Heterogeneous condensation in dense media

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Abstract

The theoretical description of the heterogeneous nucleation kinetics is presented. This description takes into account the perturbation of the vapor phase initiated by the growing droplets. The form of the density profile around the growing droplet is analyzed which leads to some special approximations. Then the process of nucleation in the whole system is described. As the result all main characteristics of the process are determined analytically.

Among numerous examples of the first order phase transitions a case of condensation is extracted by a relative simplicity. This case is well investigated experimentally and is traditionally regarded as the base for application of some new theoretical methods. A "classical theory of condensation" (see, for example [1]) gives the solid ground for further theoretical constructions. Numerous modifications and reconsiderations (see, for example [2]) allow to consider an example of condensation as well analyzed both theoretically and experimentally.

One has to stress that practically all investigations were intended to determine the rate of nucleation and didn’t give the global picture of the phase transition. Some theoretical descriptions of a global evolution appeared later than the classical theory of nucleation has been created and they were not so numerous. Among them one can extract the descriptions of a metastable phase decay by Wakeshima [3], Segal’ [4] and Kuni, Grinin [5]. A process of condensation which occurs during a smooth variation of external conditions was considered in [3]. Nevertheless the theoretical description of the global picture of a whole condensation kinetics have ignored some important features of this process. Namely, an exhaustion of a metastable phase near a
growing embryo of a new phase have not been taken into account in a proper way. Certainly, this exhaustion is explicitly taken into account in expression for the rate of embryos growth in continuous model (i.e. in the "diffusion regime" of the embryos growth). This effect was carefully analyzed both in stationary and non-stationary aspects in many publications mainly in the field of mechanics of continuous media. But the presence of the gap of a metastable phase density near a droplet will act on the intensity of the new droplets formation. This effect hasn’t been taken into account in all previous theoretical descriptions of the global evolution in the first order phase transition. But as it is shown in [8] this gap can lead to big numerical effects in the description of the whole process.

The reason why the mentioned effect was not considered is rather trivial. Even under a spatial homogeneous consumption of the metastable phase the mentioned descriptions were rather complicate [5]. Then ordinary the condensation process was described under the free molecular regime of growth where there is will be no such a gap. This was a serious restriction of the theoretical description.

In some publications (see, for example [9]) the regime of the droplets growth was the diffusion one. This requires to consider the gap of the density near the growing droplet but in [9] the vapor consumption was regarded to be homogeneous in space. As far as this effect is very important one can not present a reliable description without taking it into account. Here we shall present a more realistic picture of a phase transition which allows an analytical solution.

Qualitatively the picture of the condensation process is rather simple. A process of nucleation (i.e. a formation of supercritical embryos of liquid phase) leads to a vapor exhaustion which stops the nucleation process. But the supercritical embryos continue to consume a vapor phase. All surplus substance of a metastable phase will be accumulated in the embryos of a new phase. One can say that the process of condensation is completed.\footnote{A further evolution includes the consumption of some relatively small embryos by some relatively big ones. It will be seen later that when all surplus substance is consumed then all droplets have approximately one and same size and we don’t analyze this process here.}

The global picture of homogeneous condensation with explicit account of the density profiles was presented in [8] where the giant numerical effects were observed. But ordinary the process of nucleation occurs on heterogeneous
centers. This radically complicates the theoretical description due to the centers exhaustion which has essentially non-linear character.

During the nucleation process one can see that heterogeneous centers become the centers of the supercritical droplets which are growing irreversibly in time. But the nucleation process diminishes the number of free (unoccupied by droplets) heterogeneous centers. In some cases the total exhaustion of free heterogeneous centers interrupts the nucleation, in some cases the partial exhaustion seriously influences upon the nucleation rate. This effect has to be also taken into account.

A simple analytical description of heterogeneous condensation will be presented here with proper account of all mentioned problems. As the result all main characteristics of the condensation process will be expressed through the parameters of external conditions behavior and substance parameters by some explicit analytical formulas. The error of the presented description will be estimated.

The structure of the theory will be as follows:

- At first we shall analyze the density profile around the solitary droplet and construct some approximations. It has much in common with the case of homogeneous condensation considered in [8] and will be considered briefly.

- Then we shall construct some models for kinetics of process. We have to show that these models estimate the time evolution of the system during the nucleation period. As far as these models will give the similar results one can state that the approximate description of the nucleation kinetics is given. The error of description is, thus, estimated.

- When the solution is already obtained we can compare it with formulas given by the previous approach and see the numerical effect of account of the gap near the growing droplets.

The small parameter of the theory will be the inverse number of molecules inside the critical embryo of a new phase. The small value of this parameter isn’t a restriction of our theory - it comes from the possibility of thermodynamic approach to calculate the free energy of the critical embryo. There is no other reliable way to calculate the free energy except the thermodynamic

\[2\text{Also it is more simple to observe heterogeneous case experimentally.}\]
approach\[3\]. To use the thermodynamic approach it is necessary to have at least a few dozens of molecules inside the embryo.

Also we shall require the barrier character of nucleation. It means that to begin to grow irreversibly every embryo has to overcome the activation barrier of essential height. This height is less than for the homogeneously (pure fluctuation) formed embryo but still attains several thermal units\[4\]. Certainly, one can imagine the situation when there is no activation barrier. Then all embryos begin immediately to grow irreversibly. The number of droplets (i.e. the irreversibly growing embryos) will be equal to the total number of centers and the kinetics of the process will be relatively simple.

We shall speak only about the density profiles around the droplet and ignore the heat extraction in the nucleation process. Really, the mathematical structure of a diffusion equation is absolutely identical to the structure of a heat transfer equation. So, all constructions for the condensation heat extraction will be the same as for the substance consumption. It will lead only for some renormalizations. That’s why only some corresponding remarks will be given. Any detailed results can be found in \[10\].

We shall consider the situation of a metastable phase decay. It means that in the initial moment of time all substance is in the vapor phase. All heterogeneous centers are free from droplets.

1 Profile around the solitary droplet

Due to the external influence in the initial moment of time one can observe in the system the homogeneous mother metastable phase with the particle number density $n$ which is equal to some value $n_0$. All heterogeneous centers are distributed rather homogeneously in space with the number density $\eta_{tot}$.

The process of condensation can begin only when $n_0$ is greater than the molecule number density $n_{\infty}$ in the vapor saturated over the plane liquid. The power of metastability of vapor will be characterized by the value of a supersaturation $\zeta$ defined as

$$\zeta = \frac{n}{n_{\infty}} - 1$$

\[3\] All microscopic models requires very complex calculations which can not be fulfilled directly.

\[4\] All energy-like values will be measured in thermal units.
The initial value of the supersaturation will be marked by \( \zeta_0 \).

Practically immediately around every center there will be formed an equilibrium embryo which has \( \nu_e \) molecules of the condensing substance. The value of \( \nu_e \) is relatively small\(^5\) and there is no need to consider the density profile around the equilibrium embryos\(^6\).

The number of the equilibrium embryos in the unit volume\(^7\) will be equal to \( \eta_{tot} \). During the condensation process the number of the equilibrium embryos \( \eta \) will be decreased due to the exhaustion of the free heterogeneous centers

\[
\eta = \eta_{tot} - N
\]

where \( N \) is number of the supercritical embryos which will be called as the droplets.

The last equation illustrates the main specific feature in kinetics of heterogeneous condensation. Despite the simple form of the last relation the effect is very complicate because \( N \) depends on time in a very complicate manner.

The effects of the density profile will be essential also for \( N \) and one can not directly apply the results of \([5]\). One has to determine the effect of the influence on \( N \) even for the density profile of the solitary droplet.

We shall call an approach where the law of embryos growth is found from continuous model but there is no account of the profile around the droplets as the ”Additive approach” (AA).

Then one can formulate the evident

Statement 1

The duration of the nucleation period\(^8\) and the characteristic sizes of the droplets at the end of nucleation period are greater than those calculated in AA

\(^5\)In comparison with the characteristic number of molecules inside the droplet during the nucleation period.

\(^6\)In fact it will disappear rather fast. This leads to the slight variation of the equilibrium embryo characteristics. This variation will act on the gap. But the final relaxation will be rather rapid.

\(^7\)The system of a unit volume will be considered.

\(^8\)The period of nucleation is the period of the relatively intensive formation of the droplets. It can be proven that the end of this period is well defined due to the cut-off of the intensity of the droplets formation.
Really, the existence of the density profile means that the part of substance is going to be consumed from the regions where there is already no droplets formation. This substance is consumed from the gap instead of unexhausted regions as it is done in AA.

