Dispersion of nucleation under the smooth variation of external conditions

Victor Kurasov

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Abstract

A simple method to calculate dispersion of the total number of droplets appeared in the process of nucleation caused by the smooth variation of external conditions has been presented. The analytical result for dispersion is compared with results of numerical simulations and the coincidence has been observed. The role of stochastic appearance of several first droplets in formation of dispersion has been analyzed.

One of the evidently characteristic features of a nucleation process is an occasional appearance of embryos of a new phase. The occasional manner of the new embryos appearance leads to generally stochastic corrections in a total number of droplets $N_{tot}$. In every particular process of phase transition the number $N_{tot}$ differs from the mean value $<N_{tot}>$ averaged over many particular attempts of nucleation in the given system. Since the process of condensation is essentially non linear one the mean value $<N_{tot}>$ which is a result of averaging of particular processes differs from the value $N_{tot \ T\ AC}$ calculated in the theory based on averaged characteristics (TAC) [4]. In a free molecular regime of droplets growth considered here the number $<N_{tot}>$ approaches to the value calculated on the base of averaged characteristics $N_{tot \ T\ AC}$. It occurs when the volume $V$ of the system is infinitely big which explains notation $N_{tot \ T\ AC} = <N_{tot}(V = \infty)>$. One has to take this property into account in all theoretical descriptions of kinetics of the global process of phase transition.

Earlier stochastic effects were investigated in [6, 5, 7], but here it will be shown that the consideration made in [6, 5, 7] isn’t satisfactory. Still
the structure of analysis proposed in [6], [5], [7] can be adopted in general features for further considerations. From the general limit theorem for the chain of stochastic events it is clear that the distribution $P(N_{tot})$ has to be a gaussian distribution with some mean value $< N_{tot} >$ and dispersion $\sqrt{D}/2$. The task is to determine these values.

From the first point of view $D$ equals to the value

$$D_0 = 2 < N_{tot} >$$

of dispersion of distribution of independent events. But the nonlinearity of kinetics of the nucleation process leads to the deviation of $D$ from $D_0$. Namely this deviation will be the subject of investigation in this paper.

Here the situation of the smooth variation of external conditions will be studied. Namely in this situation the method proposed in [6], [5], [7] leads to the most striking error.

The plan of investigation will be the following

- In the first part we shall see why the previous publications [6], [5], [7] can not be applied, what are the errors made in these publications.

- In the second part a method to determine dispersion will be presented. This method is based on the monodisperse approximation proposed in [11]. To calculate dispersion one has to take into account the specific internal balance property in the nucleation process. As a result a very simple method to calculate dispersion is given.

- In the third part the role of the several first droplets in formation of dispersion is analyzed. The result of this section is a simple method with clear physical reasons which can be applied for practically all significant relative deviations of $N$ from $< N >$.

1 Two cycle models of nucleation process

The formulation of the problem is described in [6], [5], [7] in details and one can omit it here. To investigate stochastic effects in kinetics of the nucleation process one has to write analytical approximations to the size spectrum and then to variate parameters of these approximations.

The most traditional way to get analytical approximations is the iteration procedure. Originally started by Kuni [9] it was seriously modified in [2], [4]
and became a powerful tool to describe nucleation kinetics. But here one can not use iteration procedure due to the following reasons:

- The simplest effect which can cause the difference $D$ from $D_0$ is the influence of stochastic deviation of the rate of formation from the mean value on the rate of formation of droplets in next moments of time.

- The first iteration in the iteration procedure corresponds to the ideal rate of growth. So, there is no influence of the deviation of the rate of formation of droplets of big sizes on formation of new droplets.

- The second iteration can not be calculated analytically.

- The standard approximations [8] which allow to calculate further iterations correspond to some model approximation to the size spectrum. In these approximations one can not effectively calculate the influence of stochastic deviation of the rate of formation from the mean value on the rate of formation of droplets in next moments of time.

The mentioned difficulties is the reason to calculate stochastic effects on the base of some simple models of evolution.

To present the models for the size spectrum one has choose a renormalization in the corresponding theory based on averaged characteristics:

- The evolution equation for the renormalized number of molecules $g$ in a new phase looks like

$$g(z) = A \int_{-\infty}^{z} (z - x)^3 \exp(x - g(x))dx$$

Here

$$\phi \equiv \exp(x - g(x))$$

is the size spectrum.

