Abstract

Kinetics of the first order phase transition is investigated. In some rather widespread situations the property of avalanche growth of the objects of a new phase doesn’t take place. This radically complicates the theoretical description of the nucleation kinetics and this case was completely investigated here. The power-like dependencies with decreasing absolute value of derivative on time were chosen as the model laws of embryos growth. All main characteristics of the nucleation period including the spectrum of sizes of the new phase objects were obtained. An analytical approximate description of nucleation in different external conditions was fulfilled. The errors of such description are found and proved to be small.
Kinetics of nucleation for the decreasing rate of
the new embryos growth

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1 Introduction

Kinetic description of a system under the phase transition is typical namely for
the phase transition of the first order. The driving force of the first order phase
transition implies the existence of metastability of a mother phase. Namely
this metastability can be regarded as a "source" of the substance transfor-
mation from an unstable "mother" phase to a stable "new" phase. Thus, kinetic
investigation of the phase transformation is rather actual for the phase tran-
sition of the first order. For example, such an important characteristic as the
number of objects of a new phase can be calculated only on the base of kinetic
consideration.

Traditionally the physical model situation for the first order phase transition
was the case of the supersaturated vapor condensation into the phase of liquid
droplets. It was chosen as the base for theoretical and experimental investigation
due to the rather simple description of the bulk phase. Namely in this case
the classical theory of nucleation was created in [1]. This gave the base for
construction of the kinetic description of the global evolution of the system
under the first order phase transition which was done in [3], [4]. That’s why we
shall borrow the terminology from the case of condensation [3], [4]. For example,
the supercritical embryos of a new phase will be called as droplets, the process of
the phase transformation will be called as condensation, the period of formation
of the main quantity of the droplets will be called as nucleation, etc.

One of the main features which allows to fulfill analytical constructions in
[3], [4] was the property of the avalanche consumption of the mother phase by
droplets. This means that the quantity of the mother phase molecules absorbed
by a small droplet is many times smaller than the number of molecules absorbed
during the same time by a droplet of a big size.

In a free molecular regime of the substance exchange one can write that
absorption coefficient $W^+$ is proportional to the surface of droplet, i.e. to the
square of the droplet radius $R$. Then $W^+$ grows in time $t$ under the constant
power of metastability as $W^+ \sim t^2$ and the number of molecules $\nu$ accumulated
by a droplet grows as $t^3$. The big power 3 allows to apply in [3], [4] some effective
methods which can be reduced to the first steps in some iteration procedures, formulated there.

Under the diffusion regime one can get $\nu \sim t^{3/2}$ and even this not so rapid growth is also sufficient for the application of the methods from [4] based on the first iterations.

All possible regimes of the substance consumption lies between the free molecular regime and the diffusion regime and namely this property allows to establish in [5] the general feature - the avalanche consumption of metastable phase. This property isn’t only the key to get the numerical results but allows to combine the collective regime of the metastable phase consumption and the existence of the density profiles in a unique approach [3], [5]. This possibility plays the fundamental role in the justification of approaches formulated in [3].

But sometimes the rate of droplets growth decreases in time. This property doesn’t allow to apply iteration methods from [4], [5]. This situation requires a special consideration which will be given below. The situation with decreasing rate of growth takes place rather often in the processes of cementation, structural transformations, morphological transitions, etc.

Rigorously speaking one has to state that the avalanche consumption is the characteristic feature of phase transition, the justification is based on the geometrical features (i.e. on the dimensionality of space). So, the situation with the decreasing rate of growth isn’t characteristic for the pure transition in a rigorous sense. But in practice the decreasing rate of growth is also considered in frames of the first order phase transition in an ordinary sense. So, it is worth doing here through a presentation of the analytical theory of the process.

We shall consider two types of external conditions which seems to be typical and are widely spread both in theoretical and practical investigations. The first type is a situation of decay. It takes place when the power of metastability is attained in the system rather rapidly and later there is absolutely no external influence upon the system. The power of metastability is fully determined here by the condensation processes.

The second type typical external conditions are conditions of dynamic type. Really, ordinary practically all external conditions have rather smooth behaviour in time. It means that the metastability is created gradually. Formation of droplets and mainly the process of growth consume vapor and the power of metastability begins to fall. As the result the process nucleation stops and one have the formed spectrum of sizes of droplets with rather simple law of evolution.

