Multicomponent nonisothermal nucleation. 1. 
Kinetic equation

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The first order phase transition ordinary occurs in the systems with many different condensating components. During the process of nucleation, i.e. formation of droplets, the heat of condensation is extracted which changes the rate of nucleation. The theoretical description has to take into account these two features. So, one can see that creation of the nonisothermal theory for the multicomponent nucleation is rather actual.

The adequate theoretical description of the nucleation stage was given for many different situations starting from the pure isothermal nucleation of one component (one substance). Even in this situation described by the so-called classical theory of nucleation there is no coincidence between theoretical predictions and experimental results. Nevertheless, this disagreement can not be the reason to reject all further modifications of the theory to grasp the effects of the heat extraction and to extend the theory for the multicomponent case.

The first theory where the thermal effects were taken into account rather adequately was presented by Kantrowitz [1]. In this publication embryos of given size were characterized by the unique average temperature. Only the so-called "weak thermal effects" were considered there. But the really essential decrease of the nucleation rate occurs under the "strong thermal effects" considered by Kuni [2].

Certainly, there exists the distribution of the embryos of given size over the temperature. Feder et al. [3] took this phenomena into account for the weak thermal effects. The energy distribution of embryos under the strong thermal effects was investigated by Kuni and Grinin [4].
The standard way to construct kinetic equation is to use the Fokker-Planck approximation. Then kinetic equation can be solved in the stationary situation by approach of Langer [5] or by approach of Kuni et al. [6] in the nonstationary situation.

The methods described in [5] allow to study some different situations. Namely the situation of the binary situation was studied by Lazaridis and Drossinos [7] under the Fokker-Planck approximation.

Concerning the mentioned publication [7] one has to note that due to a rather big quantity of the molecular heat extracted in the act of condensation the restriction by the Fokker-Planck approximation isn’t sufficient. Then kinetic equation contains high derivatives and one has to use the Chapman-Enskog procedure to solve it.

Until the current moment one can say that the most advanced approach for the nonisothermal nucleation is the application of the Chapman-Enskog procedure which was suggested by Kuni, Grinin in the case of one component nucleation [4]. In [8] this approach was spread to the binary nucleation. Unfortunately it was not done in the appropriate way. So, the subject of this publication appears rather naturally in the context of the theoretical methods development.

Particularly, this publication is aimed to present the nonisothermal theory of nucleation in the multicomponent mixture and to correct the errors in [8]. We shall present the self consistent theory which gives the analytical expression for the nucleation rate. Some parts of the theory where it is quite analogous to the known results (for example, the solution of kinetic equation in the Fokker-Planck approximation) are omitted.

In this publication we shall use all standard definitions of the classical nucleation theory, consider the unit volume, take all values with the energy dimension in the units of the elementary thermal energy $k_bT$ ($k_b$ is the Boltzmann constant and $T$ is the temperature), and all values with the heat capacity dimension in the $k_b$ units.

1 Substance exchange

Here we shall derive kinetic equation from the balance equation for the distribution $n$ over the embryos sizes. This balance equation can be written in
the following form
\[ \frac{\partial n}{\partial t} = V + G \]
where \( V \) is the operator associated with the substance exchange between
the embryo and the environment (one also has to take into account here the
energy exchange due to the extraction of the condensation heat) and \( G \) is
the operator associated with the energy exchange due to the difference of the
temperature \( T \) of the embryo from the temperature \( T_0 \) of the environment
(the effects of the heat extraction are already included into \( V \)).

The function \( n \) is the number of embryos of given size in a unit volume.
Later we shall specify variables of the embryos state description.

At first we shall study kinetic equation without thermal relaxation by a
passive gas, i.e. in the form
\[ \frac{\partial n}{\partial t} = V \] (1)
and then we shall study thermal relaxation, i.e. operator \( G \).

Suppose that there exists a vapor mixture with \( i_0 \) condensating com-
ponents. All these components can be found both in the vapor and in the
embryo (in contrary of the passive gases which can be found only in the vapor
phase). The distribution \( n(\{\nu_i\}, t) \) of embryos is the function of \( i_0 \) variables
of the number of molecules \( \nu_i \) of the \( i \)th component (substance) inside the
embryo and also the function of time \( t \).

The process of the absorption of a molecule of \( j \)th component occurs with
intensity \( W_j^+ \alpha_{j \text{ cond}} \) where \( W_j^+ \) is the intensity of collision of the given embryo
with an arbitrary molecule of \( j \)th component and \( \alpha_{j \text{ cond}} \) is the condensation
coefficient for \( j \)th component. The most natural is to suppose that the length
of the free motion in the gas media strongly exceeds the linear size of the
embryo (so-called free molecular regime of the substance exchange). Then
the value \( W_j^+ \) can be easily found by the gas kinetic theory
\[ W_j^+ \sim S n_j \]
where \( S \) is the surface square of the embryo and \( n_j \) is the molecular num-
ber density of the \( j \)th component\(^1\). Due to the small relative size of the

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\(^1\)One has also to note that in the nearcritical region all embryos are in the quasiequi-
librium with the surrounding vapor. This quasiequilibrium also leads to the small unhom-
genities in the vapor phase. These unihomogeneties would lead to the diffusion flows on
nearcritical region we can see that \( W_j^+ \) remains practically constant in the nearcritical region.

