(zK_B)^2 \exp(zK_B) + 6zK_B \exp(zK_B) - 6(\exp(K_B z) - 1)]))$$

have the step-like behavior. This is the central point of our calculations. This property can be directly seen by calculations.

The possibility to see the step-like behavior of exponent of the supersaturation deviation directly on the base of explicit expressions is the evident advantage of the iteration method. Otherwise we have to prove this property in the general situation taking into account that exponent of the supersaturation deviation lies between $\exp(-z^4)$ and $\exp(-z^3)$ after the suitable renormalization.

Now to calculate $\theta_A$, $\theta_B$ we have to define the values $z_{2A}$, $z_{2B}$ by equations

$$\Gamma_A(G_{A2}(z_{2A}) + G_{B2}(z_{2A})) = 1$$
$$\Gamma_B(G_{A2}(z_{2B}) + G_{B2}(z_{2B})) = 1$$

Then

$$\theta_A = \exp(-K_A[\Theta(z_{2A} - z) + \Theta(z - z_{2A})z_{2A}])$$
$$\theta_B = \exp(-K_B[\Theta(z_{2B} - z) + \Theta(z - z_{2B})z_{2B}])$$

The calculation of $G_{3A}$ and $G_{3B}$ can be done by the following way

$$G_{A3} = F_A \int_0^z (z - x)^3 \exp(-\Gamma_A(G_{A2} + G_{B2})) \exp(-K_A[\Theta(z_{1A} - x) + \Theta(x - z_{1A})z_{1A}])dx$$

$$G_{A3} = F_A \int_0^z (z - x)^3 \Theta(z_{2A} - x) \exp(-K_A[\Theta(z_{1A} - x) + \Theta(x - z_{1A})z_{1A}])dx$$

$$G_{B3} = F_B \int_0^z (z - x)^3 \exp(-\Gamma_B(G_{A2} + G_{B2})) \exp(-K_B[\Theta(z_{1B} - x) + \Theta(x - z_{1B})z_{1B}])dx$$

$$G_{B3} = F_B \int_0^z (z - x)^3 \Theta(z_{2B} - x) \exp(-K_B[\Theta(z_{1B} - x) + \Theta(x - z_{1B})z_{1B}])dx$$
\[ G_{B3} = F_B \int_0^z (z - x)^3 \Theta(z_{2B} - x) \exp(-K_B[\Theta(z_{1B} - x)x + \Theta(x - z_{1B})z_{1B}]) \, dx \]

These integrals can be easily taken in analytical form. For \( G_{A3} \) one can get

- For \( z > z_{2A} \) with arbitrary \( z_{1A} \) we have
  \[ G_{A3} = \sum_{i=0}^{3} z^i p_{Ai} \]
  where
  \[ p_{Ai} = \frac{(-1)^i 3!}{i!(3-i)!} F_A \int_{z_{1A}}^{z_{2A}} x^i \exp(-K_A z_{1A}) \Theta(x - z_{1A}) + \exp(-K_A x) \Theta(z_{1A} - x) \, dx \]
  can be calculated analytically.

- For \( z < \min\{z_{1A}, z_{2A}\} \)
  \[ G_{A3} = F_A \int_0^z (z - x)^3 \exp(-K_A x) \, dx \]
  has been already calculated.

- For \( z_{1A} < z < z_{2A} \)
  \[ G_{A3} = \sum_{i=0}^{3} z^i p_{Ai} + F_A \frac{(z - z_{1A})^4}{4} \exp(-K_A z_{1A}) \]
  where
  \[ p_{Ai} = F_A \frac{3!(-1)^i}{i!(3-i)!} \int_{z_{1A}}^{z_{2A}} x^i \exp(-K_A x) \, dx \]

All \( p_{Ai} \) are constants and can be calculated analytically.

For \( G_{B3} \) one can get
• For \( z > z_{2B} \) with arbitrary \( z_{1B} \)

\[
G_{B3} = \sum_{i=0}^{3} z^i p_{Bi}
\]

where

\[
p_{Bi} = \frac{(-1)^i 3!}{i!(3-i)!} F_B \int_{z_{1B}}^{z_{2B}} x^i \left[ \exp(-K_B z_{1B}) \Theta(x - z_{1B}) + \exp(-K_B x) \Theta(z_{1B} - x) \right] dx
\]

• For \( z < \min\{z_{1B}, z_{2B}\} \)

\[
G_{B3} = F_B \int_{0}^{z} (z - x)^3 \exp(-K_B x) dx
\]

has been already calculated.

