Late periods of the condensation process

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Abstract

The full evolution during the late periods of the condensation process is described in the analytical form. The process is split into several periods and for every period the simple approximate solution is given.

1 Introduction

The first order phase transition is characterized by the temporal duration - the process of the condensation lasts in time and consists of several characteristic periods. The kinetics of the first order phase transition is one of the actual problems in the phase transformations.

Ordinary it is supposed that the final stage (period) of the phase transition is the stage of coalescence. This name goes from the theory given by Lifshic and Slezov [1]. This terminology is not absolutely correct - formally the coalescence means the adhesion of the embryos. But the Lifshic-Slezov (LS) consideration does not take into account the adhesion, the evolution in the LS picture is the competition between the embryos through the exhaustion of the vapor environment. One has to clarify this difference. In the case of adhesion we shall speak about the coagulation and when the Lifshic-Slezov mechanism takes place we shall speak about the over-condensation.

The over-condensation means the competition between the already formed embryos when the embryos of the relatively big sizes eat the embryos of the relatively small sizes not directly but through the exhaustion of the

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metastable old phase until such a degree that the mentioned small embryos become the pre-critical ones and begin to eject the molecules in the vapor. These embryos begin, thus, to disappear.

Beside this opportunity it is possible to see in the open systems the situation when all embryos continue to grow until all volume of the system will be transformed into a new phase. Certainly this situation takes place when there is an effective source of the substance in the old phase. This is also an alternative possibility for the final of the phase transition. So, we see that the final stages of the phase transformation can be very different.

Here we shall speak about the over-condensation and consider the closed system. The effect of coagulation is not taken here into account. The temperature of the system is supposed to be fixed. The mentioned restrictions are not the crucial ones.

The methodology of analysis of such systems is given by Lifshic and Slezov in [1]. Strictly speaking the results of Lifshic and Slezov can not be directly applied for the systems with the diffusion regime of the substance exchange (as it was done in [1]) because in this case around every embryo there will be a profile of the metastable (old) phase substance. The profiles around different embryos overlap. This changes the rates of growth. Then one has to consider an interaction between the density profiles. So, one can not directly take the integral form of the balance equation as it is done in the theory of Lifshic-Slezov. The last task to describe the interaction of profiles is extremely difficult and the precise analytical solution of this problem is hardly possible.

The ignorance of the diffusion profiles leads to the necessity to consider the situation with the free molecular regime of interaction when there is no profiles. This was done by Wagner [2] and we shall follow this regime of the substance exchange below.

The fundamental fact is that the LS asymptotics was confirmed experimentally (see [3], [4], [5]). Here one has to stress that according to the notation made in [6] the accuracy is not very high - one can speak only about the qualitative confirmation of the form of the spectrum and about the precise confirmation of the power-like law of evolution of parameters of the spectrum (in some sense the power-like law is rather evident and it can be derived from some simple qualitative remarks). Also it is necessary to stress that according to the references from [6] the form of the size spectrum is more sharp than it follows from the leading term of the LS theory.

The next step in modification of the LS approach was done by Osipov and
Kukushkin in [6] where the "regular asymptotic" was constructed. Since the first two terms in asymptotic decomposition in the LS theory are universal (independent from the initial size spectrum) it is possible to introduce such variables (coordinates) where already the initial approximation is equivalent to the first two terms of the LS decomposition. So, the modification of Osipov and Kukushkin seems to be natural. But this modification is important because it allows to speak on the level of the regular asymptotics already from the very beginning.

The LS asymptotics has an amazing feature - it allows to establish the universal form of the size spectrum. One can admit that the power of metastability has some universal asymptotics, but one can hardly believe that the spectrum of the embryos sizes is universal. This will be the matter of discussion in this paper. Below it will be shown how the real spectrum of sizes approaches the form given by LS theory.

2 Some remarks initiated by technique of Lifshic and Slezov

Now we shall consider the simplest model leading to the over-condensation. At first we shall consider the embryos with linear sizes which strongly exceed the critical size. We shall call them as the supercritical embryos. The growth of the supercritical embryo in time \( t \) is given by the following equation

\[
\frac{d\rho}{dt} = \frac{\zeta}{t_1}
\]

Here \( \rho \) is the cubic root of the number of molecules inside the embryo (it plays the role of the linear size), \( \zeta \) is the supersaturation of the metastable phase, \( t_1 \) is some characteristic time (this is simply the constant coefficient). The supersaturation is defined as the ratio of the surplus density of the metastable phase (with respect to the saturated phase) to the density of the saturated phase or the ratio of the real density of metastable phase to the density of the saturated phase minus one.

The simplest asymptotic correction to the asymptotic law of growth will be the following

\[
\frac{d\rho}{dt} = \frac{\zeta}{t_1}(1 - u^{-1})
\]
Here

\[ u = \frac{\rho}{\rho_c} \]

is the ratio of \( \rho \) to the critical size \( \rho_c \) to have the zero rate of growth for the critical embryo. It is quite possible that this ratio has been changed by an analogous ratio in some power but this does not lead to the essential reconsideration of this approach.

One can give the interpretation of the last correction term as the leading term in the asymptotic expansion in inverse powers of the linear size. It is possible that this decomposition starts from the non-integer power as it takes place in construction of series for solutions of the linear second order differential equations. It is also possible that the law of growth for the supercritical embryos has some power of the linear size which grows with a constant velocity. Namely this situation takes place in the diffusion regime of the metastable phase exchange. In both cases the technique described below can be applied.

So, since one can see that

\[ \frac{(d\rho/dt)}{(d\rho/dt)_{\text{asym}}} = (1 - 1/u) \]

or there is some function of \( u \) in the rhs it is convenient to consider \( du/dt \) instead of \( d\rho/dt \). For the derivative \( du/dt \) we get an additional term

\[ \frac{d\rho}{dt} = \rho_c \frac{du}{dt} + u \frac{d\rho_c}{dt} \]

which is linear on \( u \). So,

\[ \frac{du}{dt} = \frac{\zeta}{t_1} (1 - u^{-1}) - u \frac{d\rho_c}{dt} \]

In the LS theory there exists a hidden supposition that \( \rho_c \) depends on time droningly. This supposition was reexamined in approach which predicts the periodic formation of the tail of the size spectrum and then the consumption of this tail. But nevertheless this supposition is rather natural at least at the asymptotics. If we adopt this supposition then all values depending on time are the values depending on the critical size. At least one can consider the intervals of the monotonous dependence.
The generalization of this law on other regimes of growth leads to

\[
\frac{du}{dt} = \phi_1(t)u^\alpha(1 - u^{-1}) - u\phi_2(t)
\]

The functions \(\phi_1, \phi_2\) are the functions of time. The function \(\phi_1\) can be excluded by transition to the rescaled time \(\tau\). The same can be done with \(u^\alpha\).

The right hand side of the last equation (let it be \(\Gamma\)) can not attain asymptotically the positive value at some argument - then the substance balance will be violated. The balance equation will be violated also when the rhs is negative at all values of argument \(u\). Hence, the unique possibility is to touch the zero level at the main maximum. Then it is necessary that the rhs as a function of \(u\) has a maximum and then by the correct choice of \(\varphi\) one can put the maximum to the zero level. The class of functional dependencies which allow this operation forms the class of dependencies where the LS technique can be applied at least formally. The fine unjustified supposition here is the monotonous approach (in time) of the maximum to the zero level. It is quite possible that this maximum oscillates near zero - at some moments is it greater than zero, at some times it is less than zero. This possibility is considered in \([8]\). Here we do not consider the oscillating scenarios.

For the function \(\varphi\) we get

\[
\varphi = \gamma_0
\]

where \(\gamma_0\) is some constant. Even when this supposition is adopted the velocity at the maximum is zero and the balance equation is violated. Then it is necessary to be:

\[
\varphi = \gamma_0(1 + \varepsilon^2(\tau))
\]

with \(\varepsilon \to 0\) at \(\tau \to \infty\).

The reason that \(\gamma_0\) is a constant lies in the form of equation for \(du/d\tau\). It would be interesting to consider equations which do not belong to the established form and to get the evolution analogous to the over-condensation.

Let the argument of the main maximum be \(u_m\). One can see that at \(\varphi = \gamma_0\) the embryos with \(u > u_m\) can be dissolved only at the infinite time (the diffusion is not considered here).

Now we shall establish the function \(\varepsilon(\tau)\). To find this function one has to analyze the solution near the maximum of \(\Gamma\). We introduce the variable

\[
z = (u - u_m)/\varepsilon
\]
Then we see that
\[ \frac{du}{d\tau} = \frac{d(u - u_m)}{d\tau} = \frac{dz\varepsilon}{d\tau} = \varepsilon\frac{dz}{d\tau} + z\frac{d\varepsilon}{d\tau} \]
and
\[ \varepsilon\frac{dz}{d\tau} = \Gamma(\gamma_0(1 + \varepsilon^2)) - zk_1 \]
where \( k_1 \) is the coefficient equal to \( \frac{d\varepsilon}{d\tau} \). In the last equation it is necessary to express \( u \) in the function \( \Gamma \) through \( z \) and \( \varepsilon \). Then we rescale the time to exclude the coefficient in the rhs and then we get an equation which allows (or does not allow according to the reasons mentioned above) the analysis analogous to the already made one. If equation allows such analysis one can get the correction term of the asymptotic.

One has to get the equation binding \( d\varepsilon/d\tau \) and \( \varepsilon \). In the power-like laws of growth this equation is trivial and has the form \( f(\varepsilon)\frac{d\varepsilon}{d\tau} = \text{const} \) with some known function \( f \). It is interesting whether one can get any more complex form of this equation. It is quite possible that some more complex form can lead to some new physical effects. Here we do not consider this question and assume that the dependence \( \varepsilon \) on \( \tau \) for the correction term is established.

Having calculated one correction term after another we establish all asymptotic series until the step when we can not perform the procedure described above because the obtained equation does not allow to put maximum to the zero level. In the natural physical situations only the initial and the first correction term can be established. It is worth seeking the situations where one can make more steps.

In the Osipov-Kukushkin approach we get the correction term already as the initial approximation since one can choose such variables where the correction term can be treated as the initial one. Certainly, it is possible to continue this procedure but it appears that under the natural regimes of the substance exchange it is impossible to choose parameters in equations for correction terms that the main maximum will touch the zero level. It is interesting to find situations where all corrections are the universal ones.

One can see that the account of the diffusional term in the evolution equation can not lead to another asymptotics because the diffusion process along \( u \) becomes negligible at the infinitely big time. In correction terms it is necessary to check that the diffusion process is really negligible in account of corrections. It would be interesting to seek the situations where the account of the diffusion process changes the correction terms.
The unpleasant fact for the LS theory is the following one. In the zero approximation the time of the dissolution of the embryo with \( u > u_m \) is infinite and has to be refined. But in the first approximation the time of dissolution of every finite embryo is the finite one and it means that every finite size spectrum will be dissolved (dissolved at the finite time). After the spectrum is dissolved the balance equation will be certainly violated.