Any reliable information about the condensation coefficient \( \alpha_{j\,\text{cond}} \) is absent (in the literature one can found rather different estimates). But we believe that \( \alpha_{j\,\text{cond}} \) is rather smooth function of the embryo state and can be regarded in the nearcritical region as some constant value.

The process of absorption of the molecule leads to the variation of the number of the molecules inside the embryo

\[ \{\nu_i\} \rightarrow \{\nu_{i\neq j}, \nu_j + 1\} \]

and also to the extraction of the condensation heat \( \beta_j \) (which is measured in the natural thermal units) which is going to increase the temperature of the embryo \( T \) by the value

\[ T \rightarrow T + \frac{\beta_j}{\sum c_i \nu_i} \]

where \( c_i \) are the heat capacities per one molecule in the liquid phase (taken in units of \( k_b \)), the sum is taken over all components.

The value \( W_j^+ \) depends only on the state of a vapor-gas mixture. Contrary to \( W_j^+ \) the intensity of the ejection of the molecule of the \( j \)th component \( W_j^- \) strongly depends on the temperature of the embryo. The embryo has to be characterized by the temperature \( T \) of the embryo or some function of the temperature. Instead of \( T \) one can introduce the value of additional energy \( E \) according to

\[ E = \left( \frac{T}{T_0} - 1 \right) \sum c_i \nu_i \]

where \( T_0 \) is the temperature of the media, \( c_i \) are molecular specific heats expressed in units of \( k_b \). The evident advantage of \( E \) is that the equilibrium value coincides with the zero point. Now we shall normalize \( E \) in order to

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2One can use the standard classical nucleation theory for this estimate.
3This follows also from the model where \( \alpha_{j\,\text{cond}} \) appears as the probability to overcome the energy barrier near the surface of the liquid phase.
4We suppose that the temperature relaxation inside occurs very rapidly. It can be justified by estimates analogous to \( \text{[4]} \).
5They are close to those defined under the constant pressure.
have no coefficient in the square form of the equilibrium distribution\footnote{\(n^e\)} along additive energy near \(E = 0\):

\[ n^e \sim \exp(-\mu^2) \]

To find \(\mu\) we shall start with Clapeyron-Clausius formula for the molecular number density \(n_{\infty j}\) of the saturated vapor under a plane surface of liquid

\[ n_{\infty j}(T) = n_{\infty j}(T_0) \exp(\beta_j \frac{T - T_0}{T_0}) \]

As far as\footnote{Here we suppose that the surface tension doesn’t depend on the embryo’s temperature. Details of this approximation can be found in \cite{9}.} for the planar surface

\[ W_j^-(n_{\infty j}) = W_j^+(n_{\infty j}) \sim n_{\infty j} \]

one can come to

\[ \frac{W_j^-(T)}{W_j^-(T_0)} = \frac{n_{\infty j}(T)}{n_{\infty j}(T_0)} = \exp(\beta_j \frac{T - T_0}{T_0}) \]

One the other hand

\[ W_j^-(E)n^e(E) = W_j^+(E - \beta_j)n^e(E - \beta_j) \]

and

\[ W_j^-(E = 0)n^e(E = 0) = W_j^+(E = 0)n^e(E = 0) \]

which leads to

\[ W_j^-(E) = \frac{n^e(E - \beta_j)}{n^e(E)} W^-(E = 0) \frac{n^e(E = 0)}{n^e(-\beta_j)} = W^-(E = 0) \exp(E\beta_j \frac{\partial^2 F}{\partial E^2}) \]

where \(F\) is the free energy of the embryos formation and it is taken into account that the equilibrium distribution \(n^e \sim \exp(-F)\).
Both approaches will coincide when
\[
\frac{\partial^2 F}{\partial E^2} = \left( \sum_i c_i \nu_i \right)^{-1}
\]

Then
\[
\mu = \frac{E}{(2 \sum_i c_i \nu_i)^{1/2}}
\]

One can write kinetic equation (1) in variables \( \{\nu_i\}, \mu \) in the following form
\[
\frac{\partial n(\{\nu_i\}, \mu, t)}{\partial t} = \sum_j \left[ J_j(\{\nu_{i \neq j}, \nu_j - 1\}, \mu - \tau_j) - \sum_j W_j^+ n(\{\nu_{i \neq j}, \nu_j\}, \mu) - \sum_j W_j^- n(\{\nu_{i \neq j}, \nu_j + 1\}, \mu + \tau_j) \right]
\]

where
\[
\tau_j = \frac{\beta_j}{(\sum_i c_i \nu_i)^{1/2}}
\]

One can present the following split of the last equation
\[
\frac{\partial n(\{\nu_i\}, \mu, t)}{\partial t} = \sum_j [J_j(\{\nu_{i \neq j}, \nu_j - 1\}, \mu - \tau_j) - J_j(\{\nu_{i \neq j}, \nu_j\}, \mu)]
\]

where the flow \( J_j \) is defined by
\[
J_j(\{\nu_i\}, \mu) = W_j^+ n(\{\nu_{i \neq j}, \nu_j\}, \mu) - W_j^- n(\{\nu_{i \neq j}, \nu_j + 1\}, \mu + \tau_j)
\]

Now we have to substitute the finite differences by derivatives.

One has to mention that the elementary steps 1 along \( \nu_i \) are small in comparison with the characteristic scale corresponding to the essential variation of exponent of the free energy. This allows to substitute the finite difference along \( \nu_i \) only by the first derivative\(^9\).

More carefully it can be done in terms of the finite differences.\(^{10}\)

\(^{9}\)More carefully it can be done in terms of the finite differences.

