Colloids and Surfaces A: Physicochem. Eng. Aspects 483 (2015) 307–315

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

The stage of nucleation of supercritical droplets with thermal effects in the regime of nonstationary diffusion and heat transfer

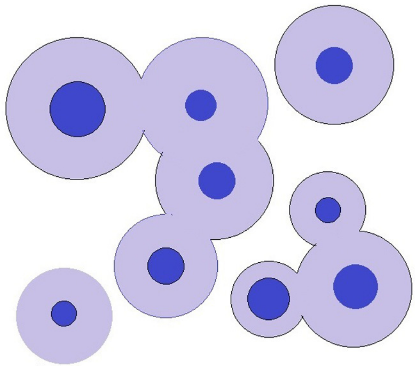
Anatoly E. Kuchma, Alexander K. Shchekin*, Maxim N. Markov

Department of Statistical Physics, Faculty of Physics, St. Petersburg State University, Ulyanovskaya 1, Petrodvoretz, St. Petersburg 198504, Russian Federation

HIGHLIGHTS

- Extended excluded-volume theory with overlapping diffusion shells.
- Theory of nonisothermal nucleation with nonstationary transfer.
- Identity of different approaches at small nonstationarity.
- Analysis of the nearest-neighbor approach.

GRAPHICAL ABSTRACT



$$\ln\frac{V_1(t)}{V}=-\frac{4\pi\mu\bar{I}_0}{3(1+k)}\int_0^t d\tau\left(2Db(t-\tau)\right)^{3/2}\frac{V_1(\tau)}{V}$$

ARTICLE INFO

Article history:
Received 11 February 2015
Received in revised form 1 April 2015
Accepted 2 April 2015
Available online 21 April 2015

Keywords:
Nucleation
Condensation
Droplet
Diffusion
Thermoconductivity
Excluded volume

ABSTRACT

Previously the stage of nucleation of supercritical droplets in the vapor–gas medium at instantaneously generated vapor supersaturation had been described within the mean-field, excluded-volume and stochastic probability (nearest neighbor) approaches which are based on different physical assumptions. Here we have formulated an extended excluded-volume theory which reconciles these approaches. The theory takes into account the drop of the nucleation rate in vicinities of growing supercritical droplets and mean-field mixing of vapor concentration and temperature at outer boundaries of the nonstationary diffusion shells around the droplets due to stochastic overlapping of the shells. The theory gives the distribution of supercritical droplets in sizes and predicts the vapor concentration profiles at any moment of the nucleation stage as well as duration of the nucleation stage, the total number of nucleating supercritical droplets and the mean droplet size to the end of nucleation stage. These characteristics are compared with the estimates obtained within the stochastic probability (nearest neighbor) approach. A generalization of the isothermal excluded-volume theory with the overlapping diffusion shells has been done to include the thermal effects of nonisothermal nucleation and the nonstationary transfer of heat in the vapor–gas medium. It has been shown that the mean-field and excluded-volume approaches lead to identical results in the limit of small nonstationarity of vapor diffusion and thermal conductivity.

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* Corresponding author. Tel.: +7 9119495666; fax: +7 8124287240.
E-mail address: akshch@list.ru (A.K. Shchekin).

http://dx.doi.org/10.1016/j.colsurfa.2015.04.020
0927-7757/

1. Introduction

At instant creation of vapor supersaturation in a vapor–gas system, the stage of nucleation of supercritical droplets starts after incubation stage and is very important in the whole nucleation process since the droplet size-distribution function is formed just during nucleation stage. The next stage develops as a process of subsequent growth of the supercritical droplets that already appeared on the nucleation stage. The theory of the nucleation stage had been initially formulated on the assumption that vapor supersaturation decreases due to condensation in growing supercritical droplets uniformly and simultaneously for the whole system [1–5]. Below we call such theory as the mean-field approach. It had been elaborated for any regime of supercritical droplet growth, from kinetic to diffusion. For diffusion growth of supercritical droplets, the approximation of the mean-field vapor supersaturation can be strictly justified if the diffusion vapor shells around 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, i.e., if these shells considerably overlap. In the case when the number of nucleating droplets is small and they grow due to nonstationary diffusion, the corresponding diffusion shells of neighbor droplets may overlap only at the end of the nucleation stage. Nucleation of new droplets during this stage occurs in the vapor–gas media with nonuniform vapor supersaturation profiles around droplets formed earlier. The rate of nucleation of new supercritical particles is suppressed in spherical diffusion region where the local vapor supersaturation is depleted by the growing droplet. Therefore a volume excluded from nucleation is formed around such droplets. The theory of the nucleation stage based on the concept of the excluded volume had been considered in several forms [6–14], and we further call it as the excluded-volume approach. Another development of the theory which takes into account the vapor inhomogeneity on the nucleation stage by considering the stochastic probability for the distance between nearest nucleating droplets [15] is called below as the nearest-neighbor approach.

