Kinetic effects of multi-component nucleation

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Abstract

The process of multicomponent condensation is considered. The theory taking into account several channels of nucleation is constructed. The analytical approximate description of the whole condensation process is given. The specific phenomena of the secondary nucleation is described analytically. The possibility of the partial reverse condensation is discussed.

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1 Introduction

Multicomponent nucleation is widely spread in nature and the task to describe it theoretically is rather actual. Creation of the classical theory of nucleation [1] allows to investigate the case of multicomponent nucleation. The stationary rate of multicomponent nucleation was found in [2], solution of a stationary kinetic equation with appropriate boundary conditions was given in [3]. These results gave the opportunity to describe kinetics of the global evolution during the whole phase transition. The final period of evolution is known - it is the period of the recondensation (coalescence) and it is described by the Lifshic-Slezov theory [4]. But coalescence is mainly the redistribution of surplus substance and the real transition of practically all surplus substance occurs earlier. Before the coalescence, in fact, a phase transition takes place. To describe the phase transition it is necessary to determine the total number of droplets appeared in the process of nucleation. This quantity is the quasiintegral of evolution after the end of nucleation and before the coalescence. The characteristic times of coalescence ordinary strongly exceeds the characteristic times of experimental

\footnote{\text{Certainly, during the coalescence a small part of the surplus substance is gradually going from the mother phase to the new phase.}}
observations and the characteristic time of a practically all surplus substance consumption exceeds the time of nucleation (i.e. the duration of the intensive appearance of droplets). Then the problem to determine the number of droplets is the central one and it will be solved here when many channels of nucleation are important.

The problem to determine the global evolution until coalescence for multicomponent case was investigated in [2], [5], [6], [7], [10]. Recent publications [8], [9] repeat the consideration made in [6], [7], [10]. The mentioned publications gave the consideration of the most spread case of multicomponent condensation when the droplets of the sole composition will appear in the system. Then as it is noted in [6], [7], [10], [5] the method of description of the nucleation can be reduced by renormalizations to the one component case. Therefore it was sufficient to give in [6], [7], [10], [5] the corresponding references to the one component case [16]. Nevertheless in [8], [9] in consideration of the binary condensation the method of solution of one component situation was reproduced and unfortunately it was done with many errors. This requires to give here detailed analysis of this problem.

Besides the consideration of nucleation with a sole composition of components in droplets the case of multiple compositions will be considered here. To see that the consideration based only on the sole composition isn’t complete we can imagine the following simple example. Let us suppose that the system contains two immiscible substances and both substances in a vapor phase are supersaturated. Then it is evident that the two separate processes of condensation will take place. As the result there will be droplets of the first substance and of the second substance. So, it is evident that consideration of multicomponent nucleation should contain the consideration of multiple channels of droplets formation. It will be done below. The effect of multiplicity of channels of nucleation is well known, it is deeply investigated by Ray [11]. It is rather strange that in [9] (where [11] is considered as the base for constructions) these conclusions of Ray are ignored.

From the first point of view it seems that this problem can be solved by the simple generalization of the case with the sole composition of substances in droplets. This illusion is wrong. The situation when there is absolutely no interaction between separate processes of nucleation of droplets with different compositions is exclusive. Normally there is such interaction and it has to be taken into account. This interaction forms the main content of multicomponent nucleation.

To speak about kinetic effects of multicomponent nucleation one has to specify external conditions. We shall consider the process of the metastable phase decay. In the initial moment of time we have a metastable mixture of gases.

\[2\] But contain some wrong statements, which will be corrected here.

\[3\] Certainly, these processes can interact by a heat release effects, but when these effects are small (it can be ensured by sufficient quantity of passive gas) one will observe two absolutely separate processes of the one component nucleation.

\[4\] Due to the entropy of mixing there can be some species of the other substance in droplets of the given dominating substance.
The stable phase is the liquid droplets phase, which will gradually appear in the system. Liquid phase droplets will consume metastable vapor molecules and the supersaturation of the mother phase is gradually falling. It leads to the cessation of appearance of new droplets and stops the process of nucleation. This is the qualitative picture of metastable phase decay, which will be described quantitatively.

We consider the free molecular regime of vapor consumption. In [12] it is shown how renormalizations can reduce the situation with an arbitrary regime of vapor consumption to the case of the free molecular regime. Below some corresponding remarks will be given.

The absence of thermal effects of condensation is supposed. Formally speaking this absence can be attained by sufficient quantity of a passive gas. The generalization on the thermal effects of nucleation is rather evident and can be done in a manner quite similar to [17].

We take the classical thermodynamic expression for the free energy of a critical embryo. This requires that the critical embryo has to contain many molecules of every component. Only then we can use the approximation of a liquid solution in the embryo. Otherwise one can consider the molecules of a rare component as heterogeneous centers, but the requirement to have many molecules of all substances in the critical embryo remains. Certainly, one can argue about the discrepancy between theoretical and experimental results in nucleation rates even in the one component homogeneous case, but it seems rather evident that this discrepancy can be eliminated by some fitting (normalizing) constants, which are very smooth functions of all ordinary thermodynamic parameters of the systems including supersaturation and temperature. So, we can use the classical expression for the stationary nucleation rate as a brick for constructions made in this paper. It can be done because the variations in thermodynamic parameters essential for nucleation will be very small (details see later).

The system is supposed to be homogeneous in space. The unit volume is considered, all energy like values are measured in units of a mean thermal energy.

## 2 Channels of nucleation

### 2.1 Asymptotic thermodynamic channels

It is supposed that in the system there are $l$ different substances, which can be found later in droplets of liquid. They will be called as components. Different components are marked by lower index. The molecular number densities are marked by $n_i$, in the initial moment of time $t$ they are known and equal to $n_i(0)$. The number of molecules of $i$-th component in the embryo is marked by

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5Or some modified approach. As it can be seen below only some general features of the free energy (such as smoothness on the power of metastability of a mother phase) are required.

6The theory for heterogeneous decay is given in [18].
\(\nu_i\), the total number of molecules - by
\[\vartheta = \sum_i \nu_i.\]

The embryo can be described by the set \(\{\nu_i\} \equiv \vartheta.\) Then the concentration \(\xi_i\) of component inside the embryo will be\(^7\)
\[\xi_i = \nu_i / \vartheta.\]

It can be done for every component and the vector \(\vec{\xi} = \{\xi_i\}\) can be introduced\(^8\). Then one can speak about the molecular number density of a vapor of \(i\)-th component saturated over a liquid of concentration \(\xi\) with a plane surface. It is marked by \(n_{ie}\). According to standard definitions
\[n_{ie} = n_{i\infty} f_i(\vec{\xi}),\]
where \(n_{i\infty} \equiv n_{ie}(\xi_i = 1)\) and \(f_i\) are activity coefficients. Ordinary they satisfy conditions\(^9\)
\[f_i(\xi_i \to 1) \to 1, \quad \partial f_i / \partial \xi_i (\xi_i \to 1) \to 0.\]

In approximation of ideal solution \(f_i \equiv 1.\)

The free energy of an embryo is marked by \(F\). One can speak about \(F\) only for an embryo near the state of initial equilibrium. For the bulk liquid phase the free energy is given by \(F_b = -\sum_i \nu_i \Delta \mu_i\) where the differences of chemical potentials are given by \(\Delta \mu_i = \ln(n_i / n_{ie}),\) which implies that the vapor phase can be regarded as an ideal gas\(^10\). Having extracted extensive variable \(\vartheta\) one can rewrite \(F_b\) as
\[F_b = -\vartheta \sum_i \xi_i \ln(n_i / n_{ie})\]
and extract the function
\[B_b = -\sum_i \xi_i \ln(n_i / n_{ie}).\]

On the base of \(B_b\) one can formulate the necessary condition for the possibility of nucleation - function \(B_b\) has to be negative at least at some \(\xi.\)

The form \(F_b = \vartheta B_b(\vec{\xi})\) leads to existence of the thermodynamic asymptotic channels of nucleation. These channels are straight lines in plane \(\vec{\xi}, \vartheta\), they are perpendicular to \(\vec{\xi}\)-plane. The coordinates \(\xi_i c\) are extracted by conditions
\[\frac{\partial B_b}{\partial \xi_i} = 0, \quad S_q(B_b) \equiv \sum_{i,j} \frac{\partial B_b}{\partial \xi_i \partial \xi_j} (\xi_i - \xi_i c)(\xi_j - \xi_j c) \geq 0.\]

\(^7\)We don’t take into account here the surface enrichment effects. It will be done later.
\(^8\)Here one concentration is absent due to \(\sum_i \xi_i = 1.\)
\(^9\)We shall use in this paper two sets of variables for the embryo description \(\{\xi_i\}, \vartheta\) and \(\{\nu_i\}.\) Sometimes \(\vartheta\) will be changed by the volume of the embryo. So, it is clear what variables will be fixed in partial derivatives.
\(^10\)Certainly, virial corrections can be introduced here and this allows to describe many real situations.
These conditions can be satisfied at some $\xi^c$. Let the number of $\xi^c$ be equal to $l_0$.

One can see that $B_b$ can be presented as

$$B_b = -\sum_i \xi_i (\ln(n_i/n_{i\infty}) - \ln \xi_i - \ln f_i(\xi))$$

The term $-\ln(\xi_i)$ ensures that

$$\frac{\partial B_b}{\partial \xi_i}|_{\xi_i=0} = -\infty,$$

$$\frac{\partial B_b}{\partial \xi_i}|_{\xi_i=1} = \infty.$$

This leads to the following properties of asymptotic behavior of $F_b$:

- (A) The asymptotic thermodynamic channel can not be at $\xi_i = 1$ or $\xi_i = 0$ precisely.

- (B) The previous property doesn’t mean that $B_b$ goes to infinity, the equality $x \ln x|_{x\to+0} \to 0$ ensures that at $\xi_i = 0; 1$ the function $B_b$ attains some finite values. Here it is supposed that all $f_i(\xi)$ have regular behavior.

The first property allows later to make some conclusions about the properties of nucleation channels. The second property establishes the possibility to include the unary nucleation into the multicomponent picture and to see the almost pure channels of nucleation, which will be important here.

We shall denote coordinates of channels by $\xi_{as\;c}$. Consider now the binary case, we enumerate the channels to have

$$\xi_{as\;c\;1} < \xi_{as\;c\;2} < ... < \xi_{as\;c\;l_0}$$

Every channel has the zone of interaction. The boundaries of interaction zones are defined by relations

$$\frac{\partial B_b}{\partial \xi_i} = 0, \quad \frac{\partial^2 B_b}{\partial \xi_i^2} < 0$$

The boundaries of these zones are straight lines in plane $\xi, \vartheta$. They are perpendicular to $\xi$-plane. We have to get the coordinates of these lines. We shall denote these coordinates as $\xi_{as\;b\;i}$ (the first index marks component, the last is the number, index ”$b$” means ”boundary”). The total number of these coordinates is $l_0 - 1$. They are distributed as

$$\xi_{as\;b\;1} < \xi_{as\;b\;2} < ... < \xi_{as\;b\;l_0-1}$$

One can see that

$$\xi_{as\;c\;i-1} < \xi_{as\;b\;i-1} < \xi_{as\;c\;i}, \quad \xi_{as\;b\;i-1} < \xi_{as\;c\;i} < \xi_{as\;b\;i}$$

\(^{11}\)Under the regular behavior of $f_i$. 

The boundaries of the zone of interaction for the first channel are: the lower boundary is \( \xi_{j} \approx b_{0} \equiv 0 \), the upper boundary is \( \xi_{j} \approx b_{1} \). The boundaries of the zone of interaction for the last channel are: the upper boundary is \( \xi_{j} \approx b_{l+1} \equiv 1 \), the lower boundary is \( \xi_{j} \approx b_{l_{0} - 1} \). The boundaries of the zone of interaction for other channels (number \( i \)) are: the upper boundary is \( \xi_{j} \approx b_{i} \), the lower boundary is \( \xi_{j} \approx b_{i - 1} \).

One can determine the time of relaxation for every channel. It is necessary only to linearize the system of equations for the law of the embryos moving in plane \( \nu_{i} \) near the coordinates of the channel. Then we have the ordinary differential equations with constant coefficients with known solution as relaxation exponents\(^{12}\).

One has to note that for the two component case this picture is exact, but for multi component case the situation is more complex: in plane \( \xi \) together with focuses we have saddle points. The analysis in this case here is the standard one for the theory of dynamic systems.

The main ground for this analysis is the reduction of \( F \) into the product of intensive part \( B \) and extensive part \( \vartheta \) ensures that the thermodynamic channels bottoms (when \( \vartheta \) is fixed) are straight lines. The same is true for the bounds of interaction zones - they are also straight lines in plane \( \xi, \vartheta \), perpendicular to the \( \xi \) plane.

Also one has to note that even in the two component case there exist some illegal channels among channels of nucleation. They are situated in the region of the miscibility gap, which is defined by condition \( B_{b} > 0 \).

One can give an interpretation of the function \( B_{b} \) as \( \bar{\Delta} \mu \) - it is the mean value of chemical potential excesses

\[
B_{b} = -\bar{\Delta} \mu = - \sum_{j} \xi_{j} \Delta \mu_{j}
\]

An interesting question, which will have important consequences is a question whether it is possible to see the asymptotic thermodynamic channel at some \( \xi_{i} \approx 0 \) or at least at very small \( \xi_{i} \). We shall these channels as the “pure” channels. The statements (A) and (B) show that it is quite possible but requires the specific behavior of activity coefficients \( f_{i} \). One can extract the following properties of such channels.

- (C) Dependence of \( f_{i} \) over \( \xi \) must be sharp.
  It means that for some \( \xi_{j} \) the inequality \( |\partial f_{i}/\partial \xi_{j}| \gg 1 \) near the coordinate of the pure channel \( \xi_{i} \approx 0 \) has to be satisfied.

- (D) The pure channels are narrow and deep\(^{13}\).
  The qualitative explanation is the following. The property \( |\partial f_{i}/\partial \xi_{j}| \gg 1 \) means that near the coordinate of channel bottom the absolute value of

\(^{12}\)Here for the asymptotic channels the relaxation resembles the relaxation in the kinetic channel, which will be considered below.

\(^{13}\)For the narrow channel the characteristic variations of \( \xi_{j} \) are many times less than 1.
ordinary (not precise) attains big values. The existence of a channel together with monotonous behavior of \( \ln(\xi_j) \) at small concentrations means that \( f_i \) has a minimum near the coordinate of a channel. The channel becomes deep. The non-linear behavior of \( \ln(\xi_i) \) at \( \xi_i \approx 0 \) ensures that the pure channel is narrow.

- (E) Positions (coordinates) of channels are rather insensible to \( n_i \).

Since \( f_i \) has a deep minimum it means that slight variations of \( n_i \) can not lead to essential variation of coordinates \( \xi_i \) as \( c \) of a pure channel.

The term "pure channel" doesn't mean that this channel corresponds to the absolutely pure condensation of one component. The entropy terms \( \ln(\xi_i) \) lead to existence of other components as species. This will be the main source of specific kinetic behavior discussed below.

It seems now that the situation with the pure channel is rather rare in nature. Really, the behavior of \( f_i \) is required to be rather specific. But it is an illusion. Ordinary, in the situation with immiscible components we have the mentioned behavior and the pure channels of nucleation.

### 2.2 Real thermodynamic channels

Now we shall include into consideration the surface term \( F_s = S\sigma \), where \( S \) is the surface of an embryo and \( \sigma \) is the surface tension. The free energy of an embryo formation will be \( F = F_b + F_s \). This form is the so-called capillary approximation. All other correction terms are neglected here. The term \( F_s \) is asymptotically negligible.

We shall try now to repeat all constructions for \( F \) instead of \( F_b \). Really it is possible to do as far as \( F \) can be presented in the following form

\[
F = +\Omega B(\xi) + \Omega^{2/3},
\]

where \( \Omega = (S\sigma)^{3/2} \), then

\[
B(\xi) = \frac{B_b(\xi)}{\sigma^{3/2}(\xi)\bar{v}^{1/2}}
\]

Here \( \bar{v} \) is the mean value of the volume per one molecule in a liquid phase defined as

\[
\bar{v} = \sum_j v_{l_j} \xi_j
\]

and \( v_{l_j} \) is the volume occupied by a molecule of \( j \)-th component in a liquid phase. Then

\[
F_c = \Omega^{2/3}/3
\]

(index \( c \) marks the critical embryo) and the ordinary Gibbs rule takes place.

Later we suppose that there are no irregularities in behavior of \( f_i, v_{l_i} \) and \( \sigma \) as functions of \( \xi \).
Now we can see the maximum over the extensive variable $\Omega$ and again we see the set of channels defined by the extremums of function $B$. We can reproduce here all arguments and constructions as we have done for $F_b$. Again we observe properties (A)-(E). Certainly, the numerical values of coordinates of channels will be another. We shall call these channels as ”thermodynamic channels of nucleation”.