Now we shall discuss the law of the droplets growth. Here we shall use the power-like dependencies of the droplets growth. The power-like dependencies are explained by the absence of some characteristic dimensional scale like in the scaling theory for the second order phase transitions. The diffusion regime and the free molecular regime have also the power-like laws of growth. So, we shall also take the power-like regimes here. Namely

$$\nu = t^\alpha$$

with parameter $\alpha$. We shall call the power dependencies with $0 < \alpha < 1$ as the slow rates of growth.
We shall use all results and definitions formulated in [3], [4], [5]. But, certainly the methods used in these papers have to be reconsidered. They can not be directly applied under the slow rate of growth and a new methods have to be developed.

We investigate the case of homogeneous phase transition. The heterogeneous case can be investigated analogously to [4]. In [4] it is shown that the homogeneous case can be effectively applied as the base for the consideration of heterogeneous case. The same takes place here also.

2 Evolution equations

The situation with the slow rate of growth is more complex because now not only the droplets with relatively big sizes are the main consumers of vapor. Here all droplets takes place in the consumption of vapor. But there is one simplifying feature which states that now there is no need to consider the density profiles or profiles of metastability [3], [5]. Really the characteristic scale of the diffusion blurring is

\[ R_{\text{diff}} \sim \sqrt{t - t'} \]

where \( t \) is the current moment of time, \( t' \) is the time of the perturbation appearance. The same is valid for the thermal blurring. So, when \( \alpha < 3/2 \) the diffusion blurring destroys the density profile and we come to the collective regime of vapor consumption (see [3], [5]).

The procedure of derivation of the evolution equation is absolutely the same as in [4], one has only to substitute the power 3 or 3/2 by the new power \( \alpha \). The statement about the leading role of the supercritical embryos in the substance balance used in [4] is so strong, that it remains valid until \( \alpha \to 0 \). But the case \( \alpha \to 0 \) can be investigated explicitly without this assumption which will be done separately (due to the simple conservation laws) below. The same is valid for the statement about the applicability of the quasistationary approximation for the rate of nucleation (the rate of appearance of droplets).

The power of metastability will be characterized by the value of supersaturation

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

where \( n \) is the molecular number density of the mother phase, \( n_\infty \) is the same value for the saturated mother phase.

The evolution equation for the situation of decay can be written as

\[ G = A \int_0^z (z - x)^\alpha \exp(-G)dx \]

with a positive parameter \( A \), which has the sense of the spectrum amplitude. The spectrum looks like

\[ f \sim \exp(-G) \]
In the situation of dynamic conditions we can linearize the power of metastability in the absence of nucleation as we have done in [4]. Then we have

\[ G = A \int_{-\infty}^{z} (z - x)^\alpha \exp(bx - G) \, dx \]

with the additional parameter of the mentioned linearization \( b \). Here

\[ f \sim \exp(bx - G) \]

In the derivation of these equations we have used the following approximation for the stationary rate of nucleation

\[ f_s(\zeta) = f_s(\zeta_0) \exp(D(\zeta - \zeta_0)) \quad (1) \]

as a function of the supersaturation \( \zeta \) where index 0 characterizes the base of decomposition. Here \( D \) is the derivative of the free energy of a critical embryo formation over \( \zeta \).

This approximation isn’t something special but simply the Klapeiron-Klausius equation. Ordinary this equation is used for the dependence of \( n_\infty \) over temperature but there is no difference to what characteristic we shall apply this procedure of approximate derivation. We have to mention that renormalizations to describe the nucleation kinetics in non isothermal conditions are based on the Klapeiron-Klausius equation for the density of the saturated vapor. Here the analogous renormalizations in order to take into account the non isothermal effects can be also done.

3 Decay of metastable state

At first we shall investigate the evolution of the system under external conditions of the decay type. Certainly, one can act in the manner analogous to the approach of the universal solution [5] for the case of the avalanche consumption of the mother phase. After the evident rescaling \( z \rightarrow A^{1/4} z, x \rightarrow A^{1/4} x \) one can come to

\[ G = \int_0^{z} (z - x)^\alpha \exp(-G) \, dx \]

with no parameters. Then \( G \) is the universal function and the zero momentum \( M_0 = \int_0^{\infty} \) is the universal constant. Since \( M_0 \) is the coefficient in the asymptotically leading term \( M_0 z^\alpha \) in expression for \( G \) after the end of nucleation we have got all information necessary for the further evolution. This solves the problem of the nucleation description.

Having determined the duration of the nucleation period \( \delta z \) as

\[ N(\delta z) = N(\infty)(1 - \epsilon) \]

with some small \( \epsilon \) and \( N(z) \) as the number of droplets appeared before \( z \) one can get for \( \delta z \) some fixed constant. The value \( N(z) \sim \int_0^{z} \exp(-G) \, dx \) is also the
universal function and $\delta z$ as the root of equation with no parameters will be the universal function.

