Monodisperse approximation in the metastable phase decay

V.Kurasov

Victor.Kurasov@pobox.spbu.ru

Abstract

A new simple method for the first order phase transition kinetics is suggested. The metastable phase consumption can be imagined in frames of the modisperse approximation for the distribution of the droplets sizes. In all situations of the metastable phase decay this approximation leads to negligible errors in the total number of droplets appeared in the system. An evident advantage of the presented method is the possibility to investigate the situation of the metastable phase decay on several sorts of heterogeneous centers.

Attempts to give a theoretical description for the first order phase transition appeared practically simultaneously with creation of the classical nucleation theory [1]. An idea to give the global description of the first order phase transition was attractive and induced many publications (for example, see Wakeshima [2], Segal' [3]). But all of them were intended only to estimate the main characteristics of the phase transition. The time of the cut-off of the nucleation clearly observed in experiments was adopted in these publications without any proper justification. The first theoretical description with explicit determination of time behavior of supersaturation was given in [4] where a homogeneous condensation was investigated. The method used in [4] was an iteration solution of integral equation of a substance balance.

To give a global picture of phase transition one has to take into account a presence of active centers of condensation. The iteration method can be spread on heterogeneous condensation on similar centers (see [5]), but for condensation on several types of centers one can not calculate iterations with

a proper accuracy (see also [5]). The system of condensation equations becomes so complex that it can not be directly solved without simplifications. As the result it would be rather attractive to suggest some simple approximations which can be used in the complex situation of the condensation on several types of centers. Certainly, this approximation has to be well based.

Here we shall suggest a monodisperse approximation of the droplets size distribution to calculate the number of molecules in the liquid phase. From the first point of view this approximation is strange - we have already attracted attention to the necessity to know the behavior of a supersaturation which determines the form of the droplets size spectrum. But here we are going to show that with an appropriate choice of the cut-off (which can be also justified) one can give an adequate description of a nucleation period.

The monodisperse approximation presented here differs from the total monodisperse approximation used in [7] for description of the intensive consumption of the metastable phase and can not be applied during a nucleation period. Here we use a special modification of the mentioned approximation which allows to describe the period of nucleation.

This publication is intended to give the main idea of the monodisperse approximation which would be clear for experimenters. That's why we start from situations of homogeneous condensation and heterogeneous condensation on similar centers which can be solved even without this approximation. Some technical details are excluded to give the most clear version (for example, a complete version of limit situations and monodisperse approximation in the intermediate situation is described in [6], the overlapping of the intermediate and limit situations is analysed in [8], the transition of the special monodisperse approximation to the total one is discussed in [9]).

We use the physical model of nucleation kinetics described in [5]. It is rather standard but to avoid misunderstanding we shall consider [5] as the base of references.

1 Homogeneous nucleation

The condensation kinetics equation for the number G of the molecules in the liquid phase can be written in a well known form [4], [5]

$$G(z) = f \int_0^z dx (z - x)^3 \exp(-\Gamma G(x)) \tag{1}$$

where parameter f is the amplitude value of the droplets sizes distribution Γ is some fixed positive parameter.

One can analyse behavior of subintegral function g defined by

$$G(z) = \int_0^z g(z, x)dx \qquad (2)$$

as a function of a size $\rho = z - x$, z. This function has the sense of the distribution of the number of molecules in droplets over their sizes ρ.

In some "moment" z (or $t(z)$) it can be presented in the following form

- When $\rho > z$ it is equal to zero (there are no droplets with such a big size)

- When $\rho < 0$ it is also equal to zero (there aren't droplets with a negative size)

- At the intermediate ρ it grows rather quickly with a growth of ρ. It is easy to note that it grows faster than ρ^3 grows.

Really, if one takes into account that supersaturation decreases in time then we get $g \sim \rho^3$. But supersaturation falls in time and there aren't so many droplets of the small size as of the big size.

As the result one can see that the function g as the function of ρ has the sharp peak near $\rho \approx z$. This property takes place under the arbitrary z (or $t(z)$).

The sharp peak of g allows to use for g the monodisperse approximation - a representation in the δ-like form with a coordinate corresponding to a position of the peak of function g, i.e.

$$g \sim \delta(\rho = z)$$

As the result one can state that the monodisperse approximation is based now. But it is necessary to determine the number of droplets in this approximation.