• For \( z_{1B} < z < z_{2B} \)

\[
G_{B3} = \sum_{i=0}^{3} z^i p_{Bi} + F_B \frac{(z - z_{1B})^4}{4} \exp(-K_B z_{1B})
\]

where

\[
p_{Bi} = \frac{3!(-1)^i}{i!(3-i)!} \int_{0}^{z_{1B}} x^i \exp(-K_B x) dx
\]

All \( p_{Bi} \) are constants and can be calculated analytically.

One can easily see that \( z_{1A} < z_{2A}, \ z_{1B} < z_{2B} \) and the third opportunity can take place.

Moreover, if we define \( z_{iA}, z_{iB} \) by equalities

\[
\Gamma_A(G_{Ai}(z_{iA}) + G_{Bi}(z_{iA})) = 1
\]

\[
\Gamma_B(G_{Ai}(z_{iB}) + G_{Bi}(z_{iB})) = 1
\]

then we can get the following chains of inequalities

\[
z_{1A} < z_{3A} < \ldots < z_{2i+1A} < \ldots < z_{A} < \ldots < z_{2iA} < \ldots < z_{4A} < z_{2A}
\]

\[
z_{1B} < z_{3B} < \ldots < z_{2i+1B} < \ldots < z_{B} < \ldots < z_{2iB} < \ldots < z_{4B} < z_{2B}
\]
where \( z_A, z_B \) are defined by

\[
\Gamma_A(G_A(z_A) + G_B(z_A)) = 1
\]

\[
\Gamma_B(G_A(z_B) + G_B(z_B)) = 1
\]

Then we can calculate \( G_{A4}, G_{B4} \). In the initial expressions

\[
G_{A4} = F_A \int_{0}^{z} (z - x)^3 \exp(-\Gamma_A(G_{A3} + G_{B3})\theta_{A3})dx
\]

\[
G_{B4} = F_B \int_{0}^{z} (z - x)^3 \exp(-\Gamma_A(G_{A3} + G_{B3})\theta_{B3})dx
\]

we have to use two characteristic lengths \( z_2 \) and \( z_3 \). Then

\[
G_{A4} = F_A \int_{0}^{z} \Theta(z_{3A} - x)(z - x)^3 \left[ \exp(-K_A x)\Theta(z_{2A} - x) + \exp(-K_A z_{2A})\Theta(x - z_{2A}) \right]dx
\]

\[
G_{B4} = F_B \int_{0}^{z} \Theta(z_{3B} - x)(z - x)^3 \left[ \exp(-K_B x)\Theta(z_{2B} - x) + \exp(-K_B z_{2B})\Theta(x - z_{2B}) \right]dx
\]

These integrals can be easily taken in an analytical form. For \( G_{A4} \) one can get

- For \( z > z_{3A} \) with arbitrary \( z_{2A} \)

\[
G_{A4} = \sum_{i=0}^{3} z^i p_{Ai}
\]

where

\[
p_{Ai} = \frac{(-1)^i 3!}{i!(3 - i)!} F_A \int_{0}^{z_{3A}} x^i \left[ \exp(-K_A z_{2A})\Theta(x - z_{2A}) + \exp(-K_A x)\Theta(z_{2A} - x) \right]dx
\]

- For \( z < \min\{z_{2A}, z_{3A}\} \)

\[
G_{A4} = F_A \int_{0}^{z} (z - x)^3 \exp(-K_A x)dx
\]

has been already calculated.
• For $z_{2A} < z < z_{3A}$

$$G_{A4} = \sum_{i=0}^{3} z^i p_{Ai} + F_A \frac{(z - z_{2A})^4}{4} \exp(-K_A z_{2A})$$

where

$$p_{Ai} = F_A \frac{3!(-1)^i}{i!(3 - i)!} \int_0^{z_{2A}} x^i \exp(-K_A x) dx$$

All $p_{Ai}$ are constants and can be calculated analytically.