Now we shall determine the form of the size spectrum of droplets explicitly. The iteration procedure isn’t effective because the initial approximation is too rough. To propose another iteration procedure we shall establish the new property of the droplets growth typical for the regime of the slow growth.

**The property of effective size of growth**

Let us consider the law of the the vapor consumption by a separate droplet. It is shown in fig. 1. For every moment $z$ (or $t(z)$) we can find the boundary $z_0$ with two properties

- $z_0 \ll z$
- $\nu(z) - \nu(z_0) \ll \nu(z)$

One can see that for $z_0 = \alpha z/p$, $p \sim 2 \div 3$ both properties are satisfied.

It means that the qualitative picture is the following: rather soon the droplet accumulates the main quantity of vapor and during the rest of the evolution time the accumulation isn’t too important. Certainly, this moment of accumulation grows in time.

This picture allows to suggest the following initial approximation:

*For every $z$ one can imagine that practically immediately the number of molecules of a given droplet (with coordinate $z$) attains the value $\nu(z_0)$ and then the droplet doesn’t grow.*

One has to stress that for different $z$ the values $z_0$ are also different.

This property allows to use the approximation with $\alpha = 0$ as initial approximation, which has an evident advantage.

Here one can see the property of a real collective consumption of vapor -

Practically all droplets (except small ones with sizes less than $z_0$) consume vapor in approximate equal quantities. This is really the collective consumption of vapor (Earlier this term was used simply for vapor consumption in a fixed point by many droplets in different quantities. Now droplets consume vapor in equal quantities and we shall speak about the equal collective consumption.)

The case $\alpha = 0$ can be solved analytically, because it can be reduced to the ordinary differential equation of the first order. This leads to

$$\exp(-G) = \frac{1}{1 + z}$$

One has to note that the last equation leads to the infinite number of droplets appeared in the process of nucleation. This is an error. This error is initiated by the inapplicability of approximation \(1\) at small supersaturations. Really, at $G \sim n - n_\infty$ the rate of nucleation has to be vanished, but approximation \(1\) gives the finite value of the nucleation rate at any $G$.

Nevertheless we aren’t interested at the long tail $\sim z^{-1}$ of the size spectrum because this tail can not be directly seen in experiment and all integral values can be explicitly calculated. Really, the total number of droplets can be easily obtained, it is convenient to do even in initial variables.
The case $\alpha = 0$ corresponds to a fixed number $\nu_{\text{fin}}$ of a number of molecules inside the droplet. This quantity doesn’t depend on time, in rescaled units $\nu_{\text{fin}} = 1$. The total number of droplets is

$$N_{\text{total}} = \frac{n - n_{\infty}}{\nu_{\text{fin}}}$$

Formally we can choose the cut-off of the spectrum at the size where $N(z)$ equals to $N_{\text{total}}$.

**Iteration procedure**

One can see that even in the case of small positive $\alpha$ the spectrum of sizes is well localized which allows to use the iteration procedure

$$G_{i+1} = \int_{0}^{z} (z - x)^{\alpha} \exp(-G_{i}) \, dx$$

Here the lower index denotes the number of iteration. As initial approximation we choose here the analytical solution for $\alpha = 0$, i.e.

$$G_{0} = -\ln(x + 1)$$

This radically differs from consideration of the situations with avalanche regimes of growth, where $G_{0} = 0$.

The first iteration can be easily calculated. We have

$$G_{1} = \int_{0}^{z} (z - x)^{\alpha} \frac{1}{1 + x} \, dx$$

which can be easily calculated

$$G_{1} = -\frac{z^{\alpha+1}}{z + 1} \Phi(-\frac{z}{z + 1}, 1, \alpha + 1)$$

where

$$\Phi(z, s, v) = \sum_{k=0}^{\infty} \frac{z^{k}}{(v + k)^{s}}$$

is the standard special function [2].

The spectrum based on $G_{1}$, i.e. $\exp(-G_{1})$ can be considered as a rather precise approximation. It can be shown analytically and numerically. Namely, the relative error in the number of droplets, i.e. in

$$N(z) = \int_{0}^{z} \exp(-G(x)) \, dx$$

is less than 0.05 for $\alpha < 0.5$. The values $\alpha$ from $1/2$ up to $3/2$ can be considered analogously on the base of iterations started from solution with $\alpha = 1$. This solution can be also found analytically since the evolution equation can be reduced to the second order ordinary differential equation with no explicit dependence on the argument, which can be easily integrated. Then is is necessary
only to take one iteration step and then to integrate \( \exp(-G_1) \) over time to get the number of droplets.