Then having repeated all constructions from [5] one can see

**Statement 2**

*The characteristic size of the droplets at the end of the nucleation period is many times greater than the size of the critical embryo. The main role in vapor consumption is played by the supercritical embryos.*

and

**Statement 3**

*The characteristic time of the nucleation period duration is many times greater than the time of relaxation to the stationary state in the nearcritical region. Then one can use the stationary rate of nucleation as the intensity of the droplets formation in every current moment of time.*

Due to the statement 2 one has to investigate the profile around a growing droplet. The problem is whether one has to consider the interference of profiles around different droplets.

To solve this problem one has to use the small parameter of the theory. Due to the statement 3 the rate of nucleation is equal to the stationary one. It can be taken from [1]

\[ I_s = Z \eta \exp(-\Delta F) \]

where \( \Delta F \) is the height of activation barrier (taken in thermal units), \( \eta \) is the number of free (unoccupied by the supercritical embryos) heterogeneous centers, \( Z \) is Zeldowitch factor. Zeldowitch factor is the smooth function of the supersaturation which is given by

\[ Z = \frac{W}{\pi^{1/2} \Delta \nu_c \Delta \nu_e} \]

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\(^9\) In [5] the AA was formulated for external conditions of dynamic type. For the situation of decay the required hierarchical inequalities can be proven by the same way. One can note that in [5] there is no special reference on the type of condition when the required estimates are proven.

\(^10\) The barrier character of nucleation is required here. It means that the magnitude of the activation barrier height has the same order as the free energy of the homogeneous critical embryos (may be it is 4 or 3 times smaller).
where $W$ is kinetic factor, $\Delta \nu_c$ is the halfwidth of the nearcritical region, $\Delta \nu_e$ is the width of the equilibrium region.

Due to the rather small size of the critical embryo it is reasonable to use the free molecular regime of the substance exchange\textsuperscript{11}. Namely, in this regime an expression for the nucleation rate is well based. One has also to note that the critical embryo is in equilibrium (unstable one) with the metastable phase which implies no profiles of vapor density and regime of the substance exchange is the free molecular one.

Under the free molecular regime $W$ can be calculated as

$$W = 3 \zeta + \frac{1}{\tau} \nu_c^{2/3} \alpha$$

where $\nu_c$ is the number of molecules inside the critical embryo, $\alpha$ is the condensation coefficient,

$$\tau = 12\left[(36\pi v_l^2)^{1/3}n_\infty v_T\right]^{-1}$$

is the characteristic time, $v_l$ is a volume per one molecule in a liquid phase, $v_T$ is the mean thermal velocity of a molecule.

The value of $\Delta \nu_c$ is the halfwidth of the nearcritical region and it can be calculated as

$$\Delta \nu_c = \sum_{\nu \leq (\nu_c + \nu_e)/2} \exp(-F_c + F_\nu) \pi^{-1/2}$$

where $\nu$ is the number of the molecules inside the embryo, $F_\nu$ is the free energy of the embryo of $\nu$ molecules, $F_c$ is the free energy of the critical embryo. In continuous approximation it can be calculated as\textsuperscript{12}

$$\Delta \nu_c = \left|\frac{2}{\pi v_T^2} |_{\nu=\nu_c}^{1/2} \right|$$

The value of $\Delta \nu_e$ can be calculated as

$$\Delta \nu_e = \sum_{\nu \leq (\nu_e + \nu_c)/2} \exp(-F_\nu + F_e)$$

\textsuperscript{11}As long as the characteristic size of the droplet during the nucleation is many times greater that the critical size the diffusion regime of growth for the characteristic droplets is quite reasonable.

\textsuperscript{12}Ordinary $\Delta \nu_e$ is smaller than $\Delta \nu_c$ and an explicit summation for $\Delta \nu_e$ is quite reasonable.
where $F_e$ is the free energy of the equilibrium embryo.

Both $\Delta \nu_c$ and $\Delta \nu_e$ are rather smooth functions of the supersaturation.

One can see that $I_s$ is a very sharp function of the supersaturation. It means that the relatively small fall of the supersaturation leads to the interruption of the droplets formation.

At least for all $\zeta > \zeta_0/2$ one can show that $d^2\zeta/dt^2 > 0$ and there is no long tail of a size spectrum with a small intensity. It means that the interruption of the droplets formation leads to the interruption of the nucleation process. So, the relative fall of the supersaturation during the nucleation process is small. One can come to the following statement

**Statement 4**

*During the nucleation period the relative variation of supersaturation is small.*

The last statement shows that there is no need to consider the interference of profiles in order to change the rate of droplets growth.

On the base of mentioned expressions and the smallness of the relative fall of supersaturation one can see the validity of the following approximation

$$I_s(\zeta) = I_s(\zeta_0) \exp(\Delta F(\zeta_0) - \Delta F(\zeta))$$

for the nucleation period.

Moreover one can linearize the height of the activation barrier over the supersaturation and get

$$I_s(\zeta) = I_s(\zeta_0) \exp(-\frac{d\Delta F(\zeta)}{d\zeta}|_{\zeta=\zeta_0}(\zeta - \zeta_0))$$

(1)

The validity of the last approximation depends on the concrete type of heterogeneous centers but for the majority of the heterogeneous centers types the last approximation is valid. For example, this validity can be directly proven for ions.

One can explicitly calculate the derivative in the last expression

$$\frac{d\Delta F}{d\zeta} = -\frac{1}{\zeta + 1}(\nu_c - \nu_e)$$

13Here we assume the vapor to be an ideal gas and suppose the possibility to present the free energy of critical and equilibrium embryos as an analytical function of an inverse embryo radius.
The smooth character of the last expression shows the validity of (1) one more time.

Then (1) can be rewritten as

\[ I_s(\zeta) = I_s(\zeta_0) \exp(\Gamma \frac{\zeta - \zeta_0}{\zeta_0}) \]  \hspace{1cm} (2)

where

\[ \Gamma = -\zeta_0 \frac{d\Delta F}{d\zeta} \bigg|_{\zeta=\zeta_0} = \frac{\zeta_0}{\zeta_0 + 1}(\nu_c(\zeta_0) - \nu_e(\zeta_0)) \]

As far as the value of \( \nu_c \) in going in the presented theory to infinity the value of \( \Gamma \) is also going to \( \infty \). The real value of \( \Gamma \) is very big. Certainly, one can consider the possibility of compensation between \( \nu_c \) and \( \nu_e \) in the expression for \( \Gamma \). Then one has to mention that due to the barrier character of nucleation at least \( \nu_c - \nu_e \geq \Delta \nu_c \). Having estimated \( \Delta \nu_c \) by the homogeneous value \( \Delta \nu_c \sim \nu_c^{2/3} \) one can see that \( \Gamma \gg 1 \) in any case.

The small value of \( \Gamma^{-1} \) will be very important in further constructions.

We see that essential dependence over the supersaturation occurs through the height of activation barrier. It allows to give the interpretation of the stationary rate of nucleation as the probability for the given embryo to overcome the activation barrier. After the interpretation of \( I_s \) as the probability we can apply it to the arbitrary spatial point of spatially unhomogeneous system. To use this interpretation the natural requirement is the weak unhomogeneity of the system. Namely, the volume of the regions where

\[ \frac{\zeta(r) - \zeta(r + \sqrt{4Dt_s})}{\zeta(r)} \ll \Gamma^{-1} \]

is violated has to be relatively small.

Here \( D \) is the diffusion coefficient, \( t_s \) is the time of relaxation in the nearcritical region which can be estimated according to Zeldowitch [1]

\[ t_s \sim \frac{\Delta \nu_c^2}{W} \]

One can use instead of \( t_s \) the time \( Z^{-1} \) which can be interpreted as the mean time to overcome the nearcritical region.
Both these estimates are observed. Actually we need them only for those regions where the intensity of the droplets formation isn’t too small in comparison with initial intensity. Certainly, the required property is observed there.

Now we have to turn to the rate of embryos growth. According to the Statement 2 the characteristic size of droplets is rather big. Then it is more reasonable to use the diffusion regime of droplets growth. Under the intermediate Knudsen numbers one has to use an interpolation law for the rate of embryos growth (for example, see [4]). It will be important that all expressions for the embryos growth lead to the avalanche character of the substance consumption.

The avalanche character of the substance consumption means that the quantity of substance accumulated by a droplet strongly increases in time. The most evident manifestation of the avalanche consumption can be seen in the free molecular regime of the substance consumption. The most ”weak” effect of the avalanche consumption can be seen under the diffusion regime of the substance consumption.

The force of the iterations convergence in [5] is based on this property. The property of avalanche consumption will be extremely important in the further constructions also. That’s why we take the diffusion regime to have the worst situation and to grasp errors in all possible cases.

In the diffusion regime of the vapor consumption the law of growth for a droplet (i.e. for the supercritical embryo) can be written in the following way

\[
\frac{d\nu}{dt} = \kappa \zeta \nu^{1/3}
\]

where

\[
\kappa = \left(\frac{2}{3}\right)^{-1/3} 4\pi n_\infty D\left(\frac{v_l}{2\pi}\right)^{1/3}
\]

is some constant.