- The characteristic time $t_*$ necessary for decompositions (see [4], [2]) is chosen to get at $z = 0$ the maximum if the spectrum (or the maximum of spectrum in the first iteration). It leads to

$$A \equiv 1/6 \approx 0.189$$
The manifestation of stochastic effects requires to have at least two effects - the effect of stochastic deviations and the effect of further reaction on these deviations. So, the simplest model is the two cycle model where during the first cycle the independent stochastic deviations appear and during the second cycle the reaction on these deviation takes place. The ”minimal” model is the two cycle model and now we shall investigate this model.

At first we shall consider approximation proposed in [7]. The approximation is the following one

- Before \( z = x_b \equiv 0 \) the rate of nucleation is supposed to be the ideal one.

- After \( z = x_b \equiv 0 \) the rate of nucleation \( I \) (in renormalized units) is given by

\[
I = \exp(x - g_-)
\]

where \( g_- \) is the renormalized number of molecules in the droplets formed before \( x = x_b \)

In the theory based on the averaged characteristics

\[
g_- = A \int_{-\infty}^{0} \exp(x)(z - x)^3 dx
\]

which explains the sense of approximation.

It is clear that this approximation is very rough. The boundary parameter \( x_b \) was chosen in a bad style. The reasons of such conclusion are the following:

1. The spectrum has very discontinuous character. The jump at \( x_b \) is very big. It can be seen in fig.1
   We see that the region \( x > 0 \) is approximately negligible in the calculation of total number of droplets. But namely this tail will be the main source of the deviation of dispersion from the standard value.

2. For arbitrary \( x_b \) one can calculate the number \( < N_{tot}(V = \infty) > \) of the total number of droplets. But always we get the number which is greater than the precise value \( < N_{tot}(V = \infty) >= 1.002 \). The figure 2 shows the number of droplets as function of \( x_b \).

One can see that the number of droplets has minimum at \( x_{boundary} = -0.85 \). This value seems to be more realistic because the jump in the spectrum (this jump must be in every model of such a type) isn’t so giant. The spectrum is shown in figure 3.
Figure 1: The form of approximation with a boundary value $x_{\text{boundary}} = 0$

The models with two cycles of evolution where the first cycle is an ideal one and the second cycle is formed under the influence of the first cycle will be referred to as "two cycle models".

The models where the spectrum in the first cycle is determined explicitly on the base of ideal conditions of the embryos formation will be called "explicit two cycle models".

From figure 2 one can see that explicit two cycle models cannot reproduce the right number of droplets. But these models have still more bad features concerning with calculation of dispersion.

2 Numerical calculation of dispersion

The best way to check the theoretical calculation of dispersion in the presented model is to compare it with the results of numerical simulation.
Figure 2: The total number of droplets given by the theory based on averaged characteristics as a function of $x_b$

the following type of numerical simulation will be presented: The evolution of the system of the volume $V$ starts from big negative $z$ ($z \approx -15$ is sufficient) and at every step $dz$ the random number between 0 and 1 is generated $V$ times. Every time the generated random number is compared with $f \ast dz$ where $f$ is the rate of nucleation in TAC and can be calculated as

$$f = \exp(z - g(z))$$

To know $g$ one has to know four integrals $I_i$, $i = 0, 1, 2, 3$ and $g$ is determined as

$$g = I_0 \ast z^3 - 3z^2 \ast I_1 + 3z \ast I_2 - I_3$$

The integrals $I_i$ are determined in TAC as

$$I_i = \int_{-\infty}^{z} x^i f dx$$
In application to the random appearance of embryos it means that at every attempt when the random number is greater than \( f \ast dz \) the integrals have to be increased as
\[
I_i \rightarrow I_i + z^i \ast 1
\]
Certainly, at every step \( z \) moves to \( z + dz \).

In the current calculations the step is \( dz = 0.001 \), at every \( V \) around 1000 nucleation processes were performed and then the mean value and dispersion were calculated.