Figure 2 shows the relative error in the total number of droplets as a function of \( \alpha \). The integration is fulfilled up to \( z = 10 \) which is absolutely sufficient for any case except \( \alpha = 0 \) and in this case the error is zero (certainly with artificial cut-off the same will be numerically). The deviation from zero at small \( \alpha \) is initiated only by a finite step of integration. One can see that the relative error is rather small. This can be shown not only numerically but also analytically.

Figure 3 shows the characteristic forms of spectrums. Two cases are shown - \( \alpha = 0.2 \) and \( \alpha = 1 \). One can see two pairs of curves coinciding at the beginning and approximately at the end. Every pair corresponds to one case and presents the precise solution and our approximation. The case \( \alpha = 1 \) has analytical solution and it is out of consideration here but one can see that even in this case our approximation works good. In this case the back side of spectrum is more sharp than for \( \alpha = 0.2 \). One can also notice the relative invariancy of the form of spectrum to the concrete choice of \( \alpha \) for small \( \alpha \).

One has to mention that the consumption of vapor by all droplets requires to reconsider slightly the characteristic size of consumers in the statements about the quasistationarity of the nucleation rate and about the size of the main consumers of vapor [3]. But even with these modifications both statements can be proven (and under dynamic conditions also).

4 Dynamic conditions

The simple rescaling \( z \rightarrow z A^{1/\alpha} \), \( x \rightarrow x A^{1/\alpha} \) brings evolution equation to

\[
G = \int_{-\infty}^{z} (z - x)^{\alpha} \exp(bx - G)dx
\]

and allows to cancel parameter \( A \). But it isn’t too simple to cancel parameter \( b \) because earlier it the condition, which allows to cancel this parameter was the following: The point of decompositions has to be chosen as the maximum of supersaturation (or as the maximum of \( f \))

In situation with \( \alpha = 0 \) one can not satisfy this condition. Moreover, \( f \) increases in time. The analytical solution in the case \( \alpha = 0 \) is the following

\[
f = \exp(bx - \ln(\frac{\exp(bx)}{b} + 1)) \equiv f_0
\]

This solution can be got after differentiation of the evolution equation which brings it to

\[
\frac{dG}{dx} = \exp(bx - G(x))
\]

One can easily integrate this equation

\[
\int \exp(G)dG = \int \exp(bx)dx
\]
and come to \( \mathbb{2} \).

When \( \alpha \neq 0 \) one can see the maximum of \( f \) and when \( \alpha = 0 \) the explicit analytical solution has been presented.

For \( \alpha > 0 \) one can put condition on maximum. Then for \( \alpha \neq 0 \) we have the universal solution depended on \( \alpha \). This solution satisfy the following universal equation

\[
-\ln(f) + \alpha \int_{-\infty}^{0} (z-x)^{\alpha-1} f(x) dx = \int_{-\infty}^{z} (z-x)^{\alpha} f(x) dx
\]

the ideology here is absolutely analogous to the already investigated situations.

**Iteration steps**

Now we shall present the methods to get the explicit form of the size spectrum. The main feature which has to be taken into account is the long infinite tail of the spectrum for \( \alpha = 0 \). The explicit form of spectrum in this case for \( b \sim 1 \) is drawn in figure 4. One can see that the curve is slightly blurred because here an approximation which will be discussed later is also drawn.

The most interesting region here is the region of the rapid increasing of \( f \).

If we choose \( b = 1 \) we get this region at \( x \sim 0 \). Later we shall see that it is reasonable to put \( b \sim 1 \) for all \( \alpha \).

One can formulate an important feature: Certainly, for \( \alpha > 0 \) the spectrum \( f \) lies lower than the spectrum \( f_0 \) in the case \( \alpha = 0 \). Having used the property of effective size of growth one can come to conclusion that the maximum of \( f \) lies near \( x = 0 \) when \( b = 1 \). So, then one can put \( b = 1 \) for all cases with small \( \alpha \).

We shall use \( f_0 \) as initial approximation in the iteration procedure

\[
G_{i+1} = \int_{-\infty}^{z} (z-x)^{\alpha} \exp(bx-G_i) dx
\]

\[
G_0 = -\ln(f_0) + bx
\]

The first iteration can be presented as

\[
G_1 = \int_{-\infty}^{z} (z-x)^{\alpha}(\frac{\exp(bx)}{b} + 1)^{-1} \exp(bx) dx
\]

