Effective interaction of exhausted regions in kinetics of nucleation

Victor Kurasov

Abstract

An effect of overlapping of exhausted regions around droplets of a new phase is analyzed. Several approximation to take overlapping into account are suggested. The small parameter responsible for convergence is extracted. The multi particle effects of overlapping are described.

Introduction

Kinetics of the first order phase transitions includes many aspects of evolution. One of such aspects is the exhaustion of the volume where the embryos can appear. Since A.N.Kolmogorov [1] has solved a problem of exhaustion for the case of crystallization this problem is considered to be analyzed completely.

Nevertheless in the case of nucleation of a supersaturated vapor into a liquid state of droplets kinetics of nucleation is governed by another mechanisms which depends on the Knudsen number characterizing the nucleating system. Under the small Knudsen numbers the kinetics of nucleation was described in [2]. Under the big Knudsen numbers kinetics resembles kinetics of crystallization but with some modifications. These modifications were described in [3]. Here the precise solution of this problem is absent. The source of difficulties lies in a very specific behavior of exhausted regions. In this paper the further investigation of this problem is presented.
1 Direct regions

The rate of nucleation $J$ as it is shown in [3] is proportional to the volume $V_{\text{free}}$ of the non-exhausted region

$$J \sim V_{\text{free}}$$

The total volume of the system $V_{\text{tot}}$ is supposed to be the unit one. Our task is to determine $V_{\text{free}}$ as accurate as possible.

Certainly,

$$V_{\text{free}} = 1 - V_{\text{exh}}$$

where $V_{\text{exh}}$ is the volume of the region exhausted by already existed droplets.

Around the formed droplet there will be an exhausted region formed by the vapor consumption by this very droplet. This region will be called as a "direct region".

For $V_{\text{exh}}$ one can write the following representation:

$$V_{\text{exh}} = \int_{0}^{t} J(t') V_{cl}(t, t') dt'$$

Here $t = 0$ is the initial moment of time, $t$ is the current moment of time. The value $V_{cl}(t, t')$ is the (mean) volume which is exhausted at the moment $t$ from $V_{\text{free}}$ by the embryos formed at $t'$. For the last value one can suggest several approximations.

1.1 Kolmogorov’s result

In crystallization Kolmogorov justified the following result

$$V_{cl}(t, t') = V_{0}(t, t')$$

Here $V_{0}(t, t')$ is the volume of the region which is exhausted at $t$ elsewhere by embryos formed at $t'$.

In crystallization

$$V_{0} \sim (t - t')^{d}$$

where $d$ is the dimensionality of space. The linear size $R \sim V_{0}^{1/d}$ of the direct region grows linearly in time. This is the crucial point in justification of the Kolmogorov’s result.
In general situation of nucleation asymptotically at \( t - t' \to \infty \) one can see that
\[
O(t - t')^{d/2} \leq V_0 \leq O(t - t')^d
\]

It means that the linear size grows as
\[
O(t - t')^{1/2} \leq R \leq O(t - t')
\]
So, the non-linearity is not too strong and this will be the source of several approximations considered below.

In any situation the dependence \( R(t - t') \) is known. Ordinary \( R \sim (t - t')^{1/2} \).

### 1.2 Stochastic approximations

In stochastic approximation the following approximation
\[
V_{cl}(t, t') = V_{free}(t)V_0(t, t')
\]
is taken.

This approximation implies stochastic overlapping of volumes \( V_0 \) coming from different droplets. Why for the volume \( V \) depending oh \( t \) and \( t' \) the overlapping is taken at \( t' \)? More reasonable is to take the half-sum
\[
V_{cl}(t, t') = \frac{(V_{free}(t) + V_{free}(t'))}{2}V_0(t, t')
\]
or
\[
V_{cl}(t, t') = \int_{t'}^{t} V_{free}(t'')dt''V_0(t, t')
\]

The approximate linearity of \( R(t - t') \) leads to the approximate similarity of all approaches.

### 2 Approximation of pair interaction

Consider the auxiliary problem which is formulated as following:

*Consider the droplet born at \( t'' \). The question is what will be the part of \( V_0 \) occupied by direct regions from other droplets.*

One can approximately suppose that outside direct region of this droplet the rate of nucleation is not perturbed and inside the direct region the rate of nucleation is zero.
Then the problem is purely geometrical one. One has simply to calculate the overlapping of spheres. The value \( V_{\text{over}}(r''', t''', r', t') \) is the volume of overlapping for the droplet born at \( t'' \) in the point \( r''' \) and the droplet born at \( t' \) in the point \( r' \). It is calculated purely geometrically.

Also purely geometrically one can calculate the boundary \( r'_b \) of the direct region and the time \( t_b \) when the given \( r''' \) is attained by the boundary of this direct region.

