Surface effects in droplet nucleation

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ABSTRACT

The classical nucleation theory (CNT) concept of a nucleus as a fragment of the bulk new phase fails for nanosized nuclei. An extension of CNT taking into account the properties of the transition region between coexisting bulk phases is proposed. For this purpose, the finite-thickness layer method which is an alternative to Gibbs' one is used; the transition region is considered as a separate (surface) phase. The nucleus inhomogeneity (difference in the properties of surface and bulk phases) is shown to result in the dependence of surface tension on radius and temperature. An equation for the work of nucleus formation is derived which is basic for the multivariable theory of nucleation; it takes into account the dependences of surface tension on radius (the curvature effect) and temperature. The Kelvin formula for the equilibrium vapor pressure is extended to small radii. It is shown that the ratio of the isothermal nucleation rate to that of CNT can achieve several orders of magnitude due to the curvature effect. The analysis of different dependences of the Tolman length on radius, $\delta(R)$, obeying the condition of limiting (spinodal) vapor supersaturation suggests that the curvature effect in the nucleation region is determined by the value of $\delta(0)$ which is positive, rather than by the asymptotic value δ_∞. The equilibrium temperature of a noncritical droplet is shown to differ from the vapor temperature due to the dependence of surface tension on temperature. Therefore, the calculated mean steady state overheat of droplets relatively the vapor temperature consists of the kinetic (due to the release of the condensation heat) and thermodynamic parts.

1. Introduction

CNT (Frenkel, 1946; Volmer, 1939; Zeldovich, 1942) is based on the so-called drop model (or the capillarity approximation): the work of formation of a new phase nucleus is represented as the sum of volumetric and superficial parts. The superficial part is proportional to the nucleus surface area; the proportionality factor is the surface tension of planar interface. Thermodynamic parameters of the volumetric part are taken the same as for the bulk phase. In other words, the nucleus is represented as a small fragment of the bulk phase and the presence of the transition region (or the surface layer) between the new and old phases is neglected. At the same time, the typical radius of a critical nucleus is about 1 nm, so that the homogeneous (bulk) phase inside this nucleus is absent and it entirely consists of the inhomogeneous surface layer with thermodynamic parameters different from those of the bulk phase.

The development of the density functional theory (DFT) (Lutsko, 2007, 2008; Nyquist, Talanquer, & Oxtoby, 1995; Oxtoby & Evans, 1988; Zeng & Oxtoby, 1991) was intended to take into account the inhomogeneity of a new phase nucleus and thereby to improve the predictive ability of the nucleation theory; this new theory was named non-classical. It made significant progress in the description of nucleus properties; density profiles, nucleation barriers, etc. were calculated. The DFT uses certain models for the structure of substance, in particular, a certain form of the intermolecular potential and therefore it is related to the first-principles theories.

At the same time, it is of interest to study the given problem within a thermodynamic approach for the following reasons. First, as

is known, thermodynamic relations have a great generality. Even relations in the form of inequalities are useful for the analysis of processes. Second, the use of macroscopic kinetic equations for the description of nucleus evolution (Alekseechkin, 2006, 2012, 2013, 2014, 2015) in the multivariable nucleation theory (Alekseechkin, 2006; Feder, Russell, Lothe, & Pound, 1966; Langer, 1969; Reiss, 1950; Stauffer, 1976; Trinkaus, 1983; Wilemski, 1999) requires a thermodynamic expression for the nucleation work. Third, an analytical theory allows obtaining predictions which cannot be obtained in numerical models; in particular, this concerns the behavior of thermodynamic quantities in the spinodal limit (when the critical-nucleus radius tends to zero).