The interesting value is the ratio \( D/D_0 \) which is plotted in figure 4. Since there is no evidence what total number of droplets one has to take in calculation of \( D_0 \) (there are two variants \( D_0 = 2 < N_{tot} > \) and \( D_0 = 2 < N_{tot}(V = \infty) > \) ) two curves are presented. Since \( < N_{tot} > \) is very close to \( < N_{tot}(V = \infty) > \) these curves are close. The jumps of curves correspond to stochastic nature of calculations and one can see what characteristic error is
caused by averaging only over 1000 attempts.

Figure 4: Relative square of dispersion as the function of the volume in precise simulation.

One can see that the value of dispersion goes with increase of $V$ to a limit value around 9.5 rather quickly. Really in a volume unit there will be around

$$A \int_{-\infty}^{\infty} \exp(x - g(x)) \approx A = 1/6$$

droplets. So, at $10 \div 15$ droplets the limit value is already attained.

Now one can turn to the analytical calculations of dispersion. At first we shall present calculation according to formulas presented in [7]. Since the approach in [7] is absolutely analogous to approach [5] we don’t mention all mistakes made in [7], [5]. They are mentioned in [12], [12] where these mistakes were corrected.

The result of calculation is shown in figure 5. Instead of [7], [5] we consider the model with an arbitrary $x_b$ instead of $x_b = 0$. Here one can see the relative square of dispersion as function of $x_b$. 

8
We plot the parameter $\epsilon = D/D_0$ in the Gaussian distribution

$$P \sim \exp\left(-\frac{(N_{\text{tot}} - \langle N_{\text{tot}} \rangle)^2}{2\epsilon < N_{\text{tot}}>}\right)$$

![Figure 5: Relative square of dispersion as function of $x_b$](image)

We see that the dependence of dispersion on $x_b$ is rather essential and there is no evidence of the choice of $x_b$.

It is seen that the result of the model with $x_b = 0$ is two times smaller than a real result. But the "optimal choice" $x_b = -0.85$ gives the value of dispersion which is rather close to the real result. It seems that here the coincidence is attained. But further considerations will show that this coincidence in no more than occasional.
3 Disadvantages of two cycle model

Having seen the results of two cycle models one has to mention that the calculation in these models is connected with technical difficulties and requires serious simplifications to come to the final result. Beside many unnecessary restrictions (see [12], [12]) the linearization of the action of stochastic fluctuations of already appeared droplets on the rate of formation of new droplets has been done. This linearization is necessary to perform analytical calculations but it kills all possible deviations of the mean number of droplets from the value calculated in the theory based on averaged characteristics. So, the conclusion about the absence of this shift made in [5], [7] is out of justification, it is direct consequence of linearization. A special question why there is no shift in the mean number of droplets will be the matter of further analysis and now the dispersion with all non-linear terms of the two cycle model will be calculated.

The most simple and effective way to see the non-linear corrections in the two cycle model is to fulfill the numerical simulation corresponding to this model. Then one has to change the calculation of $f$. Instead of $f = \exp(x - g(x))$ one has to use

$$f = \exp(x)$$

for $x < x_b$ and

$$f = \exp(x - g_-(x))$$

for $x < x_b$. The value of $g_-$ is calculated analogously to $g$ but the values of $I_i$ have to be taken here at $x_b$ (no further increase is allowed). So, from the first point of view there are absolutely no difficulties in simulation of this model.

The numerical simulation of explicit two cycle model shows new weak features of this model.

The first principal difficulty is the divergence of the model. Really, there is a fixed small probability that until $x = x_b$ no droplets at all will be formed. This probability can be taken from Gaussian distribution as

$$P(0) \sim \frac{1}{\sqrt{2\pi} < N_{\text{tot}}>} \exp\left(- \frac{< N_{\text{tot}}>}{2}\right)$$

but here there is no reasons to take the Gaussian distribution valid for many events (here there are no events). It is more reasonable to take Poisson
distribution but even with this distribution one has to come to

\[ P(0) \sim \exp(-l) \]

Here \( l \) is the number of possible events until \( x_b \). For \( l \) one can get

\[ l \sim \int_{-\infty}^{x_b} \exp(x) dx = \exp(x_b) \]

So, with a fixed probability (it is very small) there will be no droplets until \( x_b \). Then \( g_- = 0 \) and the size spectrum \( f = \exp(x - 0) \) grows infinitely.