For $G_{B4}$ one can get

• For $z > z_{3B}$ with arbitrary $z_{2B}$

$$G_{B4} = \sum_{i=0}^{3} z^i p_{Bi}$$

where

$$p_{Bi} = \frac{(-1)^i 3!}{i!(3 - i)!} F_B \int_0^{z_{2B}} x^i \left[ \exp(-K_B z_{2B}) \Theta(x - z_{2B}) + \exp(-K_B x) \Theta(z_{2B} - x) \right] dx$$

• For $z < \min\{z_{2B}, z_{3B}\}$

$$G_{B4} = F_B \int_0^{z} (z - x)^3 \exp(-K_B x) dx$$

has been already calculated.

• For $z_{2B} < z < z_{3B}$

$$G_{B4} = \sum_{i=0}^{3} z^i p_{Bi} + F_B \frac{(z - z_{2B})^4}{4} \exp(-K_B z_{2B})$$

where

$$p_{Bi} = F_B \frac{3!(-1)^i}{i!(3 - i)!} \int_0^{z_{2B}} x^i \exp(-K_B x) dx$$
All $p_{Bi}$ are constants and can be calculated analytically.

One can easily see that $z_{3A} < z_{2A}$, $z_{3B} < z_{2B}$ and the third opportunity can not take place.

One can calculate by the same way all further iterations.\footnote{That’s why we left all possibilities in the last expressions.}

We see that due to the difference of the relations between parameters $z_{Ai}$, $z_{Bi}$ even the functional form of the iterations will be different. But it is quite easy to see that calculations of further iterations will be done absolutely analogously. Moreover, the functional forms of all odd further iterations will be similar. The functional forms of all even iterations will be also similar.

Then one can extract these functional forms and it is necessary to obtain the values of parameters $z_{Ai}$, $z_{Bi}$ in these forms.

Moreover, one can put one and the same values of "final" parameters $z_A$, $z_B$ in equations for $G_A$, $G_B$, $\theta_A$, $\theta_B$. This leads to the following result

In the initial expressions

\[
G_A = F_A \int_0^z (z - x)^3 \exp(-\Gamma_A(G_A + G_B))\theta_A dx
\]

\[
G_B = F_B \int_0^z (z - x)^3 \exp(-\Gamma_A(G_A + G_B))\theta_B dx
\]

Then

\[
G_A = F_A \int_0^z \Theta(z_A - x)(z - x)^3 \exp(-K_A x) dx
\]

\[
G_B = F_B \int_0^z \Theta(z_B - x)(z - x)^3 \exp(-K_B x) dx
\]

These integrals can be easily taken in analytical form.

For $G_A$ one can get

- For $z > z_A$

  \[
  G_A = \sum_{i=0}^3 z^i p_{Ai}
  \]

  where

  \[
p_{Ai} = \frac{(-1)^i 3!}{i!(3 - i)!} F_A \int_0^{z_A} x^i \exp(-K_A x) dx
  \]
For $z < z_A$

$$G_{A4} = F_A \int_0^z (z - x)^3 \exp(-K_A x) dx$$

has been already calculated.

All $p_{Ai}$ are constants and can be calculated analytically.

For $G_B$ one can get

- For $z > z_B$

$$G_B = \sum_{i=0}^{3} z^i p_{Bi}$$

where

$$p_{Bi} = \frac{(-1)^i 3!}{i!(3-i)!} F_B \int_0^{z_B} x^i \exp(-K_B x) dx$$

- For $z < z_B$

$$G_{B4} = F_B \int_0^z (z - x)^3 \exp(-K_B x) dx$$

has been already calculated.

All $p_{Bi}$ are constants and can be calculated analytically.

As the result now we know the functional form for $G_A, G_B, \theta_A, \theta_B$. The condensations equations system now determines the characteristic values $z_A, z_B$.

The step-like behavior of $\varphi$ occurs due to the avalanche character of the vapor consumption. The avalanche character of the vapor consumption has to be considered as the main feature of the first order phase transition kinetics. This feature was described in [5] in details. Meanwhile it is possible to make the theory more accurate taking into account the regime of the droplets growth.

Note that all functions $\varphi$ are lying between $\exp(-x^4)$ and $\exp(-x^3)$ after the suitable renormalization. Namely, they are more sharp than $\exp(-x^3)$ and more smooth than $\exp(-x^4)$. Note that

$$\int_0^\infty \exp(-x^4) dx \approx \int_0^\infty \exp(-x^3) dx \approx 0.9 \equiv D$$

Then one can make results of the theory more accurate if we take

- instead $\Theta(z_{iA} - x)$ the function $\Theta(Dz_{iA} - x)$
• instead $\Theta(z_{iB} - x)$ the function $\Theta(Dz_{iB} - x)$
• instead $\Theta(x - z_{iA})$ the function $D\Theta(x - Dz_{iA})$
• instead $\Theta(x - z_{iB})$ the function $D\Theta(x - Dz_{iB})$

and multiply all parameters $z_{iA}, z_{iB}$ on $D$.