There are two thermodynamic approaches to studying surface phenomena: Gibbs' theory of capillarity (Gibbs, 1957) and the finite-thickness layer (FTL) method (Rusanov, 1967, 1978). According to Gibb's approach, the real surface layer is replaced by the geometrical surface possessing the tension σ and to which the excess energy, E_{Σ}, entropy, S_{Σ}, and numbers of particles (or masses), N_{Σ}^i, are related (the superficial quantities). While Gibbs' approach operates with superficial quantities, the FTL method deals with real quantities having simple physical meaning and relating to the surface layer which is considered as a separate phase. As a consequence, the interpretation of results is greatly simplified in comparison with Gibbs' approach (especially in the case of a multi-component system); also, one can use some clear approximations in calculating the nucleation work. The values of surface layer parameters included in thermodynamic equations can be estimated within the statistical- mechanical approach as well as obtained from the DFT or computer simulations. The FTL method was first introduced by Dutch physicists (Bakker, 1928; v. d. Waals & Kohnstamm, 1927), in particular, by Guggenheim (1940) for planar interfaces. As applied to curved interfaces, this method was developed in detail by Rusanov (1967, 1978).

The aim of the present report is to consider the termodynamics and kinetics of droplet nucleation within the FTL method. The outline of the paper is as follows. In Section 2, a basic equation for the nucleation work is derived and analyzed with the use of thermodynamic fundamental equations given in Appendix 1. The dependences of surface tension on radius and temperature are considered in Section 3. The extension of Kelvin's formula to small radii is given in Section 4. The results of Sections 2–4 are applied to studying the thermodynamics and kinetics of droplet nucleation in Sections 5 and 6. Numerical estimates of the curvature- and nonisothermal effects in droplet nucleation are given in Sections 7 and 8. Some remarks on the method employed and comparison with other approaches in Section 9 as well as the summary of results in Section 10 finalize the paper.

2. Equation for the work of nucleus formation

We consider the three-phase system consisting of new phase α, parent phase β and the surface layer between them which is phase σ (Fig. 1). The effective thickness τ of the surface layer is determined by Rusanov (1967) as that covering the region of essential change of all properties ξ_i (e.g., density, tangential pressure, concentration); outside this layer, all these properties have their bulk values up to fluctuations. The rms of ξ_i fluctuations can therefore serve as a quantitative measure in determining τ, while the dependence of ξ_i on distance can be derived within statistical mechanics. The thickness τ is a state parameter and can be uniquely connected with temperature, pressure and other thermodynamic parameters. So, with this definition of the quantity τ, the surface layer becomes an *autonomous* phase – the "surface phase". The fundamental thermodynamic equations for a surface layer are given in Appendix 1.

The complex consisting of phases α and σ is the *density fluctuation* (DF) (Kashchiev, 2003a) within phase β which was named "globule" by Gibbs (1957). Considering the DF appearance, we mean that it occurs in a large amount of phase β playing therefore the role of a thermostat, so that its parameters do not change at this event: temperature T^{β}, pressure P^{β}, and composition $\mathbf{x}^{\beta}$ are *constant*; hence, the chemical potential $\mu_i^{\beta}(T^{\beta}, P^{\beta}, \mathbf{x}^{\beta}) = const$, where $\mathbf{x}^{\beta} \equiv (x_1^{\beta}, x_2^{\beta}, ..., x_{n-1}^{\beta})$. The particles that make up the DF form the subsystem in phase β which goes from one phase state (state 1) to another (the DF, state 2). As is known from thermodynamics (Kubo, 1968; Landau & Lifshits, 1976), the minimum (reversible) work done by the medium (phase β) in such a process is given by the following expression:

$$W = \Delta E - T^{\beta}\Delta S + P^{\beta}\Delta V \tag{1}$$

where the changes in energy, ΔE, entropy, ΔS, and volume, ΔV, relate to the substance in the DF (Fig. 1). Since the state of phase β does not change under the DF formation, these changes can be attributed to the *whole* system also. Eq. (1) is a consequence of the first and second laws of thermodynamics only.

Before the DF appearance (state 1), the volume, entropy, and energy of our system are respectively V_1, S_1, and
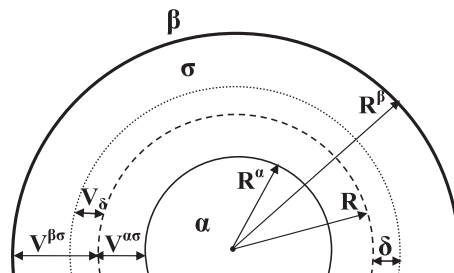

Fig. 1. Phases α, σ, and β. The density fluctuation is bounded by bold line; the surface of tension and the equimolecular surface are shown by dashed and dotted lines, respectively.