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Nucleation stage in supersaturated vapor with inhomogeneities due to nonstationary diffusion onto growing droplets

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HIGHLIGHTS

- A theory of the nucleation stage is given on the basis of the excluded volume approach.
- Self-similar solution of the nonstationary diffusion equation has been used.
- Characteristics of the nucleation stage are compared with those in the mean-field approach.
- The limits of the mean-field approach have been considered.

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ABSTRACT

An analytical description of the nucleation stage in a supersaturated vapor with instantly created supersaturation is given with taking into account the vapor concentration inhomogeneities arising as a result of depletion due to nonstationary diffusion onto growing droplets. This description is based on the fact, that the intensity of the nucleation of new droplets is suppressed in spherical diffusion regions of a certain size surrounding previously nucleated droplets, and remains at the initial level in the remaining volume of the vapor–gas medium. The value of the excluded volume (excluded from nucleation) depends on the explicit form of the vapor concentration profile in the space around the growing droplet, and we use for that the unsteady self-similar solution of the time-dependent diffusion equation with a convective term describing the flow of the gas–vapor mixture caused by the moving surface of the single growing droplet. The main characteristics of the phase transition at the end of the nucleation stage are found and compared with those in the theory of nucleation with homogeneous vapor consumption (the theory of mean-field vapor supersaturation). It is shown that applicability of the mean-field approach depends on smallness of the square root of the ratio of the densities of metastable and stable phases. With increasing the temperature of the supersaturated vapor or for liquid or solid solutions, this smallness weakens, and then it would be more correct to use the excluded volume approach.

1. Introduction

The traditional approach used to describe kinetics of the liquid phase formation at the nucleation stage (i.e., the stage of formation of super-critical, i.e., steadily growing, droplets), assumes that the consumption of vapor by growing droplets leads

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to a simultaneous and uniform-over-volume (for the whole ensemble of droplets) decrease of the vapor supersaturation [1–5]. In the case of diffusion growth of sufficiently large super-critical droplets after the incubation stage of nucleation (i.e., the stage of formation of steady-state distribution for small critical and near-critical droplets), one should recognize that the approximation of a homogeneous vapor supersaturation in the system (the mean-field supersaturation) can be justified only on the assumption that the sizes of diffusional vapor shells (from which the droplets consume the vapor) surrounding growing droplets are large not only in comparison with the sizes of the droplets themselves, but also with respect to the average distance between the droplets. If the shells are thin and small, the main volume is not affected by growing droplets. The condition of diffusional mixing can be realized on the final stages of nucleation, like the stage of the considerable vapor consumption and the Ostwald ripening stage [3,5]. However, this condition is certainly not satisfied at the stage of nucleation of super-critical droplets (which follows the incubation stage), when the average distance between the droplets can be very large. At nonstationary diffusion to a droplet, the corresponding diffusion shell in the vapor–gas medium has a finite thickness around the droplet, and such shells for neighboring droplets may overlap only to the end of the nucleation stage. At the same time, the nucleation intensity (i.e, nucleation rate) is exponentially sensitive to the local vapor supersaturation. It has been recently shown for bubble nucleation in supersaturated by gas solution [6,7], that nonstationary diffusion inhomogeneity is responsible for strong swelling effects for the solution which cannot be explained within the stationary diffusion approach. As a consequence, the problem to develop a description of the kinetics of nucleation stage, which would explicitly take into account the heterogeneity of the field of vapor concentration caused by nonstationary vapor diffusion onto consuming droplets, becomes an important one.

The effect of vapor heterogeneity caused by vapor diffusion to a growing droplet on the stage of nucleation of super-critical droplets had previously been considered in several works employing different approaches [8–13]. In a very close context, this problem was raised in Refs. [8,9] where the average nucleation rate per unit volume of vapor–gas medium notion of "clearance volume" around the droplet was introduced. It was noted in Refs. [10,11] that using the stationary diffusion approximation for the density profile around the droplet is not appropriate, and the nonstationary density profile should be taken into account with recognizing the presence of a shell around the droplet where nucleation of new droplets is absent. It was proposed [10,11] to utilize an integral equation for the available for nucleation vapor volume with calculation of the vapor profile around droplets in the approximation of non-moving droplet surface (i.e., for vapor diffusion onto droplet at typical boundary condition at fixed droplet radius). Grinin et al. [12,13] calculated the probability of the nearest-neighbor droplet nucleation in the diffusion profile of a previously nucleated droplet found under condition that material balance maintains between the droplet and the vapor, even though the droplet boundary is a moving one. Their approach operated with the mean distance to the nearest-neighbor drop and the mean time to its appearance which provide estimates for the duration of the nucleation stage and the number of drops formed per unit volume during the nucleation stage. There were also other theoretical and experimental studies of similar effects associated with primary and secondary nucleation and coarsening in different physical systems [14,15].

In this paper, we assume as well as in Refs. [8–13] that the intensity of nucleation of new droplets is suppressed in spherical diffusion layers of certain thickness surrounding the previously nucleated drops, and stays at the initial level in the remaining volume of the gas–vapor mixture. It can be called the excluded volume approach because the total volume of such diffusion spheres with droplets at their centers is excluded from nucleation process. At the first glance such an approach looks too simplified, but it should be noted that the value of the excluded volume depends on the explicit form of the vapor concentration profile in the space around the growing droplet, and the clear and regular procedure for determining this value is required for self-consistent theory. As new important elements of the analysis, we propose such procedure and use for that the most accurate unsteady self-similar solution of time-dependent diffusion equation with a convective term describing the flow of the gas–vapor mixture caused by vapor condensation and moving surface of the growing droplet. Earlier, a similar approach was used to describe the stage of nucleation of bubbles in gas-supersaturated solution [6,7]. However it should be noted that the physical appearance of the "excluding" mechanism is different for growing bubbles and droplets, and the differences will be outlined in Section 3. As a part of excluded volume approach for droplets, we calculate the main characteristics of the phase transition (the duration of the nucleation stage, the number of nucleated droplets per unit volume, the maximal and average radii of the droplets) set at the end of the nucleation stage, and the results are compared with the results of the theory of mean field of vapor supersaturation.

The article is organized as following. First, in Section 2, we reformulate the basics of the theory of the nucleation stage in the approximation of the mean-field vapor concentration in the convenient for subsequent comparison form. Description of nucleation in the framework of the excluded volume approach is constructed in Section 3. In Section 4 we will compare the results from Sections 2 and 3 and make conclusions.

2. Nucleation stage in the mean-field approximation for vapor concentration

Let us formulate the basic principles of the theory of the stage of nucleation of super-critical droplets at instantly created vapor supersaturation in the mean-field approximation for vapor concentration [1–5]. The main characteristics of the state of droplets, reached to the end of the nucleation stage as the second stage of the whole nucleation process are: the total number of super-critical droplets, their maximum and average sizes, the time of duration of the nucleation stage. The theoretical problem is to link these main characteristics of the final state of droplets in the end of the nucleation stage (which are experimentally observable) to initial value of supersaturation in the system. As we said in Introduction, the mean-field