The difference between consideration of the real thermodynamic channel and the asymptotic thermodynamic channel is only in the process of relaxation. For the asymptotic channel one can not observe the saddle point in thermodynamic channel. So, there is no use to speak about the quasi equilibrium along $\vartheta$ in the precritical region. For the real thermodynamic channel one can speak about the quasi equilibrium. Then one can estimate the time of relaxation $t_r$ over $\xi$ in a way it had been done by Zeldovitch for the near critical region and come to

$$t_r \sim \vartheta^{1/3}.$$ 

Also one has to add to this time the time of regular motion to the viscosity of the ”bottom” of the channel, i.e. from initial values to the region $|\xi_i - \xi_i| \sim \nu_i^{-1/2} |\partial^2 B/\partial \xi_i^2|^{-1/2} \vartheta^{1/2}$. Since $B$ is arbitrary, we prefer not to give the final expressions here, because it can be done only on the base of the behavior of $B$ after the evident integration.

Here it is necessary to outline the meaning of $\bar{v}$. One has to keep in mind the Gibbs absorption equation or the Gibbs-Duhem relations. In application to the embryo description it means the phenomenological rule, which states that having come to $\bar{v}$ and $\bar{\xi}$ one can simply neglect all derivatives of $\bar{v}$ over $\xi_i$. The same has to be done with derivatives of $\sigma$ over $\xi_i$, which is known as the so-called Wilhemsky-Renninger effect [13]. This rule, which is very useful in practice, can be shown on the base of Gibbs absorption equation.

In transition from $F_b$ to $F$ the surface tension have appeared. Surface tension can have rather arbitrary behavior on concentration. Can it violate the previous conclusions? The typical behavior of $\sigma$ as function of $\xi$ is the following: as long as possible there exists an enrichment of a surface layer and the surface tension doesn’t variate essentially. Certainly, the entropy of mixture has to be contained in $\sigma$. Only when there is practically no molecules of component with a small $\sigma$, then the value of $\sigma$ begins to grow and attains for the pure substance the value corresponding to $\sigma$ for this pure substance. It means that the pure thermodynamic channel of nucleation for component with maximal $\sigma$ is practically impossible$^{14}$.

This picture of the surface tension behavior has one important qualitative consequence. Precisely speaking the asymptotic thermodynamic channels have nothing in common with precise thermodynamic channels and are useless. Certainly, for the ideal solution (all $f_i \equiv 1$) the additional entropy of mixture is

$$\left(\frac{n_{surf}}{n_{surf} + n_{surf}}\right) \ln\left(\frac{n_{surf}}{n_{surf} + n_{surf}}\right) +$$

$$\left(\frac{n_{surf}}{n_{surf} + n_{surf}}\right) \ln\left(\frac{n_{surf}}{n_{surf} + n_{surf}}\right) -$$

$^{14}$Certainly, the sharp dependence of $\sigma$ can be compensated by peculiar behavior of $f_i$. 8
where \( n_{i \text{ surf}} \) is the density of given component in the surface layer, \( n_{i \text{ bulk}} \) - the same value for the bulk phase, \( n_{i \text{ surf}} \) - the density of all other components in a surface layer, \( n_{i \text{ bulk}} \) - the same value for the bulk phase\(^{15}\). Then the sum over all components has to be taken. We see that the additional entropy of mixture at moderate \( \xi_i \) cannot be a sharp function of concentration. Under the rough generalization one can speak about the flat region - the region of the flat behavior of \( \sigma \) as function of \( \xi_i \) and about the sharp region - the region of the sharp dependence of \( \sigma \) on \( \xi_i \). In the sharp region the thermodynamic channel of nucleation can be hardly situated, then this region isn’t important. In the flat region the derivative of surface tension is small and it means that the position of the thermodynamic channel can not be essentially changed by inclusion of the surface term. So, one can use the asymptotic (bulk) thermodynamic channels as initial approximation to find the coordinates of the real thermodynamic channels.

One has to show inclusion of the picture obtained in consideration of \( F_b \) into the picture in consideration of \( F \) when \( \vartheta \) goes to infinity. Precisely speaking the roots of \( B \) don’t coincide with the roots of \( B_b \). This is because the roots of \( B \) are coordinates of channels when the extensive variable \( \Omega^{3/2} \) is fixed and the roots of \( B_b \) are coordinates of channels when \( \vartheta \) is fixed. Certainly, these coordinates will be different even when the channels would be the same ones\(^{16}\). To compare channels one has to go from \( \Omega \) to \( \vartheta \) according to

\[
\Omega = \sigma^{3/2} 6 \pi^{1/2} \bar{v} \vartheta .
\]

Then the necessary inclusion will be evident.

2.3 Kinetic channels of nucleation

Now we shall turn to the definition of kinetic channels of nucleation. Really, the mentioned thermodynamic channels of nucleation are important for transition over the activation barrier, but when the droplets are moving along the slope of the free energy profile then kinetic terms are extremely important. At the sizes strongly greater than the critical sizes one can not speak about the absolute extremums and saddle points, which are independent from kinetic factors. Now we shall investigate embryos with \( \nu_i \) more than three-four times greater than the corresponding critical values.

Now we have to investigate kinetic equations and to determine their stationary points. The simplification here is the possibility to use only the regular laws

\(^{15}\)Here we suppose that the function \( \bar{v}(\tilde{\xi}) \) is very smooth.

\(^{16}\)When \( \Omega \to \infty \) or \( \vartheta \to \infty \) then \( |F - F_b| \ll F \), but this doesn’t mean the similarity of coordinates of channels.
of growth\textsuperscript{17} for embryos (since they are supercritical embryos here they will be called as droplets).

The regular laws of motion

\[ \frac{d\nu_i}{dt} = W_i^+ - W_i^- , \]

where \( W_i^+ \) and \( W_i^- \) are direct and inverse flows on the embryo (the coefficients of condensation are included in these flows) lead to expression for

\[ \frac{d\xi_i}{dt} = -\xi_i \vartheta^{-1} \sum_j \frac{d\nu_j}{dt} + \vartheta^{-1} \frac{d\nu_i}{dt} . \]

So, the coordinate of a kinetic channel \( \xi_{i,k} \) is determined\textsuperscript{18} by

\[ -\xi_i \sum_j \frac{d\nu_j}{dt} + \frac{d\nu_i}{dt} = 0 . \]

It is necessary to stress that the last equations will be equations on \( \vec{\xi} \), the dependence on \( \vartheta \) is absent here. Really, one can write for \( W_i^+ \) the following formulas from a simple gas kinetic theory (it is supposed that gas is an ideal one and the regime of substance exchange is the free molecular one)

\[ W_i^+ = \frac{1}{4} v_i \tau S_{n_i} \alpha_i \]

Here \( v_i \tau \) is the mean thermal velocity of a molecule of component \( i \), \( \alpha_i \) is condensation coefficient\textsuperscript{19}. The surface square of an embryo \( S \) is the same as in the expression for the free energy, it differs only in microscopic corrections. The kinetic coefficient \( W_i^- \) can be obtained on the base of \( W_i^+ \) by the detailed balance relation

\[ W_i^- (\vec{\nu}, \nu_i) = W_i^+(\vec{\nu}, \nu_i - 1) \exp(-F(\vec{\nu}, \nu_i - 1)) \exp(F(\vec{\nu}, \nu_i)) \]

In the supercritical region near the bottom of the channel the function \( \exp(-F(\vec{\nu}, \nu_i - 1)) \exp(F(\vec{\nu}, \nu_i)) \) doesn’t depend on \( \vartheta \) when \( V = \sum_i v_i \nu_i \) is going to infinity and one can easily see that \( d\xi/dt \) can be presented as \( \vartheta \) multiplied by some given function of \( \vec{\xi} \). It allows to speak about the line as a limit of kinetic channel in a plane \( \vartheta, \vec{\xi} \). Now we shall determine this line concretely. Instead of the previous relation one can write

\[ W_i^- (\vec{\nu}, \nu_i) = W_i^+(\vec{\nu}, \nu_i - 1) \exp(\partial F(\vec{\nu})/\partial \nu_i) \]

\textsuperscript{17}This requires a special justification for the supercritical embryos - the embryos, which contain much more molecules of every component than the critical ones. This justification can be given analytically.

\textsuperscript{18}Here and later the lower index \( k \) denotes the stationary characteristics in the kinetic channel.

\textsuperscript{19}It can be included into the mean thermal velocities \( v_i \tau \).
Calculation of $\partial F(\vec{\nu})/\partial \nu_i$ leads to

$$\partial F(\vec{\nu})/\partial \nu_j = -\ln\left(\frac{n_j}{n_j \infty \xi_j f_j(\xi)}\right) + \left(6\pi^{1/2}/3\right)^2 \sum_i v_i \nu_i)^{-1/3} \sigma v_j + G.D.$$  

Here $G.D.$ marks the terms, which according to the Gibbs-Duhem relation have to be cancelled\(^{20}\).

The Gibbs-Duhem equation for this case can be written as

$$\sum_j \sum_{j'} \nu_j \frac{-\partial \ln\left(\frac{n_j}{n_j \infty \xi_j f_j(\xi)}\right)}{\partial \xi_{j'}} \frac{\partial \xi_{j'}}{\partial \nu_i} + \sum_j \left(6\pi^{1/2}/3\right)^2 \sum_{j'} \frac{\partial}{\partial \xi_{j'}} \left[\sigma \left(\sum_j \nu_j f_j\right)^{2/3}\right] \frac{\partial \xi_{j'}}{\partial \nu_i} = 0$$

for arbitrary $i$. This Gibbs-Duhem relation isn’t the standard one because it contains the term, which has a low dimension. This equation appears as a combination of the Gibbs-Duhem equation for the bulk phase and the Gibbs-Duhem equation for the surface layer. One has to keep in mind that due to the surface enrichment the concentration $\xi_i$ in a bulk solution of an embryo can not be precisely defined as $\nu_i/\vartheta$. This note leads to the last relation.

One can see that the term $\left(6\pi^{1/2}/3\right)^2 \sum_i v_i \nu_i)^{-1/3} \sigma v_j$ is negligible in comparison with $\ln(n_j/(n_j \infty \xi_j f_j(\xi)))$ when the volume of an embryo $\sum_i v_i \nu_i$ is big enough. So, one can neglect the correction term and come to

$$dF(\vec{\nu})/d\nu_j = -\ln\left(\frac{n_j}{n_j \infty \xi_j f_j(\xi)}\right).$$

This relation is typical for asymptotic kinetic channels of nucleation. Here one can already speak about the straight channels of nucleation because the rhs doesn’t contain extensive terms and $d\nu_j/dt$ can be presented as $S$ multiplied by a function of intensive terms.

The Gibbs-Duhem relation becomes here also more standard and can be written as\(^{21}\)

$$\sum_j \sum_{j'} \nu_j \frac{-\partial \ln\left(\frac{n_j}{n_j \infty \xi_j f_j(\xi)}\right)}{\partial \xi_{j'}} \frac{\partial \xi_{j'}}{\partial \nu_i} = 0.$$  

This form is absolutely typical for the bulk solution with standard definition of concentration $\xi_i$ as $\nu_i/\vartheta$.

For asymptotic kinetic channel the relaxation to the stationary value of concentration is practically evident. The absence of curvature here is very important in contrast to the thermodynamic channels in the under-critical or near-critical regions. The matter is that the variable $\vartheta$ in the super-critical region has

\(^{20}\)One can argue whether the Gibbs absorption relation can be applied to a growing embryo, but we have to adopt this equation in order to have concrete calculable results.

\(^{21}\)Here appears a special question whether it is possible to consider $\nu_i$ as $d\xi_i$ and to take $\partial d\xi_i$ instead of $\partial \nu_i \ln(n_j/(n_j \infty \xi_j f_j(\xi)))$ instead of $\partial \nu_i \ln(n_j/(n_j \infty \xi_j f_j(\xi)))$ in two previous Gibbs-Duhem relations. Since the channels of nucleation are rather narrow ($\xi_i - \xi_i c \sim \vartheta^{-1/2}$) this can lead only to correction terms with negligible order in powers of $\vartheta$. 

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to be regarded as the fast variable. This lies in contradiction with consideration of the near-critical region (where $\xi$ are the fast variables and $\vartheta$ is the slow one).

Consider the near-critical region. Having calculated $dF/d\Omega$ and $dB/d\xi$, one can easily see that if there are no small parameters in $W^+_i$, $f_i$ and their derivatives, then the relaxation to the bottom of thermodynamic channel takes place and the characteristic time of this relaxation is estimated as $\sim \vartheta^{1/2}/W^+_i$.

The time to overcome the barrier in the near-critical region has the estimate $\sim \vartheta^{2/3}/W^+_i$ and one can see that there exist the hierarchy between these characteristic times, which provides that along the stable variable $\sim (\xi - \xi_c)$ there is the quasi equilibrium.

The opposite situation takes place in the super critical region. As we shall see later the variable $\vartheta$ grows very rapidly, this property will be called as the avalanche consumption of metastable phase (see [22]). When the channel is straight one then there is no difference whether $\vartheta$ is the fast variable or not and one can see such a relaxation. But when the channel is curved there can be no relaxation to the bottom (the term "bottom" at the slope becomes rather relative). So, here the asymptotic disappearance of curvature plays a very important role. Really, the velocity $^{22}\vartheta/dt$ allows the estimate $^{23}$

$$d\vartheta/dt \sim \vartheta^{2/3} \rightarrow \infty,$$

$$d(\xi - \xi_k)/dt \sim \vartheta^{-1} d\nu/dt \sim \vartheta^{-1/3} \rightarrow 0.$$  

Fortunately $\vartheta \sim t^3$ and

$$\int \frac{d(\xi - \xi_k)}{dt} dt \sim \int dt/t \sim \ln t \sim \infty .$$

So, relaxation really takes place, but it isn’t the exponential, but the power relaxation$^{24}$. Here the straightness of the channel plays the principal role.

We shall enumerate kinetic channels by the number of thermodynamic channels, which this kinetic channel will be attained from (So, the kinetic channel can have several numbers or no number at all. Kinetic channel can be described by one of its possible numbers.).

One can not investigate in details the transition from the critical region to the region of sizes, which strongly exceed the critical sizes. One of effective approximations is the $\delta$-function approximation suggested in [2]. Let some stationary value of concentration $\xi$ (it is one dimensional variable for the binary system) be $\xi^+$. The characteristic width $\Delta\xi$ along $\xi$ allows the estimate

$$\Delta\xi \sim \vartheta^{-1/2}.$$ 

The last value is relatively small. So, in the law of growth one can put $\xi \approx \xi^+$.

Then

$$\frac{d\vartheta}{dt} \sim \vartheta^{2/3} ,$$

$^{22}$When the embryo is moving near the stationary value, i.e. the concentration alterations are small.

$^{23}$Here and later the lower index $k$ denotes the equilibrium value in kinetic channel.

$^{24}$All details can be seen in [2], Appendix 1 and Appendix 2.
which leads to $\vartheta \sim t^3$. The characteristic deviation in plane $\nu_i$ can be estimated as $(\xi_i - \xi_i +)\vartheta$ and has a characteristic value $\vartheta^{1/2}$. Having rewritten the last estimate as a function of time we get $(\xi_i - \xi_i +)\vartheta \sim t^{3/2}$. We see that this width grows faster than the width of the diffusion blurring $\sim t^{1/2}$. Then one can consider the pure diffusion over $\hat{\xi}$. The solution of this problem is known. The distribution $n$ over $\vartheta, \vec{\xi}$ with $\delta$-like initial conditions will be presented as

$$n \sim n_{\vartheta} \prod_i n_{\xi_i},$$

where $n_{\vartheta} \sim \int d\vec{\xi} n$ is simply a translation of initial conditions (i.e. the boundary conditions at small $\vartheta$) and $n_{\xi_i}$ approximately satisfies the diffusion equation

$$\partial n_{\xi_i}/\partial \vartheta \sim D_i \partial^2 n_{\xi_i}/\partial \xi_i^2$$

with characteristic diffusion coefficient $D_i$ and looks like the Green function of diffusion on the flat energy profile

$$G \sim \exp\left(-\frac{(\xi_i - \xi_i +)^2}{(4D_i t)}/(4\pi D_i t)^{1/2}\right)$$

Approximation $D_i \approx \text{const}$ as the function of size, which was used to get the previous relation isn’t too suitable. Now we shall extract coordinates with a real physical meaning.

Having noticed that $\vartheta \sim t^3, \partial/\partial \vartheta \sim \partial/\partial \vartheta^{1/3}$ we can write instead the previous diffusion equation the following equation

$$\partial n_{\xi_i}/\partial \vartheta \sim D_{0i} \partial^2 n_{\xi_i}/\partial \xi_i^2.$$

Here $D_{0i}$ is the new diffusion coefficient for evolution in $\vartheta, \vec{\xi}$ plane. The really significant variables are namely these variables. A solution of the last equation has a good approximation also in the form of the Green function

$$G \sim \exp\left(-\frac{(\xi_i - \xi_i +)^2}{(4D_{0i} \vartheta)}/(4\pi D_{0i} \vartheta)^{1/2}\right).$$

The diffusion over the plane surface can not lead to the approaching of $\xi_i$ to $\xi_i +$. To see this approach one has to take into consideration the terms corresponding to the regular growth.