\(^{10}\)This produces certain restrictions which will limit later the Chapman-Enskog expansion.
An elementary step $\tau_j$ along $\mu$ corresponds to essential violation of exponent of the free energy. So, one has to substitute the finite difference by the whole Tailor seria. As the result we have

$$\frac{\partial n(\{\nu_i\}, \mu, t)}{\partial t} = \sum_j \sum_{l=1}^{\infty} \frac{(-\tau_j)^l}{l!} \frac{\partial^l}{\partial \mu^l} J_j(\{\nu_i \neq j, \nu_j - 1\}, \mu)$$

$$- \sum_j \frac{\partial}{\partial \nu_j} J_j(\{\nu_i \neq j, \nu_j\}, \mu)$$

We have to note that the possibility to substitute $J_j(\{\nu_i \neq j, \nu_j - 1\}, \mu) - J_j(\{\nu_i \neq j, \nu_j\}, \mu)$ by $-\frac{\partial}{\partial \nu_j} J_j(\{\nu_i \neq j, \nu_j\}, \mu)$ can be made when we consider the situation near the quasistationary one. Then in one dimensional projection on $\nu_j$ we shall get the small value for $J_j(\{\nu_i \neq j, \nu_j - 1\}, \mu) - J_j(\{\nu_i \neq j, \nu_j\}, \mu)$ which allows to substitute it only by the first derivative.

The flow $J_j$ can be expressed with the help of a function

$$f(\{\nu_i\}, \mu) = \frac{n(\{\nu_i\}, \mu)}{n^e(\{\nu_i\}, \mu)}$$

as

$$J_j(\{\nu_i \neq j, \nu_j\}, \mu) = W^+_j n^e(\{\nu_i\}, \mu) \left[ f(\{\nu_i \neq j, \nu_j\}, \mu) - f(\{\nu_i \neq j, \nu_j + 1\}, \mu + \tau_j) \right]$$

The analogous substitution of the finite differences by the Taylor seria gives

$$J_j(\{\nu_i \neq j, \nu_j\}, \mu) = W^+_j n^e(\{\nu_i\}, \mu, t)$$

$$[- \frac{\partial}{\partial \nu_j} f(\{\nu_i \neq j, \nu_j + 1\}, \mu) - \sum_{m=1}^{\infty} \frac{\tau_j^m}{m!} \frac{\partial^m}{\partial \mu^m} f(\{\nu_i \neq j, \nu_j + 1\}, \mu)]$$

To be close to the standard form of one component nonisothermal theory we shall use instead of function $f$ the following function

$$P(\{\nu_i \neq j, \nu_j\}, \mu) = \frac{n(\{\nu_i \neq j, \nu_j\}, \mu)}{\exp(-\mu^2)}$$

The free energy $F$ of the embryos formation can be split as

$$F(\{\nu\}, \mu) = F(\{\nu\}, \mu = 0) + \mu^2$$
which gives
\[ f(\{\nu\}, \mu) = P(\{\nu\}, \mu) \exp(F(\{\nu\}, \mu = 0)) \]

One can present expression for \( J_j \) in terms of function \( P \) as
\[
J_j(\{\nu_{i \neq j}, \nu_j\}, \mu) = W_j^+ n^e(\{\nu_i\}, \mu) \left[ -\frac{\partial}{\partial \nu_j} \exp(F(\{\nu\}, \mu = 0)) P(\{\nu_{i \neq j}, \nu_j\}, \mu) - \exp(F(\{\nu_{i \neq j}, \nu_j + 1\}, \mu = 0)) \sum_{m=1}^{\infty} \frac{\tau_j^m}{m!} \frac{\partial^m}{\partial \mu^m} P(\{\nu_{i \neq j}, \nu_j + 1\}, \mu) \right]
\]

or
\[
J_j(\{\nu_{i \neq j}, \nu_j\}, \mu) = W_j^+ n^e(\{\nu_i\}, \mu) \left[ -\frac{\partial}{\partial \nu_j} \exp(F(\{\nu\}, \mu = 0)) P(\{\nu_{i \neq j}, \nu_j\}, \mu) - (1 + \frac{\partial F}{\partial \nu_j} + \frac{1}{2} \frac{\partial^2 F}{\partial \nu_j^2} + \frac{1}{2} \frac{\partial F}{\partial \nu_j}) \exp(F(\{\nu_{i \neq j}, \nu_j + 1\}, \mu = 0)) \sum_{m=1}^{\infty} \frac{\tau_j^m}{m!} \frac{\partial^m}{\partial \mu^m} P(\{\nu_{i \neq j}, \nu_j + 1\}, \mu) \right]
\]

Having introduced an operator
\[
L_j = -W_j^+ \frac{\partial F}{\partial \nu_j} + \frac{\partial}{\partial \nu_j}
\]

one can present the last expression for \( J_j \) as
\[
J_j(\{\nu_{i \neq j}, \nu_j\}, \mu) = \exp(-\mu^2) L_j P(\{\nu_{i \neq j}, \nu_j\}, \mu) - (1 + \frac{\partial F}{\partial \nu_j} + \frac{1}{2} \frac{\partial^2 F}{\partial \nu_j^2} + \frac{1}{2} \frac{\partial F}{\partial \nu_j}) \exp(-\mu^2) W_j^+ \sum_{m=1}^{\infty} \frac{\tau_j^m}{m!} \frac{\partial^m}{\partial \mu^m} P(\{\nu_{i \neq j}, \nu_j + 1\}, \mu)
\]

According to the smooth dependence along \( \nu_j \) one can substitute the argument \( \nu_j \pm 1 \) of function \( P \) by \( \nu_j \).