It would be wrong to include the total number of already appeared droplets in this peak. Really, in the spectrum of sizes there are many droplets with small sizes. One can not describe these droplets as containing the same substance as the droplets of a big size. It would be more correct to exclude

them from the substance balance. So, it is necessary to cut off the small droplets. It can be done according to two recipes.

The first recipe is the differential one. One can note that during all times which don't exceed the time of nucleation essentially the function g near maximum is close to

$$g_{appr} = f\rho^3$$

This approximation corresponds to the constant value of supersaturation.

One can cut off this approximation at a half of amplitude value (i.e. at a level $fz^3/2$). Then one can get for the width $\Delta_{diff}z$ the following expression

$$\Delta_{diff}z = (1 - 2^{-1/3})z$$

This cut off means that all droplets $\rho < z - \Delta_{diff}z$ are excluded from consideration and all droplets with $\rho > z - \Delta_{diff}z$ are taken into account in a δ-like peak.

The second recipe is the integral one. One can integrate g_{appr} and require that

$$\int_0^z g_{appr}(z, x)dx = Nz^3$$

An integration gives

$$\int_0^z g_{appr}(z, x)dx = f\int_0^z (z-x)^3 dx = f\frac{z^4}{4}$$

The width of spectrum is defined from condition that the number of droplets has to be equal to the amplitude multiplied by the width of spectrum $\Delta_{int}z$:

$$N = f\Delta_{int}z$$

This gives the following expression

$$\Delta_{int}z = z/4$$

One can see that $\Delta_{diff}z$ and $\Delta_{int}z$ practically coincide. This shows the high selfconsistency of this approximation. The second recipe will be more convenient for concrete calculations.

In fig.1 one can see the application of the monodisperse approximation in the homogeneous case.

As the result one can say that all parameters of approximation are defined. Now it will be used to solve (1).

Instead of (1) one can get

$$G(z) = N(z/4)z^3$$

where

$$N(z/4) = fz/4$$

is the number of droplets formed until $t(z/4)$. This leads to

$$G(z) = fz^4/4$$

which coincides with the resulting iteration in the iteration method [4], [5]. It is known (see [4], [5]) that this expression is very accurate which shows the effectiveness of the monodisperse approximation. Here the cut off of the tail of the sizes spectrum compensates the unsymmetry of the initial spectrum.

The main result of the nucleation process is the total number of the droplets which can be found as

$$N_{tot} = f \int_0^\infty dx \exp(-\Gamma G(x))dx$$

or

$$N_{tot} = f \int_0^\infty dx \exp(-f\Gamma z^4/4) = f^{3/4}\Gamma^{-1/4}D$$

where

$$D = \int_0^\infty \exp(-x^4/4)dx = 1.28$$

The error of this expression is less than two percents (it is the same as in the iteration method).

2   Heterogeneous condensation on similar centers

The condensation equations system can be written in the following form [5]

$$G(z) = f \int_0^z dx(z-x)^3 \exp(-\Gamma G(x))\theta(x)$$

$$\theta(z) = \exp(-b \int_0^z \exp(-\Gamma G(x))dx)$$

with positive parameters f, b, Γ. An appearance of a new function θ which is a relative number of free heterogeneous centers requires the second equation.

The first equation of the system is rather analogous to the homogeneous case. The subintegral function here is also sharp. A function θ is a decreasing function of time according to the second equation of the system. Then the function g which is again determined by (2) is more sharp than in the homogeneous case. As far as the supersaturation has to fall one can see that g is more sharp than g_{appr}. It allows to use here the monodisperse approximation for all z or $t(z)$.

As the result the monodisperse approximation is based for heterogeneous condensation. One needs here only the sharp peak of $g(\rho)$ which can be easily seen.

The successive application of the monodisperse approximation in the homogeneous case shows that all droplets necessary for a metastable phase consumption at $t(z)$ were formed until $t(z/4)$. In the heterogeneous case the exhaustion of heterogeneous centers increases in time. So, all essential at $t(z)$ droplets were formed before $t(z/4)$.

At the same time the presence of a long tail in the situation of a weak exhaustion of heterogeneous centers requires to cut off the spectrum for the monodisperse approximation. As far as the long tail is essential in the situation of a weak exhaustion one has to cut off the spectrum by the same recipe as in the situation of the homogeneous condensation: one has to exclude all droplets formed after $z/4$ which have the sizes $\rho < z - \Delta_{int}z = z - z/4$.

One can see in fig. 2 the monodisperse approximation in the situation of the heterogeneous condensation on similar centers. The form of the spectrum in this situation is illustrated in fig. 3. So, the way to construct approximation is known. Now one can turn to concrete calculations.