The last expression is written in stationary approximation. The non-stationary effects were investigated in many publications in details and they are rather small ones.

One can see that the rate of the droplet growth is proportional to \(\zeta\). So, the rate of growth can be essentially changed only by the essential relative variation of \(\zeta\). Then according to Statement 4 one can see that

Statement 5
The rate of droplets growth during the nucleation period can be approximated as a constant one.

The last statement is extremely important because it allows to analyze the profile of the density initiated by a solitary droplet. Now this case will be considered.

The approximately constant value of the supersaturation allows to integrate the law of growth and get

\[ \nu(t) = \gamma t^{3/2} \]

where

\[ \gamma = (4\pi)^{3/2} \left( \frac{3v_l}{4\pi} \right)^{1/2} \left( \frac{2\zeta n_{\infty} D}{3} \right)^{3/2} \]

and \( t \) is the duration of the irreversible growth for the given droplet.

Consider the spherical system of coordinates with a center in the center of droplet. Diffusion equation will be written as

\[ \frac{\partial n}{\partial t} = D \Delta n \]

where \( \Delta \) is the Laplace operator. Diffusion coefficient \( D \) is supposed to be approximately constant (there is a lot of a passive gas and the density of a gas mixture is approximately constant).

The boundary conditions are the following

\[ n|_{r=\infty} = n(\infty) \]

\[ n|_{r=R_d} = n_\infty \]

where \( R_d \) is the radius of a droplet. The values \( n_\infty \) and \( n(\infty) \) are known parameters. The variable \( r \) is the distance until the center of the embryo.

The stationary approximation is suitable for the rate of droplets growth. The errors are analyzed in [4] and they are small. But the stationary solution can not give any reasonable result for the density far from the droplet. Really, the stationary solution is the following

\[ n(r) = n(\infty) - \frac{R_d}{r} (n(\infty) - n_\infty) \]

and has a very long tail. This tail leads to the infinite value of

\[ G = \int_0^\infty 4\pi r^2 (n(\infty) - n(r)) dr \]
which has to be the integral excess of the substance. This quantity has to be in the droplet. This contradiction shows that it is absolutely impossible to use the stationary approximation for the density profile around the droplet. One has to introduce another approach.

One can see that if the first boundary condition will be changed by

\[ n|_{r=\infty} = n(\infty)(1 - \Gamma^{-1}) \]

then the rate of embryos growth will be changed unessentially. But the level \( n(\infty)(1 - \Gamma^{-1}) \) is the level when the nucleation stops. So, one can see that during the nucleation period there is no interaction between droplets through the change of the growth rate. Certainly, two droplets can appear too close and act one upon another but the probability of such coincidence is too small. That is why one can come to the "Principle of a separate growth of droplets during the nucleation period".

Now one has to prove that at the distances \((5 \div 10) R_d \) from the droplet one can observe the quasistationary profile.

One has to note that

\[ \frac{v_l}{v_v} \ll 1 \quad (4) \]

where \( v_v \) is the partial molecule volume in a vapor phase. Really, the last ratio is very small (for example, this ratio is 0.001 for water in normal thermodynamic conditions). But contrary to \( \Gamma^{-1} \) one can not consider it in all cases as zero.

Now one can introduce a formal parameter \( l \) which attains big values

\[ l \gg 1 \]

but satisfies the following condition

\[ l^2 \frac{v_l}{v_v} \ll 1 \quad (5) \]

Due to \( (4) \) it is possible to do.

In the region \( r \leq lR_d \) the stationary profile is established after

\[ t_h = \frac{l^2 R_d^2}{4D} \]

It is necessary to show that

\[ s \equiv \frac{R_d(t + t_h) - R_d(t)}{R_d(t)} \ll 1 \]
Really,

\[ s \approx \frac{dR_d}{dt} \frac{t_h}{R_d} \]

and

\[ s \sim \lambda \frac{v_l}{v_v} \]

which is a small value according to (3). So, the stationary form of profile in the region \( r < R_d l \) is proven.

As far as \( \Gamma \gg 1 \) and at least \( \Gamma \gg l \) one can see that in the region \( r < lR_d \) there is no formation of new droplets. Then this region isn’t interesting for the theory and one can only observe the region \( r > lR_d \).

The previous notation is rather important. Namely this property allows to use the model with a point source. Really, one can consider only the distances greater than \( lR_d \). But at these distances the droplet can be interpreted as a point.

Certainly, the point approximation of a droplet can not give an expression for the rate of droplets growth because the boundary condition at \( r = R_d \) is absent. But the rate of growth is already known and can be used directly as a known function of time. Really,

\[ \frac{d\nu}{dt} = \lambda t^{1/2} \]

where

\[ \lambda = 2^{5/2} \pi v_l^{1/2} \zeta^{3/2} v_v^{3/2} D^{3/2} \]

The action of a point source of a vapor consumption can be described in a simple and suitable manner under the Green function formalism. The Green function for the diffusion equation can be written in a following form

\[ G_r = \Theta(t) \frac{\exp(-r^2/4Dt)}{(4\pi Dt)^{3/2}} \]

Then one can get the density profile by a simple integration

\[ n(r) = n(\infty) - \int_0^r \frac{\lambda x^{1/2}}{(4\pi D(t-x))^{3/2}} \exp\left(-\frac{r^2}{4D(t-x)}\right) dx \]
After evident transformations one can come to

\[ \frac{\zeta_0 - \zeta}{\zeta_0} = \sqrt{\frac{2}{\pi}} \sqrt{v_f} f(\beta) \]  

(6)

where

\[ \beta = \frac{r}{\sqrt{4Dt}} \]

and

\[ f(\beta) = \int^\infty_\beta \left( \frac{1}{\beta^2} - \frac{1}{x^2} \right)^{1/2} \exp(-x^2) dx \]

It is important that the profile dependence on \( t \) and \( r \) is now going through \( \beta \).

Concrete form of \( f(\beta) \) is drawn in fig. 1. One can get for \( f(\beta) \) an expression through special functions

\[ f(\beta) = \frac{1}{2} \Gamma\left(\frac{3}{2}\right) \exp(-\beta^2) \Psi\left(\frac{3}{2}, \frac{3}{2}; \beta^2\right) \]

Here \( \Gamma \) is the Gamma-function, \( \Psi \) is the confluent hypergeometric function.

One can get asymptotes for \( f(\beta) \) at small and big values of \( \beta \). At small values

\[ f(\beta) \sim \frac{\sqrt{\pi}}{2} \frac{1}{\beta} \]  

(7)

which corresponds to the stationary solution \( \Box \).

At big values of \( \beta \) one can come to

\[ f(\beta) = \exp(-\beta^2) \frac{1}{2\beta^3} \int^\infty_0 x^{1/2} \exp(-x) dx \sim \frac{\exp(-\beta^2)}{\beta^3} \]  

(8)

One can see that this asymptote radically differs from the stationary solution. Namely this tail behavior ensures the convergence of the integral for \( G \). Certainly, the Green function formalism ensures a precise value for \( G \) which is introduced here as an external object.

Now one can turn to construct some approximation for the nucleation rate around the growing droplet.

One can see that according to \( \Box \) the behavior of the supersaturation is important when \( \zeta_0 - \zeta \leq (2 \div 3)\zeta_0/\Gamma \). When \( \zeta_0 - \zeta \geq (2 \div 3)\zeta_0/\Gamma \) the intensity
of the droplets formation is negligibly small. From (1) one can see that

\[ I_s(\zeta(r)) = I_s(\zeta_0) \exp(-\Gamma \sqrt{\frac{2}{\pi v_l} f(\beta)} \sqrt{\frac{v_l}{v_v}}) \]

Then one can extract a positive parameter

\[ \sigma \equiv \Gamma^2 \frac{v_l}{v_v} \]

which will be important in further constructions.

Due to \( \Gamma \gg 1 \) one can easily see that \( \sigma \gg 1 \)

The last condition isn’t necessary for further constructions, but it will be rather important for manifestation of profile effects in the nucleation process.

The last condition is also the most doubtful one because \( v_l/v_v \ll 1 \) and one has the ration of two big parameters with generally unknown result. It is necessary to stress that condition \( v_l/v_v \ll 1 \) isn’t so strong as \( \Gamma \gg 1 \). In frames of thermodynamic description \( \Gamma \gg 1 \) is the main condition necessary to give the thermodynamic description and \( v_l/v_v \ll 1 \) is the supplementary condition which isn’t absolutely necessary but slightly simplifies the theory.

In the situation of homogeneous condensation one has the ”hidden contradiction between the thermodynamic description and the relatively intensive nucleation”. Really, as far as in the homogeneous condensation \( \Delta F = F_c \sim \nu^{2/3} \) the limit \( \nu \to \infty \) means \( \Delta F \to \infty \) and the rate of nucleation goes to zero. So, there is the contradiction between thermodynamic limit in the critical embryo description and the observable rate of nucleation.