We can see that the generalization of the presented approach to the multicomponent case is quite evident. But here the number of unknown parameters $z_A$ will be equal to the number of the sorts of heterogeneous centers. The problem how to solve this system is rather actual and here we shall propose a way to do it.

We shall choose the sorts of heterogeneous centers as to have

$$\Gamma_A > \Gamma_B > \Gamma_C > \Gamma_D > ....$$

Then

$$z_A < z_B < z_C < z_D < ....$$

At first we shall determine $z_A$. Note that the behavior of the system after $z_A$. Then we can put all all $\Gamma_B, \Gamma_C$ etc. to be equal to $\Gamma_A$ and $z_B, z_C$ etc. to be equal $z_A$. Then we have only one parameter $z_A$ and can determine it from one algebraic equation analogous to those described in [6] (the situation is absolutely analogous to the intermediate situation).

Now $z_A$ is determined and $G_A, \theta_A$ are known. It allows to go to the determination of $z_B$. It can be done by the same procedure. We have to consider $G_A, \theta_A$ as known values and put all $z_C, z_D$ etc. to be equal to $z_B$. Then the analogous equation can be solved and it gives $z_B, G_B, \theta_B$. This procedure can be continued. Note that at first this way was described in [6] for the special monodisperse approximation.

3 Special monodisperse approximation

The task to give the theoretical description of the complex systems required new approximations for some characteristic functions. As the result the monodisperse approximation for $G_A$ and $G_B$ was suggested in [4]. The monodisperse approximation can be used in two variants - the first one is the monodisperse approximation with fixed number of droplets which is suitable when $G_A, G_B$ are really important, the second one is the monodisperse...
approximation with a floating number of droplets involved in this approximation. A special recipe allows to get approximation which is suitable during all times.

The second variant of approximation is necessary for the systems with the strong hierarchy between the probabilities of droplets formation on different sorts of centers. Nevertheless in solution of the system by the procedure analogous to the already described in the end of the last section it is possible to use only the first type of approximation. This states the significance of the first type of approximation. But as far as we follow here the iteration procedure it will be necessary to use the second variant of approximation.

The problems to calculate iterations appear in the second approximation:

\[ G_{A2} = F_A \int_0^z (z-x)^3 \exp(-\Gamma_A(F_A + F_B)\frac{x^4}{4}) \exp(-K_Ax) dx \]

\[ G_{B2} = F_B \int_0^z (z-x)^3 \exp(-\Gamma_B(F_A + F_B)\frac{x^4}{4}) \exp(-K_Bx) dx \]

The justification of the monodisperse approximation has been already presented many times (see [4], [5]) and we shall use it here without discussion. Then

\[ G_{A2} \approx F_A z^3 \int_0^{z/4} \exp(-\Gamma_A(F_A + F_B)\frac{x^4}{4}) \exp(-K_Ax) dx \]

\[ G_{B2} \approx F_B z^3 \int_0^{z/4} \exp(-\Gamma_B(F_A + F_B)\frac{x^4}{4}) \exp(-K_Bx) dx \]

The real advantage of consideration of the monodisperse approximation on the level of iterations is the possibility to calculate the error of approximation explicitly. This error is small.

One can make the iteration approximation more accurate by the substitution of \( \exp(-K_Ax) \) by

\[ \theta_{2A} = \exp(-K_A \int_0^z \exp(-\Gamma_A(F_A + F_B)\frac{x^4}{4}) dx) \]

and by the substitution of \( \exp(-K_Bx) \) by

\[ \theta_{2B} = \exp(-K_B \int_0^z \exp(-\Gamma_B(F_A + F_B)\frac{x^4}{4}) dx) \]
This leads to
\[ G_{2A}(z) = F_A(1 - \theta_{2A}(\frac{z}{4}))z^3/K_A \]
\[ G_{2B}(z) = F_B(1 - \theta_{2B}(\frac{z}{4}))z^3/K_B \]

When monodisperse approximation is used it convenient to use the following way to construct iterations
\[
G_{A_{i+1}}(z) = F_A \int_0^z (z - x)^3 \exp(\Gamma_A(\zeta_i(x) - \Phi))\theta_{A_{i+1}}(x) dx
\]
\[
G_{B_{i+1}}(z) = F_B \int_0^z (z - x)^3 \exp(\Gamma_B(\zeta_i(x) - \Phi))\theta_{B_{i+1}}(x) dx
\]

All other formulas remain the same. Certainly the chains of inequalities will be slightly violated, but this can not leads to divergence of iterations. Moreover, one can simply add the difference between sequential \( \theta \) to the error between sequential iterations.