The number of the droplets formed until $t(z/4)$ has to be calculated as

$$N(z/4) = \frac{f}{b}(1 - \theta(z/4))$$

An approximation for G has the form

$$G(z) = \frac{f}{b}(1 - \theta(z/4))z^3$$

The total number of droplets can be determined as

$$N_{tot} = \frac{f}{b}(1 - \theta(\infty))$$

or

$$N_{tot} = \frac{f}{b}(1 - \exp(-b \int_0^\infty \exp(-\Gamma G(x))dx))$$

or

$$N_{tot} = \frac{f}{b}(1 - \exp(-b \int_0^\infty \exp(-\Gamma \frac{f}{b}(1 - \theta(z/4))z^3)dz))$$

or

$$N_{tot} = \frac{f}{b}(1 - \exp(-b \int_0^\infty \exp(-\Gamma \frac{f}{b}(1 - \exp(-b \int_0^{z/4} \exp(-\Gamma G(x))dx))z^3)dz))$$

The last expression has a rather complicate form. It contains several iterations in a hidden form which ensures the high accuracy.

The last expression can be simplified. One of the possible recipes is the following. One can note that an expression for G is necessary at $\Gamma G \sim 1$. Then z attains some values $\Delta_\zeta z$. But until $\Delta_\zeta z/4$ the value ΓG is small and $\exp(\Gamma G(z))$ is close to unity. This leads to simplification of last expression which can be written in the following form

$$N_{tot} = \frac{f}{b}(1 - \exp(-b \int_0^\infty \exp(-\Gamma \frac{f}{b}(1 - \exp(-bz/4))z^3)dz))$$

Then one can fulfil calculation according to the last formula. The relative error is less than two percents. Here it is a little bit greater than in the homogeneous case because the form of initial spectrum is changed and there is no full compensation of the unsymmetry of spectrum and an exclusion of the tail. The relative error in the situation of heterogeneous condensation on similar centers is drawn in fig. 4.

Now one can turn to explicit calculation of the integral in the last expression. After the appropriate renormalization the subintegral function is more sharp than $\exp(-x^3)$ and more smooth than $\exp(-x^4)$. Both these functions have a sharp back front of spectrum. It allows to introduce the characteristic scale Δz by equation

$$\frac{f}{b}\Gamma(1 - \exp(-b(\Delta z)/4))(\Delta z)^3 \approx 1$$

Then
$$\int_0^\infty \exp(-\Gamma\frac{f}{b}(1-\exp(-bz/4))z^3)dz = \Delta z\frac{A+B}{2}$$
where
$$A = \int_0^\infty \exp(-x^3)dx = 0.89$$
$$B = \int_0^\infty \exp(-x^4)dx = 0.90$$

Now the calculation is reduced to some algebraic manipulations. The error of the last approximation is less than one percent.

As the result
$$N_{tot} = \frac{f}{b}(1-\exp(-b\Delta z\frac{A+B}{2}))$$

One can note that it is possible to formulate the recipe already in terms of Δz. The long way is adopted here to give the most clear picture for the monodisperse approximation.

3 Nucleation on several types of heterogeneous centers

The main advantage of monodisperse approximation is the possibility to use it for the condensation on the several types of centers. The iteration procedure can not be applied in this case successfully. The result of calculations according to [5] shows this fact explicitly. The reason is the existence of the cross influence of the different types of centers through vapor consumption.

In the condensation on similar heterogeneous centers in the situation of exhaustion the influence of this phenomena on the vapor consumption isn't important because in the situation of consumption the converging force of the heterogeneous centers exhaustion is extremely high. But in the situation with two types of heterogeneous centers the exhaustion of the first type centers can have a certain influence on a vapor consumption but the exhaustion of the second type centers is weak and there is no converging force due to the weak exhaustion of the second type centers.

This effect in very thin and it can not be taken into account in the second iteration. But one can not calculate the third iteration analytically and this stops an application of iterations. Really, this phenomena isn't evident from

the first point of view but it exits and leads to the error of the second iteration in many times.

The application of the monodisperse approximation is based on the sharpness of function g. This property takes place already in this situation. So, there are no objections to apply the monodisperse approximation here.

Here we shall reproduce the same formulas but with the lower indexes which determine the sort of heterogeneous centers.