As the result one can easily calculate the total volume of overlapping by integration

\[
V_{\text{ol}} = \int_0^{t_b} dt' \int_0^{2R(t'-0)} dr S_d V_{\text{over}}(0, t''', r, t')
\]

Here \( t_b \) is a minimum of \( t \) and \( t_b, S_d \) is the surface square of a sphere of radius \( r \) in a space with dimension \( d \).

The problem is that the supposition that outside direct region of the droplet the rate of nucleation is not perturbed and inside the direct region the rate of nucleation is zero is no more than an approximation.

Another approximation is that the rate of nucleation outside is \( J(t') \) taken from another approximation, for example, from the previous one. Then

\[
V_{\text{ol}} = \int_0^{t_b} dt' \int_0^{2R(t'-0)} dr S_d J(t') V_{\text{over}}(0, t''', r, t')
\]

Unfortunately, the rate of nucleation \( J(t') \) strongly depends here on \( r \). To see this we can analyze the region (it will be called ”an inverse region”) where the region is forbidden to have the free point \( r, t' \). This region can cross the direct region for the droplet born at \( 0, t'' \).

It means that in the outside region near \( r'_b \) the rate of nucleation is higher than far from \( r'_b \).

This correlation is missed here.

### 3 Approximations for estimates

The effective approach is to note that \( d \gg 1 \) and use this fact. For example for \( d = 3 \) the droplets appeared until the first quarter of the nucleation period in decay conditions occupy the small part of the whole volume and later all evolution is governed namely by these droplets. This fact allows to construct approximations as it is shown in [4].
4 Inverse region

Inverse region for the droplet born at $r', t'$ is the geometrical place of points where the formation is forbidden to have the possibility to form droplet at $r', t'$. Certainly, this region is situated symmetrically to the direct region of the same droplet.

In the case of the Kolmogorov’s solution $R = A(t - t')$ with some constant $A$. Then any inverse region can not cross any direct region.

Having required that at the bottom of inverse region there is no formation of droplets one can see that there is no traces of direct regions in the whole inverse region. Then the Kolmogorov’s approximation really takes place.

Consider now the general situation. Let $P_-(t)$ be a probability that in the point $r = 0$ at $t$ there is a free point. For $P_-(t)$ one can write

$$P_-(t) = \int_0^t dt' \int_0^{r_b} dr' S_d P_-(t', r')$$

where $P_-(t', r')$ is the probability that the point $r', t'$ is free.

Let $r', t'$ be inside th inverse region formed at $r = 0, t$. For $P_-(t', r')$ one has to construct the inverse region. This region can go outside the inverse region of $r = 0, t$. This is the difficulty. For $P_-(t', r')$ one can then write

$$P_-(t', r') = \int_0^{t''} dt'' \left[ \int_{V_{\text{exhausted}}} d\vec{r}'' P_-(t'', r'') + \int_{V_{\text{non-exhausted}}} d\vec{r}'' P_-(t'', r'') \right]$$

Here $V_{\text{exhausted}}$ is the inverse region based on $r', t'$ which lies inside the inverse region based on $0, t$ and $V_{\text{non-exhausted}}$ is the inverse region based on $r', t'$ which lies outside the inverse region based on $0, t$.

The last separation is artificial but it will be essential in further approximations.

The integral equation is the linear one. Moreover, in dimension $d = 3$ there exists a cylinder symmetry.

The suitable way is an iteration solution based on the smallness of overlapping

$$P_{-(i)}(t', r') = \int_0^{t''} dt'' \left[ \int_{V_{\text{exhausted}}} d\vec{r}'' P_{-(i-1)}(t'', r'') + \int_{V_{\text{non-exhausted}}} d\vec{r}'' P_{-(i-1)}(t'', r'') \right]$$

The initial approximation is evident: $P = 1$ in $V_{\text{exhausted}}, P = P_{\text{mean}}$ in $V_{\text{non-exhausted}}$. Here $P_{\text{mean}}$ is some mean rate of nucleation calculated by
other approximations. The smallness of overlapping ensures the convergence of iterations.

This consideration is also some approximation. Here we do not take into account the possibility to born the third droplet with its own inverse region which causes the change of $P_-$.

5 Approximate simplification

If one approximates $J$ by initial intensity $J_0$ in $V_{\text{exhausted}}$ and by the mean intensity $\bar{J}$ in $V_{\text{non-exhausted}}$ then one can see a very simple expression

$$J(t', r') = \int_0^{t'} dt''[J_0 V_{\text{exhausted}} + \bar{J} V_{\text{non-exhausted}}]$$

The last approximation is both simple and accurate one.

Earlier the effects of interaction (overlapping) of three and more regions were not taken into account. Since the effects of overlapping are small, the influence of effective interaction of several particles are small.