Then as far as
\[
(1 + \frac{\partial F}{\partial \nu_j} + \frac{1}{2} \frac{\partial^2 F}{\partial \nu_j^2} + \frac{1}{2} \frac{\partial F}{\partial \nu_j}) \mid_{\nu \rightarrow \nu + 1} = (1 + \frac{\partial F}{\partial \nu_j} - \frac{1}{2} \frac{\partial^2 F}{\partial \nu_j^2} + \frac{1}{2} \frac{\partial F}{\partial \nu_j})
\]

Later it will be seen that \( \partial / \partial \nu_j \) produces some small parameter as far as the action of \( \partial F / \partial \nu_j \). We write this equation in the first two orders of this parameter. This corresponds to the order essential in the isothermal version of the theory.
then kinetic equation can be presented as

\[ \exp(-\mu^2) \frac{\partial P\{\nu_i\}, \mu}{\partial t} = \sum_j \sum_{l=1}^{\infty} \frac{(-\tau_j)^l}{l!} \frac{\partial^l}{\partial \mu^l} \]

\[ \exp(-\mu^2)L_j(1 - \frac{\partial}{\partial \nu_j})P\{\nu_i\}, \mu) - \]

\[ (1 + \frac{\partial F}{\partial \nu_j} - \frac{1}{2} \frac{\partial^2 F}{\partial \nu_j^2} + \frac{1}{2} (\frac{\partial F}{\partial \nu_j})^2) \exp(-\mu^2)W_j^+ \sum_{m=1}^{\infty} \frac{\tau_j^m}{m!} \frac{\partial^m}{\partial \mu^m} P\{\nu_i\}, \mu) - \]

\[ \sum_j \frac{\partial}{\partial \nu_j} \exp(-\mu^2)P\{\nu_i\}, \mu) - (1 + \frac{\partial F}{\partial \nu_j})(1 + \frac{\partial}{\partial \nu_j}) \exp(-\mu^2)W_j^+ \sum_{m=1}^{\infty} \frac{\tau_j^m}{m!} \frac{\partial^m}{\partial \mu^m} P\{\nu_i\}, \mu) \]

The action of \( \partial/\partial \mu \) on \( \exp(-\mu^2)\psi \) where \( \psi \) is the arbitrary function is obviously given by

\[ \frac{\partial^l}{\partial \mu^l} \exp(-\mu^2)\psi = \exp(-\mu^2)(\frac{\partial^l}{\partial \mu^l} - 2\mu)^l \psi \]

Certainly one can not take \( 2\mu \) away from \( \frac{\partial^l}{\partial \mu^l} \) and has to consider \( (\frac{\partial^l}{\partial \mu^l} - 2\mu)^l \) as sequential action of operators in brackets. This turn kinetic equation to

\[ \frac{\partial P\{\nu_i\}, \mu}{\partial t} = \sum_j \sum_{l=1}^{\infty} \frac{(-\tau_j)^l}{l!} \frac{\partial}{\partial \mu^l} \]

\[ [L_j(1 - \frac{\partial}{\partial \nu_j})P\{\nu_i\}, \mu) - W_j^+ (1 + \frac{\partial F}{\partial \nu_j} - \frac{1}{2} \frac{\partial^2 F}{\partial \nu_j^2} + \frac{1}{2} (\frac{\partial F}{\partial \nu_j})^2) \sum_{m=1}^{\infty} \frac{\tau_j^m}{m!} \frac{\partial^m}{\partial \mu^m} P\{\nu_i\}, \mu) - \]

\[ \sum_j \frac{\partial}{\partial \nu_j} [L_j P\{\nu_i\}, \mu) - W_j^+ (1 + \frac{\partial F}{\partial \nu_j} + \frac{\partial}{\partial \nu_j}) \sum_{m=1}^{\infty} \frac{\tau_j^m}{m!} \frac{\partial^m}{\partial \mu^m} P\{\nu_i\}, \mu) \]

The last equation present the final form of kinetic equation.

We decompose the finite differences along \( \nu_j \) until the second derivatives (or the second order of the small parameter) because in the classical theory of isothermal one-component nucleation two derivatives have to be taken into account (An account of the first derivative couldn’t lead to the suitable rate of nucleation).
One can easily note that operators

\[ S_{1j} = 1 - \frac{\partial}{\partial \nu_j} \]
\[ S_{2j} = 1 + \frac{\partial F}{\partial \nu_j} - \frac{1}{2} \frac{\partial^2 F}{\partial \nu_j^2} + \frac{1}{2} \left( \frac{\partial F}{\partial \nu_j} \right)^2 \]
\[ S_{3j} = 1 + \frac{\partial F}{\partial \nu_j} + \frac{\partial}{\partial \nu_j} \]

are absent in [8]. Really, in the first two steps of the Chapman-Enskog procedure described later these terms will not be essential. But it occurs only in frames of the Chapman-Enskog procedure and can not be seen directly from this equation. We shall call \( S_{1j} \), \( S_{2j} \), \( S_{3j} \) as the shift operators.

Now we shall turn to the thermal relaxation by the passive gas in order to include it in the presented equation.