For $\xi_i$ near $\xi_i +$ one can restrict the regular law of growth only by linear terms in $(\xi_i - \xi_i +)$ series. For diffusion terms one can take the ordinary coefficient of diffusion. So, we observe the evolution in a square potential. Then one can prove that it is possible to use the Fokker-Planck approximation.

The Fokker-Planck equation in multi dimensional harmonic potential has a well known solution. Multidimensional square potential in $\hat{\xi}$ is invariant over...
Lorenz transformation, which leads to the separation of variables. We shall denote the new variables also by $\xi_i$ here.

Since Lorenz transformation is a linear one, it can not lead to any terms except linear ones along $\vartheta$. Now we have $(l - 1)$ separate diffusion problems with known solutions (the Green function is known, the eigenfunctions and eigenvalues of harmonic oscillator are known, one can act in both approaches).

2.4 The coordinates of channels

Now we shall speak mainly about asymptotic kinetic channels and forget about the curved kinetic channels. The reasons will be the following:

- When the channel is curved it means that the current characteristics aren’t too far from the critical ones. Then the the derivatives $\partial F/\partial \nu_i$ are small ones and one has to take into account the diffusion. The interesting situation is far from the critical region where the channel is straight.

- The characteristic size of relaxation to the stationary value of concentration strongly exceeds the distance where the curvature of a channel is essential.

- Later namely the characteristic sizes corresponding to the asymptotic channels will be important for construction of the global kinetics of the process.

We shall mark the coordinates of asymptotic kinetic channels also by the subscript $k$. We shall call the asymptotic kinetic channels simply as the kinetic channels.

To determine this coordinate of equilibrium in the kinetic channel one has to write the laws of regular growth

$$\frac{d\nu_i}{dt} = \frac{1}{4} Sv_i \alpha_i (n_i - n_i \infty \xi_i f_i (\vec{\xi}))$$

at the supercritical asymptotics.

The surface square $S$ is given by $S = (6\pi^{1/2})^{2/3} \vartheta^{2/3} (\vec{\xi}) \vartheta^{2/3}$, which leads to

$$\frac{d\xi_i}{dt} = \frac{(6\pi^{1/2})^{2/3}}{4\theta^{1/3}} \vartheta^{2/3} [\alpha_i \nu_i \iota (n_i - n_i \infty \xi_i f_i (\vec{\xi})) - \xi_i \sum_j \alpha_j \nu_j \iota (n_j - n_j \infty \xi_j f_j (\vec{\xi}))]$$

Here one can extract the function

$$K_i = [\alpha_i \nu_i \iota (n_i - n_i \infty \xi_i f_i (\vec{\xi})) - \xi_i \sum_j \alpha_j \nu_j \iota (n_j - n_j \infty \xi_j f_j (\vec{\xi}))]$$

Equations

$$K_i = 0$$

for all $i$ together with

$$\sum_j \xi_j = 1$$
form the system of nonlinear equations for coordinates \( \xi_i \). This system has at least one solution when the vapor mixture is metastable. It can be derived from the boundary behavior. But sometimes this system can have several solutions (this corresponds to several channels).

Near \( \vec{\xi}_k \) one can rewrite the previous equation as

\[
\frac{d\xi_i}{dt} = (6\pi^{1/2})^{2/3} \frac{dK_i(\vec{\xi})}{d\xi_i} |_{\xi_i = \xi_i, k} (\xi_i - \xi_i, k) \bar{v}^{2/3} |_{\bar{v} = \xi_i, k}
\]

Equation for \( \vartheta \) will be

\[
\frac{d\vartheta}{dt} = (6\pi^{1/2})^{2/3} \frac{d^2(\bar{v}(\vec{\xi}))^{2/3}}{d\xi_i} \sum_i v_i t \alpha_i (n_i - n_i, \infty \xi_i f_i(\vec{\xi}))
\]

or

\[
\frac{d\vartheta}{dt} = \vartheta^{2/3} P(\vec{\xi})
\]

where

\[
P(\vec{\xi}) = (6\pi^{1/2})^{2/3} \bar{v}(\bar{\xi})^{2/3} \sum_i v_i t \alpha_i (n_i - n_i, \infty \xi_i f_i(\bar{\xi}))
\]

One can suggest the simple approximation when \( \xi_i \) is near \( \xi_i, k \) for all \( i \) (here some given channel is already chosen)

\[
\frac{d\vartheta}{dt} = \vartheta^{2/3} P(\vec{\xi}_i, k)
\]

This equation can be easily integrated

\[
\vartheta^{1/3}(t) = (t - t_0) P(\vec{\xi}_i, k) / 3
\]

where \( t_0 \) is the time of appearance of a droplet in a supercritical region\(^{30}\).

It allows to rewrite the equation for \( d\xi_i / dt \) as

\[
\frac{d\xi_i}{dt} = \frac{(6\pi^{1/2})^{2/3}}{4} \frac{1}{P(\vec{\xi}_i, k)/3} \frac{dK_i(\vec{\xi})}{d\xi_i} |_{\xi_i = \xi_i, k} (\xi_i - \xi_i, k) \bar{v}^{2/3} |_{\bar{v} = \xi_i, k}
\]

with solution

\[
(\xi_i - \xi_i, k) = \text{const}(t - t_0)^L
\]

and unknown \( \text{const} \) where

\[
L = \frac{(6\pi^{1/2})^{2/3}}{4} \frac{1}{P(\vec{\xi}_i, k)/3} \frac{dK_i(\vec{\xi})}{d\xi_i} |_{\xi_i = \xi_i, k} \bar{v}^{2/3} |_{\bar{v} = \xi_i, k}
\]

\(^{29}\)It is necessary that the square form \( \sum_i \sum_j (\partial^2 F/\partial \xi_i \partial \xi_j) |_{k} (\xi_i - \xi_i, k) (\xi_j - \xi_j, k) \) will be positively defined. Later only these \( \xi_i, k \) will be considered.

\(^{30}\)Initial size can be put to zero.
If one can spread the last equation until $\xi_i = \xi_{i\,c}$ (index $c$ marks the critical value) one can very approximately get

$$\text{const} = (\xi_{i\,c} - \xi_{i\,k})/(t_c - t_0)^L$$

where $\xi_{i\,c}$ is the concentration of the critical embryo (one has to decide, which critical point has to be chosen), $t_c$ is the time when according to the regular law of growth the embryo attains the critical value of $\vartheta$.

One has to stress that there appear at least three problems, which have to be solved

- 1. how one can get the critical values of $\vartheta$ and $\vec{\xi}$, i.e. $\vartheta_c$, $\xi_{i\,c}$;
- 2. how one can get the asymptotic values of $\vartheta$ and $\vec{\xi}$;
- 3. how one can decide, which asymptotic channel corresponds to the given critical point (i.e. to the given thermodynamic channel).

The first two problems are purely algebraic ones. One can only note that to solve the first problem one has to use the Kelvin relation instead of direct search of minimum of function $B$ because of deviation of the bulk concentration from the integral definition, which occurs due to the Gibbs absorption isotherm.

As an initial approximation for solution of the first problem one can take the roots of the function $dB/d\xi_i$, where it is necessary to forbid the differentiation of $\sigma$. Then one can see the regions of interaction for all channels having calculated $d^2B/d\xi_i d\xi_j$ and decided whether the suspicious root is the bottom of the channel, the top of the hill or the saddle point. Then $dB/d\xi_i = 0$ leads to

$$\bar{\nu} \frac{d\Delta \mu_i}{d\xi_i} = \Delta \mu_i \frac{d\bar{\nu}}{d\xi_i}.$$  

This leads to

$$\frac{\Delta \mu_i}{\bar{\nu}} = \frac{\Delta \mu_j}{\bar{\nu}} = \frac{\Delta \mu}{\bar{\nu}},$$

which is the known Kelvin relation.

Function $B_b$ can be found from $B$ when $v_i$ have approximately the same values and $\sigma$ is independent on the concentration. sometimes the search of the roots $dB_b/d\xi_i = 0$ is more simple than the search of the roots $dB_b/d\xi_i = 0$ and can be regarded as some initial approximation. When all $v_i$ have approximately the same values then asymptotic thermodynamic channels lies near the real thermodynamic channels.

To fix the positions of asymptotic kinetic channels of nucleation sometimes one can use the approximation of strong supersaturations. This approximation means that in $K_i$ the value $n_i \sim \xi_i f_i(\xi)$ is neglected in comparison with $n_i$. Then

$$K_i = \alpha_i \nu_i v_i n_i - \xi_i \sum_j \alpha_j v_j n_j.$$
and together with $\sum \xi_i = 1$, (which now is trivial) we have the system of linear equations with known solution

$$\xi_i = \frac{\alpha_i v_i m_i}{\sum_j \alpha_j v_j m_j}$$

Here the solution is unique.

Another promising approximation is approximation of ideal solution. In this approximation one can formally split the system into two components: the first component and all other components. Then one can get kinetic coefficients for these two components and solve the two-component case where the equation of the concentration of the first component will be the following (obtained by D.Stauffer in [2])

$$\alpha_1 v_1 (1 - \xi_1) (n_1 - n_1 \infty \xi_1) = \alpha_2 v_2 \xi_1 (n_2 - n_2 \infty (1 - \xi_1))$$

(it has two solutions: one for the bottom (stable stationary value) of the channel and one for the top (unstable stationary value), also it is necessary to check boundary values at $\xi_1 = 0; 1$ as possible channels). The problem is that $n_2 \infty$ is unknown because the composition of the second complex component is unknown, but now for this component the number of substances is reduced and we can continue this procedure having chosen in the second component two composing components, etc. As a result we shall get the equation for concentration. This completes the method of approximation of ideal mixture.

In the general case one can speak about invariant

$$\alpha_i v_i (n_i - n_i \infty \xi_i f_i) / \xi_i = inv$$

and write equation on this value. This way was described in [18].

The third problem is rather hard to solve but one can note some essential properties:

- Ordinary one can use the regular velocities of droplets growth and ignore fluctuation terms. Only under a very specific behavior of properties the fluctuation terms are essential. This can take place only when there explicitly exist some small parameters.

- Rather often it is possible to act in a following simple manner: It is sufficient to get the regions of interactions for kinetic channels and then to see to the region of what kinetic channel belongs the given thermodynamic channel. This way is very effective for practical needs. The probability to make an error is very low.

- In any case it is impossible that droplets can cross the miscibility gap. Results presented in [9] are wrong. Really, in the miscibility gap the slope is positive (with increase of $\vartheta$ the value of free energy also increases). So here the kinetic channels will be thermodynamic ones (if we don’t take into account the disappearance of the embryo), which have no saddle points.
3 Standard nucleation

Nucleation is a period of a rather intensive formation of droplets. To begin the investigation of the nucleation process one can note that the number of thermodynamic channels have nothing in common with the number of compositions of solution in droplets, i.e. with the number of kinetic channels. The illusion of such connection was presented in [9], but there are no reasons to justify this illusion.

According to the ordinary adopted classification one can extract in the condensation the first period - the period of intensive formation of droplets and the second period - the period after the nucleation but before the coalescence. But it is necessary to stress that even at the first period the variations of the vapor densities $n_i$ or of activities $\zeta_i$ are rather important. This is in contradiction with the statement made in [9] (page 391) where it is noted that $n_i$ during the period of nucleation are constant. Under such assumption it is impossible to get any spectrum of the droplets sizes different from the constant amplitude. Nevertheless in [9] some attempts to get the spectrum of sizes were made without any citations of the already presented theory in [5], [10], [6], [7]. They follow instructions of [5], [10], [6], [7] to consider the one dimensional equation instead of the system of condensation equations, which also were presented in [4], [10], [6], [7].

As it was noticed earlier $\xi_i \approx \xi_{i k}$. It means that the quantity of the molecules of component $i$ in droplets (i.e. $g_i$) satisfies equality

$$g_i/\xi_{ik} = g_j/\xi_{jk}$$

for two different components. This takes place when the characteristic size of droplets during the nucleation period (the first period) strongly exceeds the critical size and one can assume that the evolution is mainly determined by rather big droplets, which have $\xi_i \approx \xi_{ik}$. The process of relaxation was described above.

Namely this relation is the base for reduction of multi-component case to the one component condensation. The relaxation processes haven’t been mentioned in [9] at all. Really, having marked the initial densities of vapor as $n_i(t = 0)$ and the current densities as $n_i(t)$ ($t$ is time) one can easily see that

$$\frac{(n_i(0) - n_i(t))/\xi_{ik}}{(n_j(0) - n_j(t))/\xi_{jk}}$$

for two different components $i$ and $j$. This forms the base for reduction to the one component case.

We see that this reduction isn’t the consequence of some functional approximations used in [5], [6], [10] and repeated in [9]. So, it is more than symbolic that to get the reduction to the one dimensional case [9] also uses the functional exponential approximation and approximation of a regular growth (they

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$^{31}$Here and later the size of the droplet will be the characteristic, which grows with the velocity independent of this characteristic. For the free molecular regime such characteristic will be $\nu_i^{1/3}$. The concentrations here are fixed.
are also from [5], [6], [10], which isn’t necessary here and is the little defect of narrative

One can directly show that the droplets of big sizes are the main consumers of vapor phase. One has specially stress attention on this property despite it was considered in [10] because in [9] in was announced (p.391) that "this hardly influences the results of our theory but significantly simplifies the mathematical expressions". The cited conclusion is wrong\(^{33}\). This property can be shown by the set of simple qualitative estimates. We omit here these estimates because this property will be directly seen from the final results. Also it can be directly shown that the quasi-stationary approximation for the droplets, which sizes \(\vartheta\) two or three times exceed the critical size \(\vartheta_c\) really takes place (the concentrations here are arbitrary, but in reality the quasi-stationary distribution is essential only for concentrations near the stationary value in the given channel).

Both these properties are based on the possibility of the thermodynamic description of the critical embryo. In [9] the possibility of analytical derivation of these properties hasn’t been mentioned at all.

On the base of the last statements one can write the balance equation in the following form

\[ n_i(0) = n_i(t) + g_i(t) \]

where \(g_i(t)\) is the number of molecules in the liquid phase and it can be presented as

\[ g_i(t) = \int_0^t dt' p_i(t') \nu_i(t', t') dt' \]

Here \(\nu_i(t, t')\) is the number of molecules inside the droplets born at \(t'\), \(p_i(t')\) is the intensity of formation of droplets. Our next task is to determine this intensity.

The intensity of the droplets formation depends on the height of the activation barrier of nucleation. Since there are several saddle points it seems that there are several possibilities for embryos to become the supercritical objects of the liquid phase. Ordinary, the leading channel is the unique one. The intensity of formation is proportional to \(\exp(-F_{c_j})\) (here \(F_{c_j}\) is the height of activation barrier in the \(j\)-th thermodynamic channel). It follows from the standard classical consideration (see [1]) in stationary conditions because the nucleation rate can be calculated in stationary approximation. Here it is sufficient to keep only the leading term and not to think about the preexponential factor, which is the matter of numerous discussions [2], [3]. It is important that the normalizing factor of the equilibrium distribution for every thermodynamic channel is one and the same since all channels go from the origin of coordinates.

One can choose the channel with the lowest \(F_{c_j}\). Let it be the first one. If there is another channel with \(|F_{c_j} - F_{c_1}| \leq 1\) the theory presented below

\(^{32}\)It this derivation it is supposed that the equilibrium concentrations do not change too fast, which has to be proven (and can be done).

\(^{33}\)It isn’t clear how after this conclusion in [9] it was possible to consider only the droplets of big sizes without the logical destruction of the theory.
has to be slightly modified. But the probability of such coincidence is very low since $F_{c_j} \gg 1$. All these estimates have to be done at initial values $n_i = n_i(t = 0)$ when there is no depletion. At first we shall investigate the period of intensive formation of droplets in the first channel. This period doesn’t cover all nucleation possibilities but as we shall see later namely this period will be the main in nucleation.

From the first point of view it seems that the variations of $n_i$ can lead to the variations of $\Delta F_{i_c}$ and sometimes the channel, which was the first one can be changed by some other channel, which becomes the most energetically profitable one. Fortunately the leading channel remains the main one at least until the end of intensive nucleation in this channel.

The droplets consumes vapor and this effect strongly diminishes the intensity of nucleation rate. To see this one can simply calculate the derivatives of the free energy of the critical embryo:

$$\frac{dF_c}{dn_i} = -\frac{1}{n_i} \nu_{i_c}$$

The last relation can be seen directly from the explicit expression for the free energy $F(\bar{\nu})$ if we notice that in

$$\frac{dF_c}{dn_i} = \frac{\partial F}{\partial n_i} + \sum_j \frac{\partial F}{\partial \nu_j} \frac{\partial \nu_j}{\partial n_i}$$

the term $\sum_j \frac{\partial F}{\partial n_i} \frac{\partial \nu_j}{\partial n_i}$ vanishes as far as $\frac{\partial F}{\partial \nu_j} = 0$ at the point of extremum (i.e. at the saddle point). This equality is a concrete realization of nucleation theorem in the multi-component nucleation (see [6], [7] for the first derivation in the application to the multicomponent condensation kinetics, but generally this result was mentioned in [14]).