The mentioned difficulty has a fundamental character which is confirmed by further constructions in frames of the LS theory. It is reasonable to connect the finite time of dissolution with the possibility to find the universal form of the size spectrum. The authors of the LS approach treat the universal distribution as the distribution which is the limit of the relaxation process. But it evident that namely the initial form of the size spectrum determines the whole further evolution. Under the regular and only under the regular law of growth we have

\[
p(\rho, t) d\rho = f(\rho', t') d\rho'
\]

where \( p \) and \( f \) are the old spectrum and the new spectrum of sizes and \( \rho \) at the moment \( t \) has to come by the regular growth into \( \rho' \) at \( t' \). Then

\[
p(\rho, t) \frac{d\rho}{dt} = f(\rho', t') \frac{d\rho}{dt} \bigg|_{t=t', \rho=\rho'}
\]

Since for \( d\rho/dt \) we have the concrete given expression it is hardly possible to change the form of the size spectrum to come to the universal form of the LS theory. If one determines the velocity of growth from comparison of the initial form of spectrum and the final universal form of spectrum it leads to the unpleasant contradiction.

The alternative is the following: to have the size spectrum prescribed by the initial distribution or to see the leading role of diffusion (at least at some time).

It appears that the universal form of the size spectrum has absolutely another sense - this form of spectrum is such a form which corresponds to the already established asymptotics for the critical size precisely or at least ensures the optimal relaxation to the established asymptotics for the velocity of growth. With the real form of the size spectrum this asymptotic form of the size spectrum has no direct connection. Then the asymptotic for the velocity of growth corresponding to the ideal size spectrum will be never attained at finite time.
3 Asymptotic form of the size spectrum

One can get the universal form of the size spectrum in the LS formalism rather simply. In the LS approach it is supposed that the main quantity of the substance is in the region $u < u_m$. Then the balance of the substance leads to

$$\int_0^{u_m} \rho^3 f(\rho, t) d\rho = \text{const}$$

where $f(\rho, t)$ is the distribution function. From this function we come to the distribution over $u$, namely to $\phi(u, \tau)$. Then

$$\phi(u, \tau) du = f(\rho, t) d\rho$$

The substance balance can be rewritten as

$$\rho_c^3 \int_0^{u_m} u^3 \phi(u, \tau) du = \text{const}$$

The form of the function $\phi$ can be determined from the continuity equation

$$\frac{\partial \phi}{\partial \tau} = -\frac{\partial \phi v_u}{\partial u}$$

where $v_u$ is the velocity of the growth for $u$. The solution of this equation is rather simple

$$\phi(u, \tau) = \theta(\tau - \tau(u))/v_u$$

where $\tau(u)$ is the time for the embryos to attain $u$. Instead of the last function one can write the function of $u - u(\tau)$, where $u(\tau)$ is the size attained at the given time. The sense of solution is that the dependence over two variables is performed through the dependence over one variable. The concrete form of this dependence is determined by initial conditions (in the LS approach it is determined by asymptotic relations).

The transformation to the variable $u$ is made to ensure the constant value of the upper limit of integration.

Ordinary the concrete form of the functional dependence of $\theta$ has to be determined from the initial conditions. But in the LS formalism this form is determined from the asymptotic balance equation which can be written as

$$\rho_c^3 \int_0^{u_m} u^3 \theta(\tau - \tau(u))/v_u du = \text{const}$$
The function \( v_u \) depends only on \( u \), but not on \( \tau \). This is the consequence of the fact that in the zero approximation for \( du/d\tau \) one can take \( \gamma_0 \) which excludes the dependence on time.

The function \( \rho^2_c \) at the already established asymptotic is the known function of time. This dependence has to be cancelled by the true choice of the functional dependence for \( \theta \). Namely this cancellation is the recipe to choose the true form of the function \( \theta \).

The simple dependence (but may be not the unique one) is the following one

\[
\theta(\tau - \tau(u)) = g(\exp(\tau - \tau(u)))
\]

where the function \( g \) satisfies the relation

\[
g(ab) = g_1(a)g_2(b)
\]

for any \( a \) \( b \). As this function one can take the power function. Since we have to cancel only the leading term in asymptotic the choice of the power-like function is quite satisfactory.

So, the solution is announced. But is it well justified?

Really, the ordinary solution of the problem (not the asymptotic one) is very simple it is already presented in the form of the function \( \theta \), i.e. in the fact that \( \theta \) is the function of only one variable. Certainly, this function has to coincide with the initial spectrum of sizes at the initial moment of time. It is sufficient to calculate the origin of the given embryo taking into account the known supersaturation, then to take the initial distribution and divide it on the velocity of growth in the given point (or on the ratio of the velocities of growth in corresponding points).

We shall speak here about the evolution scenario. This scenario is in contradiction with the LS scenario. It conserves the explicit dependence on the initial distribution. It is clear that the evolution scenario is more correct in comparison with the LS scenario. The LS scenario has at least two disadvantages

- The absence of the spectrum at \( u > u_m \)
- The spectrum is determined to ensure the asymptotic, but it is more reasonable to get the asymptotic on the base of spectrum.

The first disadvantage can be ignored by notation that every finite spectrum sooner or later will leave the region \( u > u_m \).
The second disadvantage is more serious because it destroys the methodology of the LS approach. It seems that it is the crucial point and the real size spectrum will differ from the result of the LS theory.

But one can see the amazing fact - the similarity between the form of the LS spectrum and the results of experiment. We shall explain this similarity below.

4 Approximate similarity between the real size spectrum and the results of the LS approach

We start to consider the strange fact - why the form of the size spectrum prescribed by initial conditions will resemble the universal result of the LS theory?

At first one has to stress the low accuracy in the experimental determination of the size spectrum form. As an example one can consider the style of discussion in [6]. In [6] one can see not only the account of the initial approximation but already of the first correction in the form of the size spectrum. The form of the size spectrum with the first correction essentially differs from the form in the zero approximation. This fact is very important and leads at least to two essential conclusions

- the correction term in the asymptotic expansion is not small at least for the size spectrum - one can not see the parameter with a property: the small value of this parameter leads to the size spectrum in the zero approximation. Moreover, one can state that there is no such parameter because the size spectrum in the first approximation is universal one. This shows that there is no reliable way to determine the size spectrum because the next correction can change the form of the size spectrum radically.

One can also give an interpretation which is not favorable for the LS approach - the modified zero (Osipov-Kukushkin) approximation is only the starting point and all further terms of decomposition depend on the initial size spectrum. So, there is no reason to speak about the universality.
- the accuracy of the experimental results is rather low. Really, the difference between the size spectrum in the zero (LS theory) and in the first approximation is very essential. Earlier the experimental results confirmed the LS spectrum in the zero approximation. Now experiments confirm the Osipov-Kukushkin result. It can be only when the accuracy is low. So, one can speak only about the experimental observation of some tendencies in the form of the size spectrum.

In the analysis of experimental results one has to note that some authors speak about the diffusional blurring of the size spectrum which corresponds to experiment.

But one can show analytically that it is possible to neglect the diffusional term in the LS technique. It does not mean that in the evolution scenario one can neglect the diffusion - at least there are some periods when the diffusion is the driving force of evolution. Also one can see that in the case of the finite size spectrum one has to include diffusion.

As the result of these facts one has to conclude that there exists a tail of the size spectrum (it is the exponential one - this is explained by the diffusion process) at $u > u_m$ (in any other region it can not be noticed). This tail is observed experimentally. What is the reason for this tail? The LS formalism can not give an answer. Below this answer will be given.

Kinetics of the new phase embryos formation has some characteristic features which help to determine the characteristic features of the over-condensation. Roughly speaking, the "initial" size spectrum belongs to a narrow class of functional dependencies. So, we use the evolution approach and construct the sequence of stages for the process of condensation and over-condensation.

The process of condensation (the periods before the over-condensation) is investigated in [7]. This investigation gave the total number of the embryos and the form of the size spectrum. For the further regular evolution it is necessary to know the first three (and the zero) momenta of the size spectrum

$$\mu_i = \int_{-\infty}^{\infty} f(x)x^i dx$$

or of the distribution function $f(x)$ of the variable $x$, defined as the deviation of the coordinate $\rho$ from the size $z$ of the maximal value of this variable corresponding to the embryo formed at the very beginning of the condensation process.
4.1 The period of the initial relaxation

The relatively intensive formation of droplets stops at the relative decrease of the supersaturation equal to the value reciprocal to the quantity of the molecules in the critical embryo.

The number of molecules in the critical value is a big value. The relatively small decrease of the supersaturation stops the nucleation (formation of new embryos) and later the size spectrum moves along the $\rho$-axis without any change of the form. To ensure the essential exhaustion of the metastable phase the spectrum has to move along $\rho$-axis for a rather long distance. So, at the end of this evolution the spectrum of sizes can be considered as the monodisperse one.

The balance equation can be written in the following form

$$\Phi = \zeta + \sum_{j=0}^{3} \frac{3!}{i!(3-i)!} z^{(3-i)} \mu_i$$

or

$$\Phi = t_1 \frac{dz}{dt} + \sum_{j=0}^{3} \frac{3!}{i!(3-i)!} z^{(3-i)} \mu_i$$

which is the ordinary first order differential equation without the explicit dependence on the argument. So, it can be easily integrated. The result is the monodisperse spectrum and the relaxation of the spectrum coordinate to the critical size (or more correct the relaxation of the critical size to the coordinate of the spectrum).

Here we use the law of growth for the supercritical embryos. It can be replaced by the precise law of embryos growth. Really, in the law

$$\frac{dz}{dt} = \frac{\zeta}{t_1} (1 - \frac{z3\zeta}{2a})$$

we replace $\zeta$ by $\Phi - \sum_{j=0}^{3} \frac{3!}{i!(3-i)!} z^{(3-i)} \mu_i$ and get equation

$$\frac{dz}{dt} = \frac{\Phi - \sum_{j=0}^{3} \frac{3!}{i!(3-i)!} z^{(3-i)} \mu_i}{t_1} (1 - \frac{z3(\Phi - \sum_{j=0}^{3} \frac{3!}{i!(3-i)!} z^{(3-i)} \mu_i)}{2a})$$

which can be easily integrated. Here it is ignored that during the evolution the momenta $\mu_i$ will be changed which is considered as a correction. In any case we need only the initial approach to the critical size where the rough
monodisperse approximation is sufficient. Then there will be no problem with changing momenta.

One can show that the account of the diffusional term will be essential only when the coordinate of the size spectrum is rather close to the critical size. This is the end of the relaxation stage and the beginning of the new period.

4.2 The period of the diffusional blurring of the size spectrum

The result of the previous period is the relaxation of the spectrum coordinate to the critical size. The spectrum resembles the delta-like function. The spectrum width $\delta \rho$ is many times less than the coordinate $\rho$ or $\rho_c$ which is the spectrum coordinate.

If there would be no diffusion then the spectrum will remain near the critical coordinate until the end of the whole evolution. But after the time of relaxation at the previous period the diffusion becomes the main driving force of the process.

Kinetics of the diffusion blurring is rather simple and it is described in [8]. It is possible to approximate evolution by diffusion blurring without any regular growth with a boundary condition

$$f(\rho = 0) = 0$$

and the initial condition

$$f(t = t_{initial}) \sim \delta(\rho - \rho_c)$$

The method to solve this problem is the combination of the Green functions at the infinite interval. The method of images allows to construct solution by addition of the negative gaussian in the symmetrical point.

So, we write the diffusional equation in the following form

$$\frac{\partial f}{\partial t} = W_c \frac{\partial^2 f}{\partial \rho^2}$$

Here $W = W^+ + W^-$ is the generalized kinetic coefficient equal to the weighted sum of the adsorption coefficient $W^+$ and the ejection coefficient $W^-$. One can take these coefficients in the critical point marked by the index
c. Then one can assume that $W_c = 2W_c^+$. Taking into account the evident relation

$$W^+ = Sv_t/4 = 3\rho^2(\zeta + 1)/t_1$$

where $v_t$ is the mean thermal velocity, $S$ is the surface square of the embryo one can determine the dependence of $W_c$ on $\rho$. Then it is necessary to go from $\rho$ to a new variable $r$ which is $\rho$ in some constant power, i.e. $\rho^{const}$. This transition excludes the dependence of the diffusion coefficient on the size at least asymptotically. It occurs at $\rho d\rho \sim ds = d\rho^2$.