In the case of heterogeneous condensation there is no such contradiction if there are some active centers of condensation. Then the height of the activation barrier has no direct connection with a number of molecules inside the critical embryo. For example, the halfwidth of the nearcritical region estimated by a homogeneous value has a value \( \sim \nu^{2/3} \) and goes to infinity when \( \nu \to \infty \), but the free energy decreases at the boundary of the nearcritical region only by one thermal unit. So, in certain sense the case of heterogeneous condensation is more preferable for theoretical description.

\(^{14}\)Which isn’t too small.
As a compensation for this advantage one has to note that the Statement 1 and Statement 2 are based on the homogeneous estimate for the activation barrier height. These properties can be violated. But as far as these Statements are based on very strong inequalities one can accept their validity. The influence of nonstationary effects will be analyzed in a separate publication where the complete theory has been constructed.

Now one can analyze the profile of intensity of the droplets formation around the already existing droplet. This nucleation rate profile is a rather sharp function which has a step-like behavior.

To show this we shall introduce two characteristic values of $\beta$ ($\beta_{st}$ and $\beta_{fin}$) by relations

$$f(\beta_{st}) = \frac{\sqrt{\pi}}{2} \sqrt{\frac{v_0 \exp(-1/2)}{v_t}} \Gamma$$

$$f(\beta_{fin}) = \frac{\sqrt{\pi}}{2} \sqrt{\frac{v_0 \exp(1/2)}{v_t}} \Gamma$$

In the region $\beta > \beta_{st}$ the rate of nucleation practically coincides with the unperturbed value $I_s(\zeta_0)$. In the region $\zeta < \zeta_{fin}$ the rate of nucleation is negligible in comparison with the unperturbed value, i.e. $I_s(\zeta(r)) \ll I_s(\zeta_0)$.

In some moment $t$ the values $\beta_{st}$, $\beta_{fin}$ initiate the space distances $r_{st}$, $r_{fin}$ by the following expressions

$$r_{st} = \beta_{st} \sqrt{4Dt}$$

$$r_{fin} = \beta_{fin} \sqrt{4Dt}$$

For $\sigma \gg 1$ one can come to

$$f(\beta_{st}) \ll 1$$

$$f(\beta_{fin}) \ll 1$$

and

$$\beta_{st} \gg 1$$

$$\beta_{fin} \gg 1$$

Then one can use the asymptote (8) and see that

$$\frac{|\beta_{st} - \beta_{fin}|}{\beta_{st} + \beta_{fin}} = \frac{1}{4\beta_{st,fin}} \ll 1$$
\[
\frac{|r_{st} - r_{fin}|}{r_{st} + r_{fin}} = \frac{1}{4\beta_{st,fin}} \ll 1
\]

The real picture of nucleation is going in the time scale. In a fixed space point \( r \) one can introduce two characteristic times \( t_{st} \) and \( t_{fin} \) by expressions

\[
t_{st} = \frac{r^2}{4\beta_{st}^2 D}
\]

\[
t_{fin} = \frac{r^2}{4\beta_{fin}^2 D}
\]

Before \( t_{st} \) one can not observe any essential deviation of the nucleation rate from the unperturbed value. After \( t_{fin} \) the rate of nucleation is very small.

One can get for the relative deviation

\[
\delta \equiv \frac{t_{fin} - t_{st}}{t_{st,fin}}
\]

the following expression

\[
\delta \sim \frac{1}{\beta_{st,fin}}
\]

So, the relative deviation is small.

Even in the situation of small \( \sigma \) one can show with the help of the asymptote that \( \delta \) is rather small.

The step-like behavior of intensity profile allows to introduce some characteristic parameter \( \beta_{eff} \) and consider the region as the exhausted region where there is no nucleation more and in the region \( \beta > \beta_{eff} \)

the rate of nucleation is unperturbed.

---

\textsuperscript{15}This step can take place even for \( \beta > \beta_{st} \) when \( \sigma \ll 1. \)

\textsuperscript{16}At \( \sigma \ll 1 \) the value of \( \beta_{eff} \) can be greater than \( \beta_{st} \) and \( \beta_{fin}. \)

\textsuperscript{17}In all cases \( \beta_{eff} > \beta_{fin}. \)
One has to choose $\beta_{\text{eff}}$ carefully. The problem is the possibility of existence of a long tail of a density profile. To grasp the situation of a small values of $\sigma$ one has to introduce $\beta_{\text{eff}}$ in an integral manner.

One can introduce the excess of nucleation rate $\Delta I_s$ by the following formula

$$\Delta I_s = I_s \int_0^\infty (1 - \exp(-\frac{\Gamma(\zeta_0 - \zeta(r))}{\zeta_0})) 4\pi r^2 dr$$

when $I_s$ is the unperturbed rate of nucleation.

On the base of the last expression one can get the excess of $N$ due to the existence of the solitary profile. This value will be marked by $\Delta N_{\text{sol}}$ and can be found as

$$\Delta N_{\text{sol}} = I_s \int_0^t \int_0^\infty (1 - \exp(-\frac{\Gamma(\zeta_0 - \zeta(r))}{\zeta_0})) 4\pi r^2 dr dt'$$

Having used equation (6) one can come to

$$\Delta I_s = 4\pi (4Dt)^{3/2} I_s \int_0^\infty (1 - \exp(-\sqrt{\frac{2}{\pi}} \sqrt{\frac{v_l}{v_v}} f(\beta))) \beta^2 d\beta$$

Parameter $\Gamma \sqrt{\frac{2}{\pi}} \sqrt{\frac{v_l}{v_v}}$ has a constant value.

The value $\Delta N_{\text{sol}}$ can be now found as

$$\Delta N_{\text{sol}} = 4\pi (4Dt)^{3/2} I_s \int_0^t \int_0^\infty (1 - \exp(-\sqrt{\frac{2}{\pi}} \sqrt{\frac{v_l}{v_v}} f(\beta))) \beta^2 d\beta dt'$$

The step-like approximation of the nucleation profile will lead to

$$\Delta I_s^0(\beta_{\text{eff}}) = 4\pi (4Dt)^{3/2} I_s \int_0^{\beta_{\text{eff}}} x^2 dx$$

The value $\beta_{\text{eff}}$ has to be determined from

$$\Delta I_s^0(\beta_{\text{eff}}) = \Delta I_s$$

Certainly, the value of $\beta_{\text{eff}}$ depends of $\Gamma \sqrt{\frac{2}{\pi}} \sqrt{\frac{v_l}{v_v}}$.

The value of $\beta_{\text{eff}}$ initiates

$$r_{\text{eff}} = 2\beta_{\text{eff}} D^{1/2} t^{1/2}$$
Inside the volume

\[ V_{\text{eff}} = \frac{4}{3} \pi r_{\text{eff}}^3 \]

there is no nucleation and outside this volume the rate of nucleation is unperturbed.

Then one can imagine that around every droplet there exists the exhausted region (ER) where there is no nucleation and the unexhausted region (UR) where the nucleation remains unperturbed. The whole space now is divided into two regions.

The volume \( V_{\text{eff}} \) grows in time in the following way

\[ V_{\text{eff}} = \frac{32}{3} \pi \beta_{\text{eff}}^3 D^{3/2} t^{3/2} \]

In a free molecular regime \( V_{\text{eff}} \) will grow even faster.

For \( b_{\text{eff}} \) one can get the simple expression

\[ \beta_{\text{eff}}^3 = 3 \int_0^\infty (1 - \exp(-\Gamma \sqrt{\frac{2}{\pi} v_l v_v f(\beta)})) \beta^2 d\beta \]

or

\[ \beta_{\text{eff}}^3 = 3 \int_0^\infty (1 - \exp(-\sigma^{1/2} \sqrt{\frac{2}{\pi} f(\beta)})) \beta^2 d\beta \]

For \( \Delta N_{\text{sol}} \) one can obtain

\[ \Delta N_{\text{sol}} = I_s(\zeta_0) \int_0^t dt' V_{\text{eff}} = \int_0^t dt' \frac{4}{3} \pi r_{\text{eff}}^3 \]

One can easy integrate the last expression and get

\[ \Delta N_{\text{sol}} = I_s(\zeta_0) \frac{64}{15} \pi \beta_{\text{eff}}^3 D^{3/2} t^{5/2} \]

One can see that \( \Delta N_{\text{sol}} \) is growing in time rather rapidly. Namely this property illustrates the feature of the "avalanche consumption during the first order phase transition" in application to the heterogeneous nucleation.