As a result we see that in explicit two cycle models there appears a singularity which is certainly a main peak in integration over all possible situations. So, it completely destroys the possibility to get reasonable results in the two cycle models.

To overcome this difficulty one has to see what happens when the number of droplets \( N_{eff} \) appeared before \( x_b \) deviates from the mean value \( \langle N_{eff} \rangle \). Since the problem is formulated on the level of the number of droplets\(^1\) it will be very profitable to express evolution in terms of the number of droplets. Fortunately it is possible to do. In [10] a monodisperse approximation for the evolution in the theory based on the averaged characteristics has been presented for the situation of the metastable phase decay. In [11] the same task was solved for the smooth variation of external conditions. Now we shall use results of [11] for our purposes.

Briefly speaking one can say that according to results of [11] during the nucleation period the vapor is consumed in the unit volume by \( N_0 \equiv \langle N_{eff}(V = \infty) \rangle = 1/27 \) droplets and this value in renormalized values is one and the same.

What will happened when at \( z = -3 \) (this is the average value for the position of formation of the maximum of droplets) the number of appeared droplets will be less than \( 1/27 \)? The system will wait until the moment when there will be \( 1/27 \) droplets in the unit of volume. It will occur at some moment later than \( z = -3 \), i.e. at \( z = -3 + \delta \). Later the evolution will be the same but in the shifted \( z + \delta \).

We see that if we calculate the number of droplets precisely at \( x = x_b \) then the parameter in a functional approximation for the rest of size spectrum

\(^1\)It is really the most important characteristic, but generally speaking one can investigate some other characteristic, for example \( I_i(\infty) = \int_{-\infty}^{\infty} dx \exp(x - g(x)) \).
will be smaller or greater than the necessary value. In the monodisperse approximation this functional approximation is

\[ f = \exp(x - N_0(x - x_b)^3) \]

In explicit two cycle boundary it is

\[ f = \exp(x - g_-(x)) \]

When we put the smaller \( N_0 \) than \( 1/27 \) then the validity of approximation will be violated. One simply can not use approximation when the value of parameter seriously differs from the value \( 1/27 \).

The same is valid also for approximation (1). Approximation (1) can be used only if all \( I_i \) are near \( \int_{-\infty}^{x_b} x^i \exp(x) dx \). The use of (1) for all deviations (also corresponding to the small values if \( I_i \)) is the serious mistake. Namely this mistake doesn’t allow to use the two cycle models with a fixed boundaries.

To formulate the two cycle models with floating boundary one has to formulate the balancing property of the kinetics of nucleation.

\section{Balance property in kinetics of nucleation}

The calculations of stochastic effects are so complex that they can be made only in some primitive models of evolution in frames of mean values of characteristics. So, we have to present simple and rather precise models of evolution.

At first we consider the situation of decay. In the situation of decay there are two sources of balancing force. The first one is evident. Suppose that imaginary the whole period is divided into two arbitrary parts. Let the number of droplets in the first part be greater that the average value. Then these droplets will consume metastable phase with greater intensity and the second part of nucleation will be shorter. Then the supposed number of droplets born in the second part will be smaller. This balances the number of droplets near the average value.

The second balancing reason is more specific. Suppose that the first droplet isn’t going to appear. What will be changed in kinetics? Nothing. The start of nucleation process is the moment of appearance of the first droplet and the system will simply wait until this moment without any
changes. The process of nucleation is invariant to the starting point which is the appearance of the first droplet.

Denote as $t_{st}$ the moment of appearance of the first droplet. Then

$$\frac{< dN_{tot} >}{dt_{st}} = 0$$

in the situation of decay.

Consider now the situation of smooth variation of external conditions. To get the analytic approximations one has to choose some model of kinetics. The model of monodisperse spectrum is rather simple and precise [11]. We shall follow this model.

Certainly the first reason of balancing effect takes place also in dynamic conditions. But the second reason doesn’t take place. The problem is that there is no fixed initial point such as $t_{st}$ in decay.