The Green function at the infinite interval is written in the following form

$$G(s, t|s_0, t_0) \sim \exp\left(-\frac{(s - s_0)^2}{4D(t - t_0)}\right)$$

where $D$ is the diffusion coefficient (this is the known constant value), $s_0$ is the point of appearance of elementary disturbance at the moment $t_0$, $s$ is the point of observation at the moment $t$.

Here one can take as $s_0$ the critical size and the time $t_0$ has to correspond to the time of the end of relaxation (actually it is the time of relaxation).

To observe the boundary condition $f(s = 0) = 0$ it is necessary to take the combination

$$f_0 = f_+ + f_-, \quad f_+ = G(s, t|s_0, t_0), \quad f_- = G(s, t|s_0, t_0)$$

This gives the solution of this problem.

Consider the behavior of the critical size $\rho_c$. It is important to know $\rho_c$ because $u = \rho/\rho_c$. One can propose the equilibrium critical size $\rho_{ce}$ which can be determined on the base of the size spectrum as

$$\int_{-\infty}^{\infty} f(\rho, t)3\rho^2(1 - \frac{\rho_c}{\rho})d\rho = 0$$

This corresponds the stationary value of the critical size, i.e. $d\rho_c/dt = 0$.

It is clear that never $\rho_c$ equals $\rho_{ce}$ because this means the stationary value of $\rho_c$ and of the supersaturation $\zeta$. But approximation $\rho_c \approx \rho_{ce}$ is rather good. Namely, at the beginning of the diffusion blurring this equality takes place. So, the critical radius $\rho_c$ (we shall mark it $\rho_{c0}$ for initial time) is given by condition

$$\int_{0}^{\infty} f_0(\rho)v_\rho(\rho_{c0})d\rho = 0$$
Here \( v_\rho \) is the velocity of growth of the variable \( \rho \). It is supposed that the size spectrum is relatively narrow. Another variant taking into account the different volumes of embryos is the following

\[
\int_0^\infty f_0(\rho) \rho^2 v_\rho(\rho,0) d\rho = 0
\]

Also one can propose to extract the deviation of \( \rho_c \) from \( \rho_{ce} \)

\[
y = (\rho_c - \rho_{ce})/\rho_{ce}
\]

and see that ordinary \( y \) is small. Then one can analyze the evolution of the system through decomposition on \( y \).

When \( y \) is big it means that the size spectrum is essentially greater than \( \rho_c \). But this corresponds to the evolution via supercritical embryos where we have extremely simple law of growth \( d\rho/dt = \zeta/t_1 \). So, the combination of the consideration of supercritical embryos and decompositions on \( y \) with restriction in the first several terms (actually the first non-zero term) can be very effective.

Now we return to the diffusion blurring. The result of the diffusion blurring is very optimistic for the final conclusions. It sounds as following: The distribution function is the universal one and does not undergo the change of the form any more. So, one can see that the asymptotic solution is found. But the situation is not so simple.

Really the function \( f_0 \) after scaling in units of \( \rho_{ce} \) will be the universal function without any parameters.

On the base of distribution we can calculate the behavior of the critical radius. Note that it is impossible to find the critical size directly from the balance equation \( 2a/3\rho_c + \int_0^\infty \rho^3 f(\rho,t) d\rho = \text{const} \) because here \( \int_0^\infty \rho^3 f(\rho,t) d\rho \approx \text{const} \) and the error radically increases. Instead of the direct balance equation one can use the differentiated variant \( 2(a/3\rho_c^2)(d\rho_c/dt) = 3 \int_0^\infty \rho^2 f(\rho,t) d\rho \) which allows to find \( \rho_c \).

If the size spectrum will be the universal function then the critical size will be also the universal function.

The special question is the correct boundary condition at small sizes. The velocity of the dissolution of the small embryos is a rather complex function of size and the regular dissolution exists. One can not neglect this regular dissolution. But fortunately the small embryos are dissolved very quickly with the growing velocity. So, one can suppose that they disappear
immediately at \( \rho = \rho_f = (0.6 \div 0.8)\rho_c \). So, the zero boundary condition has to be put at \( \rho_f \) and all further considerations remain without reconsideration. Certainly, to keep the boundary condition we have to put the negative Green function symmetrical to \( s \) with respect to \( s_f \).

In the situation with \( s_f \) we have also the universal spectrum and the universal behavior of the critical size.

But this universal asymptotics is only the intermediate asymptotics. Now we shall introduce the regular growth and destroy this universality. It is necessary to put some boundary of the type

\[
\rho_r = (2 \div 3)\rho_c
\]

and for the sizes greater than \( \rho_r \) one has to consider the regular motion with the asymptotic velocity. The choice of \( \rho_r \) can be made also on the base of the LS analysis.

It is trivial to refine the solution by investigation of the transition zone explicitly.

The growth of the supercritical tail leads to the growth of the size \( \rho_c \) which can be calculated in approximation of the following iteration procedure: On the base of initial \( \rho_{c0} \) we find the tail \( f_{\text{tail}} \) of the size spectrum

\[
f_{\text{tail}}(\rho, t) = f_0(\rho_r, t')v_\rho(\rho_r)/v_\rho(\rho)
\]

where

\[
t - t' = \int_{\rho_r}^{\rho} \frac{1}{v_\rho(\rho')} \, d\rho'
\]

(the explicit dependence of \( v_\rho \) on \( t \) is weak or it can be expressed via \( t \) iteratively).

The new distribution function \( f_1 \) will be the superposition of the initial part \( f_0 \) and the tail. Then from the balance equation

\[
\int_0^\infty f_1(\rho)\rho^2v_\rho(\rho|\rho_{c1}) \, d\rho = 0
\]

we find \( \rho_{ce1} \). This will be the new equilibrium critical size. It will be near the real critical size unless the tail begins to play the main role in the metastable phase consumption.

The period of the diffusion blurring come to the end when the velocity of the growth for the critical embryo becomes to be comparable with the velocity of the growth for the tail.
One has to analyze an attractive possibility to consider the process of diffusion in the region \( s < s_r \) with the linear on \( s - s_c \) rate of growth. Here \( s_r \) has to be determined as the boundary between the linear and the asymptotic rates of the embryos growth. It seems from the first point of view that the linear rate of growth in the near critical region is preferable instead of the absence of the regular growth considered above.

The Fokker-Planck equation under the linear rate of growth has the following form

\[
\frac{\partial p}{\partial t} = \gamma \frac{\partial y p}{\partial y} + D \frac{\partial^2 p}{\partial y^2}
\]

Here the zero value of the coordinate as the critical size is taken, \( \gamma \) and \( D \) are some constants. Here \( \gamma \) is negative. The Green function for the positive \( \gamma \) at the infinite interval is well known and has the following form

\[
G(x, t|x', t') = \frac{\gamma}{\sqrt{2\pi D(1 - e^{-2\gamma(t-t')})}} \exp\left(\frac{-\gamma(x - e^{-\gamma(t-t')}x')^2}{2D(1 - e^{-2\gamma(t-t')})}\right)
\]

Now it is necessary to take the combination of two Green functions and the answer is ready. The further analysis is absolutely the same.

This approach seems to be more precise than the previous one but it has many disadvantages. The first disadvantage is the following: one can see that here \( \gamma \) has to be negative and then at some time the half width of the gaussian goes to infinity. So, the solution becomes illegal.

The second disadvantage is how to take into account the drift of the critical size. Now it appears in the rate of growth and then in the final formulas. The solution with a moving critical size is illegal also.

But the idea to consider the law of growth as a combination of the linear dependence at \( \rho < \rho_r \) and the asymptotic law at \( \rho > \rho_r \) is very attractive. Really the term \( 1 - \rho^{-1} \) in the traditional law of growth can be treated as a correction term in the asymptotic decomposition. Here this asymptotic is taken over the positive powers of \( \rho_r \). The decomposition on the positive powers is not less justified in comparison with the decomposition on inverse powers. But the last approximate rate of growth allows an explicit integration and then the LS technique can be analyzed explicitly.

One can try to construct the approximate Green function for the case of the presence of the regular growth in the following manner. We construct this function for initial perturbation at \( x_0 = 0 \) which is an equilibrium value for the regular growth \( v_x(x = 0) = 0 \). We suppose that there are no other
points where $v_x = 0$ and $v_x(x) = -v_x(-x)$. Then we seek the Green function in the ordinary form

$$G(x, t|t_0) = A(t, t_0) \exp\left(-\frac{x^2}{\Delta(t, t_0)^2}\right)$$

where the amplitude $A$ can be reconstructed on the base of normalizing equation $\int Gdx = 1$ and the width $\Delta$ is found by relation

$$\Delta = \sqrt{4D(t - t_0) + \int_{t_0}^{t} v_x(\Delta(t'))dt'}$$

or

$$\Delta = \sqrt{\int_{t_0}^{t} D(\Delta(t'))dt' + \int_{t_0}^{t} v_x(\Delta(t'))dt'}$$

for varying $D$. The last equation can be easily solved iteratively

$$\Delta_{i+1} = \sqrt{\int_{t_0}^{t} D(\Delta_i(t'))dt' + \int_{t_0}^{t} v_x(\Delta_i(t'))dt'}$$

$$\Delta_0 = \Delta(t_0)$$

To ensure the correct boundary condition it is necessary to add the symmetrical negative Green function.

To refine the solution one can also use here the values of effective diffusion coefficient and effective law of the regular growth velocity from consideration made in [9].

4.3 The period of the dissolution of the head of the size spectrum

The tail of the size spectrum grows and earlier or later the main role of the metastable phase consumption will belong to the tail. This opens the period of dissolution of the head of the spectrum.

This period allows a rather trivial description since the high accuracy is not important here. Inevitably the head of the spectrum will be dissolved and this marks the end of this period.

The most primitive description is the following. We split the substance between the tail $G_{tail}$ and the head $G_{head}$. The spectrum in the head is described by $f_0$. The spectrum in the tail $f_{tail}$ is the direct translation of
the blurring part of the head which comes to the zone $\rho > \rho_r$ by the regular growth with the known supersaturation. The supersaturation corresponds in the first iteration loop to the stationary position of the critical size. Then we can calculate the dissolution of the head, the growth of the tail and replace the critical size on the base of the balance equation. We know a new value of supersaturation. This closes the iteration loop.

Here it is impossible to use the model of the growth with a zero value of growth for $\rho > \rho_f$ and the zero value of $\rho$ for all $\rho < \rho_f$ (otherwise it produces the jumps in the supersaturation value). One has to use the explicit law $d\rho/dt = (2a/3\rho_c)(1 - (\rho_c/\rho))$.

Another style of description is to use the methods from description of the dissolution of the tail of the size spectrum which is analyzed below. Since the method is the same we do not consider it here explicitly. Certainly, the exponential tail like $\exp(-\text{const } \rho)$ has to be changed to the head of the size spectrum $f_0$.