## 2 Thermal relaxation

The physical reason to consider the interaction of the embryo with the passive gas is rather simple. Really, due to heat extraction the temperature of the embryo is higher than the temperature of environment and the embryo heats the molecules of the passive gas. Certainly, the temperature of the embryo falls which reduces an ejection rate. This has to be taken into account and the consideration of the interaction with the passive gas is important.

In the previous consideration the condensation of the molecule can be described by some fixed values of the the condensation heat \( \beta_j \). An obvious restriction only by the regular term in the presence of the big quantities of the passive gas will lead to the thin spectrum in the energy scale of the \( \delta \)-function form. Certainly, this doesn’t coincide with the equilibrium distribution. Thus, one has to use at least the Fokker-Planck approximation. The physical reason is rather obvious - molecules of a passive have the different velocities and equilibrium distribution in energies. This has to be taken into account and leads at least to the Fokker-Planck approximation. As far as the variation of the energy in the elementary act of interaction is small in comparison with the characteristic scale of the variation of the equilibrium
distribution one can restrict this description by the Fokker-Planck approximation.

In Fokker-Planck approximation the kinetic equation can be written as

\[ \frac{\partial n}{\partial t} = B \frac{\partial}{\partial \mu} n^e \frac{\partial}{\partial \mu} f \]

where \( B \) is kinetic coefficient. It can be determined by consideration of the limit situation where the last equation transforms into an equation only with the regular term

\[ \frac{\partial n}{\partial t} = B \frac{\partial}{\partial \mu} [2\mu + \frac{\partial}{\partial \mu}] n \rightarrow B \frac{\partial}{\partial \mu} 2\mu n \]

This form form has to be reproduced by the standard analysis. We begin with the balance equation

\[ \frac{\partial n}{\partial t} = W^+ n(\mu + \delta \mu) - W^+ n(\mu) \rightarrow W^+ \delta \mu \frac{\partial n}{\partial \mu} \]

where \( W^+ \) is the rate of collisions of the given embryo with the molecules of the passive gas, the regular variation \( \delta \mu \) is given by

\[ \delta \mu = \frac{c_g}{\sum c_j \nu_j} \mu \]

and \( c_g \) is the molecule heat capacity of the passive gas. This leads to

\[ B = W^+ \frac{c_g}{2 \sum c_j \nu_j} \]

Now the kinetic equation can be written in the following form

\[ \frac{\partial n}{\partial t} = W^+ \frac{c_g}{2 \sum c_j \nu_j} \frac{\partial}{\partial \mu} n^e \frac{\partial}{\partial \mu} f \]

One has to put the coefficient of thermal accommodation \( \alpha_{acc} \) to \( W^+ \) in order to take into account that thermal accommodation occurs with some probability.

The generalization of the previous equation on the mixture of passive gases leads to

\[ \frac{\partial n}{\partial t} = \sum_{i'} W_{i'}^+ \alpha_{acc} i' \frac{c_g i'}{2 \sum c_j \nu_j} \frac{\partial}{\partial \mu} n^e \frac{\partial}{\partial \mu} f \]
where indexes with prime denote different passive gases.

One has to take into account that the condensating substances also take part in the cooling. With the probability \((1 - \alpha_c)\alpha_{acc}\) the act of cooling takes place. The molecules accumulated by embryos also have to be taken into account. As the result one can get

\[
\frac{\partial n}{\partial t} = \sum_{i'} W_{i'}^+ \alpha_{acc} i' \frac{c_g}{2 \sum c_j \nu_j} \frac{\partial}{\partial \mu} n^e \frac{\partial}{\partial \mu} f + \\
\sum_i W_i^+ (1 - \alpha_{c,i}) \alpha_{acc} \frac{c_i}{2 \sum c_j \nu_j} \frac{\partial}{\partial \mu} n^e \frac{\partial}{\partial \mu} f + \\
\sum_i W_i^+ \alpha_{c,i} \frac{c_i}{2 \sum c_j \nu_j} \frac{\partial}{\partial \mu} n^e \frac{\partial}{\partial \mu} f
\]

It is quite obvious that now to get the general kinetic equation we have to add the part associated with the condensating substance. So, it is necessary to formulate the part under consideration in terms of function \(P\). Here one has to fulfill the same actions and get

\[
\frac{\partial P}{\partial t} = \sum_{i'} W_{i'}^+ \alpha_{acc} i' \frac{c_g}{2 \sum c_j \nu_j} \left( \frac{\partial}{\partial \mu} - 2 \mu \right) \frac{\partial}{\partial \mu} P + \\
\sum_i W_i^+ (1 - \alpha_{c,i}) \alpha_{acc} \frac{c_i}{2 \sum c_j \nu_j} \left( \frac{\partial}{\partial \mu} - 2 \mu \right) \frac{\partial}{\partial \mu} P + \\
\sum_i W_i^+ \alpha_{c,i} \frac{c_i}{2 \sum c_j \nu_j} \left( \frac{\partial}{\partial \mu} - 2 \mu \right) \frac{\partial}{\partial \mu} P
\]