Ordinary the coordinate of monodisperse spectrum is $z = -3$. We shall call this coordinate $z_b$. Then the distribution function has the form

$$f = f_\ast \exp(x - N_{eff}(x + 3)^3)$$

where the effective number of droplets $N_{eff}$ is given by

$$N_{eff} = \frac{6c}{27}, \quad c = 0.189$$

or

$$N_{eff} = \frac{1}{27}$$

The value $N_{eff}$ has the gaussian distribution

$$P(N_{eff}) \sim \exp\left(-\frac{(N_{eff} - < N_{eff} >)^2}{2 < N_{eff} >}\right)$$

where $< N_{eff} >$ is the mean value.

Consider what will happen when at $z = -3$ the required number of droplets $N_{eff}$ will be less than $< N_{eff} >$. The system will simply wait until $< N_{eff} >$ will be attained. And then the evolution will be absolutely the

\footnote{In free molecular regime when the distribution function has a maximum at $z = 0$.}

\footnote{Certainly, it is simplification to grasp the main features.}
same. But the evolution will occur with a shifted value of argument $z$ which corresponds to the shift in the amplitude value

$$f_* \rightarrow \exp(k\delta z)f_*$$

where $\delta z$ is the shift in $x$ and $k$ is the coefficient, which can be put to 1 by appropriate scale of variables $z, x$. We keep here $k$ to show that the effects don’t occur due to the special renormalization.

Then the mean total number of droplets $<N_{tot}>$ will be shifted as

$$<N_{tot}>ightarrow<N_{tot}>&\exp(k\delta z)$$

Our task is to obtain the shift $\delta z$ or the distribution of shifts $\Pi(\delta z)$. This distribution is connected with $P(N_{eff})$.

One can present $<N_{eff}>$ as

$$<N_{eff}>=f_*\int_{-\infty}^{z_b}\exp(kx-g(x))dx$$

or approximately

$$<N_{eff}>=f_*\int_{-\infty}^{z_b}\exp(kx)dx$$

Then

$$\frac{dN_{eff}}{dz_b} = f_*\exp(ksz_b)$$ (2)

Then

$$P(N_{eff}) = \Pi(\delta z)(\frac{dN_{eff}}{dz})^{-1} = (f_*\exp(ksz_b))^{-1}\Pi(\delta z)$$

or

$$\Pi(\delta z) = \exp(-kz_b)f_*^{-1}\exp\left(-\frac{(N_{eff}-<N_{eff}>)^2}{2<N_{eff}>}\right)$$

One can also write the last relation as

$$\Pi(\delta z) \sim N_{eff}^{-1}\exp\left(-\frac{(N_{eff}-<N_{eff}>)^2}{2<N_{eff}>}\right)$$

Then one can speak about the density distribution $\Xi(N_{tot})$ of the total number of droplets because $N_{tot} =<N_{tot}>&\exp(k\delta z)$ Then

$$\Xi(N_{tot}) \sim \Pi(\delta z)k\exp(k\delta z)$$
This leads to
\[ \Xi(N_{\text{tot}}) \sim P(N_{\text{eff}}) \]
and there is no effect of shift. The distribution of the total number of droplets is a gaussian distribution with the ordinary mean value.

The last relation leads to the absence of shift effect also in the case of dynamic conditions.

Certainly, one can mention that the absence of shift takes place only approximately. Really, having used in (2) the same parameter \( k \) we supposed that the difference between ideal supersaturation and real supersaturation is absent. But the difference isn’t absent, it is only small. Then instead of (2) we come to
\[
\frac{dN_{\text{eff}}}{dz} = f_s \exp\left(\frac{\Gamma}{\Phi_s}(\zeta - \Phi_s)\right)
\]
The sense of parameters is explained in [4]. For us now it is only important that at \( z = z_b = -3 \) the coefficient \( k \) will be approximately\( k' = k(1 - \exp(-3)) \)

Then
\[ \Xi(N_{\text{tot}}) \sim P(N_{\text{eff}}) \exp(kz_b(1 - (1 - \exp(-3)))) \]
or
\[ \Xi(N_{\text{tot}}) \sim P(N_{\text{eff}})N_{\text{eff}}^{\exp(-3)} \]

Because \( \exp(-3) \) is very small one can not see this effect clearly in experiment or in comparison with numerical simulation.

In fact the existence of the last effect is rather doubtful and it is more preferable to speak about the absence of the regular shift in the considered situation.