For those situations where \( \sigma \gg 1 \) one can get

\[ \beta_{\text{eff}} \approx \beta_{st} \approx \beta_{\text{fin}} \]
and $\beta_{\text{eff}}$ satisfies the simple equation

$$
\exp(-\beta_{\text{eff}}^2) = \beta_{\text{eff}}^3 \sqrt{\frac{v}{v_l}} \sqrt{\frac{\pi}{2 \Gamma}}
$$

The last equation can be easily solved by iterations as far as $\beta_{\text{eff}} \gg 1$ and $\exp(-\beta^2)$ is the most sharp function of the supersaturation.

Earlier when the principle of the separate growth was discussed then the reason of the absence of interaction between droplets was the low probability to appear too close one to another only due to the smallness of such space volume. Now one can see that the growing ER helps to exclude the interference. Really, the essential deviation of the supersaturation from the ideal one can be seen in the region $r < R_{dl}$. It means that the distance between the droplets with an interference must have the order $2R_{dl}$ Then the time distance between the moments of formation of these droplets must be shorter than

$$
\Delta t_{\text{init}} \sim \left(\frac{R_{dl}}{\beta_{\text{eff}} D^{1/2}}\right)^2
$$

This time interval is many times shorter than the duration of the nucleation period.

Every droplet forms rather rapidly after formation the ER of such a size which guarantees that the rate of growth of the given droplet can not be perturbed by a vapor consumption by the other droplets.

## 2 Kinetic models of the global evolution

Now one can construct the picture of nucleation in a whole system. The main problem is to take into account the interference of the density profiles. The interference through the rate of growth is absent, but there is a simple overlapping of profiles which leads to the deviation of the total nucleation rate over the volume from those calculated with account of the additive excesses around every droplet.

The overlapping of ER (even when this approximate formalism is used) is very complex and can not be directly taken into account in precise manner. Instead of writing the long expressions which can not be explicitly calculated one can act in another manner: some simple approximate models for kinetics of the nucleation process will be formulated. From these models it will be
seen that they estimate the nucleation characteristics from below and from above and lead practically to the similar results. So, it will be shown that the complex details of the ER overlapping has no strong influence on the real characteristics of the phase transition.

At first one can consider the common feature of all models concerning the exhaustion of free heterogeneous centers.

The rate of nucleation $I$ depends on time $t$ and on spatial point $r$ (the last behavior is the most complex). So, it is reasonable to consider the mean (over the space) value of $I$ denoting it by $<I>$. For $<I>$ one can write the following expression

$$<I>=\frac{W_{\text{free}}}{W_{\text{tot}}} \frac{\eta}{\eta_{\text{tot}}} I_0$$

where $I_0$ is the unperturbed rate of nucleation. Here $W_{\text{free}}$ is the volume of a region where the rate of nucleation is unperturbed, i.e. the UR of the whole system. The value $W_{\text{tot}}$ is the total volume of the system (it equals to unity and is written only to clarify the consideration).

Then as far as

$$N = \int_0^t <I>(t') dt'$$

one can get

$$\eta = \eta_{\text{tot}} - \int_0^t <I>(t') dt'$$

In the differential form the last relation can be written as

$$\frac{d\eta}{dt} = -<I>$$

and with the help of (9) it can be rewritten as

$$\frac{d\eta}{dt} = -\frac{\eta}{\eta_{\text{tot}}} \frac{W_{\text{free}}}{W_{\text{tot}}} I_0$$

After the integration of the last expression one can come to

$$\eta = \eta_{\text{tot}} \exp\left(-\int_0^t \frac{W_{\text{free}}(t')}{W_{\text{tot}}} \frac{I_0}{\eta_{\text{tot}}} dt'\right)$$

One has to note that heterogeneous centers aren’t distributed homogeneously with respect to the ER (or UR). Only free heterogeneous centers are
distributed homogeneously with respect to ER. This fact has to be also taken into account.

The problem is to determine the value of \( W_{\text{free}} \). In different models it will be determined in different forms.

The model without overlapping.

One can write

\[
W_{\text{free}} = W_{\text{tot}} - W_{\text{exh}}
\]

where \( W_{\text{exh}} \) is the volume where there is no further formation of the droplets. Very approximately one can present it as the sum of ER around all appeared droplets

\[
W_{\text{exh}} \approx \sum_i V_{\text{eff}}
\]

(the sum is taken over all already formed droplets). Certainly, the last approximation is rigorous only when there is no overlapping of the ER around different droplets.

Having used an expression for \( V_{\text{eff}} \) one can come to

\[
W_{\text{exh}} = \int_0^t dt' < I > (t')^{3/2} \frac{32}{3} \pi \beta_{\text{eff}}^3 D^{3/2} (t - t')^{3/2}
\]

Having used an expression for \( < I > \) one can come to the closed system of nucleation kinetics equations

\[
W_{\text{free}} = W_{\text{tot}} - \int_0^t dt' \frac{\eta}{\eta_{\text{tot}}} \frac{W_{\text{free}}}{W_{\text{tot}}} I_0 \frac{32}{3} \pi \beta_{\text{eff}}^3 D^{3/2} (t - t')^{3/2}
\]

\[
\eta = \eta_{\text{tot}} \exp(- \int_0^t \frac{W_{\text{free}}(t')}{W_{\text{tot}}} \frac{I_0}{\eta_{\text{tot}}} dt')
\]

In the quasi-homogeneous limit (when there is no essential exhaustion of centers) this system can be reduced to

\[
W_{\text{free}} = W_{\text{tot}} - \int_0^t dt' \frac{W_{\text{free}}}{W_{\text{tot}}} I_0 \frac{32}{3} \pi \beta_{\text{eff}}^3 D^{3/2} (t - t')^{3/2}
\]

which can be written after the evident renormalization \( t \to at, t' \to at' \) where

\[
a = (I_0 \frac{32}{3} \pi \beta_{\text{eff}}^3 D^{3/2})^{2/5}
\]

in the universal form

\[
W_{\text{free}} = 1 - \int_0^t dt' W_{\text{free}}(t - t')^{3/2}
\]
One has to note that in the general case the system of nucleation equations can be solved with the help of methods developed in [3]. At first one can solve the quasihomogeneous equation (it the Volterra equation with a rather simple kernel which allows to apply the Laplace transformation to solve it) and then on the base of quasihomogeneous equation one can find the final rather precise expression using the second equation as a formula for $\eta$.

Another variant is to solve numerically the universal equation for $W_{\text{free\ hom}}$:

$$W_{\text{free\ hom}} = 1 - \int_0^t dt' W_{\text{free\ hom}}(t - t')^{3/2}$$

Then one has the universal function $W_{\text{free\ hom}}$. Then one can find $\eta$ as

$$\eta = \eta_{\text{tot}} \exp(-a^{-1} \int_0^t \frac{W_{\text{free\ hom}}(t') I_0}{W_{\text{tot}} \eta_{\text{tot}}} dt')$$

The last expression leads to the formula for $<I>$ as:

$$<I> = \frac{W_{\text{free\ hom}}}{W_{\text{tot}}} \exp(-a^{-1} \int_0^t \frac{W_{\text{free\ hom}}(t') I_0}{W_{\text{tot}} \eta_{\text{tot}}} dt' I_0)$$

The justification of such approach is analogous to [3]. The physical reason is very simple: when there is no exhaustion of heterogeneous centers then the solution is found precisely, when there is an essential exhaustion of centers there is no need to know $W_{\text{free}}$ with a high precision because the converging force of the operator of the right hand of the second equation in the nucleation equations system is extremely high.

Now we shall take into account the overlapping. It can be done rather approximately.

The model with chaotic overlapping

The matter of discussion is the correct expression for $W_{\text{free}}$ which can not be got absolutely precisely. Now the more reasonable expression for $W_{\text{free}}$ will be presented. Certainly, this will lead to a more complicate equation which will be more difficult to solve.

One can use the differential approach to write the expression for $W_{\text{free}}$. Having written the evident relation

$$\frac{dW_{\text{free}}}{dt} = -\frac{dW_{\text{exh}}}{dt}$$
one has to invent an approximation for \( \frac{dW_{exh}}{dt} \). Here the following approximation

\[
\frac{dW_{exh}}{dt} \approx \frac{d \sum_i V_{eff} W_{free}}{dt} W_{tot}
\]

(the sum is taken over all droplets) will be used. It corresponds to the following approach: The probability of the absence of overlapping of the new parts of ER around the given droplet with other ER is proportional to the free volume of the system.

The last supposition seems to be rather reasonable.

The value \( \frac{d \sum_i V_{eff}}{dt} \) can be rewritten as

\[
\frac{d \sum_i V_{eff}}{dt} = \sum_i \frac{dV_{eff}}{dt}
\]

The last value can be easily expressed through \(< I >\) as

\[
\sum_i \frac{dV_{eff}}{dt} = \frac{3}{2} \int_0^t dt' < I > (t')^\frac{32}{3} \pi \beta_{eff}^3 D^{3/2} (t - t')^{1/2}
\]

(12)
due to (11).