To calculate \( G_1 \) one can act in two manners. The first one is to invent approximation for \( (z-x)^{\alpha} \). as we have already mentioned this function has behaviour drawn in figure 1. We see that that it can be well approximated by a straight line as it is drawn in figure 5. This approximation allows the analytical calculation of \( G_1 \) since the integral can be reduced to

\[
\int \frac{1}{(x+c_1)^2 - c_2} dx
\]

and to

\[
\int \frac{\ln(x + c_3)}{(x+c_4)^2 - c_5} dx = = \frac{1}{2c_5} \arctan\left(\frac{c_3x}{c_4^2 + c_5^2 + c_4x}\right) \ln[(c_3 - c_4)^2 + c_5^2] - \]
\[-\frac{1}{2c_5} Cl_2(2\Theta + 2\Phi) + \frac{1}{2c_5} Cl_2(2\Theta_0 + 2\Phi) - \frac{1}{2c_5} Cl_2(\pi - 2\Theta) + \frac{1}{2c} Cl_2(\pi - 2\Theta_0)\]

Here
\[
\tan \Theta = \frac{x + c_4}{c_5} \\
\tan \Theta_0 = \frac{c_4}{c_5} \\
\tan \Phi = \frac{c_3 - c_4}{c_5}
\]

and
\[
Cl_2(z) = -\int_0^z \ln(2 \sin(\frac{x}{2})) dx
\]
is the Klausen integral which is the standard special function.

The second method which suggests an approximation for \(f_0\) seems to be more attractive. This approximation is the following

\[
f_0 \equiv \frac{1}{1 + \exp(-x)} \approx f_{ap}
\]

where
\[
f_{ap} = \exp(x) - \exp(2x) + \frac{1}{2} \exp(3x)
\]
for \(x < 0\) and
\[
f_{ap} = 1 - \exp(-x) + \frac{1}{2} \exp(-2x)
\]
for \(x > 0\).

Namely this approximation together with precise solution is drawn in figure 4. Certainly at \(x = 0\) there is no difference between precise result and approximate one. With the help of this approximation all integral terms can be calculated in terms of Gamma-function.

When the first approximation \(G_1\) is calculated we see that the spectrum \(f_1 = \exp(x - G_1)\) in the first approximation has one maximum \(f_{1 \text{ max}}\) at \(x_{1 \text{ max}}\) and at the region \(x < x_{1 \text{ max}}\) the spectrum \(f_1\) approximates the real spectrum quite satisfactory. Moreover we have \(x_{\text{max}} \approx x_{1 \text{ max}}\), where \(x_{\text{max}}\) is the coordinate of real maximum and \(f_{\text{max}} \approx f_{1 \text{ max}}\) where \(f_{\text{max}}\) is the amplitude of a real spectrum. These facts can be proven analytically. The form of size spectrums for characteristic values of \(\alpha\) are drawn in figure 6.

One can see one important feature here. The spectrum in the first iteration rapidly turns to zero while the real spectrum has very long and smooth tail. This occurs because the amplitude of the spectrum (and also of the first iteration) is seriously less than the amplitude of the solution for \(\alpha = 0\). Now we can correct this error. When \(\alpha\) is growing then \(x_{1 \text{ max}}\) goes away from \(x_{\text{max}}\); \(f_{1 \text{ max}}\) goes away form \(f_{\text{max}}\) and \(f_0(x_{1 \text{ max}})\) goes away from \(f_{1 \text{ max}}\). But even when \(\alpha = 0.5\) (this is the realistic boundary of our constructions because for bigger \(\alpha\) one can use decompositions starting from \(\alpha = 1\)) the difference between \(f_0(x_{1 \text{ max}})\) and
$f_{1 \text{ max}}$ is small. This allows to suggest the cut-off of the zero approximation $f_{0 \text{ cut}}$ which is

$$f_{0 \text{ cut}} = f_0$$

for $x < x_{1 \text{ max}}$ and

$$f_{0 \text{ cut}} = f_0(x_{1 \text{ max}}) = f_{1 \text{ max}}$$

for $x > x_{1 \text{ max}}$.

On the base of this initial approximation one can reproduce all constructions and get the spectrum $\hat{f}_1$ in the first approximation, which lies higher than the "previous first approximation". It is drawn in figure 7 where this curve lies higher then the previous first iteration.

One can analytically show that the first advanced iteration describes the form of the hill (the head of the spectrum) satisfactorily. But there remains the long tail and it is absolutely impossible to describe it on the base of the iteration method because the duration of the back tail can be infinitely long. Then one can propose some asymptotic methods to solve this problem.