One has to note that the property of the absence of the regular shift is very important in the context of stability of kinetics. Really all proposed models have to demonstrate the property of stability in respect to the stochastic perturbations. Namely the absence of the regular shift ensures this stability.

One can also see that the property of regular shift will take place in all two-stage models. The two stage models of evolution are the models where the first part of spectrum is formed under the ideal supersaturation (it can be the monodisperse peak or explicitly the spectrum like \( \exp(x) \)) and the rest part of spectrum is formed only under the external influence and the influence of droplets from the first part of the size spectrum. In details this property will be analyzed separately.
5 Two cycle models with floating boundary

The direct result of the previous balance property is the absence of correction terms to the mean number of droplets formed under the dynamic conditions. So, the problem to determine the mean number of droplets is solved. But dispersion remains still undetermined.

But now one can formulate the true two cycle models. They must be the models with a floating boundary. The floating boundary is defined as a coordinate or the time moment \( z_f \) when the parameters of approximation concerning the first cycle attain their values used in approximation in TAC. In the monodisperse approximation there will be no difficulties - parameter \( x_f \) in every particular attempt is the coordinate when the number of appeared droplets attains \( 1/27 \).

Now we shall perform simulations for explicit two cycle models with boundaries \( x_b = 0 \) and \( x_b = -0.85 \). Results are shown in figure 6 and figure 7.

One can see that the result of the model with \( x_b = 0 \) is satisfactory but there are absolutely no reasons to choose \( x_b = 0 \) except historical ones \[7\]. The coincidence is occasional. The most reasonable model with \( x_b = -0.85 \) gives a wrong result.

In explicit two cycle models there will be a problem because different \( I_i, i = 0, 1, 2, 3 \) can attain necessary values \( \int_{-\infty}^{x_d} x_i \exp(x), x_d = 0; -0.85 \) in different moments. This is an evident disadvantage of explicit two cycle models. Having noticed the weak features of explicit two cycle models mentioned at the beginning, we see that one has to consider the monodisperse model with the floating boundary.

The model is the following:

- The effective number of droplets is \( N_0 = 6/27 \) (the number 6 appears from \( A = 6 \) in the evolution equation in TAC).

- Since the spectrum is formed in an internal point of a nucleation period one has some reasons to suppose that the subintegral function for \( g \) in a current moment of time is rather symmetrical being related to the maximum. Then the number of droplets which has to be formed before maximum has to be taken as \( N_0/2 \).

- The moment \( z_f \) of the monodisperse peak appearance is characterized by formation of \( N_0/2 \) droplets.
Figure 6: Relative square of dispersion as a function of volume in the explicit two cycle model with a floating boundary $x_b = 0$.

- After $z_f$ the spectrum is
  \[ f = \exp(x - N_0(x - x_f)^3) \]

  The numerical simulation requires to specify the procedure of calculation:
  - Until $I_0 \geq N_0/2 = 3/27$ the function $f$ is $\exp(x)$ and stochastic appearance of droplets is initiated.
  - When for the first time $I_0 \geq N_0/2$ the coordinate $z$ is referred\(^4\) as $z_f$.
  - In further evolution
    \[ f = \exp(x - N_f(x - x_f)^3) \]

\(^4\)When instead of the mentioned choice of $z_f$ we choose $z_f$ as coordinate when $I_0$ attains $N_0$ then the result of numerical simulation of this model differs from result of numerical simulation of the precise model.
Figure 7: Relative square of dispersion as a function of volume in the explicit two cycle model with a floating boundary $x_b = -0.85$.

where

$$N_f = 2 \times I_0$$

Dispersion in this model is shown in figure 8.

One can see that the coincidence between precise simulation and simulation in monodisperse model is satisfactory.