Then

\[
\frac{dW_{exh}}{dt} = \frac{3}{2} \int_0^t < I > (t')^\frac{32}{3} \pi \beta_{eff}^3 D^{3/2} (t - t')^{1/2} dt' W_{free}(t)
\]

and

\[
\frac{dW_{free}}{dt} = -\frac{3}{2} \int_0^t < I > (t')^\frac{32}{3} \pi \beta_{eff}^3 D^{3/2} (t - t')^{1/2} dt' W_{free}(t)
\]

Having used an expression for \(< I >\) one can come to

\[
\frac{dW_{free}}{dt} = -\frac{3}{2} \int_0^t \frac{W_{free}(t')}{W_{tot}} I_0 \frac{\eta}{\eta_{tot}} \frac{32}{3} \pi \beta_{eff}^3 D^{3/2} (t - t')^{1/2} dt' W_{free}(t)
\]

Together with (11) the last equation forms the closed system of the nucleation equations in the second model.

The previous equation can be integrated which gives

\[
\ln W_{free} = -\int_0^t \frac{W_{free}(t')}{W_{tot}} I_0 \frac{\eta(t')}{\eta_{tot}} \frac{32}{3} \pi \beta_{eff}^3 D^{3/2} (t - t')^{3/2} dt' + \text{const}
\]
Due to the initial conditions the \( \text{const} \) is equal to zero. Having introduced the function \( F = -\ln W_{\text{free}} \) one can get for \( F \) the following system of equations

\[
F(t) = \int_0^t \exp(-F(t'))I_0 \frac{\eta(t')}{\eta_{\text{tot}}} \frac{32}{3} \pi \beta_{\text{eff}}^3 D^{3/2} (t - t')^{3/2} dt'
\]

\[
\eta = \eta_{\text{tot}} \exp\left(-\int_0^t \exp(-F(t')) \frac{I_0}{\eta_{\text{tot}}} dt'\right)
\]

One can see that the system of condensation equations is identical to the system of nucleation equations in AA. It was completely analyzed in [5]. Certainly, the parameters in the system will be another.

The last system can be rewritten after the evident renormalization as

\[
F(t) = \int_0^t \exp(-F(t'))(t - t')^{3/2}\theta(t')dt' \equiv \hat{F}(F, \theta)
\]

\[
\theta(t) = \exp\left[-A \int_0^t \exp(-F(t')) dt'\right] \equiv \hat{\theta}(F)
\]

where \( \theta(t) = \eta(t)/\eta_{\text{tot}} \) and \( A \) is some known parameter.

This system can be solved by iterations defined as

\[
F_{i+1} = \hat{F}(F_i, \theta_i)
\]

\[
\theta_{i+1} = \hat{\theta}(F_i)
\]

with \( F_0 = 0, \theta_0 = 1 \).

For \( F_i, \theta_i \) one can get the chains of inequalities

\[
F_0 < F_2 < F_4 < \ldots < F_3 < F_1 < \ldots < F_{2i+1} < \ldots < F_{2i+1} < \ldots < F_3 < F_1
\]

\[
\theta_1 < \theta_3 < \ldots < \theta_{2i+1} < \ldots < \theta < \ldots < \theta_{2i+1} < \ldots < \theta_2 < \theta_0
\]

Then one can estimate errors in \( F_i, \theta_i \).

One can use also another methods analogous to those described in [3].

The similarity of the the condensation equations in AA and in the second model is extremely important for the transition towards collective character of vapor consumption which is analyzed in [5].

The physical ground of the considered model is the chaotic overlapping of ER. Namely, the chaotic overlapping lies in the base of approximation
used here. But due to the spherical form of every ER the overlapping isn’t absolutely chaotic.

What can be done in such a situation? In the next model we shall show that concrete type of overlapping isn’t very important.

To finish with the second model we shall show the same method of its solution as that of the first model.

One can also formulate the quasihomogeneous equation as the following one

\[ F_{\text{hom}}(t) = \int_0^t \exp(-F_{\text{hom}}(t')) I_0 \frac{32}{3} \pi \beta_{\text{eff}}^3 D^{3/2} (t - t')^{3/2} dt' \]

Then \( \eta \) can be approximately found as

\[ \eta = \eta_{\text{tot}} \exp(-\int_0^t \exp(-F_{\text{hom}}(t')) \frac{I_0}{\eta_{\text{tot}}} dt') \]

The quasihomogeneous equation can be renormalized. After renormalization \( z \rightarrow at, t' \rightarrow at' \) where

\[ a = (I_0 \frac{32}{3} \pi \beta_{\text{eff}}^3 D^{3/2})^{2/5} \]

one can transform the quasihomogeneous equation into the universal form

\[ \ln W_{\text{free \ hom}}(t) = -\int_0^t W_{\text{free \ hom}}(t')(t - t')^{3/2} dt' \]

The model with the formation of droplets inside the ER

The third model will show that the role of overlapping isn’t so essential as it can be imagined from the first point of view.

Suppose that the new droplets can appear also in the ER of the already existed droplets. Then instead of (12) one has to use

\[ \sum_1 dV_{\text{eff}} = \frac{3}{2} \int_0^t dt' \eta(t') \frac{32}{3} \pi \beta_{\text{eff}}^3 D^{3/2} (t - t')^{1/2} \]

Then

\[ \frac{dW_{\text{exh}}}{dt} = \frac{3}{2} \int_0^t \frac{\eta(t')}{\eta_{\text{tot}}} \frac{32}{3} \pi \beta_{\text{eff}}^3 D^{3/2} (t - t')^{1/2} dt' W_{\text{free}}(t) \]
and

$$\frac{dW_{\text{free}}}{dt} = -\frac{3}{2} \int_0^t I_0 \eta(t') \frac{32}{\eta_{\text{tot}}} \pi \beta_{\text{eff}}^3 D^{3/2} (t - t')^{1/2} dt' W_{\text{free}}(t)$$

Together with (11) the last equation forms the closed system of the nucleation equations in the third model.

The substance balance equation of the system can be integrated which gives

$$\ln W_{\text{free}} = -\int_0^t I_0 \eta(t') \frac{32}{\eta_{\text{tot}}} \pi \beta_{\text{eff}}^3 D^{3/2} (t - t')^{3/2} dt' + \text{const}$$

Due to the initial conditions the const is equal to zero. Having introduced the function $F = -\ln W_{\text{free}}$ one can get for $F$ the following system of equations

$$F(t) = \int_0^t I_0 \frac{\eta(t')}{\eta_{\text{tot}}} \frac{32}{3} \pi \beta_{\text{eff}}^3 D^{3/2} (t - t')^{3/2} dt'$$

$$\eta = \eta_{\text{tot}} \exp(-\int_0^t \exp(-F(t')) \frac{I_0}{\eta_{\text{tot}}} dt')$$

This system corresponds to the first iteration in the iteration solution of the second model by the method of iterations of a type ”a” described in [5]. It is also described here. But for $\eta$ the whole set of iterations has been taken (see details in [5]).

One can slightly modify the model and suppose that in the expression for $\eta$ one can use the same approximation for $<I>$ as in equation for $W_{\text{free}}$. Then the system of equation will precisely correspond to the first iteration in the iteration solution in [5].

Actually one needn’t to analyze these models in details following [5] but has only to note that all these solutions are practically similar. One can see the solution of the third model (both variants) after the same renormalizations as in the second model.

Now one has to explain why the third model is rather accurate. One can do it only with the help of results obtained in [10].

In [10] it was noted that when the power of the kernel $(t - t')$ is rather big then the solution of the quasihomogeneous equation weakly depends on concrete value of a power.

Another important notation shows that when the power of $(t - t')$ is extremely high then the ER of the given (first) droplet formed inside the ER of another (second) droplet practically can not go outside the ER of that
(second) droplet. Then the third model is absolute adequate in this situation. The same feature can be seen directly from the iteration procedure results.

Having combined these two notations one can see that on one hand the second model is close to the situation with great power of the kernel and in the situation with the big kernel the third model is suitable.

Now it is possible to explain why the overlapping isn’t so important as it can be imagined. Really, as far as the power of kernel is big and one can observe the avalanche consumption one can see the following qualitative picture

- Practically during all period of nucleation the total ER is small and there is no problem of overlapping.

- At the end of the nucleation period the total ER is going to occupy the essential part of the volume and a few moments late it occupies all the volume of the system. This process is very rapid. It stops the nucleation.

This picture shows that there is no strong influence of the overlapping on the nucleation process (except the cut-off).

As the result the nucleation description is completed. One can use both the second and the third model to get the nucleation description. How to solve these equations is also described here.

The method of universal solution

The main idea of the theory presented in [5] was to consider the quasi-homogeneous equation, to get the universal solution and then on the base of this solution to calculate the number of free heterogeneous centers. As the result one can get an expression for $< I >$ and can calculate the total number of droplets appeared on the nucleation process.