This relation plays the leading role in further analysis. To apply the thermodynamic description of the critical embryo it is necessary to have $\bar{\nu} \gg 1$. Without the thermodynamic description it is nothing to do in the quantitative theory of nucleation. To use the approximation of solution in the bulk of the embryo it is necessary to be $\nu_{i_c} \gg 1$. Otherwise we have to construct the model of liquid solution in the force field of several molecules of rare components. This problem is very hard to solve. Then it is treated as heterogeneous condensation and the molecules of rare components are considered as heterogeneous centers. The theory of heterogeneous condensation has been given in [15]. So, here we have to suppose that all $\nu_{i_c} \gg 1$ (but this doesn’t mean that $\xi_i$ essentially differs from zero for the supercritical embryos).

On the base of $-n_i dF_c/dn_i = \nu_i \gg 1$ one can easily see that even the small fall of the molecular number density leads to the interruption of intensive

\[\text{We have simply to add this intensity to the intensity in the first channel. Functional dependencies on the vapor densities will be approximately the same. One has to take into account the intensity with the smallest $\nu_{i_c}$ (see later).}

\[\text{The theory for this exclusion will be presented later.}

\[\text{The thermal effects are supposed to be absent as it has been noted earlier.}
One can see that this point of view radically differs from opinion presented in [9] where inequalities like $\frac{dF_c}{dn_i} \gg 1$ are considered (see [9] eq. (23)) as some special artificial external restrictions.

Since $n_i \frac{dF_c}{dn_i} \gg 1$ then the main dependence of the stationary intensity of formation $J_{s\ i}$ of the droplets in the $i$-th thermodynamic channel is given by

$$J_{s\ i}(n(0)) = J_{s\ i}(n(t)) \exp(-F_{c\ i}(n(0)) + F_{c\ i}(n(t)))$$

(1)

This formula is for the first channel. It is valid when

$$|n_i(t) - n_i(0)| \leq n_i(0)/\nu_i c_1 |n_i = n_i(0)|$$

(2)

This region of $n_i$ corresponds to the intensive formation of the droplets through the first channel. The last estimate restricts variation of $n_i$ and the process of formation takes place in time. One can imagine that a long tail with a small intensity can be more important than the short initial stage with a high intensity. Then the last estimate fails. Fortunately it is easy to see that every droplet grows with a growing intensity in time. Then $d^2n_i/dt^2 < 0$ and the estimate (2) really corresponds to the region essential for nucleation.

One can see one very important feature for $n_i$ satisfying (2):

- For $n_i$ satisfying (2) all values of $\xi_i c_1$ are approximately constant\footnote{The last index is the number of a channel.} (the relative variations of $\xi_i c_1$ and $1 - \xi_i c_1$ are small). For all other thermodynamic channels the relative variations of equilibrium concentrations are small if the channel is the "clear" one\footnote{The "clear channel" is the channel with relatively high sides (more than several thermal units).}.

The analogous property takes place also for kinetic channels

- For $n_i$ satisfying (2) all values of $\xi_i k_1$ are approximately constant (the relative variations of $\xi_i k_1$ and $1 - \xi_i k_1$ are small). For all other kinetic channels the relative variations of equilibrium concentrations are small if the channel is the "clear" one\footnote{Here the sides of the channel are determined $\vartheta$ being fixed.}.

These properties can be justified analytically.

The estimate (2) also allows to make decomposition in the argument of $\exp(-F_{c\ i}(n_i(t)) + F_{c\ i}(n_i(t)))$ in Tailor series. It is necessary to decide what number of derivatives has to be taken to ensure the high accuracy. In [9] the parameters of analogous decompositions were chosen in a wrong way. Really, in [9] the correction term has an order proportional to the first derivative $dF_c/dn_i$, the second derivatives were ignored. It is wrong and has a hidden supposition...
that the second derivative have the same order as the first derivative. This
supposition is too strong. Instead of this one has simply to require that

$$-F_1 c(n_1(0)) + F_1 c(n_1(t)) \approx \sum_i \frac{dF_1 c}{dn_i} |_{n_i=n_i(0)} (n_i(t) - n_i(0))$$

The last approximation has to be directly checked for every type of multicomponent mixture. It can be shown on the base of the evident inequalities

$$| -F_1 c(n_1(0)) + F_1 c(n_1(t)) | > \sum_i \frac{dF_1 c}{dn_i} |_{n_i=n_i(0)} (n_i(t) - n_i(0))$$

and

$$| -F_1 c(n_1(0)) + F_1 c(n_1(t)) | < \sum_i \frac{dF_1 c}{dn_i} |_{n_i=n_i(0)} (1 - \frac{d\nu_i c}{dn_j} |_{n_j=n_j(0)})(n_i(t) - n_i(0))$$

There is no special parameter of decomposition, the considerations made in $O$-symbols presented in [9] are irrelevant because in reality the values of $dF_1 c/dn_i$ are big, but still finite. Nevertheless it is possible to give some convincing arguments to see that the last approximation is valid. We shall show that the terms with second derivatives are small. For one component condensation the required property is obvious and can be checked by explicit formulas. In the multicomponent nucleation since there are generally unknown functions $f_i$ we can not get the general results. To estimate the second derivatives we have to consider the values $(d\nu_i c/dn_j)/\nu_i c$. They take moderate values, at least they are smaller than $\nu_i c$. To see this property one can use variables $\vartheta, \vec\xi$ and if all $f_i$ are directly independent on $n_j$ one can see that $(d\nu_i c/dn_j)/\nu_i c$ has no small or big parameters. So, $(d\nu_i c/dn_j)/\nu_i c$ takes moderate values less than the values $\nu_i c$.

According to (2) in the law of growth one can take $n_i = n_i(t=0)$ and get

$$\frac{d\nu_i}{dt}^{1/3} = \frac{1}{12} \alpha_i (6\pi^{1/2} c^{2/3} \xi_i^{2/3} v_i t (n_i(0) - n_i(0) \approx \xi_i f_i(\vec\xi))$$

The values of concentrations $\vec\xi$ have to be taken as the equilibrium values in kinetic channel corresponding to the first thermodynamic channel. Here we shall take more strong definition of the supercritical embryos. We shall call the supercritical embryos as those embryos, which are already passed the critical point and have already approached to the kinetic channel.

One has to check that even with a new definition the statement that the supercritical droplets are the main consumers of vapor remain valid. Under the conditions of applicability of thermodynamic description of the critical embryo this statement can be proven analytically with some reasonable assumptions. Also the second statement about the quasistationary value of the nucleation rate during the nucleation period has to be proved for a new definition of the supercritical embryos. We shall call the supercritical embryos as those embryos, which are already passed the critical point and have already approached to the kinetic channel.

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supercritical droplets. It also can be done analytically in conditions of thermo-
dynamic description of the critical embryo.

One can state that the same property as for thermodynamic channels can
be seen for kinetic channels. Namely, for variations of \( n_i \) satisfying (2) the
equilibrium concentrations of kinetic channel can be considered as constant
ones. This property is valid for the "clear" kinetic channels when that the
derivatives \( d\xi_i/dt \) have no small parameters in the vicinity of the equilibrium
values in kinetic channel.

For densities \( n_i \) satisfying to (2) one can take also \( \vec{\xi} \) as constant values
and get the rhs as a constant value. Then it is possible to integrate the last
equation and get

\[
\nu_i^{1/3} = \Lambda_i(t - t')
\]

where

\[
\Lambda_i = \alpha_i \frac{1}{12} (6\pi^{1/2})^{2/3} \bar{v}^{2/3} \varepsilon^{-2/3} v_i \xi_i \left(n_i(0) - n_i \propto \xi_i \right) - k f_i(\xi_i)\)

Here it is taken into account the initial condition \( \nu(t = t') = 0 \)

It is easy to see that

\[
\frac{\Lambda_i^3}{\xi_i} = \frac{\Lambda_j^3}{\xi_j}
\]

for different components.

The equation for \( g_i \) will be the following

\[
g_i = \int_0^t dt' J(t') \Lambda_i^3(t - t')^3
\]

Here \( J(t') \) is the rate of nucleation.

For \( J \) one can take according to the second statement the following expression

\[
J \approx J_{s,1}
\]

where \( J_{s,1} \) is the stationary rate of nucleation through the first thermodynamic
channel.

Then approximation (1) leads to

\[
J = J_s \exp(- \sum_i \frac{dF_1}{dn_i} |_{n_i=n_i(0)}(n_i(t) - n_i(0)))
\]

where

\[
J_s = J_{s,1}(\vec{n} = \vec{n}(t = 0))
\]

Then

\[
g_j = \int_0^t dt' J_s \exp(- \sum_i \frac{dF_1}{dn_i} |_{n_i=n_i(0)}(n_i(t') - n_i(0)))\Lambda_j^3(t - t')^3
\]

Since

\[
n_i(t') - n_i(0) = -g_i(t')
\]
we have
\[ g_j = \int_0^t dt' J_* \exp\left( \sum_i \frac{dF_1 c}{dn_i} \big|_{n_i(0)} g_i(t') \right) \Lambda_j^3 (t - t')^3 \]
and
\[ g_j = \int_0^t dt' J_* \exp\left( \sum_i \frac{dF_1 c}{dn_i} \big|_{n_i(0)} k g_j(t') \right/ \xi_j k) \Lambda_j^3 (t - t')^3 \]

Then the last equation is the one dimensional equation with solution, which describes the nucleation period. This equation is the same as the in the situation of one component nucleation. For the first time this fact was noted in [5], then it was confirmed in [6], [7], [10]. So, there are no problems in solution and in the description of the nucleation period. In [9] this known fact was presented as a new result. We need to discuss it even in the one dimensional case because the errors from [10] were accurately reproduced in [9], which points that these errors were made not occasionally but were the consequence of deep misunderstanding of the nucleation kinetics. So, these errors have to be corrected explicitly\(^\text{41}\).

The last equation can be rewritten as
\[ g_j = W \int_0^t dt' \exp\left( -P g_j(t') \right) (t - t')^3 \]
with constants
\[ W = J_* \Lambda_j^3 \]
\[ P = -\sum_i \frac{dF_1 c}{dn_i} \big|_{n_i(0)} k/\xi_j k > 0 \]

The physical sense of renormalizations made in [9] is wrong, the mentioned sense announced in [9] would be correct if all densities \( n_i \) are constant up to the end of the all surplus vapor depletion (due to the vapor depletion these densities will decrease). Actually there is no need to fulfill renormalizations with a physical sense, it is sufficient to write equation for \( G_j = P g_j(t') \) as
\[ G_j = WP \int_0^t dt' \exp\left( -G_j(t') \right) (t - t')^m; \quad m = 3 \]
The scale renormalization \( t \rightarrow (WP)^{1/4} t \) leads to
\[ G_j = \int_0^t dt' \exp\left( -G_j(t') \right) (t - t')^m; \quad m = 3 \]

One can prove that this equation has the unique solution and one can get this universal solution numerically. This approach was outlined in [15] where all details can be found. The base of application is the rapid decrease of \( J(t) \) after the end of nucleation period, which allows to present the influence of \( g_i \) after the end of nucleation via the first three moments of the distribution, i.e.

\(^{41}\)Solution of the one-dimensional equation in a more general case was presented in [6].
via $\int_0^\infty t^{i'} J(t') dt', \ i = 0, 1, 2, 3$ (including the zero moment, which is the leading term).

The iteration solution with the zero approximation $G_i = 0$ and the recurrent procedure

$$G_{j}^{(i+1)} = \int_0^t dt' \exp(-G_j^{(i)}(t'))(t-t')^m, \ m = 3$$

can be also applied. But it is necessary to stress that the reason of the rapid convergence of iterations is the big power $m = 3$ in the integral term. This fact was noticed for the first time in [17]. This property is the concrete realization of the principle of the avalanche consumption formulated in [22]. Nevertheless in [9] it was stated that already the first iteration gives the appropriate result for all positive powers $m$ instead of 3 in the integral equation. This conclusion is wrong, which can be seen from the explicit solution at $m \to +0$, namely

$$G_i = \ln(t + 1)$$

This function strongly differs from the first iteration

$$G_i^{(1)} = t \ ,$$

which is the correct form of the first iteration for $m \to +0$, and also differs from

$$G_i^{(1)} = t^4/4 \ ,$$

which was used in [9]. The most surprising fact is that the main part of [9] is devoted to get the estimates of the accuracy of the first iteration and the "necessary" estimate has been proven. Certainly, this estimate is wrong. We needn’t to follow procedure [9] but can simply compare the universal solution $G_i$ and the first iteration $G_i^{(1)}$. Both curves are $J = \exp(-G_i)$ and $J_1 = \exp(-G_i^{(1)})$ are drawn in Fig.1. and they can be hardly separated. It is very simple to show this approximate coincidence analytically.

The description of the nucleation period is completed, but the period of consumption of the main quantity of surplus substance has to be described. This period is the main in the phase transition because namely during this period the main quantity of surplus substance is going from the mother phase into a new liquid phase. Really, at the end of the nucleation period the relative quantity of the substance is small. It can be estimated as

$$g_i = \Lambda_3^3 J \frac{t_0^4}{4}$$

where the duration $t_0$ of the nucleation period can be estimated as

$$t_0 = \left( \frac{1}{4} \sum_i \left| \frac{\partial F_c}{\partial n_i} \right| [\xi_{i \ k} \Lambda_3^3 J_s] \xi_{j \ k} \right)^{-1/4}$$

\[42\] For approximation of the universal solution see [21].
(here the first channel is considered).

This estimate is based on the analytical form of the first iteration and it is clear that this estimate is too long. At least the values $g_i$ satisfy inequality

$$g_i < \left| \frac{\partial F_c}{\partial n_i} \right|^{-1} = \frac{n_i}{\nu_i c},$$

(the critical value is referred for the first channel), which shows that the relative quantity of substance in droplets is small at the end of the nucleation period.

### 3.1 Standard evolution after the end of nucleation

Now we shall describe the period of consumption of practically all surplus substance from the mother phase. Precise solution of the evolution during this period is unknown, the solution presented in [9] is wrong. This solution artificially without any comments and justifications prolongs some relations established at the nucleation period. This prolongation isn’t correct. Here we shall present some effective approximate solutions of kinetic equations. Here we have no necessity to ensure such high precision as at the nucleation period because there is no further nucleation (except the special case, which will be described in the final part). So, simply the high relative accuracy in $n_i$ is necessary.

At first we shall use the property that at the end of nucleation the relative
quantity of surplus substance is small. Then it is possible to use the monodisperse approximation for $g_i$. This approximation is the following
\[ g_i = N\nu_i \]
where $N$ is the number of droplets (it can be taken as the result of the nucleation period description) $N = \int_0^\infty J_s(t') dt' \approx J_s t_0 0.9$. Here $\nu_i$ is the coordinate of the monodisperse spectrum. When the monodisperse approximation for $g_i$ is bad, then $g_i$ is negligible in the substance balance.

It is necessary now to write kinetic equations for the time evolution of $\nu_i$. These equations can be written in approximation of the regular growth. Then
\[ \frac{d\nu_i}{dt} = \frac{1}{4} \alpha_i \nu_i S[n_i(t = 0) - N\nu_i - n_i \infty \xi_i f_i(\vec{\xi})] \quad (3) \]
\[ S = (36\pi)^{1/3} V^{2/3}, \quad V = \sum_j \nu_j \nu_i \approx \bar{\nu} \theta \]
Here and later $\alpha_i$ are included into $\nu_i$. Then
\[ \frac{dV^{1/3}}{dt} = \frac{1}{12} (36\pi)^{1/3} \sum_i \nu_i \nu_i [n_i(t = 0) - N\nu_i - n_i \infty \xi_i f_i(\vec{\xi})] \quad (4) \]
Here we conserve $\nu_i$ in $[n_i(t = 0) - N\nu_i - n_i \infty \xi_i f_i(\vec{\xi})]$, which can lead to perspective approaches when for $\nu_i$ some approximations are suggested\(^{43}\). One can rewrite the last expression as
\[ \frac{dV^{1/3}}{dt} = \frac{1}{12} (36\pi)^{1/3} \sum_i \nu_i \nu_i [n_i(t = 0) - N\xi_i \frac{V}{\bar{v}(\xi)} - n_i \infty \xi_i f_i(\vec{\xi})] \quad (5) \]
For $\vec{\xi}$ the evolution equation will be the following
\[ \frac{d\xi_i}{dt} = \frac{\bar{v}(\vec{\xi})}{V^{1/3}} \frac{1}{4} (36\pi)^{1/3} [(n_i(0) - N\xi_i \frac{V}{\bar{v}} - n_i \infty \xi_i f_i)\nu_i - \xi_i \sum_j (n_j(0) - N\xi_j \frac{V}{\bar{v}} - n_j \infty \xi_j f_j)\nu_j] \quad (6) \]
It is clear that one can not solve two last equations analytically (at least for the arbitrary coefficients of activity). The analytical solution announced in [9] as the precise one is wrong. Now we shall suggest different approximations, which allow to solve these equations.