The system of condensation equations can be written in the following form [6]

$$G_i(z) = f_i \int_0^z dx(z-x)^3 \exp(-\Gamma \sum_j G_j(x))\theta_i(x)$$

$$\theta_i(z) = \exp(-b_i \int_0^z \exp(-\Gamma \sum_j G_j(x))dx)$$

where the lower indexes denote the sorts of centers. This system can be seen by the direct generalization of the one type case.

The subintegral function in the substance balance equations is also sharp. As far as all θ_i are the decreasing functions of arguments then the function g defined by (2) (with proper indexes) is sharper than without the exhaustion of heterogeneous centers. So, due to the supersaturationdecreasing g is more sharp than g_{appr}. It allows here to use the monodisperse approximation for all z or $t(z)$.

As the result one can see that the monodisperse approximation in this case is justified on the base of the sharpness of $g(\rho)$.

The same properties as in the previous case can be also seen here. One has to cut off the spectrum at $z/4$. Here all justifications are absolutely same as in the previous section. The characteristic situation for the nucleation on two types of heterogeneous centers is drawn in fig.5. As the result the way to construct the monodisperse approximation is known. Now one can present calculations.

The number of the droplets formed until $t(z/4)$ on the centers of sort i has to be calculated as

$$N_i(z/4) = \frac{f_i}{b_i}(1 - \theta_i(z/4))$$

An approximation for G_i can be now presented as

$$G_i(z) = \frac{f_i}{b_i}(1 - \theta_i(z/4))z^3$$

The total number of droplets is defined as

$$N_{i\ tot} = \frac{f_i}{b_i}(1 - \theta_i(\infty))$$

or

$$N_{i\ tot} = \frac{f_i}{b_i}(1 - \exp(-b_i \int_0^\infty \exp(-\Gamma \sum_j G_j(x))dx))$$

or

$$N_{i\ tot} = \frac{f_i}{b_i}(1 - \exp(-b_i \int_0^\infty \exp(-\Gamma \sum_j \frac{f_j}{b_j}(1 - \theta_j(z/4))z^3)dz))$$

or

$$N_{i\ tot} = \frac{f_i}{b_i}(1 - \exp(-b_i \int_0^\infty \exp(-\Gamma$$
$$\sum_j \frac{f_j}{b_j}(1 - \exp(-b_j \int_0^{z/4} \exp(-\Gamma \sum_k G_k(x))dx))z^3)dz))$$

Now one can simplify the last expression by the same way as in the one type case.

Expressions for G_i are essential at $\Gamma \sum_j G_j \sim 1$. Then z is near $\Delta_\zeta z$. Until $\Delta_\zeta z/4$ the value $\Gamma \sum_j G_j$ is small and $\exp(\Gamma \sum_j G_j(z))$ is near unity. It leads to

$$N_{i\ tot} = \frac{f_i}{b_i}(1 - \exp(-b_i \int_0^\infty \exp(-\Gamma \sum_j \frac{f_j}{b_j}(1 - \exp(-b_j z/4))z^3)dz))$$

Now one can fulfil the calculations according the explicit formula. The relative error of the last expression is less than five percents (here it increases slightly due to the complex form of the spectrums on different sorts. The relative error in the number of droplets is drawn in fig. 6. The calculation of the last integral is absolutely analogous to the previous section. The subintegral function after renormalization lies between $\exp(-x^3)$ and $\exp(-x^4)$. It allows to get the characteristic size Δz from

$$\Gamma \sum_j \frac{f_j}{b_j}(1 - \exp(-b_j(\Delta z)/4))(\Delta z)^3 \approx 1$$

Then

$$\int_0^\infty \exp(-\Gamma \sum_j \frac{f_j}{b_j}(1 - \exp(-b_j z/4))z^3)dz = \Delta z \frac{A + B}{2}$$

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The relative error of the last expression is less than one percent.

As the result

$$N_{i\ tot} = \frac{f_i}{b_i}(1 - \exp(-b_i\Delta z\frac{A+B}{2}))$$

The formula is similar to the final expression in the previous section. But parameters in the last formula have to be determined in another manner.

The physical sense of the last expression is the separate exhaustion of heterogeneous centers. One sort of centers can influence on the other sort only through a vapor consumption. This fact can be seen also in the initial precise system of the condensation equations.