This approximation contains the precise number of effective droplets which doesn’t precisely coincide with $1/27$. So, here the number of effective droplets isn’t the absolutely constant value prescribed by analytical recipes. But it is better to follow this procedure than to threw out the fractional part of the number of droplets at $x_f$. Then even the number of droplets has the characteristic jumps at the values of volume $n/27$, where $n$ is a natural number. These jumps a rather essential at moderate volumes. It is evident that dispersion near these values has to be greater than the ordinary value.
Analytical calculation of dispersion

The last model allows very simple calculations to get the dispersion of the total number of droplets. Really, the dispersion of the first part of droplets, i.e. the droplets which are in the monodisperse peak is zero

\[ D_m = 0 \]

since the floating boundary has to be used. The monodisperse spectrum absolutely governs further evolution. It is very easy to calculate the dispersion of external influence on further evolution., Really according to balance property and the self similarity of conditions of nucleation during the nucleation period (see [11]) the relative deviation of the number of rest droplets equals to the ideal dispersion of the distribution of independent \( < N_{eff} > / 2 \)
droplets, i.e.

\[ D_{\text{ext}} = 2\langle N_{\text{rest}} \rangle / (N_{\text{eff}}/2) \rangle * \langle N_{\text{rest}} \rangle \]  \hspace{1cm} (3)

where \( N_{\text{rest}} \) is the number of remaining droplets

\[ \langle N_{\text{rest}} \rangle = \langle N_{\text{tot}} \rangle - \langle N_{\text{eff}} \rangle \]

Certainly one has to take into account that under the fluctuating conditions the droplets are formed stochastically with internal fluctuation characteristic to the independent formation of \( \langle N_{\text{tot}} \rangle - \langle N_{\text{eff}} \rangle \) droplets

\[ D_{\text{int}} = 2 \langle N_{\text{rest}} \rangle \]

Then

\[ D_{\text{tot}} = D_{\text{ext}} + D_{\text{int}} \]

Having put \( N_{\text{eff}} \rangle = 6/27, \langle N_{\text{tot}} \rangle = 1 \) one can come to

\[ D_{\text{tot}} \approx \epsilon 2 \langle N_{\text{tot}} \rangle \]

\[ \epsilon = 7 \]

The last value isn’t too far from results of simulation.

If one shall take into account the similarity of conditions of nucleation [11] then it will be reasonable to put \( \langle N_{\text{rest}} \rangle = 1 \) (the total number of droplets) and then

\[ \epsilon = 10 \]

which is practically the same result as in numerical simulations.

The advantage of this method is that it can be used as the base for further more detailed constructions taking into account some fine features of nucleation kinetics.

7 The role of first droplets in formation of dispersion

The effect of the influence of several first droplets on the deviation of the mean value of the droplets number from the value prescribed by the theory based on the averaged characteristics manifests itself in the fact that corrections
to the mean value of the number of droplets can be completely explained by formation of several first (actually the very first one) droplets. Here such a radical result does not take place, but for a wide range of volumes of systems one can effectively use the explicit role of several first droplets.

Since several first droplets (at least those in the monodisperse peak) are formed independently, the partial distribution of \( n \) droplets is the Poisson’s distribution

\[
P_n \sim l^n \exp(-l)/n!
\]

Here \( l \) is the number of possible events. Then at the initial period

\[
l = \exp(x)
\]

and

\[
P_n(l)dl = P_n(x)dx
\]

It leads to

\[
P_n(x) = \exp(nx) \exp(-\exp(x)) \exp(x)
\]

Certainly, the main influence appears due to the first droplet. The partial distribution for the waiting of the first droplet is

\[
P_0 = \exp(x - \exp(x))
\]

and it is similar to the universal distribution observed in [3].

The values of dispersions at moderate \( V \) initiated by the first droplet, by two first droplets and by three first droplets are shown in the figure 9. The increase of the number of droplets taken into account corresponds to the increase of dispersion - the lowest curve corresponds to account of only the first droplet, the highest curve corresponds to three droplets taken into account. Here the value of \( \epsilon \) referred to the number of droplets prescribed by the theory based on averaged characteristics is drawn.

It is seen that the increase in \( \epsilon \) initiated by every new curve is rather small and one can state that the main influence is initiated by the first droplet.

One can see that the account only of three first droplets ensures the correct description of the monodisperse peak for situations where \( N_{eff} \leq 3 \). It corresponds to the volume \( V_3 = 3 * 27 = 81 \) which is already sufficient for majority of real practical situation where the stochastic effects can be really observed in practice.
Figure 9: Relative square of dispersion as the function of volume initiated by several first droplets.