This period is rather short and it is not very important for the further evolution. Details of this period description can be found in [8]. But one can see that in the theory presented here the new head at the tail is not formed. Here lies the main difference between this theory and the theory from [8]. The question whether the new head is formed is rather complex. This is the question of applicability of the gaussian tails of the Green function of diffusion equation. If we adopt the model with a finite upper limit of the size spectrum then we have a new head at the tail and have to use scenarios proposed in [8]. If we believe in long gaussian tails we come to the theory presented here. To solve this question we must go ahead of the level of description taken in the diffusion approximation. Otherwise there is no sufficient statistics to solve this question. We prefer to stop here at the statement that there is no sufficient statistics. It means that concrete details will determine the scenario. For example, we adopt that the act of the molecule consumption by the embryo requires a certain elementary time and we come to the finite upper limit of the spectrum. In the opposite situation we come to the gaussian tail. Certainly this question is out of the level of consideration adopted in the nucleation theory.

4.4 The period of the gradual consumption of the tail

Now we come to the period which in some sense resembles the LS results.

The result of the previous period is the formation of the exponential tail
at \( \rho > \rho_r \). Now we consider the process of the tail dissolution. Here one can see the true competition between the embryos with different sizes. So, here it is convenient to go to the LS coordinates.

To investigate this period we simplify the rate of the embryos growth. We assume the following rate of growth

\[
\frac{du}{d\tau} \sim (1 - u^{-1}) - \gamma u
\]

If there is a sufficient tail and the heat is already dissolved then at the moment of the end of the previous period

\[
\max \{ \frac{du}{d\tau} \} \equiv v_m < 0
\]

So, we assume that \( v_m \) is negative.

We split the whole region of \( u \) into three small regions. In the region of big \( u \) we suppose

\[
\frac{du}{d\tau} \sim (1 - 0) - \gamma u
\]

This law allows integration even under the variation of \( \gamma \).

The next region is the region of the intermediate \( u \). Here we assume

\[
\frac{du}{d\tau} = v_m
\]

In the region of small \( u \) we neglect \( \gamma u \) and get

\[
\frac{du}{d\tau} \sim (1 - u^{-1})
\]

This law does not contain parameters and can be easily integrated. It means that the dissolution here is so fast that we can neglect the change of the critical size.

The boundaries \( u_1 \) and \( u_2 \) between these regions can be established from the continuity of the rate of growth.

One can also put an effective boundary of the total dissolution instead of the zero size.

It is possibly to refine the law of growth having introduced instead of \( v_m \) some other effective value of the flat region.
When the size spectrum is known then the balance of the substance becomes the transcendental equation on $\gamma$. After we found $\gamma$ we can get $\rho_c$ by integration.

One can easily follow the dissolution of the spectrum on the base of the approximate rate of growth.

We accumulate the approximate law of growth in the following formula

$$\frac{du}{d\tau} \approx (du/d\tau)_{appr}$$

This law of growth allows to know $u(\tau)$ on the base of some $u_0(\tau_0)$ for every arbitrary curve $\gamma(\tau')$

$$u(\tau) = u_0(\tau_0) + \int_{\tau_0}^{\tau} (du/d\tau)_{appr} \equiv F_{appr}(\tau|u_0, \tau_0; \gamma(\tau'))$$

For the law of growth we write

$$\frac{d\rho_c}{d\tau} = \varphi(u, \gamma(\tau))$$

Here we can take both approximate or precise law of growth.

The substance balance equation

$$\frac{d\rho_c}{d\tau} - \frac{2a}{3\rho_c^2(\tau)} = \rho_c^3(\tau) \int_0^\infty 3F_{appr}^2(\tau|u_0, \tau_0; d\ln \rho_c(\tau')/d\tau')$$

$$\varphi(F_{appr}(\tau|u_0, \tau_0; d\ln \rho_c(\tau')/d\tau'), d\ln \rho_c/d\tau) f_0(u_0, \tau_0) du_0$$

$$+ 3\rho_c^2(\tau) \frac{d\rho_c}{d\tau} \int_0^\infty F_{appr}^3(\tau|u_0, \tau_0; d\ln \rho_c(\tau')/d\tau') f_0(u_0, \tau_0) du_0$$

is now the closed equation on $\rho_c(\tau)$. Here instead of $a$ one can put the appropriate constant in accordance of normalization of the size spectrum.

It is necessary to stress that all functional dependencies here are explicit ones and except $\rho_c(\tau)$ all other dependencies are known. The best way to solve this equation is to use the steepest descent method. The methods to solve this equation will be discussed below.

This equation can be approximately simplified. Since the last term of the rhs is many times greater than the lhs one can approximately write

$$\rho_c(\tau) \int_0^\infty 3F_{appr}^2(\tau|u_0, \tau_0; d\ln \rho_c(\tau')/d\tau')$$

$$\varphi(F_{appr}(\tau|u_0, \tau_0; d\ln \rho_c(\tau')/d\tau'), d\ln \rho_c/d\tau) f_0(u_0, \tau_0) du_0 =$$

$$-3\frac{d\rho_c}{d\tau} \int_0^\infty F_{appr}^3(\tau|u_0, \tau_0; d\ln \rho_c(\tau')/d\tau') f_0(u_0, \tau_0) du_0$$
or
\[
\begin{align*}
\int_{0}^{\infty} 3F^{2}_{\text{appr}}(\tau|u_0, \tau_0; d\ln \rho_c(\tau')/d\tau') \varphi(F^{\text{appr}}(\tau|u_0, \tau_0; d\ln \rho_c(\tau')/d\tau'), d\ln \rho_c/d\tau) f_0(u_0, \tau_0) du_0 \\
3 \int_{0}^{\infty} F^{3}_{\text{appr}}(\tau|u_0, \tau_0; d\ln \rho_c(\tau')/d\tau') f_0(u_0, \tau_0) du_0
\end{align*}
\]

\[= -\frac{d\ln \rho_c}{d\tau} \equiv -\gamma\]

This equation can be solved by the same methods but it is more simple than the previous one. We outline again that except \(\gamma(\tau)\) all other dependencies here are known.

Another possible approximate variant of the balance equation is the following

\[
\rho_c^{-3} = \text{const}^{-1} \int_{0}^{\infty} F^{3}_{\text{appr}}(\tau|u_0, \tau_0; d\ln \rho_c(\tau')/d\tau') f_0(u_0, \tau_0) du_0
\]

It seems to be the most simple variant of the balance equation.

Now we shall discuss the asymptotic properties of the balance equation.

Generally speaking the problem is solved since we know the good approximation

\[
d\ln \rho_c/dt = \gamma_0 + \text{some positive small value.}
\]

We can solve this equation by decomposition in series or by some effective linearizations.

But below we shall analyze the properties of solution in order to see that the size spectrum here resembles the LS theory for the size distribution.

First of all we have to note that the tail has the exponential character. Really, the translation of the gaussian at some shift from the maximum leads to

\[
f_{\text{tail}} \sim \exp(-\text{const}/t)
\]

which can be easily approximated by the standard exponent of the argument linear on the size. Here the \(\text{const}\) is some fixed value proportional to \((s_r-s_c)^2\).

Here we have to recall that in the original paper by Lifshic and Slezov there is a reference on the exponential tail of the size spectrum. It is quite natural to check the theory on example of the exponential tail.

The exponential on \(r\) spectrum is exponential on \(u\) also in the asymptotic limit.

In frame of the steepest descent methods the utilization of the exponential tails is quite justified. One can simply refer to the steepest descent method instead of the explicit consideration made above. But one has to stress
that we follow the explicit determination of the size spectrum instead of the formal methods. Explicit decompositions also give the exponential tail of the spectrum.

If the characteristic width of the tail is many times greater than the critical size then $v_m$ is far from zero and there appears the rapid dissolution of the size spectrum. If the width of the spectrum is many times less than the critical size then $v_m$ is close to zero. It is evident that earlier or later the last situation will take place. One can give the qualitative picture of the process - The evolution at the big finite time is the slow monotonous increase of $v_m$ up to zero.

The situation of the wide tail can be investigated rather elementary. The behavior of supersaturation is governed by the consumption of the substance by the wide tail. To see this consumption one can use the regular growth. This is described in [8] under the investigation of the oscillating regime. Evidently, the consumption of the substance leads to the growth of the critical embryo and the dissolution of the tail. This process will take place until the tail (or the rest of the tail) can be considered as the wide one.

The rest of the tail earlier or later will become the narrow tail and then we can use the theory of the narrow tail.

Now we consider the situation of the narrow tail.

We consider the form of the size spectrum. We use the known formula

$$f(u, \tau) \sim -\frac{\xi(\tau - \tau(u))}{v_u}$$

where $v_u$ is the velocity in $u$-axis, $\tau(u)$ is the time for the embryo to attain $u$.

One can note that

$$\tau(u) = \int_0^u \frac{du}{v_u} \to \ln(u)$$

This asymptotics makes the size $u$ inconvenient for analysis. It is more convenient to act in the $\rho$-scale where the asymptotic rate of growth is the constant one. In experiment under the instantaneous observation the variable $u$ is proportional to $\rho$ and there is practically no difference between them.

So, it is preferable to consider at big $u$ the $\rho$-scale. In the variable $\rho$ the picture is rather simple - the exponential tail begins to be transformed according to the variation in the velocity of growth

$$f(\rho) \sim \frac{\exp(-\text{const}\rho)}{(1 - \rho_c/\rho)}$$
The amplitude of the spectrum and the width are determined from the behavior of \( \rho_c(t) \). Because of the asymptotic neighborhood of the behavior of the critical size to its behavior is the LS model these characteristics are close to the results of the LS technique.

Now we turn to the justification of the similarity of the form of the size spectrum in the LS technique and the spectrum established in this theory. Until \( u \approx u_m \) or \( \rho_0 \approx u_m \rho_c \) there is no spectrum in the LS theory. In the current theory the situation is analogous - the tail is very short.

Now we investigate the region \( u \approx u_m \). Since \( u_m \) is big the rate of growth \( dp/dt \) is close to the asymptotic value, i.e. to the constant velocity and the tail in the current model will be close to the exponential one. But what will be in the LS theory? We turn to the formula

\[
\theta(\tau - \tau(u)) = g(\exp(\tau - \tau(u)))
\]

which can be rewritten with account of an initial form of the size spectrum as

\[
\theta(\tau - \tau(u)) = \exp(const(\tau - \tau(u)))
\]

Having recall that

\[
\tau(u) = -\int_0^u \frac{du}{v_u} + const
\]

which gives under the constant value of \( v_u \) the evident relation near the maximum

\[
\tau(u) \sim u + const
\]

we see that the dependence of \( \theta \) on \( u \) (\( \tau \) is fixed but it is excluded) becomes the exponential one.

Certainly here the derivation differs from the LS analysis and we ignore the change of \( v_m \) in time which can be very essential. But qualitatively we come to the same results.

The distributions in the region with small \( u \) are formed both in the LS theory and here by the dissolution of the exponential spectrum. They are, hence, similar.

When one neglects \( \gamma u \) in comparison with \((1 - u^{-1})\) it means that we neglect the change of the height of the original spectrum because the time of the dissolution of the given embryo from the size \( u \sim u_m \) is small and the change of the critical size during this time is small. This simplification is quite possible.
So, both distributions (in the LS theory and the derived here) are similar in their dorm. The similarity is ensured by the narrowness of the tail of the size spectrum. Namely the situation of the narrow tail is the dominating one in the evolution scenario. So, the similarity is the occasional coincidence corresponding to the initial exponential form of the size spectrum tail. But namely this coincidence leads to the experimental confirmation of the LS technique.