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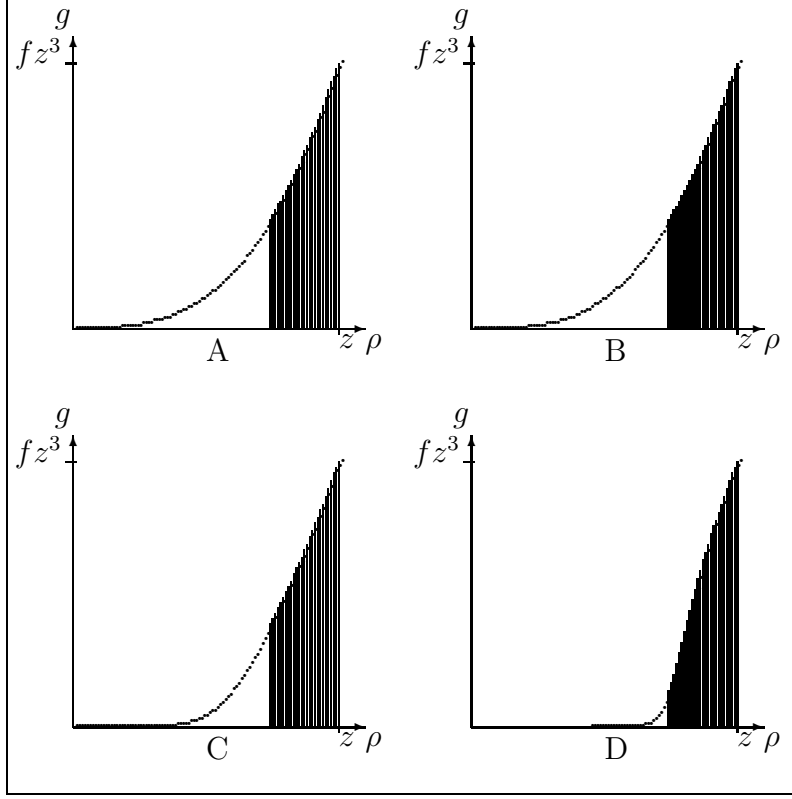
Fig.1

Monodisperse approximation in homogeneous condensation. Here one can see four pictures for different periods of time (or for different values of z. One can introduce Δz according to $\Gamma G(\Delta z) = 1$ and it will be the characteristic scale of the supersaturation fall. In part "A" $z = \Delta z/2$, in part "B" $z = \Delta z$, in part "C" $z = 3\Delta z/2$, in part "D" $z = 2\Delta z$. One can see that the spectrums in part "A" and part "B" are practically the same. It corresponds to the property of the similarity of spectrums until the end of the nucleation period.
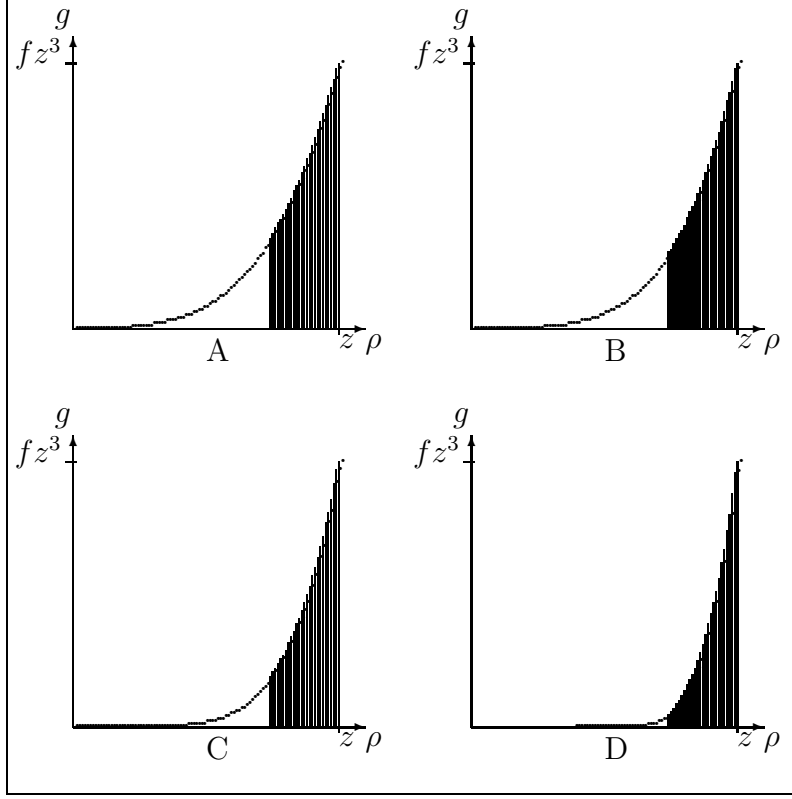
Fig.2