Now we see that in monodisperse approximation
\[
G_{iA}(z) = \frac{F_A z^3}{K_A} (1 - \theta_{Ai}(z/4))
\]
\[
G_{iB}(z) = \frac{F_B z^3}{K_B} (1 - \theta_{Bi}(z/4))
\]

So, we need to calculate only \( \theta_{Ai}, \theta_{Bi} \).

In this calculation one can use the avalanche character of the vapor consumption again. Then
\[
\theta_{2A}(z) = \exp(-K_A z_{1A})\theta(z - z_{1A}) + \exp(-K_A z)\Theta(z_{1A} - z)
\]
\[
\theta_{2B}(z) = \exp(-K_B z_{1B})\theta(z - z_{1B}) + \exp(-K_B z)\Theta(z_{1B} - z)
\]

where \( z_{1A}, z_{1B} \) are given by the previous expressions (but further \( z_{iA}, z_{iB} \) will have slightly another numerical values).

Note that in practice we don’t use such expression but can use the simple asymptotes (“essential asymptotes”)
\[
\theta_{2A} = \exp(-K_A z)
\]
\[
\theta_{2B} = \exp(-K_B z)
\]
for all $z$.

Really, we need these expressions only for $z \leq z_A, z \leq z_B$. As far as the argument is $z/4$ it means that these asymptotes can not be used only when $z_A \geq 4z_B$ or $z_B \geq 4z_A$. It can take place only when $\Gamma_A$ and $\Gamma_B$ differ more than in $4^3 = 64$ times. The last seems to be practically unrealizable.

The third iteration for $\theta$ gives

$$
\theta_{3A} = \exp(-K_A \int_0^z \exp(-\Gamma_A (F_A (1 - \exp(-K_A \frac{x}{4}))
\Theta(-\frac{x}{4} + z_{1A}) - \exp(-K_A z_{1A})\Theta(-z_{1A} + \frac{x}{4})) +
F_B (1 - \exp(-K_B \frac{x}{4})\Theta(-\frac{x}{4} + z_{1B}) -
\exp(-K_B z_{1B})\Theta(-z_{1B} + \frac{x}{4})))dx)
$$

$$
\theta_{3B} = \exp(-K_B \int_0^z \exp(-\Gamma_B (F_A (1 - \exp(-K_A \frac{x}{4}))
\Theta(-\frac{x}{4} + z_{1A}) - \exp(-K_A z_{1A})\Theta(-z_{1A} + \frac{x}{4})) +
F_B (1 - \exp(-K_B \frac{x}{4})\Theta(-\frac{x}{4} + z_{1B}) -
\exp(-K_B z_{1B})\Theta(-z_{1B} + \frac{x}{4})))dx)
$$

One can directly see that

$$
G_{A_i+1}(z) = F_A z^3 \int_0^{z/4} \exp(-\Gamma_A (G_{Ai}(x) + G_{Bi}(x)))
\exp(-K_A \int_0^x \exp(-\Gamma_A (G_{Ai}(x') + G_{Bi}(x')))dx')dx =
\frac{F_A z^3}{K_A} (1 - \exp(-K_A \int_0^z \exp(-\Gamma_A (G_{Ai}(x) + G_{Bi}(x))))dx)
$$

$$
G_{B_i+1}(z) = F_B z^3 \int_0^{z/4} \exp(-\Gamma_B (G_{Ai}(x) + G_{Bi}(x)))
\exp(-K_B \int_0^x \exp(-\Gamma_B (G_{Ai}(x') + G_{Bi}(x')))dx')dx =
\frac{F_B z^3}{K_B} (1 - \exp(-K_B \int_0^z \exp(-\Gamma_B (G_{Ai}(x) + G_{Bi}(x))))dx))
$$

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Then $G_{A_3}, G_{B_3}$ have the same structure as $G_{A_2}, G_{B_2}$ have. Certainly the numerical values of parameters $z_{Ai}, z_{Bi}$ can be slightly another. All other iteration approximations will have the same form.