Here one can follow the same idea. But one can make this idea more deep. One needn’t to formulate the universal quasihomogeneous equation. Instead of equation one can formulate the universal model.

The model will be the following

- the rate of nucleation $< I >$ can be found from

$$< I > = I_0 \frac{W_{\text{free}}}{W_{\text{tot}}} \frac{\eta}{\eta_{\text{tot}}}$$
- with intensity $I_0$ the droplet appears in the arbitrary point of the system which belongs to the free volume.

- the value $W_{free}$ can be found by exclusion of all ER around the already existing droplets.

- if the point is occupied by the ER of any droplet then the droplet can not be formed.

- the size $r_{eff}$ of ER grows in time according to

$$r_{eff} = 2 \beta_{eff} D^{1/2} t^{1/2}$$

- the initial condition is the absence of droplets and random distribution of centers.

With the proper renormalization of time $t$ and size $r$ one can cancel all coefficients. Then this process will be the universal one and as the result $W_{free}$ is the universal function of time. Then one can directly apply (11) and get the number of free heterogeneous centers (after the proper renormalization)\(^{18}\).

The modification for the dynamic conditions requires to put instead of $I_0$ the value $I_0 \exp(\alpha t)$ with some parameter $c$ determined by external conditions and to change the lower limit 0 of integration to $-\infty$ \(^{5}\).

The main constructions of the theory will be absolutely the same but the forms of characteristic curves changes radically.

### 3 Numerical results

Numerical simulation in the nucleation kinetics plays at least two important roles. The first role is the standard comparison with the approximate models to observe their quality. The second one is more specific and it is concerned with some universal dependencies in the nucleation kinetics.

In the AA to the nucleation kinetics it was shown that the adequate approach can be presented on the base of the quasihomogeneous solution \(^{4}\). Despite the dynamic conditions considered in \(^{5}\) one can observe this

\(^{18}\)This is quasihomogeneous approach method
property in the situation of the metastable phase decay also. Recall the reasons for such approach.

The formal reason is the careful analysis of the iteration procedure proposed in [5]. Really, the final result for the total number of droplets appeared in the nucleation process is given by the second iteration (see iterations of type "a" in [3]) for the relative number of free heterogeneous centers. This iteration is based only on the first iteration for the supersaturation. The value of supersaturation there is calculated without any account of the heterogeneous centers exhaustion. So, one can see that the final result can be obtained on the base of the supersaturation in the quasihomogeneous approximation. This approximation can be more sophisticated than the first iteration. Namely this approach was used in [5] where the precise quasihomogeneous universal solution was chosen as base for the final results.

The physical reason of such behavior is rather simple. The main role in the vapor consumption belongs to the droplets of relatively large sizes. We have already marked this fact. But moreover, due to the avalanche character of the vapor consumption the main role in vapor consumption is played by the relatively large droplets which are formed in the first moments of time of the nucleation period. When the effect of the centers exhaustion is essential already in the first moments of nucleation period then at the end of nucleation period already all centers will be exhausted. Then the result is evident - all centers are the centers of droplets. Due to the high force of convergence in this situation this result can be gotten under the rather arbitrary behavior of supersaturation (even including the quasihomogeneous case). In the opposite case the exhaustion of heterogeneous centers during the first moments of the nucleation period isn’t essential and one can get the quasihomogeneous behavior of supersaturation.

This effect will be called as the "approximate separation of the heterogeneous and homogeneous problems". It is based only on the avalanche consumption of the metastable phase. So, there are no objections to see this effect also in the situation with the density profiles. Then it is extremely important to get solution in the quasihomogeneous situation and clarify whether it can be presented in the universal form.

\[ \text{More precisely one can define these "first moments of time" as } 2/5 \text{ of the nucleation period duration (under the free molecular regime it is } 1/4 \text{ of the nucleation period duration). The reason for concrete value can come from the iteration procedure.} \]
The universal form of the quasihomogeneous solution can be easily seen in the situation of profiles also. In the AA there was no specific space scale because the consumption took place homogeneously from all space points of the system. Here in the situation of profiles there is the elementary space scale and one can choose the space scale as to have that the linear size of ER around the droplet is growing as \( t^{1/2} \). The time scale has to be chosen as to get that in the free volume equal to the total volume of the system one can see the appearance of one droplet in the unit of time. As long as the functional dependencies of the nucleation rate and the radius of ER are not identical one can do such a renormalization without any problems. So, we see that the pseudohomogeneous case allows the universal description.

The process of the heterogeneous centers exhaustion destroys this universality and one has to act as in \(^{21}\). The total number of droplets has to be approximately calculated as

\[
N_{\text{total}} = \eta_{\text{tot}} \left[ 1 - \exp\left( -\frac{N_{\text{hom}}}{\eta_{\text{tot}}} \right) \right]
\]  

(13)

where \( N_{\text{hom}} \) is the number of the droplets appeared in the quasihomogeneous situation (under the same parameters). This formula can be also used for all approximate models described earlier.

For the numerical simulation it was convenient to consider the cube box with a size 10. The rate of the ER growth is chosen as

\[
\frac{dR}{dt} = 100t^{1/2}
\]

where \( R \) is the radius of ER. The rate of nucleation is chosen as to have one attempt of a new droplet formation in the system during \( dt = 0.002 \). This attempt is governed by the random procedure. It may lead to the point in one of the ER and then no droplet will be formed. In the opposite situation when the point is indicated out of all ER of the already existing droplets there will be a new formation of a droplet.

One has to stress that the random procedure has one specific negative feature. In the standard numerical procedures the next random coordinate is calculated on the base of the previous ones. So, if the current coordinate

\(^{20}\)Certainly, the power has to be conserved.

\(^{21}\)Here we use slightly more simple way.
lies near the center of the already existing ER then the next coordinate will be also near the center of another ER. These correlations lead to the necessity to consider the large system. In the system under consideration the number of droplets appeared in the quasihomogeneous situation will be near 500. Nevertheless the square mean fluctuation will be about 20. The careful consideration can show that the error induced by the substitution of the periodic boundary conditions by the zero ones has the same power as the mean square error. It can be directly seen by the numerical simulation. It is explained by the evident notation that the characteristic overlapping of profiles is about the mean profile size. We shall call this feature as the property of ”moderate overlapping”. This fact can be proven analytically. One can also analytically prove that the effect of fluctuations is really caused by the mentioned phenomena.

The mean value of the total droplets number is equal to 504.8 (under the zero boundary conditions). This value has to be put into the previous formula.

The avalanche character of the vapor consumption is illustrated by fig. 2-4. Three different moments of time $t = 0.5$, $t = 1$ and $t = 1.5$ are chosen as characteristic values. The cross section is drawn. The dashed regions correspond to the ER of the already existing droplets. The black regions correspond to the overlapping of ER.

The number of heterogeneous centers in such a system can be arbitrary. Certainly the effects of the centers exhaustion will be important when the number of centers is small (in comparison with $N_{\text{hom}} = 504.8$). The pictures for $\eta_{\text{tot}} = 50$ are drawn in fig. 5-7 for $t = 1.5$, $t = 3$, $t = 6$. One can see that the number of ER is smaller than in the quasihomogeneous case. The size of ER when the free volume is going to be exhausted is larger than the size of ER in the quasihomogeneous case. The time necessary to cover all volume by ER is greater than in the quasihomogeneous case. It doesn’t mean that the duration of the nucleation period will be longer (simply all centers will be exhausted and this means the end of nucleation). Moreover, the duration of the nucleation period in the situation of the relatively small number of heterogeneous centers will be shorter than in the quasihomogeneous case.

One can also see that the avalanche character of the vapor consumption here will be more smooth than in the quasihomogeneous case. Certainly, in

\begin{footnote}
\textsuperscript{22}Only when the distance between centers is approximately the odd one.
\end{footnote}
the quasihomogeneous case the appearance of the new ER helps to consume the vapor phase in the avalanche manner. But in the situation with the small number of centers there is no need to consider the process carefully because the exhaustion of centers leads to the evident result of condensation - the number of the droplets equals to the number of centers.

Now it is evident that the main object of our interest will be the quasihomogeneous case. The relative rate of nucleation in this case is shown in fig. 8. Here the rate of nucleation is averaged over \(100dt \equiv 0.2\) and over 16 attempts. So, the rate of nucleation is rather smooth function.

The relative rate of nucleation is compared in fig. 8 with the mentioned models. Certainly, the rate of nucleation defines the spectrum of sizes when we take as the size of embryo those characteristic which has the rate of growth independent on the value of size. For the diffusion regime this characteristic is the number of molecules in the power \(2/3\).

One can see in fig. 8 three different curves and some solitary points. The solitary points correspond to the numerical simulation of the quasihomogeneous case and three curves correspond to three models in the quasihomogeneous case.