6 One limit case

In order to construct the procedure taking into account effects of overlapping (interference) of exhausted regions initiated by different droplets one has to outline the parameter responsible for the relative smallness of the many-droplets effects. Only then the effects under consideration will have the order of corrections and can be considered as some perturbations.

The small parameter $\epsilon$ of the theory will be, thus, a ratio of the square of exhausted region with overlapping to the the square of exhausted region without overlapping. We expect that $\epsilon$ is seriously less than 1.

Ordinary the growth of the linear size of the exhausted region can be well approximated by a power-like dependence

$$R(t, t') = A(t - t')^\alpha$$

with parameters $A$ and $\alpha$. The case $\alpha \to \infty$ corresponds to the maximum of $\epsilon$.

Fortunately, this case allows analytical solution.
The case $\alpha = \infty$ corresponds to instantaneous creation of the exhausted region of some radius $R_0$. Then the probability $P_-(r, t)$ to be the point $r$ free at the moment $t$ equals to

$$P_-(r, t) = \int_{S_{R_0}} dr' \int_0^t dt' P_-(r', t') I_0$$

where the space integral is taken over the sphere of the radius $R_0$ with the center $r$ and $I_0$ is the kinetic factor, i.e. the free intensity of the droplets formation.

The crucial point of consideration is that here $P_-$ can not depend on $r'$. Then

$$P_-(r, t) = 4\pi R_0^3 \int_0^t dt' P_-(r, t') I_0 / 3$$

The differentiation gives

$$\frac{\partial P_-(r, t)}{\partial t} = 4\pi R_0^3 P_-(r, t) I_0 / 3$$

The last differential equation has an evident solution

$$P_-(r, t) = \exp(-4\pi R_0^3 t / 3)$$

where initial moment of time is taken as $t = 0$.

Then it is easy to calculate the total number of exhausted regions

$$M_{tot} = \int_0^\infty dt P_-(r, t) = \int_0^\infty dt e^{\exp(-4\pi R_0^3 t / 3)} = 3/(4\pi R_0^3)$$

The absence of overlapping corresponds to the linearized version, i.e.

$$M_{lin} = \int_0^{3/(4\pi R_0^3)} dt (1 - 4\pi R_0^3 t / 3) = 3/(8\pi R_0^3)$$

So, $M_{tot} = 2M_{lin}$. Since the squares of all exhausted regions are $4\pi R_0^3 / 3$, the last ratio will be the power of overlapping, i.e.

$$\epsilon = (M_{tot} - M_{lin})/M_{lin}$$

So, in any situation $\epsilon$ and can be considered as a small parameter.
7 The scheme of calculation

Now it is worth to present a concrete effective scheme of construction of the multi-particle effects of overlapping.

The first step is the formal one - to form the first droplet at $r', t'$.

The rate of nucleation inside the exhausted region of the first droplet ($ER_1$) is zero. The question is to find the rate of nucleation outside $ER_1$.

Then it is possible to choose two alternative possibilities to go forward. The first one is to choose the rate of nucleation outside $ER_1$ to be the ideal value $I_0$. This approach is very close to the direct simulation of the process. Unfortunately, in this approach to get a suitable effect it is necessary to take into account many neighbor droplets. For example, in the plane case the number of neighbors has to be greater than six. In the free-dimensional case this number is greater than twelve.

The second possibility is more effective. Instead of $I_0$ outside the $ER_1$ one can use the average rate of nucleation $\bar{I}$. One can define the average rate of nucleation $I_V$ over the volume $V$ as

$$I_V = \frac{1}{V} \int_V dr I(r, t)$$

The value $\bar{I}$ is the limit value

$$\bar{I} = I_V$$

Namely this value is chosen as the rate of nucleation outside $ER_1$.

Corrections to the last value appear because near the boundary of $ER_1$ some droplets which might affect on a point outside $ER_1$ had been born in $ER_1$ where formation is forbidden.

The rate of this value has an order of relative volume of intersection of $ER_1$ and inverse region $IR$ of the second droplet, i.e. $IR_2$. More precise the probability $P_2$ to form the droplet at $r'', t''$ when the first droplet is formed at $r', t'$

$$P_2(r'', t''; r', t') = \frac{\bar{I}}{I_0} [1 - \frac{Vol(ER_1 \cap IR_2)}{Vol(IR_2)}]$$

Here $Vol$ means the volume. The value $Vol(ER_1 \cap IR_2)$ is the volume of the intersection of $ER_1$ and $IR_2$, etc.