Monodisperse approximation in condensation on the similar centers. The value Δz is the same as in the previous figure (i.e. it is determined without the exhaustion of centers). Now $\Gamma G(\Delta z) < 1$ and Δz will be the characteristic scale of the supersaturation fall in the situation without exhaustion. In part "A" $z = \Delta z/2$, in part "B" $z = \Delta z$, in part "C" $z = 3\Delta z/2$, in part "D" $z = 2\Delta z$. One can see that the spectrums in part "A" and part "B" aren't similar. Now all spectrums are more sharp than in the homogeneous case.
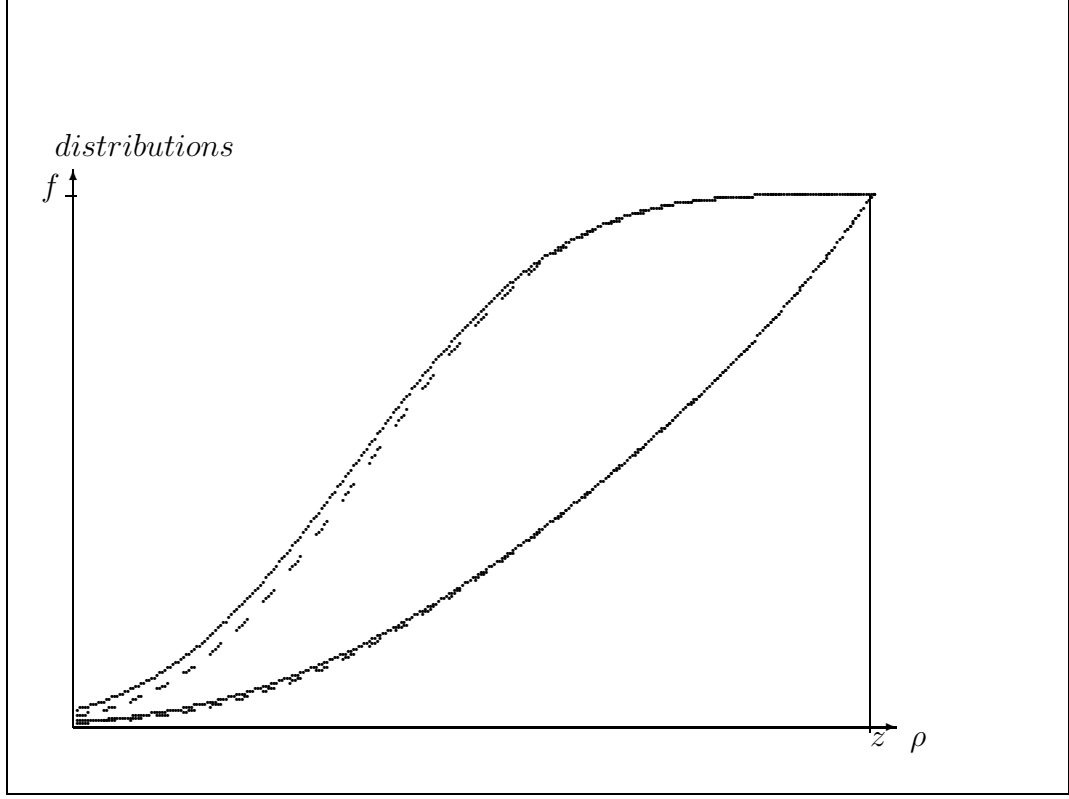
Fig.3

One can see two curves which are going from $\rho = z$ to the small sizes ρ. The lower curve corresponds to the real spectrum calculated with account of heterogeneous centers exhaustion. The upper curve corresponds to the condensation without exhaustion of heterogeneous centers which is the worst situation where there is converging force due to the centers exhaustion.

Concrete situation drawn here corresponds to $b = 2$ after renormalization (the values of parameters f and Γ can be canceled by appropriate renormalization). The value of z here equals to $3\Delta z/2$.