In this paper, we develop an extended excluded-volume theory which reconciles the results of the mean-field, excluded-volume and nearest-neighbor approaches. First, in Section 2, we reformulate the basic ideas of the excluded-volume approach in the case of isothermal formation and condensation in the supercritical droplets. In Section 3 we consider the main kinetic equation for the excluded-volume approach with overlapping diffusion shells and compare the solution of this equation with the solution of equation for the mean-field vapor supersaturation. In Section 4 we add an analysis of the ideas of the nearest-neighbor approach. In Section 5 we extend the isothermal excluded-volume approach with the overlapping diffusion shells by taking into account the thermal effects of nonisothermal nucleation and the nonstationary transfer of heat in the vapor–gas medium. Finally we summarize the results of this paper in Section 6.

2. Basics of the excluded-volume approach

Nucleation stage is the first stage in the whole nucleation process where the effects of the decrease of the vapor supersaturation by nucleating and growing droplets of supercritical size become significant. During preceding incubation stage, a quasi-steady state for small near-critical droplets and corresponding quasi-steady nucleation rate are established. On succeeding stage of supersaturation collapse (or droplet growth), the initial vapor supersaturation drops almost to zero and droplets that appeared on the nucleation stage grow considerably.

The details of the excluded-volume approach can be found in [13]. Here we formulate all the basic concepts needed for the subsequent sections. At nonuniform distribution of vapor concentration $n(\vec{r}, t)$ at the point $\vec{r}$ and time t and absolute temperature T in the vapor–gas mixture (temperature T is the same for droplets and the vapor–gas mixture and does not change under conditions of isothermal nucleation and condensation), the expression for the local nucleation rate has the form

$$I(\zeta, T) = A(\zeta, T)\exp(-\Delta F(\zeta, T)). \tag{1}$$

Here $\zeta = \zeta(\vec{r}, t)$ is the current local value of the vapor supersaturation, $\Delta F(\zeta, T)$ is the minimal work of critical droplet formation expressed in terms of thermal units k_BT, k_B is the Boltzmann constant, and pre-exponential factor $A(\zeta)$ is a much more slowly varying function of vapor supersaturation to compare with the exponential factor $\exp(-\Delta F(\zeta, T))$. The work $\Delta F(\zeta, T)$ can be written in the classical nucleation theory as

$$\Delta F(\zeta, T) = \frac{4}{27}\left(\frac{4\pi\sigma(T)}{k_BT}\right)^3\left(\frac{3}{4\pi n_l(T)}\right)^2\frac{1}{\ln^2(1+\zeta)} \tag{2}$$

where $\sigma(T)$ is the droplet surface tension and $n_l(T)$ is the number density of molecules in the liquid phase.

With ignoring a change in the pre-exponential factor $A(\zeta, T)$ in expression (1), the local nucleation rate $I = I(\zeta, T)$ at time moment t and initial nucleation rate $I_0 = I(\zeta_0, T)$ at moment $t = 0$ are related as

$$I(\zeta, T) \approx I_0 \exp[-(\Delta F(\zeta, T) - \Delta F(\zeta_0, T))] \tag{3}$$

where initial ζ_0 and current ζ values of the vapor supersaturation are defined by expressions

$$\zeta_0 \equiv \frac{n_0 - n_\infty(T)}{n_\infty(T)}, \qquad \zeta(\vec{r}, t) \equiv \frac{n(\vec{r}, t) - n_\infty(T)}{n_\infty(T)}. \tag{4}$$

Here n_0 is the initial value of vapor concentration and $n_\infty(T)$ is the equilibrium concentration of the vapor over a planar surface of its liquid phase at temperature T.

The excluded-from-nucleation volume $V_{ex}(t)$ of the vapor–gas medium around the growing supercritical droplet of radius $R(t)$ can be determined [6,9,13] from a special integral condition. This condition requires that the total number of new droplets, nucleating per unit time in a sufficiently large volume V of the vapor–gas medium around this particular particle at the current profile of vapor supersaturation $\zeta(\vec{r}, t)$ and the corresponding profile $I = I(\zeta, T)$ of nucleation rate, equals the number of droplets nucleated with the initial nucleation rate $I_0 = I(\zeta_0, T)$ outside the excluded volume, i.e.,

$$\int_V d\vec{r} I(\zeta(\vec{r}, t), T) = I_0(V - V_{ex}(t)). \tag{5}$$

For a single spherical droplet located at the center of the coordinate system, we find from Eq. (5)

$$V_{ex}(t) = 4\pi\int_{R(t)}^{\infty}\frac{I_0 - I(\zeta(r, t), T)}{I_0}r^2 dr, \tag{6}$$

where upper limit of integral has been replaced by infinity since the integrand goes sufficiently fast to zero with increase of argument r.

Applying the results of Refs. [13,16,17], where the growth of single droplet was described on the base of nonstationary diffusion equation with convection term arising from the motion of vapor–gas mixture due to the movement of the surface of growing droplet, we get the following self-similar expression for the field of vapor concentration around the droplet with radius $R(t)$