Asymptotics

We shall construct solution for $x \gg 1$. At first we can see that it is possible to write approximately evolution equation as

$$G(z) = \int_0^z (z - x)^\alpha \exp(x - G(x))dx$$

instead of

$$G(z) = \int_{-\infty}^z (z - x)^\alpha \exp(x - G(x))dx$$

Now we shall use the property of effective size of growth. Since the amplitude of spectrum doesn’t vary too rapid during this time one can take away the size $(z - x)^\alpha$ out of the integral and speak about the mean size $\bar{\rho}$. Then

$$G(z) = \bar{\rho} \int_0^z \exp(x - G(x))dx$$

For $\bar{\rho}$ one gets the following expression

$$\bar{\rho} = \frac{\int_0^z (z - x)^\alpha dx}{\int_0^z dx} = \frac{z^\alpha}{\alpha + 1} \approx z^\alpha$$

Having differentiated $G$ over $z$ one has to notice that $\bar{\rho} = z^\alpha$ is rather slow function and there is no need to differentiate it. Then

$$\frac{dG}{dt} = z^\alpha \frac{d}{dz} \int_0^z \exp(x - G(x))dx = z^\alpha \exp(z - G(z))$$

After integration we have

$$\int \exp(G)dG = \bar{\rho} \int \exp(x)dx + \text{const}$$
and

\[ G = \ln(1 + \rho \exp(z)) \]

This solution has asymptotics

\[ G \to \ln(\bar{\rho}) + z \]

This asymptotics leads to the following expression for the size spectrum

\[ f \sim \exp(x - G) = \exp(z - \ln(\bar{\rho}) - z) = (\bar{\rho})^{-1} \]

and finally

\[ f \sim \frac{1}{z^\alpha} \]

Here one can introduce the arbitrary shift \( \gamma \) and the arbitrary amplitude \( \beta \). Then

\[ f \sim \beta \left(\frac{z - \gamma}{(z - \gamma)_{\text{}}^{\alpha}} \right) \]

These parameters can be determined by requirement of the smoothness of spectrum and its derivative in the point of transition from the advanced first iteration to the asymptotics. Were shall we choose this point?

At \( z = 0 \) the spectrum begins to grow, at \( z = z_{\text{max}} \) it attains the maximum, it is reasonable to imagine the hill as symmetric one an dto say that at \( z = 2z_{\text{max}} \) the hill is over. Namely at this point we can speak about the beginning of the asymptotic.

The conditions

\[ \frac{\dot{f}_1}{dz} = -\alpha \frac{\beta}{(z - \gamma)_{\text{}}^{\alpha + 1}} \]

and

\[ \dot{f}_1 = \frac{\beta}{(z - \gamma)_{\text{}}^{\alpha}} \]

at \( z = 2z_{\text{max}} \) give the following expressions

\[ \gamma = 2z_{\text{max}} + \alpha \dot{f}_1(z_{\text{max}})/(d\dot{f}_1/dz)_{z=z_{\text{max}}} \]

\[ \beta = \dot{f}_1(z_{\text{max}})(z - \gamma)_{\text{}}^{\alpha} \]

The characteristic forms of spectrums and analytical approximations are drawn in figure 8. The letters A-E denote the pairs of curves corresponding to different \( \alpha \) from 0.1 to 0.5 with a step 0.1. The capital letters mark the precise numerical solutions, they lies near approximate solutions.

The accuracy of the theory can be estimated by the error in the droplets number

\[ \epsilon = \frac{|N - N_{\text{ap}}|}{N} \]

is drawn. Here \( N \) is precise value found from numerical solution and \( N_{\text{ap}} \) is the number of droplets found from the presented approximate solution.
In figure 9 the maximum of $\epsilon$ over $z$ is drawn as a function of $\alpha$. It can be seen that it is rather small. Here the maximum value of $z$ is chosen as 30.

Now we shall analyze the accuracy of calculations. In figure 10 the relative error for $N(z)$ at some final value is drawn. Here we consider the "final" values for $N$. Certainly, the terms "the final values" are illegal, because it is clear that for $\alpha < 1$ the finite number of droplets can not satisfy the balance of substance. So, we need to throw away the tail, which is thin but still infinite (it contains infinite number of droplets).

In consideration of extremely long asymptotic tails we have to take care about the accurate behavior of asymptotics. The combination of iteration solution and asymptotics has to be performed here in a slightly other special point. We shall mark this point as $z_{\text{bound}}$.