As the final result for the general kinetic equation one can get

\[
\frac{\partial P(\{\nu_i\}, \mu)}{\partial t} = \\
\sum_j \sum_{l=1}^{\infty} \frac{(-\tau_j)^l}{l!} \left( \frac{\partial}{\partial \mu} - 2 \mu \right) \left[ L_j S_{1j} P(\{\nu_i\}, \mu) - S_{2j} W_j^+ \sum_{m=1}^{\infty} \frac{\tau_j^m}{m!} \frac{\partial^m}{\partial \mu^m} P(\{\nu_i\}, \mu) \right] - (2) \\
\sum_j \frac{\partial}{\partial \nu_j} \left[ L_j P(\{\nu_i\}, \mu) - S_{3j} W_j^+ \sum_{m=1}^{\infty} \frac{\tau_j^m}{m!} \frac{\partial^m}{\partial \mu^m} P(\{\nu_i\}, \mu) \right] + \\
\sum_{j'} W_j'^+ \alpha_{acc} \frac{c_{g,j'}}{2 \sum c_j \nu_j} \left( \frac{\partial}{\partial \mu} - 2 \mu \right) \frac{\partial}{\partial \mu} P(\{\nu_i\}, \mu) +
\]

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\[ \sum_{i'} W_{i'}^+ (1 - \alpha_{c_{i'}}) \alpha_{acc_{i'}}^+ \frac{c_{i'}}{2 \sum_j c_j \nu_j} \left( \frac{\partial}{\partial \mu} - 2 \mu \right) \frac{\partial}{\partial \mu} P(\{\nu_i\}, \mu) + \]
\[ \sum_{i'} W_{i'}^+ \alpha_{c_{i'}}^+ \frac{c_{i'}}{2 \sum_j c_j \nu_j} \left( \frac{\partial}{\partial \mu} - 2 \mu \right) \frac{\partial}{\partial \mu} P(\{\nu_i\}, \mu) \]

Here indexes \( i' \) and \( j' \) mark the different components of the condensating substances and index \( j' \) marks the different components of the passive substances.

One can easily note that the number of components of the condensating mixture doesn’t act on the properties of passive gases. This lies in contradiction with results presented in [8] where the action of the passive gas is referred to the action of every component of condensating substance and then the direct summation over the condensation components is carried out. So, according to [8] one can speak about the separate cooling of different components (in kinetic sense, the droplet is cooling as a whole object). Here we speak about the common cooling of different components (in kinetic sense). The physical essence is another here.

### 3 Estimates of operators

Now we shall present the method to solve the last equation. The general scheme is well known. At first the extraction of the main operator with the well known eigenfunctions has to be presented. This main operator has to ensure the relaxation to the stationary state which allows to consider of the relaxation period. Such a structure allows later to apply the Chapman-Enskog procedure.

An attempt to investigate the situation of the binary nonisothermal nucleation was made in [8] but the initial kinetic equation was wrong. Contrary to [8] we shall use the correct kinetic equation. Here this equation is already generalized for the multicomponent case.

Besides the new object of investigation the approach presented here has also some new principal features.

One has to note the specific feature of the relaxation stage description fulfilled in the mentioned papers. When the main operator has only formal priority then a standard consideration of the relaxation stage requires the small value of specific parameter. This leads to the serious restriction of
the approach used in the mentioned papers. In the situations of intensive droplets formation this parameter isn’t too small and the relaxation doesn’t take place. Then the initial condition for the Chapman-Enskog procedure is violated. This doesn’t allow to apply this procedure.

We shall use another split on the r.h.s. of kinetic equation into the main operator and the additive one. As the result we come to some more complicated procedure with two sets of the main and additive operators. But still in such situation it will be possible to generalize the Chapman-Enskog procedure and come to the final formulas. It will be possible to get the relaxation to the stationary state without restriction used in [8]. One has to mention that the cited papers couldn’t overcome the main nontrivial feature of the nonisothermal condensation - the main operator extracted in these papers has only formal priority based on the presence of factorials in denominators in the Taylor’s expansion terms. So, one has to fulfill at least many steps in the Chapman-Enskog procedure. Here we shall present the way how to take into account the tails of these series and to come to the compact final results.

Now it is worth mentioning the inclusion of the present analysis into the general scheme.

One can note some specific features of the thermal effects in comparison with the general situation of the non Fokker-Planck evolution considered in [10]. Namely these features allow us to go further in comparison with [10] and to get the compact final formulas.

These features are the following ones:

- The temperature of the embryo can have an arbitrary value.
- Non-Fokker-Planck evolution occurs along the temperature of the embryo.
- Non-Fokker-Planck evolution occurs under the constant value of $\beta_j$.

The third feature is rather important. Really, as far as we have the Clapeyron-Clausius relation we can reconstruct $W^-(T)$. Then on the base of $W^+$ (it is given by the simple gas kinetics formula) and $W^-$ one can get the equilibrium distribution. The knowledge of the equilibrium distribution gives on the base of the Boltzmann formula the form of the free energy $F$ of the embryo formation (the constant shift appeared from the normalizing factor of the equilibrium distribution isn’t important). These constructions
result in a rather simple form of the free energy. In the arbitrary situation (see [10]) the form of the free energy can be more complicated and this causes the additional difficulties.

The mentioned simple form of the free energy corresponds to the simplicity of transition from the function $n$ to the function $P$ defined by

$$n = \exp(-\mu^2)P$$

Certainly $\exp(-\mu^2)$ represents here the equilibrium distribution and $\mu^2$ appears due to the square character of the free energy. This leads to the $P$ relaxation to a constant. To conserve such relaxation in the general more complicated situation one has to choose in the argument of exponent instead of $\mu^2$ another more complicated function which reflects the more complicated behavior of the free energy. As the result the eigenfunctions of the ”main” operator will be unknown.

In the general situation instead of $\mu$ in the combinations $-2\mu + \partial/\partial\mu$ in the kinetic equation appear high powers of $\mu$. This blocks the presented approach to get solution.