The volumes standing here are the simple known algebraic functions, the calculation is evident.
The effectiveness of this procedure is based on the relative smallness of the value

\[ \sigma = \frac{Vol(ER_1 \cap IR_2)}{Vol(IR_2)} \]

The average probabilities are given by

\[ P_2(r'', t''; t') = \frac{1}{V} \int_V dr' \int_{T_0}^T T \left[ 1 - \frac{Vol(ER_1 \cap IR_2)}{Vol(IR_2)} \right] \]

\[ P_2(r'', t'') = \int_0^t dt' \frac{1}{V} \int_V dr' \int_{T_0}^T T \left[ 1 - \frac{Vol(ER_1 \cap IR_2)}{Vol(IR_2)} \right] \]

Since the probability \( P_1(r', t') \) does not depend on \( r' \) the integral over \( r' \) is not more than a formal object.

It is more convenient to consider the relative deviation of \( P_2 \) from the base value \( \frac{T}{t_0} \)

\[ \Delta P_2(r'', t''; r', t') = \frac{Vol(ER_1 \cap IR_2)}{Vol(IR_2)} \]

\[ \Delta P_2(r'', t''; t') = \frac{1}{V} \int_V dr' \frac{Vol(ER_1 \cap IR_2)}{Vol(IR_2)} \]

\[ \Delta P_2(r'', t'') = \int_0^t dt' \frac{1}{V} \int_V dr' \frac{Vol(ER_1 \cap IR_2)}{Vol(IR_2)} \]

The analogous constructions can be made for the three ER overlapping.

The relative deviation in probability \( \delta P_3(r'', t''; r''', t'''; r', t') \) connected with simultaneous overlapping of three volumes is given by

\[ \delta P_3(r'', t''; r''', t'''; r', t') = \frac{Vol(ER_1 \cap ER_2 \cap IR_3)}{Vol(IR_3)} P_2(r'', t''; r', t') \]

Here there is the deviation in probability to find the third particle born at \( r''', t''' \) when the first particle was born at \( r', t' \) and the second particle was born at \( r'', t'' \).

The relative deviation in probability \( \delta P_3(r'', t''; r''', t'''; r', t') \) simply to find three particles born in positions \( r''', t''', r'', t'' ; r', t' \) is given by

\[ \delta P_3(r'', t''; r''', t'''; r', t') = \frac{Vol((ER_1 \cup ER_2) \cap IR_3)}{Vol(IR_3)} P_2(r'', t''; r', t') \]

The knowledge of \( P_1, P_2, P_3 \) solves the problem to find the rate of nucleation is one-particle, two-particle and three-particle approximation.

Certainly, \( ER(t', r') \) as a function of \( t' - t \) instead of \( t \) coincides with \( IR(t', r') \)
8 Volumes of overlapping

In two particle approximation the volume of overlapping $V_2$ can be calculated in a very simple way

$$V_2(r',t') = \int dt'' \int dr'' Vol(ER_1 \cap ER_2) P_2(r'',t'';r',t')$$

Here the argument $r'$ is not important because the system is uniform.

The partial effective volume in the two-particles approximation looks like

$$V_{eff} = Vol(ER_1) - \frac{1}{2} V_2(r',t')$$

In the three-particles approximation the volume of overlapping of three volumes is given by

$$V_{123} = \int dt'' \int dr'' \int t'' \int dr''' Vol(ER_1 \cap ER_2 \cap ER_3) P_2(r'',t'';r',t') P_3(r''',t'''';r'',t'';r',t')$$

It is necessary also to introduce the volumes of overlapping of ER of two particles in the presence of the third one. The indication of a particle which does not have ER in the two-particle overlapping stands in brackets. Then

$$V_{12(3)} = \int dt'' \int dr'' \int t'' \int dr''' Vol(ER_1 \cap ER_2) P_2(r'',t'';r',t') P_3(r''',t'''';r'',t'';r',t')$$

The volume of two-particles overlapping without the volume of the three-particles overlapping is approximately given by

$$\hat{V}_{12(3)} = \int dt'' \int dr'' \int t'' \int dr''' Vol((ER_1 \cap ER_2) - (ER_1 \cap ER_2 \cap ER_3)) P_2(r'',t'';r',t') P_3(r''',t'''';r'',t'';r',t')$$

Analogous value is given by

$$\hat{V}_{1(2)3} = \int dt'' \int dr'' \int t'' \int dr''' Vol((ER_1 \cap ER_3) - (ER_1 \cap ER_2 \cap ER_3)) P_2(r'',t'';r',t') P_3(r''',t'''';r'',t'';r',t')$$

The effective volume in three particles approximation is given by

$$V_{eff} = Vol(ER_1) - \frac{1}{2} V_{12(3)} - \frac{1}{2} V_{1(2)3} - 2 V_{123}$$

One has to stress that all volumes indicated as $Vol$ can be elementary calculated.
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