The solid lines correspond to the precise numerical solution. The dashed lines correspond to application of monodisperse approximation. One can not separate the numerical solutions from the approximate ones except the slight deviation in the region of small ρ. As far as all (precise and approximate) solutions will go to zero there will be no deviations for $z \gg \Delta z$ (i.e. we stop at the worst moment).
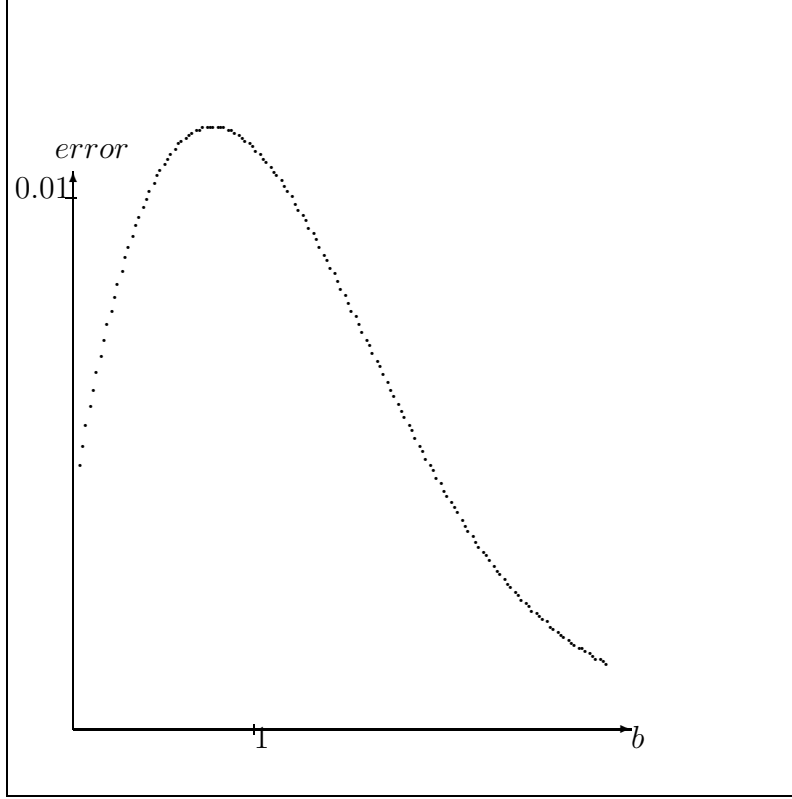
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Fig.4

The relative error of approximate solution for the nucleation on the sim-ilar heterogeneous centers. Here the values f and Γ can be canceled after renormalization and there remains only one parameter b which is the argu-ment of the function drawn here. It is clear that this function is small. All asymptotes can be checked analytically (see [9]).
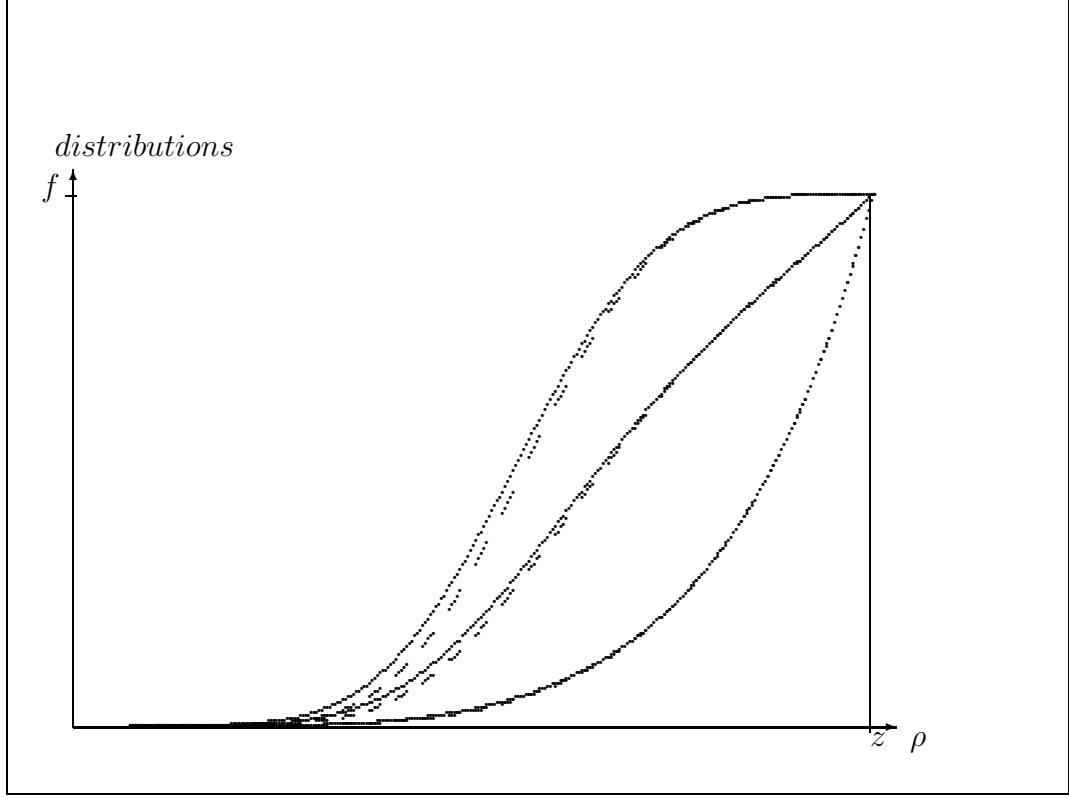
Fig.5