We are going to act in frames of the macroscopic description of the free embryo. This leads to the big parameters

$$\nu_{i\,c} \gg 1$$

for all components which are marked by index $i$. Index $c$ corresponds to the critical embryo.

The last inequality allows as it is shown in [10] to state that

- The Fokker-Planck approximation is valid to describe the evolution along $\nu_i$

- The square approximation for the free energy along $\nu_i$ in the near critical region is valid.

In [10] all specific situations appear only when the derivative of the free energy along the concentration of the solution inside the embryo provides another big parameter. Certainly the essential values of this derivative are rather ordinary in the nature but one can not consider them as the big parameter going to infinity.
Really the derivative along \( \nu_i \) has a big value in comparison with the derivative along the steepens descent line \([10]\). This appears as the base for the hierarchy in the nearcritical region \([10]\). But the value of this big parameter isn’t sufficient to compensate the influence of the big parameter \( \nu_i \) (as far as all \( \nu_i \) has one and the same power we shall drop the index \( i \) in the estimates). Namely, the halfwidth \( \Delta \nu \) along \( \nu \) has the order \( \nu_c^{1/2} \), the halfwidth along the steepens descent line has the order \( \nu_c^{2/3} \). But as far as \( \Delta \nu \) is greater than 1 (it isn’t so great as in the one component theory but it is still great) we can see that the differential form of the kinetic equation is valid.

The last result can be directly seen from the explicit expression for the free energy of the embryos formation as the function of \( \{\nu_i\} \). In the capillary approximation this expression can be written as

\[
F \sim -\sum_j b_j \nu_j + a(\sum_j v_j \nu_j)^{2/3}
\]

Here \( \nu_j \) are the molecule volumes in the liquid phase, \( b_j \) are the excesses of the chemical potentials, \( a \) is the renormalized surface tension. The surface of tension is put as to contain precisely the volume of the embryo. All \( \nu_j \) are supposed to have one and the same order, all \( \nu_c \) are also supposed to have one and the same order.

One can easy note that the halfwidth \( \Delta \nu \sim \nu^{1/2} \) in the multicomponent theory differs from the same value in the one component theory \( \Delta \nu \sim \nu^{2/3} \). The reason is the interaction between components. This phenomena doesn’t lie in contradiction with the general theory because the steepens descent line doesn’t coincide with any \( \nu_i \) and the halfwidth along the steepens descent line coincides with the halfwidth along \( \nu \) in the one component theory. But it shows that the direct differentiation of \( F \) along \( \nu_i \) without the influence of the other components taken into account cannot lead to the really small parameter. An account of the mentioned interaction is rather difficult and it is more convenient to go to variables \( \xi_i = \nu_i / \sum_j \nu_j \) and \( \kappa = a^{3/2} \sum_j \nu_j v_j \). Then the direction along \( \kappa \) coincides with the steepens descent line and due to the Gibbs-Duhem equation an account of the interaction is attained automatically.

In the set \( \{\xi_i\} \), \( \kappa \) the form of the free energy is given by

\[
F \sim B\kappa - \kappa^{2/3}
\]
where $B$ is some function of $\{\xi_i\}$. The characteristic scale of $\kappa$ can be put as to coincide with the scale of $\nu_i$.

To justify the validity of the square approximation one has to get the second and the third derivatives of the free energy. It is more convenient to use the last form of $F$. Then
\[
\frac{\partial^2 F}{\partial \xi_i \partial \xi_j} \sim \frac{d^2 B}{d \xi_i d \xi_j^\kappa}
\]
and the halfwidth along $\xi_i$ is given by
\[
\Delta \xi_i \sim \kappa^{-1/2} (B''(\{\xi_j\}))^{-1/2}
\]

As far as
\[
\frac{\partial^3 F}{\partial \xi_i \partial \xi_j \partial \xi_k} \sim \frac{d^3 B}{d \xi_i d \xi_j d \xi_k^\kappa}
\]
the action of the third term in the Taylor series is given by
\[
\frac{1}{3!} \frac{\partial^3 F}{\partial \xi_i^3} (\Delta \xi_i)^3 \sim \frac{B''(\{\xi_j\})}{(B''(\{\xi_j\}))^{3/2}} \kappa^{-1/2}
\]
As far as the function $B$ and it’s derivatives don’t contain any big parameter one can easy see that the action of the third term is small. That’s why the square approximation for the behavior of $F$ along $\xi_i$ is valid. The behavior of $F$ along $\kappa$ is similar to the one-component case. The square approximation along $\kappa$ is, thus, valid. As the result the square approximation for $F$ in the nearcritical region can be used.

These results explain why the Fokker-Planck approximation is adopted for the description of the evolution along $\nu_i$. As for the evolution along temperature the Fokker-Planck approximation isn’t sufficient. The reason is the existence of another big parameter. This parameter is $\beta_i$.

Let’s explain why $\beta_i$ can be regarded as the big parameter of the theory. When the temperature decreases from the value of the second order phase transition the value of $\nu_v$ of the molecule volume in the vapor phase grows and the value $\nu_l$ falls. So, far from the point of the second order phase transition one can come to
\[
\nu_v \gg \nu_l
\]

\[\text{The index will be omitted.}\]
\[\text{Namely in this situation some actual assumptions of the classical theory of nucleation are valid, for example the uncompressibility of liquid phase.}\]
The heat extracted in the phase transition can be presented as the difference of entropies in two phases multiplied by temperature. Then one can use the standard representation of the entropy as the logarithm of the states number. The number of states\textsuperscript{14} can be very approximately estimated as the volume occupied by the system\textsuperscript{15}. Then the last strong inequality leads to the big value of $\beta$.