Some useful approximations can be found in [6], [7] where it is shown that they can be presented as the iteration procedures with rather high rate of convergence.

\(^{43}\)For example, for fast component one can put $\nu_i$ to its final value (see later).
Approximation of ideal surface
In (3) we shall consider $S$ as known function of time. Suppose that $S$ is known in some approximation. Then one can see the following iterative procedure

$$\frac{d\nu_i^{(k+1)}}{dt} = \frac{1}{4} \nu_i \cdot S[n_i(t = 0) - N\nu_i^{(k+1)} - n_i \infty\xi_i f_i(\bar{\xi})]$$  \hspace{2cm} (7)

$$S = (36\pi)^{1/3} \left( \sum_j v_j \nu_j^{(k)} \right)^{2/3}$$

For initial $\nu_j^{(0)}$ one takes $\nu_j^{(0)} = \Lambda_j^3 t^3$. One can take in (7) $\xi_i$ as $\xi_i = \nu_i^{(k)} \sum_j \nu_j^{(k)}$ or $\xi_i = \nu_i^{(k+1)} \sum_j \nu_j^{(k+1)}$

The first opportunity leads to the linear differential equations, which can be solved and it completes the iteration step.

Approximation of the initial concentration
Consider (5) and put in this equation all $\xi_i$ to their initial values $\xi_i(0)$, which are known from the consideration of the nucleation period. Then

$$\frac{dV^{1/3}}{dt} = \frac{1}{12} (36\pi)^{1/3} \sum_i v_i \nu_i \cdot S[n_i(t = 0) - N\xi_i(0) \frac{V}{\bar{v}(\xi(0))} - n_i \infty\xi_i(0) f_i(\bar{\xi}(0))]$$

This equation can be easily integrated, which gives

$$\int^V_0 \frac{dV^{1/3}}{12 (36\pi)^{1/3} \sum_i v_i \nu_i \cdot S[n_i(t = 0) - N\xi_i(0) \frac{V}{\bar{v}(\xi(0))} - n_i \infty\xi_i(0) f_i(\bar{\xi}(0))] = t$$

Approximation of the characteristic concentration
Consider (5) and put in this equation all $\xi_i$ to their characteristic values $\xi_i(ch)$ during the most intensive consumption of the metastable phase. The characteristic value of concentration has to be chosen as some artificial parameter. Sometimes it is useful to choose the mean value between the initial and the final concentrations (the final concentration can be found without explicit solution of the evolution equation; it will be done later). Then

$$\frac{dV^{1/3}}{dt} = \frac{1}{12} (36\pi)^{1/3} \sum_i v_i \nu_i \cdot S[n_i(t = 0) - N\xi_i(ch) \frac{V}{\bar{v}(\xi(ch))} - n_i \infty\xi_i(ch) f_i(\bar{\xi}(ch))]$$

This equation can be easily integrated

$$\int^V_0 \frac{dV^{1/3}}{12 (36\pi)^{1/3} \sum_i v_i \nu_i \cdot S[n_i(t = 0) - N\xi_i(ch) \frac{V}{\bar{v}(\xi(ch))} - n_i \infty\xi_i(ch) f_i(\bar{\xi}(ch))] = t$$
Approximation of stationary concentration

Equation (6) is a typical relaxation equation, which leads to the relaxation of $\xi_i$ to the "bottom" of kinetic channel. So, it is reasonable to put $\xi_i$ to the stationary value $\xi_{i_k}$ determined by

$$0 = [(n_i(0) - N\xi_i V) - n_i \infty \xi_i f_i) v_i - \xi_i \sum_j (n_j(0) - N\xi_j V) - n_j \infty \xi_j f_j) v_j]$$ (8)

The stationary value depends on the value of $V$, i.e. $\xi_{i_k} = \xi_{i_k}(V)$, because $V$ characterizes the power of the mother phase consumption by droplets.

Then equation for evolution of $V$ will be the following

$$\frac{dV^{1/3}}{dt} = \frac{1}{12} (36\pi)^{1/3} \sum_i v_i v_i (n_i(t = 0) - N\xi_{i_k}(V) \bar{V}(\xi_k(V)) - n_i \infty \xi_i f_i(\xi_k(V))]$$

This equation can be easily integrated, which gives

$$\int_0^{V^{1/3}} \frac{dV^{1/3}}{12 (36\pi)^{1/3} \sum_i v_i v_i (n_i(t = 0) - N\xi_{i_k}(V) \bar{V}(\xi_k(V)) - n_i \infty \xi_i f_i(\xi_k(V))] = t$$

This solution is a very good approximation to the real solution. In all situations when there is no other big or small parameters (rather often the ratio $n_i \infty v_i / n_j \infty v_j$ is a small parameter$^{44}$, where $i$ and $j$ are two different components) this approximation works well.

Certainly the system of algebraic equations (8) together with $\sum_i \xi_i = 1$ has to be solved, which isn’t a simple task.

Generally speaking one can see that the problem is to get the true value for concentrations. Then the problem becomes much more simple. One can formulate here the following statement:

- (F) When some approximation $\xi_{i_{appr}}$ for the concentration is adopted then the kinetic equations can be integrated as

$$\int_0^{V^{1/3}} \frac{dV^{1/3}}{12 (36\pi)^{1/3} \sum_i v_i v_i r_i} = t$$

where

$$r_i = [n_i(t = 0) - N\xi_{i_{appr}}(V) \frac{V}{\bar{V}(\xi_{appr}(V))} - n_i \infty \xi_{i_{appr}} f_i(\xi_{appr}(V))]$$

Now we shall analyze approximations, which are suitable at different periods of condensation. One can define initial period of condensation and the final

$^{44}$This will be considered later.
period of condensation. The initial period is the period, when the quantity of
the substance in the droplets is small in comparison with the total quantity
of surplus substance. Initial period covers nucleation, which is appearance of
droplets, but does not coincide with nucleation.

The final period is the period when the quantity of remaining surplus sub-
stance in vapor is small in comparison with the quantity of substance in droplets.

These definitions will be slightly modified later.

The values which correspond to the transition\(^{45}\) of all\(^{46}\) surplus substance\(^{47}\)
to the droplets will be called the final values and will be marked by the lower
index \(\text{fin}\).

Between the initial and the final periods the intermediate period takes place.
Namely during this period the macroscopic manifestation of a phase transition
takes place.

**Approximation of different stages**

One can analyze the characteristic features of the last solution. During some
period (initial period) one can see that \(V\) grows rather fast but \(V\) is relatively
small and in \(r_i\) one can neglect \(V\). Then

\[
\int_0^{V^{1/3}} \frac{dV^{1/3}}{(36\pi)^{1/3} \sum_i n_i v_i \hat{r}_i} = t
\]

where

\[
\hat{r}_i = [n_i(t = 0) - n_i \infty \xi_i k(V = 0) f_i(\bar{\xi}(V = 0))]
\]

Then

\[
\frac{V^{1/3}}{(36\pi)^{1/3} \sum_i n_i v_i \hat{r}_i} = t
\]

The values of \(\xi_i k\) are known - they are the coordinates of kinetic channel at
initial values of \(n_i\), i.e. \(n_i(t = 0)\). So, there are no problems in integration of
the last equation. The denominator doesn’t depend on \(V\). As the result \(V \sim t^3\).

The next step in approximation is the following: The value of \(V\) grows rather
rapidly. Then in \(r_i\) there appears a rapidly growing function \(V\), which turns
\(\sum_i n_i v_i \hat{r}_i\) to zero

\[
0 = \sum_i n_i v_i \hat{r}_i .
\]

Then \(V\) stops to grow and in the system one can see some relaxation processes,
which can be described as the final period. This period is characterized by some
approximately constant and, thus, prescribed value of \(V = V_{\text{fin}}\).

At the final period the value of \(V\) becomes the function of \(\bar{\xi}\) and can be
found from the last equation, which can be written as

\[
0 = \sum_i n_i(t = 0) - N \xi_i(V) \frac{V}{\bar{v}(\xi(V))} - n_i \infty \xi_i(V) f_i(\bar{\xi}(V))
\]

\(^{45}\) The end of this transition is imaginary.

\(^{46}\) The density of vapor equals to the density of vapor saturated over the plane surface.

\(^{47}\) May be the concentration is fixed.
Later we shall write that \( V = V_{\text{fin}}(\xi) \).

Now equations on \( \xi \) can be written as

\[
\frac{d\xi_i}{dt} = \frac{\bar{v}(\xi)}{V_{\text{fin}}^{1/3}(\xi)} \frac{1}{4} (36\pi)^{1/3} [ (n_i(0) - N \xi_i \frac{V_{\text{fin}}(\xi)}{\bar{v}}) - n_i \infty \xi_i f_i v_t - \xi_i \sum_j (n_j(0) - N \xi_j \frac{V_{\text{fin}}(\xi)}{\bar{v}}) - n_j \infty \xi_j f_j v_t j ) ]
\]

This equation is the ordinary relaxation equation but certainly it is nonlinear and multi-dimensional. The analytical solution in the general case is unknown but the relaxation to the stationary value, which satisfies the system of algebraic equations

\[
[ (n_i(0) - N \xi_i \frac{V_{\text{fin}}(\xi)}{\bar{v}}) - n_i \infty \xi_i f_i v_t - \xi_i \sum_j (n_j(0) - N \xi_j \frac{V_{\text{fin}}(\xi)}{\bar{v}}) - n_j \infty \xi_j f_j v_t j ] = 0
\]

is rather obvious.

In the binary case there are no problems in solution of kinetic equation (9). It can be rewritten as equation on one concentration \( \xi_1 \)

\[
\frac{d\xi_1}{dt} = \frac{\bar{v}^{2/3}}{V_{\text{fin}}^{1/3}} \frac{(36\pi)^{1/3}}{4} R(\xi_1)
\]

where

\[
R(\xi_1) \equiv (1 - \xi_1) [ (n_1(0) - N \xi_1 \vartheta_{\text{fin}} - n_1 \infty \xi_1 f_1(\xi_1)) v_1 - \xi_1(n_2(0) - N (1 - \xi_1) \vartheta_{\text{fin}} - n_2 \infty (1 - \xi_1) f_2(1 - \xi_1)) v_2 ]
\]

and in approximation \( \vartheta_{\text{fin}} = \text{const} \) this equation can be easily integrated

\[
\int \frac{d\xi_1}{(v_1 \xi_1 + v_2 (1 - \xi_1)) (36\pi)^{1/3} \frac{1}{4} R(\xi_1)} = t
\]

Here appears a problem what extensive variable we have to fix in the last relation. When we come from \( V_{\text{fin}} \) to \( \vartheta_{\text{fin}} \) we have

\[
\int \frac{d\xi_1}{(v_1 \xi_1 + v_2 (1 - \xi_1))^{2/3} (36\pi)^{1/3} \frac{1}{4} R(\xi_1)} = t
\]

It seems reasonable to choose that extensive variable, which variations are small. The problem is what coefficients \( \lambda_i \) in extensive variable \( \sum \lambda_i \nu_i \) we have to
choose (for all \( \lambda_i = 1 \), for \( V \) we have \( \lambda_i = v_i \)). Certainly, we have to choose\(^{48}\) \( \lambda_i \) to have the smallest variations\(^{49}\) of \( \sum_i \lambda_i \nu_i \). Here we can repeat all previous constructions. For the reason of physical clearness we shall conserve below \( V \) (and \( \vartheta \)), but it is more accurate to take \( \sum \hat{\lambda}_i \nu_i \). In any case this problem is rather artificial because the concentrations approach to the stationary values.

The possibility to get analytical solution in the binary case allows to suggest the pair approximation. We choose the fastest component (due to the kinetic coefficient). All other components will be the second component\(^{50}\). Then one can get the solution presented above. The concentration of the given fast component will approach to the final value. Then the same can be done with the set of the rest (formally slow) components. This loop can be repeated up to the end.

During this relaxation such an interesting phenomena as the partial disappearance of some components from droplets can take place. Really, suppose that there is a fast component and a slow component. The chemical potential of a fast component has a minimum near \( \vec{\xi}_k (V = 0) \). The chemical potential of the slow component has a giant minimum far from \( \vec{\xi}_k (V = 0) \). What will happen in the system? At first \( \xi \approx \vec{\xi}_k (V = 0) \) and the density of vapor of the first component approaches to the value corresponding to the minimal value of the chemical potential for the fast component. But later the slow component saturates the droplets and this rises the chemical potential of the fast component from the minimum. Then the chemical potential of the fast component in the vapor has to grow. It means that the density has to grow and there is a partial disappearance of the fast component from droplets back to the vapor phase.

One can speak about the reverse phase of the phase transition for some components. Certainly, this is only the first peak of the possible oscillatory regime, which can take place here. This example shows us that many interesting phenomena were thrown out in a wrong solution presented in [9]. This redistribution of substances in droplets has nothing in common with redistribution of substance in droplets during the coalescence described by Lifshits and Slezov [4].

As the result one can speak about the inertial phenomena in the phase transition. This conclusion takes place in the multi-dimensional decay kinetics and is the principally new feature of the phase transition.

We have extracted the initial period of condensation and the final period of condensation. We recall that the period between the initial one and the final one will be called the intermediate period\(^{51}\). Do the initial and the final periods cover practically the whole period of condensation before the coalescence? Due to the avalanche consumption of surplus substance (or due to the rapid growth of \( V \) at the initial stage) one can establish the following very important fact.

\(^{48}\)With restriction \( \sum \lambda_i = 1 \).

\(^{49}\)It can be derived in some initial approximation.

\(^{50}\)Or one can divide all components into two groups.

\(^{51}\)For every component the positions of these periods are specific.
The intermediate period between the initial period and the final period is rather short (in comparison with the initial period).

Then with a small relative error one can speak about the boundary between the initial period and the final period and require the coincidence of corresponding solutions at this boundary\(^{52}\). This gives the values of arbitrary constants in the solution at the final period.

Now we shall discuss these periods in details.

**Initial stage**

To give the detailed description of the initial stage we shall write kinetic equations. It can be done as

\[
\frac{d\nu_i}{dt} = \frac{1}{4} v_i t (36\pi)^{1/3} \left( \sum_j v_i \nu_i \right)^{2/3} \left[ n_i(t = 0) - n_i \infty \xi_i f_i(\xi^2) \right] \tag{11}
\]

We see that here

\[
\xi_i = \xi_i k(t = 0)
\]

Then

\[
\nu_i^{1/3} = \Lambda_i t
\]

The same has been done in investigation of the nucleation period, but it is clear that this description can be prolonged on the whole initial stage (normally, nucleation period belongs to initial stage). One has to note that in \(^{9}\) there is no clear picture of the characteristic periods and stages during the condensation. Moreover there are many errors. For example it is stated that at the first period (nucleation period) the densities of components in vapor were considered to be constant (\(^{9}\), page 391). This conclusion is wrong. The densities are functions of time, the simplification is approximate equality of the densities to some constant values. But in consideration of nucleation, which is very sensible to the values of densities one can not consider these densities as to the constant values. Here the requirement of precision is more weak\(^{53}\) - we need only the high relative accuracy of the densities defining. So, here we can put them to constants and consider the initial stage.

One can use another possibility to enlarge the region of description by the analytical solution. This possibility lies in the approximation of high supersaturations. Let us consider this approximation.

In one component condensation one can show that the intensive condensation is possible only when

\[
n/n_\infty \gg 1
\]

This conclusion comes from the standard Gibbs rule which states that the free energy of the critical embryo is three times less than the surface energy of the

\(^{52}\)To get this boundary one has to prolong the solution at the initial period to the intermediate period. If we prolong the asymptotic solution we can incorrectly get the long intermediate period.

\(^{53}\)Except the situation with the secondary nucleation, which will be considered later.
same embryo. If \( n/n_\infty \to 1 \) then \( F_c \) is too big and the nucleation rate, which is
proportional to \( \exp(-F_c) \) is negligibly small\(^{54}\). Ordinary \( n/n_\infty \approx 3 \div 5. \)

In the situation of multicomponent condensation this requirement \( (n/n_\infty \gg 1) \) isn’t necessary because there are many components. But still there can exist some leading components, for which \( n_i/n_i \gg 1 \). Then one can neglect \( n_i \gg n_i \) in comparison with \( n_i - Nn_i \) and then get

\[
\frac{dn_i}{dt} = \frac{1}{4} v_i \xi_i f_i(\xi_i) S \left[ n_i(t = 0) - Nn_i \right]
\]

Analogously one can get a more simple equation on \( \xi_i \)

\[
\frac{d\xi_i}{dt} = \bar{\nu}(\xi_i) \frac{1}{V^{1/3}} \frac{1}{4} (36\pi)^{1/3} |(n_i(0) - N\xi_i \bar{V})v_i \xi_i - \xi_i \sum_j (n_j(0) - N\xi_j \bar{V})v_j \xi_j| \quad (12)
\]

Then the equation on the coordinates of kinetic channel will be

\[
[(n_i(0) - N\xi_i \bar{V})v_i \xi_i - \xi_i \sum_j (n_j(0) - N\xi_j \bar{V})v_j \xi_j] = 0
\]

Then the value \( (n_i(0) - N\xi_i \bar{V})v_i \xi_i \equiv c \) is some invariant (it doesn’t depend on component).