Later we return to the situation of the wide tail. Every wide tail as the narrow tail is also local in the size axis and, hence, there is the backlash in dependence of $v_u$ on time. The tail can be approximated in frames of the steepest descent method by an exponent. So, the style to construct the solution will remain the same. Hence, everything is reduced to the already analyzed situation.

One can see the following stabilizing property - the wider is the tail, the wider is the backlash and the local character is approximately conserved. This property is very important - it is responsible for the observation of the LS-like spectrum already at the moderate time.

Here the free molecular regime is adopted, this allows to write the balance equation in the integral form. The opposite case is the case of the profiles of metastability around the embryos. In this case one has to take into account the interactions between these profiles. The task seems to be extremely complex. Nevertheless the answer for the form of the size distribution is very simple. Certainly this answer is rather approximate.

Really, one can propose the following model. Since the profiles are sharp functions of the space coordinate one can imagine only the pair interactions. Such a pair battle will end by defeat on one of partners. The winner will continue to be the embryo of a new phase, the looser disappears. At the asymptotics of evolution the remaining embryo had to win many battles. With probability $p_1$ it wins the first battle, with probability $p_i$ it wins the $i$-th battle. The total probability $P_{tot}$ to win all battles is the product $\Pi_i p_i$ of all probabilities. Since $p_i$ are independent stochastic values we have for $P_{tot}$ the log-normal distribution.

Certainly this approach can be spread to the group interactions (triple, etc.) which will give the same final result.
5 Development of the model

Now we can note several important properties of the size spectrum. The first property concerns the influence of the boundary condition on the tail of the size spectrum. Consider

\[ f = -f_- + f_+ \]

\[ f_- \sim \exp(- (x + x_0)^2 / 4Dt) \]

\[ f_+ \sim \exp(- (x - x_0)^2 / 4Dt) \]

Then

\[ f_- \sim \exp(-x^2 / 4Dt) \exp(-2xx_0 / 4Dt) \exp(-x_0^2 / 4Dt) \]

\[ f_+ \sim \exp(-x^2 / 4Dt) \exp(2xx_0 / 4Dt) \exp(-x_0^2 / 4Dt) \]

\[ f_+ / f_- \sim \exp(4xx_0 / 4Dt) \]

and one can take into account in the tail only the term \( f_+ \).

One can add that the regular growth can not destroy the tail - one can speak only about the shift of the tail and the sequential cut-off of the regions preceding the tail.

The second property is the possibility to sweep out the boundaries between stages in the sequential description of the evolution. Really, does the diffusion stop after the end of diffusional blurring? Certainly, it continues and the time of diffusional blurring depends on the amplitude of the spectrum, i.e. of the rest of the tail.

One can note the following important feature - The tail blurring is so fast that it can not be overcome by the regular growth. So, the time of diffusion blurring is important and the diffusion process occurs during the whole time of evolution.

Now we specify the recipe of calculations for concrete case. We shall explicitly see what effect has the relatively small backlash in the law of growth.

5.1 Explicit calculations

We start from the law of growth

\[ \frac{dp}{dt} = \frac{\zeta}{t_1}(1 - u^{-1}) \]
for \( u = \rho / \rho_c \). Since
\[
\frac{d\rho}{dt} = \frac{d\rho_c u}{dt} = \rho_c \frac{du}{dt} + u \frac{d\rho_c}{dt}
\]
we see that
\[
\frac{du}{dt} = \frac{1}{\rho_c} \frac{\zeta}{t_1} (1 - u^{-1}) - u \frac{d\rho_c}{\rho_c} \frac{dt}{dt}
\]
Since
\[
\zeta = \frac{2a}{3\rho_c}
\]
we come to
\[
\frac{du}{dt} = \frac{2a}{3\rho_c^2 t_1} (1 - u^{-1}) - u \frac{d\rho_c}{\rho_c} \frac{dt}{t_1}
\]
or
\[
\frac{3\rho_c^2 t_1}{2a} \frac{du}{dt} = (1 - u^{-1}) - 3\rho_c t_1 \frac{d\rho_c}{2a} \frac{dt}{dt}
\]
We introduce \( \tau \) to have
\[
\frac{2a}{3\rho_c^2(t) t_1} dt = d\tau
\]
and then
\[
\frac{du}{d\tau} = (1 - u^{-1}) - \frac{1}{\rho_c} \frac{d\rho_c}{d\tau} u
\]
or
\[
\frac{du}{d\tau} = (1 - u^{-1}) - \frac{d\ln \rho_c}{d\tau} u
\]
So,
\[
\gamma = \frac{d\ln \rho_c}{d\tau}
\]
Now we find the argument \( u_m \) which provides maximum for the rate of growth \( du/d\tau \), i.e. the maximum of the curve \((1 - u^{-1}) - \gamma u\). Having differentiated \( du/d\tau \) on \( u \) we have
\[
\frac{d}{du}[(1 - u^{-1}) - \gamma u] = u^{-2} - \gamma
\]
Then
\[
u_m = \gamma^{-1/2}
\]
The height of the curve \((1 - u^{-1}) - \gamma u\) will be
\[
\frac{du}{d\tau} \bigg|_{max} = 1 - 2u_m^{-1}
\]
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It has to be zero or some small negative value $-\delta$. Namely $\delta$ is the backlash. Then

$$1 - 2u_m^{-1} = -\delta$$

and

$$u_m = \frac{2}{1 + \delta}$$

$$\gamma = \frac{(1 + \delta)^2}{4}$$

Now we reconstruct the dependence of $\rho_c$ on $t$ based on the known value of $\gamma$. We have

$$\frac{(1 + \delta)^2}{4} = \frac{d\ln\rho_c}{d\tau}$$

or

$$\frac{3t_1}{4a} \frac{d^2\rho}{dt^2} = \frac{(1 + \delta)^2}{4}$$

Then

$$\rho_c^2 \sim \frac{a}{3t_1} (1 + \delta)^2 t$$

or

$$\left(\frac{2a}{3\zeta}\right)^2 \sim \frac{a}{3t_1} (1 + \delta)^2 t$$

Then the supersaturation satisfies the asymptotic behavior

$$\zeta \approx \sqrt{\frac{4at_1}{3(1 + \delta)^2 t}}$$

### 5.2 Contradiction in asymptotics

Now we can see the concrete picture for the approximate law of growth. The asymptotics $1 - \gamma u$ at big $u$ crosses the axis $du/d\tau = 0$ at

$$u = \gamma^{-1} = \frac{4}{(1 + \delta)^2}$$

The level of the backlash $-\delta$ it crosses at

$$u_r = (1 + \delta)\gamma^{-1} = \frac{4}{(1 + \delta)}$$
The asymptotics $1 - u^{-1}$ for the rate of $u$ growth at small $u$ crosses the axis at

$$u = 1$$

and crosses the level of the backlash at

$$u_l = (1 + \delta)^{-1}$$

So, the approximate rate of growth is constructed. One has to take into account that the backlash $-\delta$ can be also the function of time $t$ or $\tau$.

Now we analyze the asymptotic behavior of big $u$. We have

$$\frac{du}{d\tau} \sim 1 - \gamma u \sim -\gamma u$$

Then

$$\ln u \sim -\gamma \tau \quad u \sim \exp(-\gamma \tau)$$

Now we can explicitly express $\tau$ on $t$ based on the known asymptotics $\rho_c$.

Really,

$$\frac{2a}{3\rho_c^2 t_1}dt = d\tau$$

or

$$\frac{2a}{3\left(\frac{at}{3t_1}\right) t_1}dt = d\tau$$

Then

$$\frac{2}{t}dt = d\tau$$

and

$$2\ln t \sim \tau$$

Then the asymptotics for $u$ in $t$-scale will be

$$u \sim \exp(-\gamma \tau) \sim t^{-2\gamma} \sim t^{-1/2}$$

Now we can see what will be the diffusional blurring $\exp(-\text{const} \ s^2/t)$. We see that

$$\exp(-\text{const} \ s^2/t) \sim \exp(-\text{const} \ \rho_c^2 u^2/t) \sim \exp(-\text{const} \ \frac{a}{3t_1}tt^{-1}/t)$$

and it seems that the diffusion blurring is the main effect. It is no more than an error. The reason is that $s$ does not grow here. Really, $\rho = \rho_c u \sim$
$t^{1/2}t^{-1/2} = const$ does not grow. This occurs because we throw away the negligible constant in the law $du/d\tau = 1 - \gamma u$. But the effect of non-zero growth of $\rho$ manifests in the constant $1$ in this law. Certainly, it will be lost in comparison with the leading term. So, we see that the variables in LS theory are very dangerous. It is forbidden to choose new irregular variables and then fulfill the asymptotic analysis.

As for the smallness of diffusional blurring one can easily see it directly. Since $d\rho/dt = \zeta/t_1$ and we already know that $\zeta \sim t^{-1/2}$ then the integration gives $\rho \sim t^{1/2}$ and $s^2 \sim t^2 \gg t$. This shows the smallness of diffusional blurring.

One can take into account the modifications of the model

- At the tail of the diffusion gaussian the regular shift is not very important.
- The initial diffusional blurring does not stop at the beginning of the regular dissolution of the tail but takes place all time long.

In the LS approach it is used that all substance is in the region less than $u_m$ without justifications. Here we shall show the analogous fact (all substance is near $u_m$) explicitly. This fact has to correspond to the smallness of the diffusion blurring. We have to show this smallness. Really, the width $s^2 \sim t$ of the diffusion blurring is many times less than the critical size $\rho_c \sim t^{1/2}$ since $s \sim \rho^2$.

### 5.3 Modifications of the model

The balance equation is the main instrument to determine the evolution of the system. It can be written in the following form

$$\rho_c^3 \int_0^\infty u^3 \phi(u, \tau) du = const$$

Precisely speaking one has to add the the supersaturation as $2a/3\rho_c$ and get

$$\frac{2a}{3\rho_c} + \rho_c^3 \int_0^\infty u^3 \phi(u, \tau) du = const$$

but the first term goes to zero. In any case it is impossible to determine the critical size from the last equation having calculated the integral term in some approximation.
We see that in analysis of the balance equation lies a dangerous possibility to get wrong results. This possibility is extremely high in the LS analysis where the size spectrum has to cancel divergence of the critical size asymptotic behavior.

To see the behavior of $\rho_c$ we have to establish the form of $\phi$ at least in the asymptotics. We write

$$\phi(u, \tau) \to \phi_{as}(u, t)$$

where $\phi_{as}$ is defined at big $u$ from the gaussian (one can show that the back side gaussian is not important here). Namely, we have the following chain of equalities

$$\phi_{as}(u, \tau)du = f(\rho, \tau)d\rho$$

$$f(\rho, \tau)d\rho = \Psi(s, \tau)ds$$

$$\Psi(s, \tau) \sim \exp\left(-\frac{s^2}{4D_s t(\tau)}\right)$$

where $s$ is $\rho^2$, $D_s$ is the diffusion coefficient over $s$ (known value).

Roughly speaking the problem is solved. But we can not combine the values of $u$, $\rho_c$ and $\tau$ until we integrate the law $du/d\tau = (1 - u^{-1}) - \gamma u$ of growth. Fortunately we can not do this with $\gamma$ varying in time. So, it is necessary to introduce approximations for this law of growth. This has been done above. Actually we are interested now in the size spectrum for the values $u > u_r$. Then we have

$$u = \tilde{u} + \int_{\tau(t_0)}^{\tau(t)} \left(\frac{du}{d\tau}\right)d\tau = \tilde{u} + \int_{\tau(t_0)}^{\tau(t)} (1 - \gamma u)d\tau$$

where $\tilde{u}$ is the size of $u$ at $t_0$. Here $t_0$ is the time when the diffusion transforms into the regular motion and $\tilde{u}$ is the corresponding size. The value of $\tilde{u}$ can be found on the base of $u, \tau$ and the initial value, then we take the initial size spectrum at $\tilde{u}$ and get the size spectrum for $u$ at $\tau$.