In reality one can not go very far from the second order phase transition temperature because the new phase transition (crystallization) occurs. Nevertheless one has to say that $\beta$ is the big parameter of the theory.

Now we come to the direct solution of the kinetic equation. We can rearrange it in the following form

\[
\frac{\partial P(\{\nu_i\}, \mu)}{\partial t} = D_1 + D_2 + D_3 + D_4
\]  \hspace{1cm} (3)

\[
D_4 = -\sum_j \frac{\partial}{\partial \nu_j} L_j P(\{\nu_i\}, \mu)
\]

\[
D_2 = -\sum_j \sum_{l=1}^{\infty} \frac{(-\tau_j)^l}{l!} \left( \frac{\partial}{\partial \mu} - 2\mu \right)^l W_j^+ S_{2j} \sum_{m=1}^{\infty} \frac{\tau_j^m}{m!} \frac{\partial^m}{\partial \mu^m} P(\{\nu_i\}, \mu)
\]

\[
D_3 = \sum_j \sum_{l=1}^{\infty} \frac{(-\tau_j)^l}{l!} \left( \frac{\partial}{\partial \mu} - 2\mu \right)^l L_j S_{lij} P(\{\nu_i\}, \mu) - \sum_j \frac{\partial}{\partial \nu_j} S_{3j} W_j^+ \sum_{m=1}^{\infty} \frac{\tau_j^m}{m!} \frac{\partial^m}{\partial \mu^m} P(\{\nu_i\}, \mu)
\]

\[
D_1 = \sum_{j'} W_{j'}^+ \alpha_{acc} j' \frac{c_g j'}{2} \sum_{j} c_j \nu_j \left( \frac{\partial}{\partial \mu} - 2\mu \right) \frac{\partial}{\partial \mu} P(\{\nu_i\}, \mu) + \sum_{i'} W_{i'}^+ (1 - \alpha_c i') \alpha_{acc} i' \frac{c_{i'}^2}{2} \sum_{j} c_j \nu_j \left( \frac{\partial}{\partial \mu} - 2\mu \right) \frac{\partial}{\partial \mu} P(\{\nu_i\}, \mu) +
\]

\textsuperscript{14}One can use quasiclassical approach.
\textsuperscript{15}We can use very approximately the model of ideal gas.
\[ \sum_{i'} W_{i'}^+ a_{c_{i'} \nu_{i'}} \frac{c_{i'}}{2 \sum_j c_j \nu_j} (\frac{\partial}{\partial \mu} - 2\mu) \frac{\partial}{\partial \mu} P(\nu_i, \mu) - \]
\[ \sum_{j} \sum_{l=1}^{\infty} (-\tau_j)^l \frac{\partial}{\partial \mu} - 2\mu \frac{\partial}{\partial \mu} W_j^+ S_{2j} \frac{\tau_j^l}{l!} \frac{\partial}{\partial \mu} P(\nu_i, \mu) \]

Now we shall estimate the actions of operators \( D_1 - D_4 \). One can easy note that the differentiation along \( \nu_i \) can be estimated as

\[ \frac{\partial}{\partial \nu_i} P \sim \frac{P}{\Delta \nu_i} \]

which produces the small parameter \( 1/\Delta \nu_i \). One has to note that as has been already noted the value \( \Delta \nu_i \) differs from the analogous value in one component case which can lead to the error made in [8]. The values \( \Delta \nu_i \) don’t estimate the size of the nearcritical region (The standard definition of the nearcritical region is given by inequality |\( F - F_c \)| ≤ 1. The infinite tails can be cut off to reduce the form of the nearcritical region to a rectangular one.). To estimate the size of the nearcritical region one can take derivatives of the free energy along \( \kappa, \xi_i \). As the result we come to the following convention: we use the notation \( 1/\Delta \nu_i \) but keep in mind that the real small parameter will be \( 1/\Delta \kappa \). Moreover one can not estimate the size of the nearcritical region by \( \Delta \nu_i \) as it was done in [8] but has to use the halfwidths along \( \kappa \) and \( \xi_i \).

The value of derivative \( \partial F/\partial \nu_i \) also contains the small parameter \( 1/\Delta \nu_i \). So the action of \( L_i \) can be estimated as

\[ L_i P \sim W_i^+ \frac{P}{\Delta \nu_i} \]

The differentiation along \( \mu \) doesn’t produce any small parameter. The characteristic value of \( \mu \) is 1.

Now we can calculate the powers of operators \( D_1 - D_4 \). As the result we see that

- Operator \( D_4 \) is the smallest one. It has the order \( 1/(\Delta \nu_i)^2 \).
- Operator \( D_3 \) is small. It has the order \( 1/\Delta \nu_i \).
- Operators \( D_1 \) and \( D_2 \) have one and the same order 1. Here operator \( D_1 \) has the formal priority because \( D_2 \) has no terms without factorials in the denominators.
The main problem of the further analysis is that the main operator $D_1 + D_2$ ensures relaxation to the state which gives zero flow of the embryos from the precritical to the postcritical region. So, this state leads to the zero value of the nucleation rate. To overcome this difficulty one can use the Chapman-Enskog procedure.
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