It is clear that the channel will be purely kinetic. It is easy to see the concentrations \( \xi_i \) can not approach to 0, because then the equality

\[ n_i(0) = \xi_i (c/v_i + N \bar{V}) \]

will be violated\(^{55}\).

One can easily get equation on \( c \). Really,

\[ \xi_i = \frac{n_i(0)}{c/v_i \xi_i + N \bar{V}} \]

Then one can get equation for \( \bar{\nu} \) via \( c \)

\[ \bar{\nu} = \sum_i v_i \frac{n_i(0)}{c/v_i \xi_i + N \bar{V}} \]

Then \( \bar{\nu} = \bar{\nu}(c) \) and because of \( \sum_i \xi_i = 1 \) one can get equation on \( c \)

\[ 1 = \sum_i \frac{n_i(0)}{c/v_i \xi_i + N \bar{V}(c)} \]

\(^{54}\)The value of surface tension referred to one molecule can not be too small otherwise one has to take into account the fluctuations of the surface and the situation will be close to the second order phase transition. So, here there is a hidden contradiction between the intensive nucleation and the possibility of thermodynamic description of the critical embryo.

\(^{55}\)When \( \bar{\nu} \) is the regular function of concentrations.
This equation can be easily solved. Ordinary it has a unique solution.

As the result we see that to observe the kinetic channel near $\xi_i = 0$ it is necessary to have really giant values of $f_i$. It means in this case that the values of $\xi_i$ are governed by $f_i$ and they are rather insensitive to the vapor depletion. Then $\xi_{i,k}$ is the quasiintegral of evolution and the stationary approximation for $\xi_{i,k}$ suggested earlier is good. Then it is easy to see the relaxation to this value.

**Final stage**

The final stage can be described by approaches described earlier. Here we shall see that the end of this stage can be described extremely simple. The final values (they can not be attained because of coelescense) can be gotten as solutions of the algebraic system

$$d\nu_i/dt = 0$$

or

$$0 = n_i(t = 0) - N\nu_i - n_i \propto \xi_i f_i(\xi) \quad (13)$$

They will be marked as $\nu_i\,_{fin}$. When $\nu_i$ are close to $\nu_i\,_{fin}$, then the kinetic equations for $\Delta\nu_i = \nu_i - \nu_i\,_{fin}$ can be rewritten as

$$\frac{d\Delta\nu_i}{dt} = -\frac{1}{4}v_t\,_{i}N S_{fin}\Delta\nu_i$$

where

$$S_{fin} = (36\pi)^{1/3}(\sum_j v_j\nu_{j\,fin}^{(k)})^{2/3}$$

These equations are linear and can be easily solved. As the result we have the solution at the end of the final stage. The solution is

$$\Delta\nu_i = c_i \exp\left(-\frac{v_t\,_{i}S_{fin}Nt}{4}\right)$$

with generally unknown negative constants $c_i$. They can be determined by coincidence of solutions at initial stage and at final stage at the boundary between these stages.

This completes the general investigation of the one-stage nucleation.

In the next section when we shall study the multi-stage nucleation process. We shall give another approximate solutions, which will be valid under some specific situations of small concentrations.

4 **Nucleation in the case of small concentration in droplets**

Why shall we pay a special attention to the further investigation of nucleation? One can recall one important feature of one component nucleation. The one component theory predicts that the number of droplets $N$ is proportional to the amplitude of spectrum $f$ in the power $3/4$. Since $f$ is proportional to $\exp(-\Delta F_c)$
it means that for two channels with $\Delta_1 F_c < \Delta_2 F_c - 1$ the strong inequalities $f_1 \gg f_2$ and $N_1 \gg N_2$ take place. This conclusion in the multicomponent condensation isn’t valid because one has to take into account specific kinetic factors which can be different for different channels.

One can also notice another important feature. In the multicomponent theory the positions of thermodynamic channels don’t observe the order. When in the one component case we analyze the dependence $F(\vartheta)$ along the thermodynamic channel we see that the higher is activation barrier the higher lies the curve $F(\vartheta)$ (along the bottom of thermodynamic channel). But since the values of surface tensions in different thermodynamic channels are different one can come to situation when the channel with the highest barrier (i.e. with the highest $F_c$) later becomes the lowest channel\(^{56}\). It means that we have to analyze all channels despite the heights of their barriers.

At first we shall describe the ordinary situation. The process of nucleation is ordinary localized in time. Really, already in the initial period

$$\nu_i = \Lambda_i \Lambda^3 t^3$$

and

$$n_i(t) = n_i(t = 0) - N \Lambda_i \Lambda^3 t^3.$$

Thus, every component leads to the fall of intensity of the droplets formation in the channel number $j$ (let us enumerate the channels according the heights of activation barriers) as

$$J(t) = J(t = 0) \exp\left(\sum_i \nu_{c_{i,j}} (n(t) - n_i(t = 0))\right) = J(t = 0) \exp(-\sum_i \nu_{c_{i,j}} N \Lambda_i \Lambda^3 t^3),$$

where $\nu_{c_{i,j}}$ is the number of molecules of $i$ component in the critical embryo for the channel number $j$. This rapid decrease of the nucleation rate $J$ according to the previous relation means that there will be no further formation of droplets. So, the process of intensive nucleation is finished in all channels. This situation has been already described in the first part of the previous section.

But still there is one important exclusion from this situation. We shall consider the nucleation in some channel which will be called as the second one. So, the last index now will merk the channel of nucleation. When the concentration $\xi$ of $i$-th component in the droplets in the first channel is small, then $\Lambda_i$ can be small and at moderate times $t$ the value $-\nu_{c_{i,2}} (n(t) - n_i(t = 0))$ is small enough when $\nu_{c_{i,2}}$ isn’t too big\(^{57}\). So, the intensive nucleation (in comparison with initial value) in the second channel continues even when the intensive nucleation in the first channel stops. Then the number of droplets appeared in the second channel becomes important and it is interesting to calculate this number.

The reason of termination of intensive nucleation in the second channel can be the vapor depletion by both droplets appeared in the first channel and

\(^{56}\)We compare channels $\vartheta$ being fixed.

\(^{57}\)We suppose this property for the second channel.
droplets appeared in the second channel. This situation becomes complex and requires a special investigation. It will be given in this section.

From the first point of view it seems that this situation is rather artificial. But as has been already noticed in introduction when we have two immiscible substances we come to two separate processes of nucleation - the first process is the nucleation of the first substance into the droplets of the first substance and the second process is the nucleation of the second substance into the droplets of the second substance. These processes have nothing in common. This situation has to be described in frames of the binary condensation also and namely this situation falls into the case, which will be considered. When there is a small miscibility of substances we have a moderate influence of the first process on the second one and have to take this interaction into account.

We shall call the situation when several channels of nucleation are sequentially important as the ”long nucleation”.

Now we shall investigate the case of long nucleation in details. We shall describe here the two component case, then the necessary remarks for generalization will be given.

We have already noticed the possibility of partial reverse condensation and shall call this as ”inertial” effects.

At first we shall analyze the general features of the process, then we shall give the theory for the process with no ”inertial” effects in the first channel, then the situation with ”inertial” effects in the first channel will be described.

4.1 General features of the ”long nucleation”

The nucleation process in the first channel has been already described and we know the number \( N_1 \) of the droplets appeared during the nucleation in this channel (earlier this quantity was denoted by \( N \)). Let us suppose that in the first kinetic channel \( \xi_1 \) is small. In the second channel \( \xi_2 \) is small. One can justify the following statement:

- **Up to the end of nucleation in the second channel the droplets appeared in the second channel can not essentially perturb the rate of growth of droplets appeared in the first channel.**

Then we can investigate the separate process of vapor depletion by the droplets appeared in the first channel.

For the evolution of droplets appeared through the first channel \( \xi_1 \ll 1 \), \( \xi_2 = 1 \), the values of concentrations are known.

The system of kinetic equations for this problem can be written in approximation of ideal solution since the solution is really the dilute one. The system of equations is given by\(^58\)

\[
\frac{d\nu_1}{dt} = \frac{v_t}{4} S(n_1(0) - N\nu_1 - n_1 \xi_1),
\]

\(^58\)For dilute solution one can use the approximation of the ideal solution (may be with renormalized parameters).
\[
\frac{d\nu_2}{dt} = \frac{v_2}{4} S(n_2(0) - N\nu_2 - n_2 \infty) ,
\]
\[
S = (36\pi)^{1/3}(v_1\nu_1 + v_2\nu_2)^{2/3} .
\]
The value of \( S \) when there is no extremely small values in ratios \( v_i/v_j \) can be presented as
\[
S = (36\pi)^{1/3}(v_2\nu_2)^{2/3} .
\]
Then it is possible to integrate these equations\(^{59}\). Equation for \( \nu_2 \) will be
\[
\frac{d\nu_2}{dt} = \frac{v_2}{4} (36\pi)^{1/3}(v_2\nu_2)^{2/3}(n_2(0) - N\nu_2 - n_2 \infty) .
\]
Since the r.h.s. doesn’t contain \( t \) this equation can be integrated
\[
\int_{0}^{\nu_2} \frac{d\nu_2}{(36\pi)^{1/3}(v_2\nu_2)^{2/3}(n_2(0) - N\nu_2 - n_2 \infty)} = t .
\]
So, now \( \nu_2 \) is the known function of \( t \). Then equation for \( \nu_1 \) can be written as
\[
\frac{d\nu_1}{dt} = \frac{v_1}{4} (36\pi)^{1/3}(v_2\nu_2(t))^{2/3}(n_1(0) - N\nu_1 - n_1 \infty\xi_1)
\]
and since \( \xi_1 \approx \nu_1/\nu_2 \) it can be rewritten as
\[
\frac{d\nu_1}{dt} = \frac{v_1}{4} (36\pi)^{1/3}(v_2\nu_2(t))^{2/3}(n_1(0) - N\nu_1 - n_1 \infty\nu_1/\nu_2(t)) .
\]
Since it is the first order linear differential equation it can be easily integrated by the known formulas.

This solution is explicit, but the model with the small concentration and ideal solution can be criticized. One can see that the limit of the last solution is
\[
n_1(t) \to 0 .
\]
The final values of \( \nu_i \in \text{fin} \) are obtained on the base of algebraic equations\(^{13}\) and they doesn’t depend on \( v_i \) and on ratios\(^{60}\) of \( n_i \infty \). So, one can easily come to the situation when \( \xi_1 \in \text{fin} \) doesn’t go to 0. The last solution doesn’t satisfy this condition.

The last remark means that we have to investigate the general situation. From the previous section we know that the solution can be composed from the part corresponding to the initial period and the part corresponding to the relaxation during the final period. So, there appeared two characteristic problems:

- 1) To describe nucleation in the second channel during the initial period

\(^{59}\)In the first equation one can neglect \( n_1 \infty\xi_1 \), which leads to
\[
\frac{d\nu_1}{dt} = \frac{v_1}{4} S(n_1(0) - N\nu_1)
\]
and the first equation can be then integrated in a very simple way.

\(^{60}\)The initial positions of kinetic channels strongly depend on \( v_i \) and \( n_i \infty \).
2). To describe nucleation in the second channel during the final period.

The last problem has to be solved in different situations. When

\[ \xi_1 \kappa f_1(\xi_1 k) > \xi_1 f_{\text{fin}}f_1(\xi_1 f_{\text{fin}}) \]

then ordinary there are no inertial effects. The rhs in the last inequality can be taken at initial values of vapor densities since as it has been noticed the channel in the situation of small concentration is very deep and concentration is here a quasiintegral of evolution. One can see here that the value \( n_1 \) constantly decreases in time. Here one has to investigate the nucleation in the second channel during the relaxation with decrease of density.

When

\[ \xi_1 \kappa f_1(\xi_1 k) < \xi_1 f_{\text{fin}}f_1(\xi_1 f_{\text{fin}}) \]

one can come to the situation when \( n_1 \) decreases at first in time to the value \( \xi_1 \kappa f_1(\xi_1 k) \). The value of \( n_1 \) can not come too close to this value. Then it begins to increase and approaches to \( \xi_1 f_{\text{fin}}f_1(\xi_1 f_{\text{fin}}) \). So, beside the problem to describe the nucleation during the decrease of \( n_1 \) it is necessary to describe the nucleation during the increase of \( n_1 \). This problem also splits into two separate problems to describe the evolution when there is essential increase of \( n_1 \) and to describe evolution when \( n_1 \) already attains the asymptotic value.

It is extremely important to note that we need the solution only when \( \xi_1 \ll 1 \). Only when \( \xi_1 \ll 1 \) we can suppose that there will be rather intensive droplets formation in the second channel. At the same time only then the solution will have a very high precision, which is necessary to describe the nucleation in the second channel.

### 4.2 Secondary nucleation during the initial stage

We shall call the appearance of droplets through the second channel as the secondary nucleation. During the initial stage of the primary condensation the equation for the density \( n_1 \) as function of \( t \) will be

\[
n_1(t) = n_1(0) - N_1(\Lambda_1 t)^3 - g_{2 \ 1}.
\]

Here \( N_1 \) is the total number of droplets appeared through the first channel (since the nucleation through the first channel is over we know this number), \( g_{2 \ 1} \) is the number of molecules of the first component in the droplets appeared through the second channel. Then having repeated for the second channel the same procedure as we had done for the first channel we get the following equation for the number of the molecules of the first component \( g_{2 \ 1} \) in the droplets appeared through the second channel

\[
g_{2 \ 1}(t) = J_2 \Lambda_2^3 \int_0^t dt' (t - t')^3 \exp(-\sum_i \nu_i c(t) N_1 \Lambda_1^3 t'^3 + \ldots)\]

\[61\] The final values here and later are taken only with account of droplets appeared through the first channel (this number is already known).

\[62\] Certainly, the opposite situation can take place.
\[ \sum_i \nu_{i \to 2} c(\tau_{i \to k} g_{2 \to 1}(t')/\xi_{1 \to k}) \]

where \( \tau = 0 \) or \( \tau \) is some characteristic value, may be at the asymptotic solution. Here \( \Lambda_{1 \to 2} \) is the constant in the law of growth

\[ \frac{d\nu_{1 \to 1}^{1/3}}{dt} = \Lambda_{1 \to 2} \]

do the molecules of the first component in the droplets appeared through the second channel, \( J_{2 \to 1} \) is the amplitude value of the stationary rate of nucleation in the second channel, \( \nu_{i \to 2} c \) is the number of molecules of \( i \)-th component in the critical embryo in second channel, \( \Lambda_{i \to 1} \) is the constant in the law of growth \( d\nu_{1 \to 1}^{1/3}/dt = \Lambda_{i \to 1} t \) of the molecules of the \( i \)-th component in the droplets appeared through the first channel, \( \xi_{i \to k} \) is the concentration of \( i \)-th component molecules in the second thermodynamic channel.

Having combined the constants we have

\[ g_{2 \to 1}(t) = J_{2 \to 1} \int_0^t dt' (t - t')^3 \exp(-At'^3 - Bg_{2 \to 1}(t')) \]

with known constants \( J_{2 \to 1}, A, B \). Both functions \( \exp(-At'^3) \) and \( \exp(-Bg_{2 \to 1}(t')) \) can be interpreted as step-like functions, which allows to state that

To get the rate of nucleation the value of \( g_{2 \to 1} \) in the r.h.s. can be calculated approximately without account of \( \exp(-At'^3) \) in frames of the first approximation in the standard iteration procedure

\[ g_{2 \to 1}(0) = 0, \quad g_{2 \to 1}(i+1)(t) = J_{2 \to 1} \int_0^t dt' (t - t')^3 \exp(-At'^3 - Bg_{2 \to 1}(i)(t')) \]

So, \( g_{2 \to 1}(1) = J_{2 \to 1} t^4/4 \) and then

\[ g_{2 \to 1}(2) = J_{2 \to 1} \int_0^t dt' (t - t')^3 \exp(-At'^3 - BJ_{2 \to 1} t'^4/4) \]

So, the rate of nucleation looks like

\[ \tilde{J} = J_{2 \to 1} \exp(-At'^3 - BJ_{2 \to 1} t'^4/4) \]

and it has the step like behavior. Moreover it is the product of two step-like functions \( \exp(-At'^3) \) and \( \exp(-BJ_{2 \to 1} t'^4/4) \). So, we can introduce two characteristic sizes

\[ \Delta_a t = A^{-1/3} \]

and

\[ \Delta_b t = (BJ_{2 \to 1}/4)^{-1/4} \]

We have to take the minimal value from \( \Delta_a t \) and \( \Delta_b t \) to determine the nucleation duration

\[ \Delta t = \min \{ \Delta_a t, \Delta_b t \} \]
Then the rate of nucleation as a function of time is
\[ J(t) = J_2 \Theta(t) \Theta(\Delta t - t) \]
and the total number of droplets \( N_2 \) appeared through the second channel is
\[ N_2 = \int_0^\infty J(t) dt = 0.9J_2 \Delta t \approx J_2 \Delta t \]
Now we have determined all main characteristics of phase transition. These characteristics can be determined with the more high accuracy using the perturbation technique and some iteration schemes. Here it is important that the base for these constructions is now given.