Now we can reformulate the system of the condensation equations because we know the functional form of $G_A, G_B$. It will be the following

$$G_A(z) = \frac{F_A z^3}{K_A} (1 - \exp(-K_A \int_0^{z/4} \exp(-\Gamma_A(G_A(x) + G_B(x)))dx))$$

$$G_B(z) = \frac{F_B z^3}{K_B} (1 - \exp(-K_B \int_0^{z/4} \exp(-\Gamma_B(G_A(x) + G_B(x)))dx))$$

In the avalanche approximation it will be the following

$$G_A(z) = \frac{F_A z^3}{K_A} (1 - \exp(-K_A z/4) \Theta(z_A - z/4) - \exp(-K_A z_A \Theta(z/4 - z_A)))$$

$$G_B(z) = \frac{F_B z^3}{K_B} (1 - \exp(-K_B z/4) \Theta(z_B - z/4) - \exp(-K_B z_B \Theta(z/4 - z_B)))$$

where $z_A, z_B$ are defined by the previous relations.

In the approximation of essential asymptotes

$$G_A(z) = \frac{F_A z^3}{K_A} (1 - \exp(-K_A z/4))$$

$$G_B(z) = \frac{F_B z^3}{K_B} (1 - \exp(-K_B z/4))$$

These algebraic equations can be easily solved.

Now one can mention some ways to go away from the avalanche approximation. In the approximation of essential asymptotes everything is clear. In the avalanche approximation one can consider the number of the free heterogeneous centers as the smooth function of $z$ and approximately consider

$$G_A(z) = \frac{F_A z^3}{K_A} (1 - \exp(-K_A \int_0^{z_A/4} \exp(\Gamma_A(G_A(x) + G_B(x)))dx))$$

$$G_B(z) = \frac{F_B z^3}{K_A} (1 - \exp(-K_B \int_0^{z_B/4} \exp(\Gamma_B(G_A(x) + G_B(x)))dx))$$

Then $G_A \sim const z^3, G_B \sim const z^3$, we have the monodisperse approximation with fixed number of droplets and need only to calculate the integrals of the type $\int_0^{z} \exp(-x^3)dx$. This leads to the necessity to take
• instead $\Theta(z_{iA} - x)$ the function $\Theta(Dz_{iA} - x)$
• instead $\Theta(z_{iB} - x)$ the function $\Theta(Dz_{iB} - x)$
• instead $\Theta(x - z_{iA})$ the function $D\Theta(x - Dz_{iA})$
• instead $\Theta(x - z_{iB})$ the function $D\Theta(x - Dz_{iB})$

and to multiply all parameters $z_{iA}, z_{iB}$ on $D$. Here

$$D \equiv \int_0^\infty \exp(-x^3) dx = 0.9$$

The generalization of the presented approach to the multicomponent case is quite evident. Our actions are absolutely identical to those described for the avalanche model. The only thing to stress is that at every step we can use “essential asymptote” for all sorts of heterogeneous centers whose $G_A$ are still undetermined. Those $G_A$ which are already determined have to be taken explicitly. Note that at first this way was described in [3].

As the result we have to conclude that approximations of the avalanche consumption or the special monodisperse approximation lead to the similarity of the iterations of the high order (at least in their functional form). So, we see now the correspondence between the iteration approach and approximations used here. The numerical calculations show that the errors of these approximations are negligible in frames of the accuracy of the modern experiment.

References

[1] Kuni F.M., Grinin A.P., Kolloidn. journ. vol.46 (1984), p.460
[2] Wakeshima H., Time lag in self nucleation J.Chem.Phys., 1954, v.22. N.9, p.1614-1615
[3] F.M. Kuni, A.P.Grinin, A.S. Kabanov, Kolloidn. journ. (USSR) V.46 (1984), p.440
[4] V.B.Kurasov, Deponed in VINITI 2594b95 from 19.09.1995, 28p.
[5] Kurasov V.B., Universality in kinetics of the first order phase transitions, SPb, 1997, 400p.

[6] Kurasov V.B., Development of the universality conception in the first order phase transitions, SPb, 1998, 125p.