The shortest spectrum is in the first model. The careful look shows that this line is doubled. This occurs because there the ideal variant of the first model is also drawn. This ideal variant corresponds to \(W_{\text{free}}/W_{\text{total}} \equiv 1\) in the subintegral function. The coincidence means that the main role in the first model is played by the relatively big droplets which were formed at \(W_{\text{free}} = W_{\text{total}}\).

The longest spectrum corresponds to the second model. This curve is very close to the intermediate curve which corresponds to the third model. The approximate coincidence of the second and the third models shows that both of them are valid and the role of the relatively big droplets here is the main one.

One also see that the first model isn’t too far from the real solution. This allows to present the rigorous estimates for the nucleation rate. Certainly the first model is the estimate of the real process from below. It gives the number of the droplets about 20 percents less than the numerical simulation.

An estimate for the nucleation rate from above can be gotten by the following way. From the first model it follows that until \(t = 0.52\) (practically this case is drawn in fig. 2) the rate of nucleation is near the ideal value and the deviation is less than 15 percents. So, one can say that the period
$0 < t < 0.52$ corresponds to the absence of overlapping (the first model is the estimate from above). Then one can consider the process where the total volume is exhausted only by the ER of the droplets appeared at $0 < t < 0.52$ in a random manner. The distribution of the centers of ER of such droplets is evidently random. This model certainly gives the estimate from above for the nucleation process. The total number of the droplets is only 15 percents greater than the result of the numerical simulation. As a conclusion one can state that two suitable estimates from below and above are obtained.

The proximity of the last estimate to the real solution justifies the supposition that the main role in vapor consumption belongs to the droplets of the relatively big sizes appeared in the system practically free from the ER. This supposition can be also justified in the analytical manner.

One can see that the second and the third models are rather close to the real solution but don’t coincide with it. There are at least two reasons of such deviation. The first one is the presence of the strong correlations in the real system - if two ER overlap in some moment of time then the power of overlapping can only grow in time. It hasn’t a random character as it is stated in the second and third models.

This effect can be taken into account in a rather simple manner. It is sufficient to consider two spheres and calculate the power of overlapping as the function of the distance and time (it is the simple geometrical problem). Unfortunately the answer can be written only in a very complicate form. If we have two ER with radii $R_1$ and $R_2$ correspondingly at a distance $l$ between their centers and $l > \max(R_1, R_2)$ then the volume of overlapping is

$$V_{\text{over}} = \frac{2\pi R_1^3}{3} (1 - 2\cos \varphi_1 + \cos^3 \varphi_1) + \frac{2\pi R_2^3}{3} (1 - 2\cos \varphi_2 + \cos^3 \varphi_2)$$

where

$$\cos \varphi_1 = \frac{-R_2^2 + R_1^2 + l^2}{2R_1 l}$$

$$\cos \varphi_2 = \frac{-R_1^2 + R_2^2 + l^2}{2R_2 l}$$

Certainly, this result can not lead to the compact form of the balance equation. It will be difficult to solve it analytically.

The second reason is the ”moderate overlapping” problem. This property means that actually there is an interaction through overlapping in ensemble of
several droplets. Earlier this property was extracted \cite{11} in a case of a special effective length of ER. Now we see that this property has a rather general sense. The way to solve this problem proposed in \cite{11} is very complicate and leads to some uncertain relations.

How one can overcome all these problems? Actually one has no need to do it. The simple numerical simulation takes into account all these effects and gives the universal solution. Really we need only one number - the total number of appeared droplets. It is known. Then one can forget about all mentioned difficulties.

Now one can analyze the heterogeneous case explicitly. The suitable approximation is given by (13). One has to substitute instead of $N_{hom}$ the number of droplets given by the corresponding model.

The relative error of approximation (13) is drawn in fig. 9 for the first model, in fig. 10 for the second model, in fig. 11 for the third model. It is rather small for all models. For the third model it is practically negligible. It is clear because the third model is based on the free volume approximation. Then the source of error can be found only in exhaustion of centers without any influence on the growing of ER. Without this influence the power of exhaustion can not essentially act on the process of nucleation.

One can fulfill the same analysis for the numerical simulation. In fig. 12 the relative error of (13) for numerical simulation is drawn. Here in (13) the value $N_{hom} = 504.8$ from the numerical simulation is used. The result is compared with the computer simulation of heterogeneous condensation. This simulation is rather simple. One can take the procedure for the quasi-homogeneous case but put the center of the new droplet with probability $\eta/\eta_{tot}$. Every time when this point will be out of ER we shall reduce $\eta$ as $\eta \rightarrow \eta - 1$.

One can see that the relative error is very small. We don’t use the averaging over (this is the reason why there is no smooth curve) many attempts in order to see that the error of (13) has the scale of the mean square error of numerical simulation\footnote{For the system with 500 droplets.}. So, there is no need to use the more sophisticated approach.

The solution of the problem now is completed.

The generalization for the conditions of dynamic type is absolutely analogous to \cite{8}. The convergence due to avalanche consumption is more weak and...
one has to use instead of approximation (13) more sophisticated procedure described in [3]. Certainly, the universal constants have to be calculated by the numerical simulation with profiles.

The generalization for the arbitrary regime of the droplets growth can be done absolutely analogous to [8]. This generalization is based on the similarity of the functional forms obtained here and in the AA. This similarity lies in the base of universality formulated in [10], [11].

One can see that the theory of condensation with profiles taken into account presents the picture which is absolutely different from the AA. Nevertheless in many situations the result of experiment coincides with the result of the AA. One has to explain this coincidence. It is rather formal one.

Really, in any experiment it is more convenient to have a small system and to get many droplets. The rate of nucleation has to be taken as a rather high one. So, the supersaturation is relatively high and parameter $\sigma^{-1}$ isn’t a real small parameter of a theory. Then as it is shown in [11] the AA gives the write qualitative result despite the wrong base of consideration. The reason lies in the fact that at small $\sigma$ the main quantity of a substance is lying in the tail of profile. The tail of profile is rather thin and can be be taken into account by the AA. In [11] the correction term for the AA at small $\sigma$ is also presented.

The last important feature to mention is the movement of the embryos boundaries. This problem is widely discussed in the determination of the rate of regular growth for the supercritical embryos. In different systems the effect of influence of the boundary movement on the rate of growth is different. We have to note that in theory presented here the rate of the embryos growth is an external value which is assumed to be known.

Another problem is the adequate account of the effect of boundary movement in construction of the ER. One can see that in the first part of publication it is already shown that the effect of the boundary movement is small. Here we shall present the abstract arguments for such conclusion.

To use the thermodynamic approach the initial power of the mother phase metastability has to be relatively small. Together with the Maxwell’s rule it leads to the following final result of the phase transition: "Only relatively

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24 It isn’t necessary for consideration here, but it has to be small due to the possibility of thermodynamic description of the critical embryo.

25 It is really known practically for all systems.
small part of the system volume is occupied by the new phase.” It isn’t in contradiction with the property that all volume is occupied by ER. So, the final state of the system is the practically saturated mother phase in practically all volume of the system and the small volume (distributed over all system) occupied by a new phase.

As the result one can see that the process of a substance consumption (extraction) leads to the saturation in a volume relatively large in comparison with a volume of the new phase embryo.

The mother phase can not be undersaturated (then there will be the disappearance of embryos). So, as long as even the saturated phase has to be spread on large distances $l_0$ one can state that the growth of embryo produces the perturbation over the large distances $l > l_0$. To have an interruption (relative interruption in comparison with an ideal nucleation rate) of a new phase formation one needs a very small reduction of the power of metastability. So, this reduction is attained at the distances $l' > l$ which are very large in comparison with the embryos linear size. Then one can use the point source approximation as it was done in the first part and forget about the boundaries movement. The negligible character of the boundary movement is proven now for all possible systems.

The heat extraction and account of all other intensive parameters of description can be done analogously to [10].

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Fig. 1
The form of $f(\beta)$. 

$latex f(\beta)$
Fig. 2
The cross section of the system at $t = 0.5$ for the quasihomogeneous situation.
Fig. 3
The cross section of the system at $t = 1$ for the quasihomogeneous situation.
Fig. 4
The cross section of the system at $t = 1.5$ for the quasihomogeneous system.
Fig. 5

The cross section of the system at $t = 1.5$ for $\eta_{\text{tot}} = 50$. 
Fig. 6
The cross section of the system at $t = 3$ for $\eta_{\text{tot}} = 50$. 
Fig. 7
The cross section of the system at $t = 6$ for $\eta_{\text{tot}} = 50$. 
Fig. 8
Comparison of different models in the quasihomogeneous situation.
Fig. 9
Relative error of the quasihomogeneous approach in the first model.
Fig. 10
Relative error of the quasihomogeneous approach in the second model.
Fig. 11
Relative error of the quasihomogeneous approach in the third model.
Fig. 12
Relative error of the quasihomogeneous approach in the universal simulation.