To get $z_{\text{bound}}$ we shall fix the beginning of nucleation more precise. On the base of iterations we get $f_{\text{max}}$. Then we get the value $f_{\text{st}}$ of the amplitude at the beginning of nucleation as $f_{\text{st}} = f_{\text{max}}/\exp(1)$. Then we can get the coordinate $z_{\text{st}}$ of the beginning of nucleation as $z_{\text{st}} = \ln(f_{\text{st}})$. Then $z_{\text{bound}}$ will be calculated according to the old recipe but with a new time of the beginning of nucleation

$$z_{\text{bound}} = z_{\text{st}} + 2(z_{\text{max}} - z - s_t)$$

In figure 11 the values of the droplets number are compared at a "final" value $z_{\text{fin}}$. Two values $z_{\text{fin}} = 50$ and $z_{\text{fin}} = 70$ are chosen here. The value of $\epsilon$ is drawn. One can see three broken lines. The shapes of two of them are approximately the same at small $\alpha$ - these lines are the relative errors in the droplets number for different $z_{\text{fin}}$. It is clear that the dependence on $z_{\text{fin}}$ at such values is very smooth and we practically attains the limit case (precisely speaking, it can not be done). The step in calculations $dx$ was chosen as $dx = 0.05$. The third line at small $\alpha$ lies below and has a more smooth shape. It is the same value $\epsilon$ for $z_{\text{fin}} = 50$ but calculated with a step $dx = 0.025$. It isn’t too far from the two mentioned curves. So, the necessary accuracy is attained.

Now one can analyze the behavior of the error. The decrease of the error at $\alpha \approx 0.7$ is caused simply by compensation of different sources of errors, the value $|N - N_{\text{ap}}|$ changes a sign here. More interesting fact is the reduction of the error at $\alpha \sim 1$. The reasons are the following: Every spectrum has the tail and the head. The head is rather short and it is localized well and can be described with the help of iteration method. The tail has to described by asymptotics. The main source of error is the absence of account of the influence of surplus substance appeared in the head of spectrum in evolution at asymptotics. When we are going to extremely long tails this influence will disappear.

When $\alpha$ attains 1 the quantity of the droplets in tail at intermediate $z$ is small in comparison with the quantity of droplets in the head. So, it is reasonable to take in to account only the head with the help of iterations (Certainly, now the number of droplets will be counted on the base of iterations not only until $z_{\text{bound}}$ but also for $z > z_{\text{bound}}$). So, now

$$N_{\text{ap}} = \int_{-\infty}^{\infty} \tilde{f}_1(x) dx$$
\[ \hat{f}_1 = \exp(x - \tilde{g}_1) \]
\[ \tilde{g}_1 = \int_{-\infty}^{z} (z - x)^{\alpha} \hat{f}_0(x) \]
\[ \hat{f}_0 = \max f_1 \]
for \( x > x_{\text{max1}} \) and
\[ \hat{f}_0 = f_1 \]
for \( x < x_{\text{max1}} \). Here \( \max f_1 \) is the maximal value of \( f_1 \) and \( x_{\text{max1}} \) is the corresponding argument. To get these values it is necessary to calculate
\[ f_1 = \exp(x - g_1) \]
\[ g_1 = \int_{-\infty}^{z} (z - x)^{\alpha} f_0(x) \]
where \( f_0 \) is the analytical solution corresponding to \( \alpha = 0 \).

The result is drawn in figure 12. Here we draw the relative error \( \epsilon \) at \( z = 50 \). The step of calculations was \( dz = 0.05 \). We see that even for \( \alpha = 3/2 \) the result is good even without asymptotics and even with initial approximation corresponding to \( \alpha = 0 \). For \( \alpha > 3/2 \) the result was presented in [5]. All situations are solved now.

We have to stress that initial approximation as the analytical solution for the case \( \alpha = 1 \) is better than initial approximation corresponding to \( \alpha = 0 \). Then the accuracy will be also better. Now we shall present the analytical solution for \( \alpha = 1 \). The evolution equation is
\[ g = \int_{-\infty}^{z} (z - x) \exp(x - g(x)) dx \]
For \( \phi = -x + g \) this equation is
\[ \phi = \int_{-\infty}^{z} (z - x) \exp(-\phi(x)) dx \]
Having differentiated two times we get
\[ \frac{d^2 \phi}{dz^2} = \exp(-\phi) \]
This second order differential equation doesn’t contain the argument explicitly, which allows to integrate it. Let \( \phi \) be the argument \( u \), \( d\phi/dz \) be the function \( y \). Then \( d^2 \phi/dz^2 = ydy/du \). Integration gives
\[ -\frac{y^2}{2} = \exp(u) + c_1 \]
From the boundary conditions we get
\[ c_1 = -\frac{1}{2} \]
Then
\[ \frac{d\phi}{dz} = \sqrt{c_1 - 2 \exp(\phi)} \]
Integration gives
\[ \int \frac{d\phi}{\sqrt{c_1 - 2 \exp(\phi)}} = x + c_2 \]
This integral can be easily taken analytically which gives the analytical expression for the spectrum in this case. The constant \( c_2 \) can be got from the limit behavior \( \phi \to -x \) when \( x \to -\infty \).

