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Kinetics of nucleation with decreasing rate of growth

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HIGHLIGHTS

- Formation of embryos with the slow rate of growth is considered analytically.
- The form of spectrum of the embryos sizes is approximately derived.
- The property of effective size for embryos with the slow rate of growth is shown.
- The head and the asymptotic tail for the spectrum of the embryos sizes are determined.
- Two basic initial approximations of iteration procedure are presented.

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ABSTRACT

Extension of analytical description of the stage of nucleation to the case of the slow growth rates of the embryos growth has been constructed. The metastable phase consumption by the already formed embryos affects the nucleation rate which leads to the non-linear evolution. The power exponentials which are smaller than that for the diffusion growth are chosen as the model laws of the embryos growth. All main characteristics of the nucleation period including the form of the embryos sizes spectrum are found. Analytical description of nucleation in the closed systems as well as in the open systems with the metastable phase influx is presented. It is shown that the relative errors of this description are small.

1. Introduction

To see the real picture of the first order phase transition it is necessary to consider kinetics of this process. The most used physical model of the first order phase transition is the case of condensation of a supersaturated vapor into a state of liquid droplets. The classical theory of nucleation [1,2] describes the appearance of embryos in this case. This theory is the base of kinetics of phase transformation [3,4]. We shall borrow the terminology from this case. So, the supercritical embryos of a new phase are droplets, the mother phase is the vapor phase, etc. The rate of embryos appearance is supposed to be a known smooth function of metastability in the system. But the metastability is unknown function of time. To get this function one has to formulate the system of condensation equations and then to solve it. This is the goal of the investigation below for the decreasing rate of the embryos growth.

One of the main features which allowed to present the analytical constructions in Refs. [3,4] was a property of the avalanche consumption of a mother phase by droplets. This property means that the intensity of absorption of vapor by a droplet rapidly increases with the growth of the droplet size.

For example, in the free molecular regime of the substance consumption one can see that the absorption intensity W^+ is proportional to the surface area of a droplet, i.e. to a square of radius R. When an embryo grows in time t under the constant power of metastability then $W^+ \sim t^2$ and the number of molecules ν accumulated by a droplet grows proportionally to t^3. The big value of the power exponential 3 allows to use in Refs. [3,4] some iteration procedures.

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In the diffusion regime of growth $\nu \sim t^{3/2}$. This growth is not so rapid but is quite sufficient for the application of methods from Ref. [3]. But there one cannot use the mean-field approach which implies that the power of metastability is considered as a value averaged over the whole volume. One has to account in this case the positions of embryos [5]. Only the situation of the free molecular growth and the situation of the diffusion regime were described in theoretical models of the nucleation kinetics.

There exist enough situations in nature when the rate of the droplets growth decreases in time. Situation with the decreasing rate of growth takes place in the processes of cementation, structural transformations, morphological transitions, etc. In the wonderful pictures of agates and malachites one can see the patterns appear due to the decreasing rate of growth of every initial embryo (and the variation of external influence). The reaction of environment of a growing object (for example, reaction of a human body on tumor) leads to the decrease of the rate of growth of a new object.

We can turn our attention to the situation of standard nucleation. One can see that the nucleation on soluble nuclei in the general formulation with several saddle points and several channels of nucleation and some fast and flow components also can lead to effective deceleration of the embryos growth. Here the condensation of the fast component leads to exhaustion of this component and as a result to the decrease of the rate of growth of the embryos with dominating other components.

The universality of the size spectrums in the avalanche regimes of growth [4] leads to a certain monotony in the properties of materials formed in these regimes. The goal to get new properties justifies the analysis of nucleation with the decreasing rate of growth of embryos.

The standard iteration methods do not work in the situation of the decreasing rate of growth of the new phase embryos. This situation requires a special consideration which will be given below.

We shall consider two types of external conditions which are widely spread both in theoretical and practical investigations. The first type is a situation of decay which takes place in the closed systems. Metastability is created in the system very quickly and later there is no external influence. The evolution of metastability is fully determined later by the consumption of vapor by droplets.

The second type of external conditions are the dynamic conditions. The smooth behavior of external influence in time takes place here. It means that the power of metastability is created gradually in time. Without the embryos formation and growth the supersaturation would increase. One can also speak here about such generalization as an open system with the effective metastable phase influx (if there was no formation of embryos the supersaturation would grow in time).

Here one can see a competition between the action of external conditions and the consumption of metastability. Both the formation of droplets and the process of the droplets growth consume vapor with a growing intensity and metastability begins to fall. The process of nucleation stops and one can see the formed spectrum of the embryos sizes. The analytical theory for this type of external conditions will be also constructed.

Here we shall use the exponential powers for the law of the embryos growth. The application of exponential powers is explained by the absence of any dimensional parameter. The diffusion regime and the free molecular regime have also this form. Namely

$$\nu = t^{\alpha} \tag{1}$$

with a parameter α. Exponential powers are smaller than that for the diffusion growth. The dependencies with $0 < \alpha < 1$ will be referred as the slow rates of growth. We shall namely this case. Dependencies with $1 < \alpha < 3/2$ are considered by the same methods as $0 < \alpha < 1$.

On the base of $\nu = t^{\alpha}$ it is very easy to introduce $z = \nu^{1/\alpha}$ to measure the time as the size of an embryo born in some characteristic moment (ordinary initial moment) of time.

We investigate the case of the homogeneous phase transition. Transition from the homogeneous case to the heterogeneous case can be investigated analogously to Ref. [3]. In Ref. [3] it is shown that the homogeneous case can be effectively used as the base for consideration of the heterogeneous case. The same approach can be used here.

2. Evolution equations

Situation with the slow rate of growth is more complex than the avalanche consumption because here not only the droplets with relatively big sizes are the main consumers of vapor. Here all droplets take place in consumption of vapor. But here one can see a simplifying feature which states that now there is no necessity to consider the density profiles or profiles of the power of metastability [5,4]. The characteristic scale of the diffusion blurring is

$$R_{diff} \sim \sqrt{t - t'} \tag{2}$$

where t is the current moment of time, t' is the time of the substance consumption. This estimate goes from the expression for the Green function of the diffusion equation. The Green function is a Gaussian and in the argument of exponent there stands $R^2/(t - t')$. So, we come to some characteristic space size R_{diff} of diffusion blurring. The same is valid for the thermal blurring initiated by the thermal effects of nucleation. So, when $\alpha < 3/2$ the diffusion blurring makes the density profile more smooth. In the characteristic region of localization of the profile there will be many droplets and we come to the collective regime of vapor consumption (see Refs. [5,4]).

Procedure of derivation of the evolution equation is absolutely analogous to Ref. [3], one has only to substitute the power 3 or 3/2 by α. The statement about the leading role of the supercritical embryos in the substance balance used in Ref. [3] is