Very approximately we can substitute the law

$$\frac{du}{d\tau} = 1 - \gamma u$$

by

$$\frac{du}{d\tau} = -\gamma u$$

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This gives
\[ u = \tilde{u} \exp(- \int_{\tau(t_0)}^{\tau(t)} \gamma(\tau) d\tau) \]
or
\[ \tilde{u} = u \exp(\int_{\gamma(t_0)}^{\gamma(t)} \gamma(\tau) d\tau) \]

But as we have seen earlier this leads to an error. Fortunately we can integrate already \( du/d\tau = 1 - \gamma(\tau)u \) explicitly without simplification (formulas will be long).

On the base of \( \tilde{u} \) one can find
\[ \tilde{\rho} = \tilde{u} \rho_c(t_0) \]
and then \( \tilde{s} \) equal to \( \tilde{\rho}^2 \).

For the distribution in \( \tilde{\rho} \)-scale it is very easy to write the gaussian
\[ G \sim \exp\left(-\frac{\tilde{\rho}^4}{D_s t(\tau)}\right) \frac{d\rho}{ds} \approx \exp\left(-\frac{\tilde{\rho}^4}{D_s t(\tau)}\right) \]

Here we ignore the jacobians arrived from transition from \( s \) to \( \rho \) scale because \( \exp(-constx^4) \) at the tail is a very sharp function. We shall ignore them below also.

We are interested now in behavior at \( u \approx u_r \). Here the true approximation will be
\[ \frac{du}{dt} = c_1 - \gamma u \]
\[ c_1 = 1 - u_r^{-1} \]
Let us take \( \gamma \approx \gamma_B = \gamma(t_B) \) (\( t_B \) is the time when \( u_r \) is attained).

Then
\[ \ln\left[\frac{u - c_1/\gamma_B}{\tilde{u} - c_1/\gamma_B}\right] = -[\tau(t) - \tau(t_0)]\gamma_B \]
So,
\[ u - c_1/\gamma_B = (\tilde{u} - c_1/\gamma_B) \exp(-\gamma_B(\tau(t) - \tau(t_0))) \]
and \( \tilde{u} \) is \( u \) at \( t_0 \). As the result we know \( \tilde{u} \) as a function of \( u \), i.e. \( \tilde{u} = F(u) \).

In any case we can integrate the equation with \( \gamma = \gamma(\tau) \) since we have the first order linear differential equation. This will give the real true result with rather long formulas. So, we use the previous formulas keeping in mind the necessity to apply the formulas with varying \( \gamma \).
Now we can see the asymptotics for the distribution function

$$
\phi(u, \tau) \sim \exp\left(-\tilde{u}(u)\rho_c^4 \frac{c_1 - \gamma_B \tilde{u}(u)}{c_1 - \gamma_B u}\right)
$$

This result is for \( u \geq u_r \).

One of important properties of this solution is the weak dependence of the form (after scaling) of the size spectrum on \( \tau \). The quantity of substance in the region \([u_r, \infty)\) can be found as

$$
G_\varphi = \rho_c^3 \int_{u_r}^{\infty} u^3 \phi(u, \tau) du
$$

Now we shall analyze the region \([u_l, u_r]\). The values at this region are marked by the subscript \( = \). Here

$$
du \over d\tau = -\delta
$$

Then

$$
\phi(u, \tau) = \phi = (u, \tau) = \phi(u_r, \hat{\tau}) \frac{du_r(\hat{\tau})}{du(\hat{\tau})}
$$

where \( \hat{\tau} \) is defined as

$$
u = \hat{u} - \int_{\hat{\tau}}^{\tau} \delta(\tau') d\tau'
$$

which is a rather complex closure. The previous equation can be rewritten as

$$
\phi(u, \tau) = \phi = (u, \tau) = \phi(u_r, \hat{\tau}) \frac{\delta(\hat{\tau})}{\delta(\tau)}
$$

More rigorous is to make a shift of \( u_r \) to exclude a slow evolution right of \( u_r \). But this does not change the qualitative behavior.

The quantity of substance \( G_\varphi \) in this region is given by

$$
G_\varphi = \rho_c^3 \int_{u_l}^{u_r} u^3 \phi = (u, \tau) du = \rho_c^3 \int_{u_l}^{u_r} u^3 \phi(u_r, \tau) \frac{\delta(\tau_r)}{\delta(\tau)} du
$$

Here

$$
u_r = u + \int_{\tau_r}^{\tau} \delta(\tau'') d\tau''
$$
Now we investigate the region $[0, u_l]$. The values at this region will be marked by the subscript $\textless$. Here the size spectrum can be given by

$$
\phi(u, \tau) = \phi(u_l, \tau') \frac{\delta(\tau')}{1 - u^{-1}}
$$

The quantity of substance is given by

$$
G_\textless = \rho \int_{u_l}^{0} u^3 \phi(u_l, \tau') \frac{\delta(\tau')}{1 - u^{-1}} du
$$

Here

$$
\tau - \tau' = \int_{0}^{u_l} \frac{du}{1 - u^{-1}}
$$

The unknown function is $\delta(t)$.

All quantities of substance $G_\textless, G_\text{=} , G_\textgreater$ have to be substituted into the balance equation which gives the equation on $\delta(t)$ with the known coefficients.

### 5.4 Steepest descent procedure

Now we shall discuss the ways to solve this equation. At first we have to get a true algebraic equation. We differentiate the balance equation on time and get

$$
\frac{d(G_\textless + G_\text{=} + G_\textgreater)}{d\tau} = 0
$$

Then we use concrete approximations to get $dG_\textless/d\tau$, $dG_\text{}/d\tau$, $dG_\text{=} /d\tau$.

For $dG_\textgreater /d\tau$ we see that the subintegral function is the product of the three functions:

1. the moderate function $3u^2$,

2. the rapidly growing function for the absolute value of the rate of growth $du/d\tau$. This function becomes very small at $u_r$ (practically it is zero).

3. the rapidly decreasing function for the initial size spectrum. This function decreases in the main term even faster than $\exp(-x^4)$ and even being multiplied by the accelerating rate of growth and by $u^2$ the product goes to zero at big $u$.  

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So, one can effectively use the steepest descent method.

For \( dG_\tau/d\tau \) we have a simple expression which is approximately proportional to the size spectrum multiplied on \( 3u^2\delta \) and due to the rapid decrease of the size spectrum we see that the subintegral function is the rapidly decreasing function of \( u \). This is the ideal situation for the application of the steepest descent method with the maximum at the boundary point (here it is \( u_l \)).

For \( dG_{<}/d\tau \) we have the integral with the subintegral function at the interval \([0, u_l] \), which is the product of three rapidly varying functions:

1. The function \( 3u^2 \) which goes to zero at \( u = 0 \),
2. The function \( du/d\tau \sim 1 - u^{-1} \) which goes to infinity at \( u = 0 \) while \( u^2(du/d\tau) \) goes to zero at \( u = 0 \),
3. the rapidly decreasing size spectrum.

This provides good conditions for the application of the mentioned steepest descent method with the point of decomposition inside the interval.

The problem which can appear here is a too sharp form of the size spectrum which can cause the maximum of the subintegral function at \( \rho = u\rho_c \) which is too small. Fortunately when such sharp size spectrum will come to the region \([0, u_l] \) the decrease of the substance in embryos will cause the decrease of \( \rho_c \). It means that until the diffusion blurring the spectrum will not be dissolved. This situation is typical for the formation of the new head which has been discussed in [8].

The mentioned approximations lead to the algebraic equation on \( \delta \). This equation allows the further simplification if we decompose \( \delta(\tau) \) in Taylor’s series on inverse time \( \xi = \tau^{-1} \)

\[
\gamma(\xi) = \gamma_0 + \sum_j a_j \xi^j
\]

with coefficients \( a_j \). The choice of \( \xi \) as a variable is recommended by the structure of the correction term in the LS procedure. Also one can use decomposition near some value \( \xi_0 \)

\[
\gamma(\xi) = \gamma(\xi_0) + \sum_j a_j (\xi - \xi_0)^j
\]

The last modifications make the analysis of the evolution a technical task.
6 Situation of wide tails

Now we shall analyze the situation of the wide tails of the size spectrum. It means that the half-width of the size spectrum in the region $\rho > \rho_r$ is many times greater than $\rho_c$. It is clear that the approximate law of growth $du/d\tau = 1 - \gamma u$ corresponds to the law of growth $d\rho/dt = \zeta/t_1$ and the distribution function moves as a whole along $\rho$-axis. The critical size $\rho$ moves faster (but with the same time dependence $t^{1/2}$) and eats the spectrum sequentially. For all distribution tails (here we take the tail multiplied by the number of molecules in the droplet $\rho^3$) which decrease like $1/\rho^i$ with $i$ greater than 1 the relative half-width will decrease. But the situation with $i < 1$ do not ensure the finite substance, it is forbidden situation. So, earlier or later the tail will be narrow. One can speak, thus, only about the intermediate asymptotics.

Since here the width remains greater than the critical radius one can speak about another asymptotic behavior, at least the intermediate asymptotic corresponding to the wide spectrum can be observed.

Kinetics of the process here will differ from the LS case. All the time the main consumers of the metastable phase substance will be the big embryos and the backlash here is very wide. The asymptotic

$$\tau(u) = \gamma \ln u$$

ensures the infinite time of the embryos dissolution for the infinitely big embryos. Then the main supposition in the LS theory fails. This argument states that to keep the balance of the substance it is impossible that some relative size will only grow and it is impossible that all relative sizes will decrease. But now it is possible to see here the situation where all sizes decrease rather intensively but the main consumers of the vapor are the big embryos with $u$ many times greater than $u_m$. In the zero approximation the evolution is very simple - the size spectrum is cut-off by the critical size (for the sizes less than the critical one the dissolution is so rapid that we can speak about the instantaneous dissolution and neglect this region). This cut off corresponds to the conservation of the substance in the system.