Characteristic behavior of size spectrums for nucleation on two types of heterogeneous centers. One can cancel f_1, Γ by renormalization. One can put $f_2 < 1$ due to the choice of centers. Here $b_1 = 2$, $f_2 = 1/2$, $b_2 = 1/2$. The value z is taken as $2\Delta z$ (see fig.1). The are three curves here. The lower one corresponds to the spectrum of droplets formed on the first type centers, the intermediate one corresponds to the droplets size spectrum for the second type centers, the upper one corresponds to the spectrum calculated without exhaustion of heterogeneous centers (the reasons are the same as in fig.3). The solid lines are the numerical solutions, the dashed lines are the approximate solutions. One can not see the difference for the lower curve. For the upper and intermediate curve one can see only very slight difference. All spectrums are renormalized to have one and the same amplitude (which is marked by f).
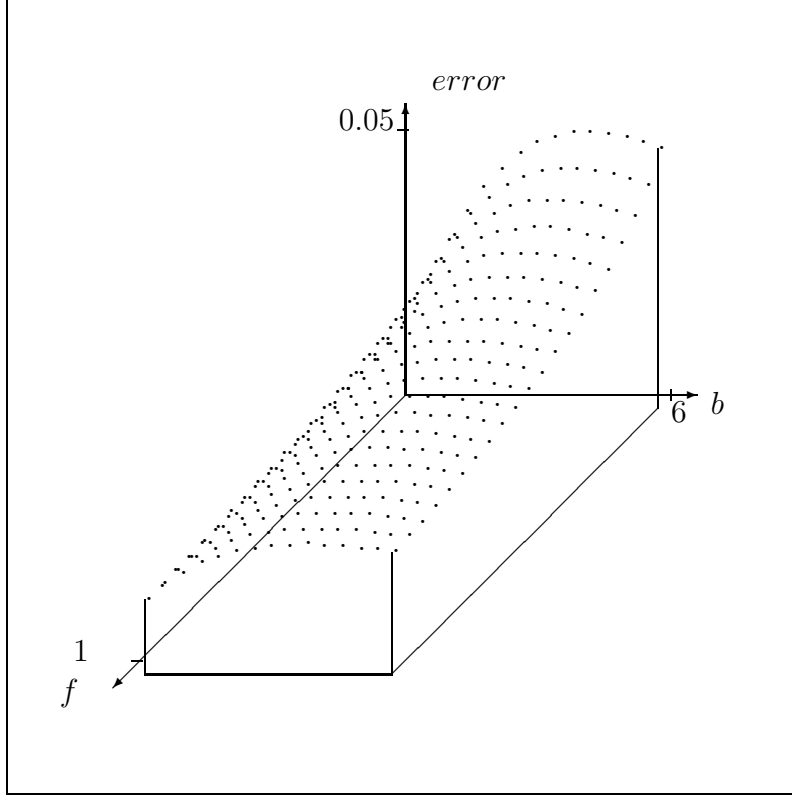
Fig.6

Relative error for the nucleation on two types of centers. For two types of centers there exists five parameters (two of them can be canceled by renormalization). We have already adopt that Γ is one and the same for different types of centers (for the reasons see [8], for numerical results see [9], for analytical estimates see [10], for recipes of calculation in this situation see [11]). We cancel here f_1, Γ. We consider $f_2 < 1$ and the first component is the leading component in the metastable phase consumption. So, the worst situation for the error in the droplets number formed on the second type centers (which is drawn here) will be when $b_2 = 0$ and the is no converging force of the centers exhaustion. So, there remain two parameters f_2 (it is marked by f) and b_1 (which is marked by b). One can see that the error is small. The calculations for the variations of all parameters give the same value of error but it is hard to reproduce these numerical results.

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