This solution is very fruitful for description of situations with \( \alpha \) close to 1. Results are given in figure 13 which is analogous to the figure 12 but with another initial approximation. One can see here the curve A, which demonstrates the error of the first iteration in direct iteration method. Here
\[ N_{ap} = \int_{-\infty}^{\infty} f_1(x)dx \]
\[ f_1 = \exp(x - g_1) \]
\[ g_1 = \int_{-\infty}^{z} (z - x)^\alpha f_0(x) \]
and \( f_0 \) is the analytical solution corresponding to \( \alpha = 1 \).

We see that the error is even greater than the error in figure 12. It is so because simply the size (the amplitude, not the shape) seriously diminishes. This is the same as we have seen for smaller powers. This diminishing is the main source of error. So, we need to reexamine the initial approximation.

The first way is to act in a style like it has been done with the advanced iterations quite above. Here
\[ N_{ap} = \int_{-\infty}^{\infty} \tilde{f}_1(x)dx \]
\[ \tilde{f}_1 = \exp(x - \tilde{g}_1) \]
\[ \tilde{g}_1 = \int_{-\infty}^{z} (z - x)^\alpha \hat{f}_0(x) \]
for \( x > x_{max} \) and
\[ \hat{f}_0 = \max f_1 \]
\[ \tilde{f}_0 = f_1 \]
for \( x < x_{max} \). Here \( \max f_1 \) is the maximal value of \( f_1 \) and \( x_{max} \) is the corresponding argument. Then
\[ f_1 = \exp(x - g_1) \]
\[ g_1 = \int_{-\infty}^{z} (z - x)^\alpha f_0(x) \]
and \( f_0 \) is the analytical solution corresponding to \( \alpha = 1 \). The results are given by the curve B.

We can act also in another manner. We can rescale the number of molecules in a liquid phase \( g \) to have the approximate equal amplitudes. One can calculate constants

\[
q(\alpha) = \int \exp(-x)x^{\alpha}dx
\]

and instead of \( g \) consider \( g/q \) (both for the current \( \alpha \) and for \( \alpha = 1 \)). This corresponds to the approximate equal \( g \) at \( z = 0 \). The error is drawn as the curve C. One can see that the error seriously diminished.

One can also require the approximate equality in derivatives of \( g \) on \( x \) at \( t_* \) as it is considered in the balance for establishing of \( t_* \) (see [4]). Then the constants \( q \) will be

\[
q(\alpha) = \alpha \int \exp(-x)x^{\alpha-1}dx
\]

The result is drawn by the curve D. It is seen that the error is practically the same. It corresponds to the property of approximate universality observed in [4]. Now we see that this approximate universality goes also for the case of intermediate 1 < \( \alpha < 3/2 \).

Here and above the values of \( q \) were calculated on the base of the ideal supersaturation, i.e. on the base of \( \exp(x) \). The results will be even better if we take \( q \) calculated of the base of solution at \( \alpha = 1 \).

One cannot calculate here iterations analytically, but can act in a manner presented in [4]. Certainly, the leading term here will be \( zN \) where \( z \) is the coordinate of the maximum of peak of spectrum.

The situation of decay is much more simple and we can use the standard iteration solution given by formulas

\[
N_{ap} = \int_0^\infty f_1(x)dx
\]

\[
f_1 = \exp(-g_1)
\]

\[
g_1 = \int_0^z (z-x)^{\alpha}f_0(x)
\]

where \( f_0 \) is the analytical solution corresponding to \( \alpha = 1 \). The error is drawn in figure 14. It is small. The slight diminution when \( \alpha \) grows is caused only by numerical errors.

One has also to keep in mind that in situation with long tails one has to take into account the higher derivatives of the free energy of the critical embryo. This account is rather easy since we know the general solution. It can be done both by iteration approach and by perturbation technique.

Also one has to take care about the validity of linearization of ideal supersaturation for the long tails. But it very simple to correct the asymptotics for deviations from the linear case.
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Figure 1
Linear approximation of the size of growth
Power $\alpha = 1/8$
The bold line presents the approximation
Figure 2
Relative error
Figure 3
Forms of spectrums
Figure 4
Forms of spectrum and approximation
for $\alpha = 0$
Figure 6
Forms of spectrums in the first iteration
Figure 7
Forms of spectrums in the first modified iteration
$\alpha = 0.2$
Figure 8
Forms of spectrums
Figure 3
Maximal relative errors
Figure
Relative errors
The length is 70
The step is 0.05
Figure
Relative errors for pure iterations
The length is 50
The step is 0.05
Figure
Relative errors for pure iterations
The length is 50
The step is 0.05
Basic power 1
Figure
Relative errors for pure iterations
The length is 50
The step is 0.05
Basic power 1
decay