Define that here the size spectrum $f_{long}(\rho)$ has the characteristic width $\Delta(f_{long})$ determined in the integral way as

$$\int_0^\infty f_{long}(\rho)d\rho = f_{long}^{max}\Delta(f_{long})$$
where \( f_{\text{long}}^{\text{max}} \) is the amplitude of the size spectrum, or in the differential way as

\[
f_{\text{long}}^{\text{max}}(\rho_m + \Delta(f_{\text{long}})) = f_{\text{long}}^{\text{max}} / \exp(1)
\]

where \( \rho_m \) is the argument for the amplitude value of spectrum. This width satisfies the strong inequality

\[
\Delta(f_{\text{long}}) \gg \rho_c
\]

The substance balance here is written as

\[
\Phi = \zeta + q_+
\]

where \( \Phi \) is the supersaturation without the embryos formation, \( q_+ \) is the substance in the tail which can be calculated as

\[
q_+ = \int_{\rho_c}^{\infty} f_{\text{long}}(\rho)\rho^3 d\rho \approx \int_{(2/3)\rho_c}^{\infty} f_{\text{long}}(\rho)\rho^3 d\rho
\]

Then in the last integral we can take for \( f_{\text{long}} \) the size spectrum fully determined by the supercritical law of growth from the "initial" spectrum \( f_0 \) (at the time \( t_{\text{init}} \)):

\[
f_{\text{long}}(\rho, t) = (\zeta(t_{\text{init}})/\zeta(t))f_0(\hat{\rho}(t, t_{\text{init}}))
\]

where \( \hat{\rho}(t, t_{\text{init}}) \) is determined from

\[
\rho = \int_{t_{\text{init}}}^{t} \zeta(t')/t_1 dt' + \hat{\rho}(t, t_{\text{init}})
\]

It is more convenient to study the initial spectrum and to see how much this spectrum is cut off. So, we introduce the initial \( \rho \)-size variable \( s \) and write a balance equation

\[
\Phi = \zeta(t) + \int_{s_c}^{s_c} \varphi(s)^3 f_0(s) ds
\]

Here \( s_c \) is the initial size of the variable \( s \) which attains at \( t \) the size \( (2/3)\rho_c \), \( \varphi(s) \) is the size which will be attained at \( t \) by the embryo with initial size \( s \)

\[
\varphi(s) = s + \int_{t_{\text{init}}}^{t} \zeta(t')/t_1 dt'
\]

The balance equation can be rewritten as

\[
\Phi = \zeta(t) + \int_{s_c}^{s} \int_{t_{\text{init}}}^{t} \frac{\zeta(t') \varphi(s)}{t_1 dt'} > (2/3) \frac{\varphi(s)^3 f(s) ds}{\pi(t)}
\]

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or since \((2 \div 3)\frac{2a}{x_t(t)}\) has to be many times smaller than the width of the spectrum then

\[
\Phi = \zeta(t) + \int_{s+\int_{t_{\text{init}}}^{t}} \frac{\varphi(t')}{x_t(t')} dt' > 0 \varphi(s)^3 f_0(s) ds
\]

Having noticed that \(s\) has to be at least positive we get the following modification of the balance equation

\[
\Phi = \zeta(t) + \int_{s>0} \varphi(s)^3 f_0(s) ds
\]

This equation can be easily solved. Having introduced the explicit equation for \(\varphi\) we come to

\[
\Phi = \zeta(t) + \int_{s>0} (s + \int_{t_{\text{init}}}^{t} \frac{\zeta(t')}{t_1} dt')^3 f_0(s) ds
\]

One can see that the integral term is the polynomial on

\[
\rho_m = \int_{t_{\text{init}}}^{t} \frac{\zeta(t')}{t_1} dt'
\]

Then

\[
\Phi = \zeta(t) + \sum_{i=0}^{3} \frac{3!}{i!(3-i)!} a_i \rho_m^{3-i}
\]

with known constants

\[
a_i = \int_{0}^{\infty} s^i f_0(s) ds
\]

It can be rewritten as

\[
\Phi = t_1 \frac{d\rho_m}{dt} + \sum_{i=0}^{3} \frac{3!}{i!(3-i)!} a_i \rho_m^{3-i}
\]

The last equation is the differential Abel equation - the ordinary first order differential equation. Since there is no explicit dependence on the argument this equation can easily integrated. This gives the solution of the problem.

Certainly, the last solution is not accurate because there all embryos remain in the integral term - they remain supercritical ones. This leads to the qualitatively wrong behavior. It is clear that the error will be essential namely when the tail stops to be really the wide tail. But nevertheless it is
possible to take into account the dissolution of the embryos. The balance equation has to be written as

$$\Phi = \zeta(t) + \int_{s > (2\pm 3)2a/3\zeta} (s + \int_{t_{\text{init}}}^{t} \frac{\zeta(t')}{t_1} dt')^3 f_0(s) ds$$

and conserves the polynomial structure on $\rho_m$.

$$\Phi = \zeta(t) + \int_{s > (2\pm 3)2a/3\zeta} (s + \rho_m)^3 f_0(s) ds$$

or

$$\Phi = \zeta(t) + \sum_j \rho_j^m \frac{3!}{j!(3-j)!} \int_{s > (2\pm 3)2a/3\zeta} s^{3-j} f_0(s) ds$$

Now the coefficients

$$a_j = \frac{3!}{j!(3-j)!} \int_{s > (2\pm 3)2a/3\zeta} s^{3-j} f_0(s) ds$$

are known (since the initial size spectrum is known) functions of $\zeta$. But it is possible to solve this equation on $\rho_m$ as the third power algebraic equation

$$\rho_m = F(\zeta)$$

or

$$\rho_m = F(t_1 \frac{d\rho_m}{dt})$$

with a known function $F$. With the help of the inverse function $F^{-1}$ we can write

$$\frac{d\rho_m}{dt} = t_1^{-1} F^{-1}(\rho_m)$$

The last equation can easily solved.

Now we take into account the growth of the embryos. The balance equation has to be written as

$$\Phi = \zeta(t) + \int_{s+\rho_m > (2\pm 3)2a/3\zeta} (s + \int_{t_{\text{init}}}^{t} \frac{\zeta(t')}{t_1} dt')^3 f_0(s) ds$$

and does not conserve the polynomial structure on $\rho_m$. It can be written analogously

$$\Phi = \zeta(t) + \sum_j \rho_j^m \frac{3!}{j!(3-j)!} \int_{s+\rho_m > (2\pm 3)2a/3\zeta} s^{3-j} f_0(s) ds$$
or in the standard form but with the coefficients

\[ a_j = \frac{3!}{j!(3-j)!} \int_{s+\rho_m>(2+3)2a/3\zeta} s^{3-j} f_0(s) ds \]

depended (since the initial size spectrum is known) on \( \rho_m \) and \( \zeta = t_1d\rho_m/dt \). So, we have the first order differential equation without explicit dependence on the argument \( t \)

\[ \Psi(\rho_m, d\rho_m/dt) = 0 \]

This equation can be integrated when we can express \( d\rho_m/dt \) via \( \rho_m \). This is an algebraic problem which can be solved at least locally in a good approximation.

7 Approximations in the explicit construction the size spectrum

The first task in construction of the size spectrum is the construction of initial distribution which will be later gradually dissolved during the over-condensation. This task is very complex. Even the elementary approximate blocks for solution do not allow the solution. We do not know the solution of the diffusion equation for the diffusion blurring of the spectrum even with the stationary value of the supersaturation. As the result of such difficulties only very approximate methods can be formulated.

To see the initial distribution it is more easy to use the \( \rho \)-scale because in this scale the asymptotic law of growth is rather simple and the velocity of growth contrary to the \( u \)-scale does not go to infinity.

The first approximate model, which allows solution is "the model of sequential evolution". We consider the period of the initial diffusion blurring. Here we have the stationary supersaturation (and the critical radius).

Consider the value of distribution at some \( \rho_f \), time being fixed. Let the initial distribution be \( \delta \)-function at \( \rho = \rho_c \). The route from \( \rho_c \) to \( \rho_f \) will be split between the diffusion blurring and the regular growth. In this model the blurring occurs up to \( \rho \) equal to some parameter \( \rho_b \). Later there will be the pure regular growth. Parameter \( \rho_b \) is reasonable to put equal to \( 2\rho_c \).

The time of the regular growth up to \( \rho_f \) will be \( (\rho_f - \rho_b)t_1/\zeta \) or \( (\rho_f - \rho_b)t_13\rho_c/2a \). Then the time to quit the diffusion blurring will be

\[ t_q = t - (\rho_f - \rho_b)t_13\rho_c/2a \]
The supercritical regular growth is the simple translation of the size spectrum, then we have to calculate the spectrum at $\rho_b$ and $t_q$ after the pure diffusion blurring (here for simplicity we do not consider the back side input $f_-$)

$$v(\rho_f, t) \sim \frac{2\rho_b}{\sqrt{4D_s t}} \exp\left(-\frac{\rho_b^4}{4D_s t_q}\right) = \frac{2\rho_b}{\sqrt{4D_s t}} \exp\left(-\frac{\rho_b^4}{4D_s(t - (\rho_f - \rho_b)t_13\rho_c/2a)}\right)$$

The function $v$ can be considered as the initial size spectrum. The problem is, thus, solved.

But the function $v$ has a certain disadvantage - the size spectrum is finite. Really, for $\rho_f$ greater than $\rho_{lim}$

$$\rho_{lim} = \rho_b + 2at/t_13\rho_c$$

the spectrum is zero.

Actually the values of $\rho$ near $\rho_{lim}$ begin to dissolve (i.e. $\rho_{lim}$ is near $\rho_r$) when the amplitude of the rest of the spectrum is extremely small. So, the relative quantity of droplets in negligibly small. It will be big only in the systems of cosmological sizes.

Nevertheless one can refine this solution. Fortunately, the diffusion process can be easily estimated even with the varying $\rho_c$ because here $\zeta$ is very small and the average number of collisions in the time unit will be $(2/t_1)(3\rho^2(t))$. Here we can take $\rho$ on the base of the regular growth and get the total number of collisions

$$n_{tot} = \int_0^t 6\rho^2(t')dt'/t_1$$

The characteristic width $\Delta_{tot}$ can be estimated as $\Delta_{tot} = \sqrt{2n_{tot}}$ with a sufficient accuracy.

Then the resulting distribution will be proportional to

$$\hat{v} = \int_{-\infty}^\infty \exp\left(-\frac{(\rho - \rho_f)^2}{2n_{tot}}\right)\hat{v}(\rho_f, t)d\rho_f$$

or

$$\hat{v} = \frac{2\rho_b}{\sqrt{4D_s t}} \int_{-\infty}^\infty \exp\left(-\frac{(\rho - \rho_f)^2}{2n_{tot}}\right) \exp\left(-\frac{\rho_b^4}{4D_s(t - (\rho_f - \rho_b)t_13\rho_c/2a)}\right)d\rho_f$$
It is quite satisfactory here to consider only the right hand wing of the distribution, i.e. to put $\rho > \rho_f$. Since the subintegral function is the product of exponents it is reasonable to use the steepest descent method.

The required result is attained by a simple combination of the regular growth and the pure diffusion. The cross effects when, for example, the stochastic increase of the embryos size leads to increase of the regular rate of growth are missed here. They can be included into consideration by consideration of the effective half-width of the diffusion blurring and the shift in regular growth proposed in [9]. Certainly, they have to be slightly reconsidered since now we start not from the very beginning of the size axis.

Now we shall show the primitive approximate way to construct the explicit form of the size spectrum for the narrow tail.

The initial distribution is supposed to be known.

We approximate the rate of growth for $u$ in rescaled time $\tau$ by the following approximation

$$\frac{du}{d\tau} \approx v_m \equiv \max\{\frac{du}{d\tau}\} = -\delta(\tau)$$

for $u \in [u_l, u_r]$.

$$\frac{du}{d\tau} \approx 1 - \gamma u$$

for $u > u_r$,

$$\frac{du}{d\tau} \approx 1 - u^{-1}$$

for $u < u_l$.

Parameters $u_l$ and $u_r$ have to be chosen to ensure the continuity of the whole approximation.

Consider $u > u_r$. The law of growth for $\rho$ corresponding to $du/d\tau \sim (1 - \gamma u)$ is $d\rho/dt = \zeta/t_1$ (the r.h.s. is precisely taken into account by transition from $t$ to $\tau$). So, the distribution in $\rho$-scale is moving as a whole without changing of the form. We know this form - it is exponential form

$$f(\rho) \sim \exp(-\alpha \rho)$$

with some parameter $\alpha$.