5 The properties of further evolution and their effects on the secondary nucleation

Now we have to consider the situation when the secondary nucleation takes place at times greater than the initial period. We know that at some intermediate times after the end of initial period but before the asymptotic final period the solution is known with essential error. Fortunately one can prove the following statement, which will help to give a simple analytical description:

- **When the process of the secondary nucleation stops after the end of the primary nucleation initial period but before the time, which two or three times exceeds the time of the end of initial period of the primary nucleation, one can simply neglect the vapor consumption by the droplets from the second channel after the end of primary initial period.**

Here we define the initial and the final periods referred to the corresponding components.

Now we shall explain this statement. At first we shall see that the period between the initial period and the asymptotic period has a rather small (in comparison with initial period) duration. We shall see this on example of the one component nucleation where the precise solution can be easily obtained. Really, the evolution equation can be reduced after the certain renormalizations to the following form
\[ \frac{dz}{dt} = 1 - z^3 \]
with the initial condition \( z(t = 0) = 0 \). Here \( z \) is the renormalized coordinate of the droplets linear size \( \vartheta^{1/3} \). The solution is the following
\[ \int_0^z \frac{dz}{1 - z^3} = t \]
and the integral can be taken analytically, which gives
\[ t = -\frac{1}{6} \ln \frac{(z - 1)^2}{z^2 + z + 1} + \frac{1}{\sqrt{3}} \arctan \frac{2z + 1}{\sqrt{3}} - \frac{1}{\sqrt{3}} \arctan \frac{1}{\sqrt{3}} \]
The last solution has the asymptotics

\[ t = -\frac{1}{3} \ln \frac{1 - z}{\sqrt{3} \exp(\sqrt{3} \pi/6)} \]  
\[ z = 1 - \exp(\sqrt{3} \pi/6) \sqrt{3} \exp(-3t) \]

at big \( t \) and

\[ z = t - \frac{t^4}{4} + \frac{3 t^7}{47} \]  \hspace{1cm} (14)

at small \( t \).

In Fig. 2 one can see the precise evolution and the asymptotics. The curves are drawn for the value of excess of density, i.e. for the normalized difference \( \Psi = n - n_{\infty} \), which is proportional here to \( 1 - z^3 \). One can see one long curve, which binds the curves, which are cut off. This long curve is the precise solution. The short curves are asymptotics. There is one asymptotic \( f_{as} \) for the big times and two asymptotics for the small times. The asymptotics for the small times differ by the number of terms for \( z \) in \( (14) \), which are taken into account. The curve \( f_{(1)} \) corresponds to the account of the first two terms in expression for \( z \) in \( (14) \) and the curve \( f_{(2)} \) corresponds to the account of the first three terms in expression for \( z \) in \( (14) \).

One can see that the period of time when both the long time asymptotics and the short time asymptotics don’t work has a rather short duration. This duration has to be compared with the duration of initial period. Since the
precise solution is known one can give the estimates but everything is clear already from the picture. One can only note that this property comes from the big power 3 in the law of droplets growth. This is the same reason as for the property of the avalanche consumption [22]. So, one can here note the following important property

• The period of consumption of the main surplus substance is rather short in comparison with the initial period.

So, one can speak also about the avalanche consumption of the all surplus substance.

This property is typical also for the case of the dynamic conditions [17]. Earlier it was only noted that the period of consumption of all surplus substance is short in comparison with the period of waiting (see [17]). Now we can state that the period of the avalanche consumption (or the intermediate period) is short in comparison with the period when the vapor density approximately equals to the density at the moment of the most intensive formation of droplets (or simply to the density at the moment of intensive formation of droplets), i.e. to the initial period.

The small parameter characteristic for the initial period in the solution of the last equation is $g = z^3$ in comparison with 1. One can see that when $m \gg 1$ the value $z^m$ will be small even when $z$ is comparable with $z_{fin} = 1$ (for example $(1/2) = 1/8 \ll 1$ can be considered as the small parameter). The small parameter for the asymptotic decompositions is \footnote{This estimate is very rough, it depends on activity coefficients $f_i$ and can be established only in the order of magnitude.}:

$$\frac{|z - z_{fin}|}{z_{fin}} \ll 1$$

where $z_{fin}$ corresponds to $V_{fin}$. Here $z_{fin} = 1$ and it means that simply $z$ is close to 1. So, we see that there is practically no gap between the initial and the final asymptotic periods.

One has to outline that there is no satisfactory approximation for the value of the vapor density or for the value of the number of molecules in the liquid phase as a function of time because namely during the intermediate period occurs the phase transition - the main quantity of substance goes from the vapor to the liquid phase. Fortunately, these values aren’t directly involved in the secondary nucleation description. But for the times of duration of characteristic periods, which are necessary for the investigation of the secondary condensation the required approximations are rather precise.

In the multicomponent case the convincing arguments are the same.

Now we shall explain why it is possible to miss already the two or three times of duration of initial period. Certainly the density attained at the asymptotics $n_{i, as}$ is essentially smaller than the initial density. So, the rate of nucleation will be many times smaller than the initial rate of nucleation. The value of the critical number of molecules of given component in the second channel can not
be very big (since the derivative of the free energy barrier on density is this value) otherwise the rate of nucleation at \( n_{i_{as}} \) will be absolutely negligible in comparison with the initial rate of nucleation. Then the period of initial peak of nucleation through the second channel will be not negligibly short in comparison with the duration of initial stage. Then we see that the number of droplets though the second channel appeared at the asymptotic can be comparable with the number of droplets through the second channel appeared in the peak of nucleation only in one case - when the duration of the whole nucleation period (including the nucleation at the asymptotics) strongly exceeds the duration of the initial period.

A special question which has been dropped out of consideration is the multiplicity of the final states. It was supposed that the "final" is unique. But the algebraic equations appeared from the conditions of the absence of the regular growth can have several roots. It means the several possible final states. This complicates the theoretical description. The first problem to solve here is to see what final state corresponds to the given channel of nucleation. We have to construct asymptotic for every final state and then to decide what asymptotic is the closest one to the solution at the initial period. this problem is the pure algebraic one and can be solved without difficulties.

The second problem is the transition between final states. Since the regular growth is absent here, we can return to the free energies of the final states (or of the droplets in the final states) \( F_{\text{fin}} \). The rate of transition between final states is proportional to \( \exp(-\Delta F_{\text{fin} \, i \, j}) \) where \( \Delta F_{\text{fin} \, i \, j} \) is the height of transition barrier (it depends on the numbers \( i \) and \( j \) of final states). The values \( \Delta F_{\text{fin} \, i \, j} \) are so giant that ordinary there is no sense to consider transitions between final states. But in some peculiar situations when the height of transition barrier isn’t too big, one can observe a very interesting kinetic behavior, which forms the problem for a separate publication. This transition may influence also on kinetics of coalescence, which is also a very interesting point of investigation. One can only note that transition between final states situated on opposite sides of metastability gap has to go through the total evaporation of embryos. This is a very slow process, its characteristic times strongly exceeds even the characteristic coalescence times. Generally speaking, kinetics of evolution of final states resembles in mathematical structure of equations the micellar evolution and, thus, we need not to give here the special description.

5.1 Secondary nucleation during the relaxation period

We need now to investigate the evolution at big times, corresponding to the asymptotic solution.

Here we have to take an explicit account of the initial peak of metastability by introduction of total number of droplets appeared through the second channel.
during this peak. This number is given by

\[ N_* = \int_0^\infty J_2 \exp(-At^3)dt' = 0.9J_2A^{-1/3}, \]

where this approximation and all parameters are described in the previous sections.

We can here also introduce the duration of nucleation peak \( \Delta t \) as

\[ \Delta t = A^{-1/3} \equiv \Delta_a t. \]

At these big times one can write for \( g_{21} \) the following expression

\[ g_{21} = N_*z^3 + \tilde{f}_2(z - \delta z)^4/4. \]

Here \( \tilde{f}_2 = J_2 s(\{n_i f_{in}\})/\Lambda_{12}(\{n_i f_{in}\}) \) is the stationary rate of nucleation \( J_2 s(\{n_i f_{in}\}) \) through the second channel attained at the asymptotic values (it can be calculated by known formulas for the stationary rate of nucleation at known final asymptotic values) divided by the rate of droplets growth \( \Lambda_{12}(\{n_i f_{in}\}) \), the value \( \delta z \) is the shortage due to the fact that initial period is already accounted (this value can be also explicitly calculated, it is coordinate \( \nu_1/3 \) attained by the droplets born at \( t = 0 \) up to the end of initial stage), \( z \) is the coordinate \( \nu_1/3 \) attained by the droplets born in the second channel at \( t = 0 \) up to the current time \( t \), i.e. \( z = \int_0^t \Lambda_{12}(\{n_i(t)\})dt \to \Lambda_{12}(\{n_i f_{in}\})t. \)

Since at asymptotic the concentration is constant and the densities are also constant, then the values \( \nu_1/3 \) grow in time with constant velocity independent on \( \nu_{12} \). Here \( \nu_{12} \) is the number of molecules of the \( i \)-th component in the droplets born in the second channel. This explains the powers 4 in the previous expressions. Sometimes it is worth to add the shift \( \delta'z \) to the coordinate \( z \) in the term \( N_*z^3 \) due to the irregularity of droplets velocity at the initial stage and at the transition from initial stage to the asymptotic solution (when \( z \) is defined as \( \Lambda_{12}(\{n_i f_{in}\})t) \).

Since \( z = \Lambda_{12}(\{n_i f_{in}\})t \) and \( \delta'z = \int_0^t (\Lambda_{12}(\{n_i(t)\}) - \Lambda_{12}(\{n_i f_{in}\}))dt \to \delta'z = \int_0^\infty (\Lambda_{12}(\{n_i(t)\}) - \Lambda_{12}(\{n_i f_{in}\}))dt \), the expression\(^{66}\) for \( g_{21} \) will be the following

\[ g_{21} = N_*(z + \delta'z)^3 + \tilde{f}_2(z + \delta'z - \delta z)^4/4. \]

We see that the expression for \( g_{21} \) is a very sharp function of \( z \). One can then speak here also about the avalanche consumption of the metastable phase, which was outlined in \(^{22}\) as the main feature of nucleation. This property allows to speak about the upper boundary. To introduce the definition of this boundary it is necessary to recall the form of spectrum as function of time

\[ \tilde{f} = \tilde{f}_2 \exp(-\sum_i \nu_{i2} f_{in} \xi_i f_{in} g_{21} / \xi_i f_{in}), \]

Again the avalanche character of vapor consumption can be proven.

\(^{66}\) The value of \( \delta z \) has to be reconsidered in the same manner.
Then the boundary $\Delta_f z$ is defined according to
\[ \sum_i \nu_i c_{2 \text{fin} \xi_i \text{fin} g_2} \frac{1}{\xi_1 \text{fin}} = 1 \]
or
\[ \left( \sum_i \nu_i \text{fin} \xi_i \text{fin} \right)^{-1} = (N_*(z + \delta'z)^3 + \frac{f_2}{4}(z + \delta'z - \delta z)^4)/\xi_1 \text{fin}. \]
This equation gives the value of $z$, which will be the boundary $\Delta_f z$ of spectrum.
The spectrum will be approximately
\[ \tilde{f} = \tilde{f}_2 \Theta(z) \Theta(\Delta_f z - z) \]
and the number of droplets is
\[ N_2 = N_* + 0.9 \tilde{f}_2 \Delta_f z \approx N_* + \tilde{f}_2 \Delta_f z. \]
Ordinary the values $\delta z$ and $\delta' z$ can be neglected here.
This completes the general investigation of the secondary nucleation but below the more accurate methods will be presented.

5.2 Description of the secondary nucleation at the decreasing asymptotic

During the asymptotic (final) period the concentrations $\xi_i$ of the droplets appeared in the first thermodynamic channel will approach the final values according to the relaxation equation. Namely, the final values $\xi_i \text{fin}$ satisfy the system of equations
\[ \left[ (n_i(0) - N \xi_i V_{\text{fin}}(\xi_{\text{fin}})) - n_i \infty \xi_i \text{fin} f_i(\xi_{\text{fin}}) \right] v_i - \]
\[ \xi_i \text{fin} \sum_j (n_j(0) - N \xi_j \text{fin} V_{\text{fin}}(\xi_{\text{fin}})) - n_j \infty \xi_j \text{fin} f_j(\xi_{\text{fin}}) \right] v_i \]
Then equation (15) can be rewritten near $\xi_i = \xi_i \text{fin}$ as
\[ \frac{d\xi_i}{dt} = \dot{L}_i(\xi_{\text{fin}})(\xi_i - \xi_i \text{fin}) \]
where
\[ \dot{L}_i = \frac{\delta \dot{S}}{\delta \xi_i} \]
and
\[ \dot{S} = \frac{\tilde{v}(\tilde{\xi})}{V_{\text{fin}}(\tilde{\xi})^{1/3}} (36\pi)^{1/3} \frac{(n_i(0) - N \xi_i V_{\text{fin}}(\tilde{\xi}))}{\tilde{v}} - \]
\[ n_i \infty \xi_i f_i v_i - \xi_i \sum_j (n_j(0) - N \xi_j V_{\text{fin}}(\tilde{\xi})) - n_j \infty \xi_j f_j v_j \]
Solution of the last system of equations is known
\[ \xi_i - \xi_{i\ fin} = C_i \exp\left(-\frac{t}{\delta_{i\ rt}}\right), \]
\[ \delta_{i\ rt} = \left|1/\hat{L}_i[\xi_{i\ fin}]\right| \]
with\(^{67}\) constants \(C_i\), which can be found from the precise solution of \(8\) by transformation to asymptotics. These solutions lead to analogous exponential solutions for \(n_i - n_{i\ fin}\), namely
\[ n_i - n_{i\ fin} = C_{n\ i} \exp\left(-\frac{t}{\delta_{n\ rt}}\right) \]
with constants \(C_{n\ i}\) and corresponding relaxation times \(\delta_{n\ rt}\).

Now we know rather precise asymptotics and can write the equation for the nucleation rate in the known exponential approximation
\[ J(t) = J_{2\ fin}(n_{\ fin}) \exp\left(\sum_i \nu_i c_{\ fin}[C_{n\ i} \exp\left(-\frac{t}{\delta_{n\ rt}}\right) - \xi_{i\ fin}\frac{g_{2\ j}}{\xi_{j\ fin}}]\right). \]
Here the lower index in \(\nu_i c_{\ fin}\) means that the critical value of \(\nu_i\) is taken at the final values of \(n_i\). The value of \(g_{2\ i}\) is the number of molecules of the \(i\)-th component in a liquid phase appeared through the second thermodynamic channel.

At first we shall analyze the case of decreasing asymptotic when even without the natural decrease (due to \(g_{2\ j}\)) of the rate of nucleation this value decreases in time.

Now we shall hold only the leading\(^{68}\) exponent, which brings the last equation to
\[ J(t) = J_{2\ fin} \exp(\nu_0 c_{\ fin}[C_{n\ 0}] \exp\left(-\frac{t}{\delta_{0\ rt}}\right)) \exp\left(-\sum_i \nu_i c_{\ fin}\xi_i \frac{g_{2\ j}}{\xi_{j\ fin}}\right) \]
\[ J_{2\ fin} = J_{2\ s}(n_{\ fin}) \],
where we have marked the leading exponent by index 0 (sometimes there are at least two leading exponents with the same times of relaxation since the sum of concentrations equals to one, so the amplitudes have to be summarized). Then
\[ J(t) = J_{2\ fin} \exp(\nu_0 c_{\ fin}[C_{n\ 0}] \exp\left(-\frac{t}{\delta_{0\ rt}}\right)) \exp(-A_j g_{2\ j}) \]
where the constant \(A_j\) is given by
\[ A_j = \sum_i \nu_i c_{\ 2\ fin}\xi_i \frac{1}{\xi_{j\ fin}} \]
\(^{67}\)If the relaxation really takes place, all \(\hat{L}_i\) are negative. 
\(^{68}\)The exponent with the greatest relaxation time.
Since \( g_{2j}/\xi_{j\ fin} \) is invariant (it doesn’t depend on \( j \)), the rhs of expression for \( J \) doesn’t depend on \( j \) also. This approximation can be used for further analysis.

At the asymptotics one can write \( \nu_{1/2}^{1/3} = \Lambda_{i\ 2}(t - t') \) where \( t' \) is the time of formation of the droplet,

\[
\Lambda_{i\ 2} = \left( 1/12 \right) (36\pi)^{1/3} \xi^{2/3} \xi_{k\ fin} \iota(n_i\ as - n_i\ i\ k\ fin) (\xi_{k\ fin}) ,
\]

\( \xi_{k\ fin} \) is the equilibrium concentration corresponding to the densities at the asymptotic for the droplets appeared through the second channel, \( n_i\ as \) is the density at the asymptotic.