8 Concluding remarks

The method proposed above is based on monodisperse approximation. This approximation is necessary because it allows to close the system of evolution equations on a level of the number of droplets. The use of explicit models with more complicated forms of spectrum used in the expression for the quantity of new liquid phase in corresponding TAC requires to write more complicated equations for other stochastic characteristics of these spectrums, which makes the problem rather more complex.

Meanwhile the applicability of the monodisperse approximation is based on the sharpness of subintegral function in expression for the quantity of new phase. In the free molecular regime of growth this function looks like $(z - x)^3 \exp(x)$ in TAC and allows the monodisperse approximation. In the diffusion regime of growth the subintegral function in TAC will be like
\[ (z - x)^{3/2} \exp(x) \] and cannot be approximated by a monodisperse peak so effectively as in the case of a free molecular regime of growth. So, there appeared some difficulties but even in this situation the predictions of monodisperse model qualitatively coincide with results of numerical simulation.

In the diffusion regime of growth one has to put the position of monodisperse peak at \( z = -3/2 \) and then the value of necessary droplets in the monodisperse peak will be \( N_{eff} = 2 \) which is approximately the same as the total precise number of droplets in TAC \( N_{TAC} = 1.96 \). Then the total number of droplets appeared in monodisperse approximation will be \( N_{tot\ mono} = 1.98 \). Here \( N_{tot\ mono} \) was calculated by the following way: at \( z = -3/2 \) the number of droplets will be the half of \( N_{eff} \) and later the number of droplets is calculated as

\[
N_{tot\ mono} = N_{eff}/2 + \int_{-3/2}^{\infty} \exp(x - N_{eff}(x + 3/2)^{3/2}) \, dx
\]

As the result we see that

\[
N_{TAC} \approx N_{eff} \approx N_{tot\ mono}
\]

It means that practically all droplets have to be in monodisperse approximation. The consequence of this is the absence of dispersion. But the property that all droplets are in monodisperse peak means that all of them at the same time govern their evolution. So, then one can attribute the dispersion of independent events. Then

\[
D = D_0
\]

Results of simulation give

\[
D = (1.2 \div 1.25)D_0
\]

which corresponds to above predictions.

Now we shall refine the model. Now at \( z = -3/2 \) the monodisperse peak is formed and we calculate the number of droplets explicitly

\[
N_{init} = \int_{-\infty}^{-3/2} \exp(x) \, dx = \exp(-3/2)
\]

Then the rest quantity of droplets is calculated by the previous formula.

The result of solution is that approximately the three quarters of droplets have to be included in monodisperse peak and the rest quarter is formed.
under the influence of this peak. The following question appears: shall one
takes into account the dispersion of droplets in the peak? The previous result
which shows the self action of the monodisperse peak onto itself requires to
take into account the dispersion of the monodisperse peak. So we have

\[ D = 3/4 * D_1 + 1/4(1 + 4/3) * D_0 \]

where \( D_1 \) is dispersion of initial peak. Certainly, for \( D_1 \) one has to take the
dispersion of independent events \( D_0 \). In the last term \( 1/4(1 + 4/3) * D_0 \) the
value 1 comes from the self dispersion of free events and term \( 4/3 \) is the
induced dispersion.

Earlier in investigation of free-molecular regime there was no use to take
into account the dispersion of initial peak because it would give addition only
6/27. This addition is so small in comparison with renormalizing factor 10
appeared earlier that there is no need to take it into account. In diffusion
regime such addition can be essential.

Then the calculation according to the last formula gives

\[ D = 4/3 * D_0 \]

Then the result is slightly greater than the result of simulation but the dif-
ference is negligible.

This result is the estimate from above because the substitution \( D_1 = D_0 \)
increases the result. The first estimate \( D = D_0 \) is the estimate from below. So,

\[ D_0 < D < 1.33D_0 \]

The interval ensured by these estimates is rather narrow and the result of
simulation lies in this interval.

One has to mention that in the diffusion regime foundations of the monodis-
perse model and of all further constructions are rather weak. So, one can not
state that our result isn’t well justified. Fortunately, in the diffusion regime
of growth kinetics of nucleation is analyzed separately \[1\] and has absolutely
another physical reasons of evolution. Also one has to take into account the
effect of compensation due to the growing volumes considered in \[12\].

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