Then the distribution $\varphi$ over $u$ is connected with $f$ by the following relation

$$\varphi(u) = f(\rho) \frac{d\rho}{du}$$
Having inserted the explicit relations for the derivatives we come to

\[ \varphi(u) = f(\rho) \frac{1 - u^{-1}}{(1 - u^{-1}) - \gamma u} \]

or in the supercritical limit

\[ \varphi(u) = f(\rho) \frac{1}{1 - \gamma u} \]

Here the distribution function is even sharper than the distribution over \( \rho \).

Now at first we shall assume that the backlash is changing in time slowly in comparison with the time of dissolution of an embryo from \( u_r \) to \( u_l \). This case will be at least the base approximation for iteration procedures to refine the solution.

The known solution in the region \( u > u_r \) leads to the known rate of appearance \( \Psi_b(\tau) \) at \( u = u_r \). This value is given by

\[ \Psi_b(\tau) = \varphi(u)|_{u=u_r} \frac{du}{d\tau}|_{u=u_r} = \varphi(u)|_{u=u_r} v_m \]

Here \( \varphi \) is the distribution over \( u \). Now it can be established. One can easily show that \( \Psi_b(\tau) \) at \( u = u_r \) is sharp decreasing function of \( \tau \).

The last function is the source at the left side of the central interval \([u_l, u_r]\). Now it is possible to solution at this interval. This solution is very simple and it is given by

\[ \varphi(u, \tau) = \Psi_b(\tilde{\tau})/\frac{du}{d\tau}|_{u=u_r} \]

or

\[ \varphi(u, \tau) = \Psi_b(\tilde{\tau})/v_m \]

The time \( \tilde{\tau} \) satisfies relation

\[ u - u_r = \int_{\tilde{\tau}}^{\tau} v_m(t')dt' \approx v_m(\tau - \tilde{\tau}) \]

Hence, the solution in the central region is constructed.

Generalization for the varying \( \delta \) is rather simple. The rate of appearance \( \Psi_b(\tilde{\tau}) \) at \( u = u_r \) is given by

\[ \Psi_b(\tilde{\tau}) = \varphi(u|\tilde{\tau})|_{u=u_r} v_m(\tilde{\tau}) \]
Here $\varphi$ is the distribution over $u$. Now it can be established.

The last function is the source at the left side of the central interval $[u_l, u_r]$. Now it is possible to solution at this interval. This solution is very simple and it is given by

$$\varphi(u, \tau) = \Psi_b(\tilde{\tau})/v_m(\tau)$$

and

$$\tilde{\varphi}(u, \tau) = \varphi(u|\tilde{\tau})|_{u=u_r(\tilde{\tau})}v_m(\tilde{\tau})/v_m(\tau)$$

The time $\tilde{\tau}$ satisfies relation

$$u - u_r = \int_{\tau}^{\tilde{\tau}} v_m(\tau')d\tau' \neq v_m(\tau - \tilde{\tau})$$

Now only the last region - the region of small $u < u_l$, has to be investigated. Here the solution is also rather simple - it is the simple translation of the source from $u_r$ under the law of growth independent on $\gamma$. Here all constructions are analogous to the previous case but the transition over the central region has to be taken into account.

The distribution $\varphi$ is given by

$$\varphi(u, t) \sim \Psi_a(\hat{\tau})/(du/d\tau) \sim \Psi_a(\hat{\tau})/(1 - u^{-1})$$

where

$$\Psi_a(\hat{\tau}) = \tilde{\varphi}(u_l(\hat{\tau}), \hat{\tau})v_m(\hat{\tau})$$

Here $\hat{t}$ is determined by the following way

$$\hat{\tau} - \tilde{\tau} = \int_{u_l}^{u_r} \frac{1}{v_m} du$$

and

$$\tau - \hat{\tau} = \int_{u}^{u_l} \frac{1}{du/d\tau} du$$

For $\delta = const$ one can simplify the last relation

$$\tau - \tilde{\tau} = \int_{u}^{u_l} \frac{1}{du/d\tau} du + (u_l - u_r)/v_m$$

or

$$\tau - \hat{\tau} = \int_{u}^{u_l} \frac{1}{1 - u^{-1}} du + (u_l - u_r)/v_m$$
The integral can be easily taken analytically and we get the explicit expression for $\tilde{t}$.

If $v_m$ does not essentially depend on time one can simply solve all these equations. The form of the size spectrum is determined, only parameter $v_m$ ($\gamma, u_r, u_l$ depend on $v_m$) is unknown. The balance equation will be algebraic equation on $v_m$ and can be easily solved since we know at least the zero approximation (for example, one can take LS asymptotic).

It is clear that the backlash is not a constant value, it changes in time. The effective way to investigate the situation of the varying backlash is to consider this variation small, then to decompose $v_m(\tau)$ in Taylor’s series, to take few first derivatives and to fulfill the same program as was done above in the case of the constant value $v_m$.

8 Finite number of embryos

Under the finite spectrum of sizes the LS asymptotic will be also destroyed. After the size of the greatest embryo attains the critical value and $\gamma$ goes to zero the diffusion blurring begins and we return to the section about the diffusion blurring and the evolution will be described by the same formulas as mentioned above. Here it is important that the diffusion term plays the main role in evolution. Certainly, diffusion begins to play essential role earlier than the biggest embryo attains the critical size.

We see that the further scenario is built on the doubtful alternative whether the size spectrum finite or not. The diffusion process through the formula for the Green function gives the infinite size spectrum. But is every concrete system the spectrum is the finite one. The answer on this question also determines the asymptotic. The type of asymptotic is determined by the time of observation and the sizes of the system under the observation. Fortunately this question is artificial because other effects (the change of the regime of growth, the thermal effects, etc.) lead to the end of applicability of the chosen physical model.

In every system the finite spectrum is the direct consequence of the finite number of embryos. So, we have to develop methods to describe the evolution with the finite number of embryos.

Suppose we have few embryos in the system. Then the evolution is determined by the laws of their regular growth (diffusion has also to be taken into account but in the manner of some stochastic adsorption and ejection of the
molecules by the embryo). The balance equation links these laws of growth in the closed system of equations. The number of these equations equals the number of embryos. When the number of embryos is less or equal to few hundreds it is preferable to solve these equations by computers explicitly.

We rewrite the law of growth for a chosen embryo in the following form

\[ \frac{d\rho_i}{dt} = \frac{\zeta}{t_1}(1 - \frac{\rho_c}{\rho_i}) \]

\[ \rho_c \equiv \frac{2a}{3\ln(\zeta + 1)} \]

(index \( i \) marks embryos), where \( a \) is the rescaled surface tension (it is a constant) and \( \zeta \) is the supersaturation. Namely through the supersaturation one can link the laws of growth having written the balance equation

\[ \zeta = \Phi - \sum_i \rho_i^3 \]

Here \( \Phi \) is the initial value of supersaturation.

One can easily solve the system of these equations at least approximately. The first method is very simple. At given initial sizes of embryos we find the value of the supersaturation. Then we reconsider the sizes having moved them according to the law of growth at the given supersaturation. The time interval has to be small. Then we recalculate the supersaturation having made one step of evolution. This method is the step by step procedure.

The stochastic adsorption and ejection of the molecules by the embryo can be taken into account by the following simple procedure. We keep in the memory of computer all coordinates of embryos \( \rho_i \) and for every embryo at the given supersaturation we determine the rate of adsorption as

\[ R_+ = 3\rho^2(\zeta + 1)\Delta t/t_1 \]

Here \( \Delta t \) is an elementary time step. The rate of ejection will be

\[ R_- = R_+ - (d\rho/dt)\Delta t \]

\[ \frac{d\rho}{dt} = \frac{\zeta}{t_1}(1 - \frac{2a}{3\zeta\rho}) \]

The rate of staying still will be

\[ R_0 = 1 - R_- - R_+ \]
We must choose $\Delta t$ enough small to have $R_0 > 0$ even for the greatest embryo.

Having put the point at the interval $[0, 1]$ stochastically we determine what action we have to do. If this point belong to interval $[0, R_-]$ we eject the molecule, i.e. we make a transition $\rho_i \rightarrow \rho_i - 1$. If this point belong to interval $[R_-, R_- + R_+]$ we accumulate the molecule, i.e. we make a transition $\rho_i \rightarrow \rho_i + 1$. If this point belong to interval $[R_- + R_+, 1]$ we keep the coordinate still, i.e. we make a transition $\rho_i \rightarrow \rho_i$.

We have to repeat this action for every embryo. Then we recalculate the supersaturation

$$\zeta = \Phi - \sum_i \rho_i$$

and fulfill the step in time.

We see that these procedures can not give the analytical properties of evolution with the finite number of embryos. Hence, the problem of the system of several embryos exists and the effective solution is absent.

Now we turn to the simplest case - the case of small quantity of embryos. The asymptotic of the process is the evident there will be the greatest embryo which will be the critical one. This embryo is in the effective potential well. Description here is analogous to the case of the several identical embryos.

Really, the law of growth

$$\frac{d\rho}{dt} = \frac{\Phi - \rho^3}{t_1} \left(1 - \frac{2a}{3 \ln(\Phi - \rho^3 + 1) \rho}\right)$$

corresponds to the regular motion in the potential

$$U = \int_0^\rho \frac{\Phi - \rho^3}{t_1} \left(1 - \frac{2a}{3 \ln(\Phi - \rho^3 + 1) \rho}\right) d\rho$$

which is very deep and only in the region of small $\rho$ it has a barrier and begins to decrease when $\rho$ decreases.

If we ignore the fluctuational formation of the new embryos then the evolution leads to the fluctuational disappearance of the last embryo. It requires absolutely giant times and at these times new supercritical embryos have to appear. So, the ignorance of the fluctuational formation of new embryos (with extremely slow rate) is illegal.

The flow of disappearance of the last embryo is many times less than the flow of appearance (formation) of the new embryo even in the system
with the practically consumed metastable phase by the giant embryo. So, one can see the formation of the second embryo. Later one can observe the competition between these embryos. Practically inevitably the second (new) embryo will be dissolved but with a small probability $\pi$ which can be estimated (very roughly because we keep the old potential $U$ appropriate only for one embryo) as

$$\pi \sim \exp(U(\rho = \rho_{\text{min}}/2^{1/3}) - U(\rho_{\text{min}}))$$

(here $\rho_{\text{min}}$ is the argument of the minimum of potential) the first embryo becomes the second one and it will be dissolved. Certainly, the above presented picture is only the rough estimate.

9 Conclusions

In the theoretical constructions presented above we came to the following results

- In Sections 2,3 we pointed out the weak features of the LS approach. In section 2 the features concerning the behavior of the supersaturation were outlined. In section 3 the weak features in construction of the size spectrum were presented.

- In section 4 the sequential analysis of the evolution was given and it is shown why the form of the size spectrum resembles the form given in the LS approach.

- In section 5 the details of the most difficult and the most important period of the tail dissolution are given.

- In section 6 the approximate way to construct the initial size spectrum for the period of the tail dissolution is given. This point is very important for qualitative results.

- In section 7 the situation of the wide tail which allows essential simplification is presented.

- Section 8 is devoted to the specifics of the case when only few embryos remain in the system.
Sections 7 and 8 are supplementary ones, the complete theory is given in sections 4 - 6. This theory gives an answer on two important questions - why LS spectrum of sizes can be really seen in nature and what is the difference between the real situation and the LS approach.

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