Now one can write equation for \( g_{2i} \) as

\[
g_{2i} = N_s(z + \delta'z)^3 + f_2 j \int_{\delta z - 0}^{\delta z} dx (z - x)^3 \exp(\nu_{0\ c\ 2\ fin} C_0 n_0 \exp(-\frac{t'}{\delta_0\ n\ r})) \exp(-A_j g_{2j})
\]

where we specify that the nucleation is going through the second channel. Here \( z = \Lambda_{i\ 2} t, x = z - \nu_{1/2}^{1/3}, t' = x/\Lambda_{i\ 2}, f_{2i} = J_2 s(n_{fin})/\Lambda_{i\ 2} \). Now this equation will be solved. It is easy to note that

\[
\int_{\delta z}^{\delta z} dx (z - x)^3 \exp(\nu_{0\ c\ 2\ fin} C_0 n_0 \exp(-\frac{t'}{\delta_0\ n\ r})) \exp(-A_j g_{2j})
\]

grows very rapidly (faster than \( z^3 \)). Then the spectrum of sizes is\(^{69}\)

\[
f = f_2 j \Theta(z) \Theta(\delta_0 z - x) \exp(\nu_{0\ c\ 2\ fin} C_0 n_0 \exp(-\frac{t'}{\delta_0\ n\ r}))
\]

plus the monodisperse peak from the initial period and \( z(t) = \Lambda_{i\ 2}(t - t_0) \) where \( t_0 \) is the time shift (it has to be associated with \( C_{0\ n} \) analogously to \( \delta z, \delta'z \)). Here \( \delta_0 z \) is the root of equation

\[
g_{2j}(\delta_0 z) = 1/A_j
\]

(\( j \) isn’t important here). The total number of droplets is approximated by

\[
N_2 = N_s + f_2 j \int_{\delta z}^{\delta z} dx \exp(\nu_{0\ c\ 2\ fin} C_0 n_0 \exp(-\frac{x}{\Lambda_{i\ 2}\delta_0 n\ r}))
\]

or after linearization

\[
N_2 = N_s + (\delta_0 z - \delta z) f_{2j} j + f_2 j \nu_{0\ c\ 2\ fin} C_0 n_0 \delta_0 n\ r\Lambda_{i\ 2}\ [\exp(-\frac{\delta_0 z}{\Lambda_{i\ 2}\delta_0 n\ r}) + \exp(-\frac{\delta z}{\Lambda_{i\ 2}\delta_0 n\ r})]
\]

Here to solve equation on \( \delta_0 z \) it is necessary to calculate \( g_{2j}(z) \) in appropriate form. One can done the following transformations: at first we shall present \( g_{2j} \) as

\[
g_{2i} = N_s(z + \delta'z)^3 + f_2 j \int_{\delta z}^{\delta z} dx (z - x)^3 (-1 + \exp(\nu_{0\ c\ 2\ fin} C_0 n_0 \exp(-\frac{t'}{\delta_0\ n\ r})) \exp(-A_j g_{2j}))
\]

\(^{69}\)Ordinary it is possible to neglect \( \delta z \), but even with \( \delta z \) taken into account the derivation will be quite similar.

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\[ +f_2 j(z - \delta z)^4/4 \]

Then we can out the upper limit in the integral to \( \infty \) and get

\[
g_{2 i} = N_\ast(z + \delta' z)^3 + f_2 i \int_{\delta z}^{\infty} dx(z-x)^3(-1+\exp(\nu_0 c_{2 fin}|C_{n 0}|\exp(-\frac{t'}{\delta_0 n r t})\exp(-A_j g_{2 j})) \\
+ f_2 j(z - \delta z)^4/4
\]

Then \( g_{2 i} \) is the polynomial of the forth power and we know the analytical structure of \( g_{2 i} \). Then the value of \( \delta_0 z \) is solution of the algebraic equation of the forth power. It can be easily solved.

When we take into account only the leading term \( f_2 j z^4/4 \) we come to the method described earlier.

### 5.3 Secondary nucleation at the increasing asymptotic

The rate of nucleation imaginary calculated without droplets appeared through the second channel will be called the ideal rate of nucleation.

All methods developed in two previous subsections can be used here. But in the case of increasing ideal rate of the droplets formation through the second channel there is a following danger - the increasing density \( n_i \) plays the role analogous to the increasing ideal supersaturation in case of dynamic conditions [15]. So, at some density it is possible to see the compensation of increase of density due to evolution of droplets appeared through the first thermodynamic channel by the molecules consumption by the droplets appeared through the second thermodynamic channel. So, here we can see the peak of intensive formation of droplets through the second channel much earlier than we attain the asymptotic. We has to investigate this situation.

The next difficulty is connected with the fact that due to increasing density the term \( N_\ast(z + \delta)^3 \) can not be now considered as the reason for the practically instantaneous cut-off of the spectrum. This radically completes the consideration.

We can introduce the natural length of spectrum \( \Delta_{nat} z \) corresponding to the given vapor densities \( n_i f_{fin} \). This length is the length of spectrum when the initial vapor densities are equal to \( n_i f_{fin} \). It is shown in [18] that the characteristic time of the spectrum formation in the situation of decay and in the situation of dynamic conditions will be approximately one and the same (see the law of inertia of characteristics of the phase transition, page 92). So, we have here some natural characteristic of duration of the spectrum formation.

The characteristic time \( \Delta_{nat} t \) will correspond to this length of spectrum. One can compare \( \Delta_{nat} t \) with the relaxation length \( \Delta_{rel} t = \delta_0 n r t \) going from the asymptotics.

When \( \Delta_{nat} t >> \Delta_{rel} t \) one can easily use the approach of the previous sections, there is nothing to change in the previous approach.

When \( \Delta_{nat} t << \Delta_{rel} t \) one has the situation described as dynamic conditions with the source, which can be effectively linearized (see [15]). So, here the
description is also known (the only specific thing is that we have to add the quantity $N_*$ to the number of droplets obtained at the second peak of densities (the first peak is the initial peak)).

When $\Delta_{nat} \sim \Delta_{rel}$ one has use the modified Gaussian method, which has been already used to investigate the nucleation on several types of heterogeneous centers in dynamic conditions (see [13]).

The method similar to the mentioned method will be described below. We shall present the simplest version which requires the minimum formulas and calculations (but isn’t too precise). We shall describe here the nucleation in dynamic condition with essentially non-linear behavior of external supersaturation (effective external conditions) in time (for external supersaturation see [20]).

We shall start with the case when the ideal supersaturation can be linearized. The integral equation, which has to be solved can be written in the following form

$$g(z) = a \int_{-\infty}^{z} (z-x)^3 \exp(c(\Phi(x) - \Phi_*) - bg(x)) .$$

Here $a, b, c$ - are some constants, $\Phi$ can be interpreted as $n_1$, index * marks the value in some characteristic moment $t_*$, which is the moment of maximum of $c(\Phi(z) - bg)$ and $z(t_*) = 0$. The values $z$ and $x$ have the same sense as in the previous section [70].

When $\Phi(z) - \Phi_*$ can be linearized the equation after the certain renormalization can be written

$$g(z) = a' \int_{-\infty}^{z} (z-x)^3 \exp(c'x - b'g(x))$$

with new values of parameters $c', b'$.

The last equation can be solved by the following approximate procedure. We know that the iterations defined according to

$$g(0) = 0 ,$$

$$g(i+1)(z) = a' \int_{-\infty}^{z} (z-x)^3 \exp(c'x - b'g(i)(x))$$

converge rather fast. Already the spectrum with $g$ as the first iteration ensures the correct number of appeared droplets [71] (a relative error is less [72] than 0.15). Why it takes place? Because the droplets appeared at the first moments of time (when $bg$ was really small) are the main consumers of vapor during the nucleation period. This takes place due to the big power 3 in the integral term. So, there exists a boundary $z = -b_0$, which have the following properties

- (') The droplets appeared before $z = -b_0$ govern the evolution during the nucleation period.

---

1. The value $\Phi_*$ can be taken as the asymptotic (without droplets appeared through the second channel) value (without any correspondence to the time $t_*$ [21]).
2. Here it is taken into account that $d^2\Phi/dt^2 < 0$.
3. One has to see this error when $\Phi - \Phi_*$ can be linearized and then to prove that for $d^2\Phi/dt^2 < 0$ the error will be smaller.
Figure 3. Precision of the method in the linear case

- (*) The inequality $bg(-b_0) \ll 1$ takes place.

It is clear that $b_0$ takes the value, which has the order of $c'^{-1}$ (more accurate it is $(0.7 \div 0.8)c^{-1}$).

So, we can suggest the following procedure: At first to calculate the value of $\tilde{g}$ defined as

$$\tilde{g} \equiv a \int_{-b_0}^{-\infty} dx (z-x)^3 \exp(c(\Phi(z) - \Phi_\ast)).$$

Then to calculate the number of droplets as

$$N \sim a \int_{-\infty}^{-b_0} dz \exp(c(\Phi(z) - \Phi_\ast)) + a \int_{-b_0}^\infty dz \exp(c(\Phi(z) - \Phi_\ast) - b\tilde{g}(z)) \quad (18)$$

This method is rather precise, the ratio $N_{\text{appr}}/N$ where $N_{\text{appr}}$ is the number of droplets calculated in (18) and $N$ is precise solution is drawn in\textsuperscript{73} Fig. 3.

Now we shall apply this method to the case under consideration.

The equation we have to study is

$$g_{2 \ 1} = f_{2 \ 1} \int_{-\infty}^z (z-x)^3 \exp(-\nu_0 c_2 f_{in}|C_0| \exp(-x/\delta_0 z)) \exp(-A_1 g_{2 \ 1}) dx,$$

\textsuperscript{73}Here the linear case is considered.
where $\delta_0 z = \delta_{0,n} 2t \Lambda_{1,2}$ and $f_{2,1}$ has the sense $J_{2,fin}$ divided by the rate of growth $\Lambda_{1,2}$. Here $C_0 \sim C_{0,0}$. So, here $\Phi - \Phi_n \sim \nu_{0,2,fin} |C_0| \exp(-x/\delta_0 z)$
and, thus,
\[
d\Phi/dx > 0 , \quad d^2\Phi/dx^2 < 0 .
\]

One has to add the term $\exp(-\sum_j \nu_j c_{2,fin} \xi_j k N_* (z_* + x)^3)$ due to the initial peak of droplets. Here $z_*$ is is the coordinate of this monodisperse peak at $t = t_*$. Then
\[
g_{2,1} = f_{2,1} \int_{-\infty}^{z} (z-x)^3 \exp(-\nu_{0,2,fin} |C_0| \exp(-x/\delta_0 z)) \cdot \\
\exp(-\sum_j \nu_j c_{2,fin} \xi_j k N_* (z_* + x)^3) \exp(-A_1 g_{2,1}) dx
\]
and inequality $d^2\Phi/dz^2 < 0$ also takes place.

Now $c(\Phi(x) - \Phi) = -\nu_{0,2,fin} |C_0| \exp(-x/\delta_0 z) - \sum_j \nu_j c_{2,fin} \xi_j k N_* (z_* + x)^3$

Due to the last inequality the method will work even better than in the linear case because here the properties (') and (") will be better. The problem is whether one can calculate $\tilde{g}$ analytically.

Actually $\tilde{g}$ is the polynomial in $z$ of the third power
\[
\tilde{g} = \sum_{i=0}^{3} z^i (-1)^{3-i} w_i \frac{3!}{i!(3-i)!} ,
\]
\[
w_i = a \int_{-\infty}^{b_0} x^{3-i} \exp(c(\Phi(z) - \Phi_n)) .
\]

Now we shall calculate $N$ and have to take definite integrals. It can be done by the quickest descent method since in the subintegral expressions there are only exponents.

6 Discussion

The theory for multicomponent condensation can not be presented in such a concrete and compact form as in the case of one component condensation. This is a result of the presence of complex and generally arbitrary coefficients of activity $f_i$. Here we have supposed only some general properties of $f_i$ such as the regularity of solution at small concentrations.

The condensation in the binary systems is much more interesting than in the one component case. The properties of reverse condensation, of the secondary nucleation are simply absent in the one component case. Now they are
predicted only theoretically and it will be very interesting to see them experimentally. Unfortunately, even the experimental results used in [9] don’t belong to the kinetics of the whole phase transition, but to the stationary rate of nucleation. The last is certainly the important characteristic but it has no direct connection with the specific phenomena of the multicomponent kinetics, which is the central point discussed here. This publication has to stimulate the experimental investigations in this direction because now it is absolutely clear what effects and characteristics are worth searching.

In the last section the description of the ”long nucleation” was done only for the period of nucleation and for the two component case. As for the description of the second period it can be done in the same manner as for the case of the ordinary nucleation. It is necessary only to consider the two channels of nucleation in all places where we speak about the initial stage of condensation and about the asymptotic stage of condensation. The situation when the evolution of the droplets from the first channel already attains the asymptotic stage (that’s why we prefer to speak about stages of condensation instead of the periods of condensation) and the droplets\textsuperscript{74} from the second channel are still at the initial stage is rather specific. But still in frames of approximations of initial stage and final stage it is easy to give the adequate description.

For different components the power of consumption of the surplus vapor can be different. That’s why at the given moment of time the different components can be at different stages. The evolution becomes unclear. In this context it is important to see the property of the global avalanche consumption, which states that the intermediate period has relatively (in comparison with the duration of the first period) short duration. Then for every concrete complex system one can act in frames of simple solutions and get the simple true kinetics of nucleation.

Here we shall briefly summarize the new items proposed in this paper:

- The consideration of kinetic and thermodynamic channels is given.
- The correct description of the relaxation to the stationary state in the channel is given.
- Essential errors of the elementary description of nucleation from [9] are corrected.
- The description of the condensation of the main quantity of substance is given. This description corrects the description proposed in [9]. It is shown that the precise solution is absent. Several effective approximations are suggested. They are rather effective.
- The situation of the ”long nucleation” is analyzed. The methods to give the adequate description of this situation are proposed.

But the main result of the article is the complete analytical description of the condensation process in the system with a mixture of substances in a metastable

\textsuperscript{74}We have to consider the initial, intermediate and the final periods with reference for every component.
phase. All main characteristics of the process such as the numbers of droplets of different sorts and the times of duration of nucleation in different channels of nucleation are determined explicitly.

We have not given the estimates for the beginning of the transformation of the condensation process into the process of coalescence (super-condensation). The necessary estimate comes from condition that the coordinate of monodisperse spectrum $\nu_i$ has to be 2 or 3 times greater than the critical size $\nu_{i,c}$ in every corresponding channel. The announced estimate can be easily checked on the base of obtained solution, which gives the estimate for the time of the end of the condensation process$^{75}$.

The generalization of the description of the "long nucleation" for the multicomponent case is rather simple. It is clear that in the $n$-component mixture condensation the maximum number of separate nucleation processes is limited by $n$. So, we have to act in the following manner: Consider the first channel of nucleation, then see what components aren’t exhausted (the corresponding concentrations in kinetic channels are small). If there are some unexhausted components we can search for the channels where only these unexhausted components are the leading ones (the concentrations of all other components at thermodynamic channel are small). We shall do it in the sequence of increasing heights of activation barriers of nucleation. May be we shall find the channel with a necessary properties. This channel may not be the second in the total sequence of the activation barriers heights, but all channels before this channel are now out of action. The nucleation through this channel will be the secondary nucleation and it is already described. Then we shall reconsider the set of unexhausted components (these components are the components, which are small in both kinetic channels) and seek for the kinetic channel with essential concentrations (concentrations, which aren’t small) from the set of previously unexhausted components. This channel will be the leading one. This completes the loop, which can be repeated again. The number of such loops is limited from above by $l$.

As the result we have the set of channels, which will be called as essential channels (both thermodynamic and kinetic). The nucleation in all channels from this set can be described analogously to the two component case. There is only one difficulty, which is specific to the multi component case. In the two component case the consumption of vapor by the droplets from the first channel occurs in the pseudo one-dimension manner (the concentration of one component is small, so the concentration of the other component is known also and, thus, all concentrations are known; moreover the value of the droplets volume is determined only by one component). In the multicomponent case there will be a real problem to describe this evolution. But with the help of methods presented in the section devoted to the second period this situation can be described analytically also.

To give the necessary description one can split the evolution into the initial

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$^{75}$Also the statement from [9] that the theory of multicomponent coalescence is absent is wrong - the results presented in [23] cover the case of multicomponent coalescence.
stage and the asymptotic stage. Since for droplets appeared from one channel the evolution is already at the final asymptotic stage and for the droplets from the other channel the evolution is at the initial stage at one and the same moment then it is preferable to speak about stages instead of periods. The initial stage and the final stage practically cover all evolution. This is the crucial point of description. Then it is rather easy to take into account the influence of the already existing spectrums of droplets appeared through the already closed channels, because we know the functional expressions for them as functions of time. So, the functional form of equations will be the same as for the binary system and it is easy to get the approximate solution in analytical form.

One have also to keep in mind that the final state corresponding to the different channels can be different. Certainly, it doesn’t produce essential difficulties.

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