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The modified Thomson equation in the theory of heterogeneous vapor nucleation on charged solid particles

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Thermodynamic theory of heterogeneous vapor nucleation on charged nanosized solid particles is considered and formulas for the condensate chemical potential in the droplet and the nucleation activation barrier are derived. A modified Thomson equation for the pressure of vapor saturated over a liquid droplet formed around the spherical charged particle is proposed. This equation determines the saturated vapor pressure as a function of the particle size, charge magnitude and sign, and the droplet radius. The approach assumes that the droplet liquid film between the particle and the vapor phase is polarized in the central electric field of the charged particle and is thin, i.e., the surface layers of the film at the boundaries with the particle and the vapor phase are overlapped and the arising disjoining pressure affects the droplet state. It is shown that the film disjoining pressure, the Maxwell stress of the film in the central electric field of the particle, the degree of the particle wetting, and the particle size interplay in determination of the threshold value of vapor supersaturation ratio at barrierless nucleation. The threshold values of the vapor supersaturation ratio are found for different model isotherms of the disjoining pressure and different relations between size and charge of the solid particles.

1. Introduction

Recently new results of several experiments were reported (Hogrefe and Keesee, 2002; Chen and Cheng, 2007; Winkler et al., 2007, 2008) to give a new insight on nucleation on different nanosized charged and uncharged insoluble solid particles. These results were related to the dependence of critical vapor supersaturations on the size and nature of investigated particles and the magnitude and sign of their charge.

The problem of nucleation induced by charged particles in the vapor has a more than century history. There are two general approaches to thermodynamics of the problem, first of them was initially proposed by J.J. Thomson and second – by M. Volmer and N.H. Fletcher. J.J. Thomson (Thomson and Thomson, 1928) addressed to ion-induced nucleation and considered nucleation on the charged particle as formation of a spherical liquid droplet in the spherically symmetric electric field of the particle concentric with the droplet. M. Volmer (Volmer, 1939) and N.H. Fletcher (Fletcher, 1958) developed a different approach addressing to nucleation on partly wettable solid surface (flat or spherical) with formation of a sessile droplet having a contact angle with the surface.

J.J. Thomson proposed a well-known equation for the pressure p_R^β of vapor saturated over charged spherical liquid droplet with radius R, which can be written as (Thomson and Thomson, 1928; Toshev, 2002)

$$k_B T n^\alpha \ln \frac{p_R^\beta}{p_\infty^\beta} = \frac{2\gamma^{\alpha\beta}}{R} - \frac{q^2}{8\pi R^4}\left(\frac{1}{\varepsilon^\beta} - \frac{1}{\varepsilon^\alpha}\right). \tag{1}$$

Here p_∞^β is the pressure of vapor saturated over flat liquid, indices α and β refer to the liquid and vapor phase, k_B is the Boltzmann constant, T is the absolute temperature of the droplet and vapor phase, n is the molecular density, $\gamma^{\alpha\beta}$ is the surface tension of the droplet at the liquid–vapor interface, q is the charge of the particle in the droplet center, ε is the dielectric permittivity. Within the frameworks of the J.J. Thomson approach, the quantities $\gamma^{\alpha\beta}$, n^α, ε^α and ε^β were considered as constant, independent of the condensing droplet size and

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particle charge, and the properties of bulk liquid phase were assumed to be reached within the droplet. The absolute maximum of the saturated vapor pressure as a function of the droplet radius at fixed charge corresponds to the threshold value of vapor supersaturation at barrierless nucleation and characterizes the nucleation activity of the particles as condensation nuclei. As a result, the approach based on Eq. (1) was able to predict a decrease in the vapor critical supersaturation due to presence of electric charge and ability of the barrierless heterogeneous nucleation above the certain threshold value of the vapor supersaturation, but failed to describe charge sign preference in nucleation and dependence on such characteristics of condensation nucleus as its size and wetting degree.

A development of the theory to include the effects of sign preference in the thermodynamics of one-component ion-induced nucleation with an ion in the center of nucleating droplet was presented in the series of papers (Rusanov and Kuni, 1982, 1984; Kuni et al., 1982, 1983a,b,c; Shchekin et al., 1984; Shchekin and Sasim, 1988). With using a thermodynamically consistent formalism of the Gibbs dividing surfaces, this theory determined the curvature and charge induced corrections to the quantities $\gamma^{\alpha\beta}$, n^{α}, and ε^{α}. It related the sign preference effect to the cubic-in-charge term added to the Thomson Eq. (1) due to nonlinear excess surface polarization (electric potential jump at the droplet surface) of the small nucleating droplet in the strong field of the central ion. The similar term was discovered by the density functional approach (Kusaka et al., 1995). An application of such thermodynamic formalism to multicomponent ion-induced nucleation had been considered by M. Noppel et al. (2003). However all these modifications of the theory of ion-induced nucleation still were not able to describe the dependence of critical vapor supersaturation on size and surface properties of condensation nuclei.

Nucleation of a droplet on uncharged wettable solid particle considerably exceeding the molecular size starts with formation a thin liquid film enveloping the particle. This film is inhomogeneous through its whole thickness due to overlapping surface layers at the film boundaries with the particle and the vapor. The overlapping surface layers give rise to the disjoining pressure Π of the thin liquid film which can be defined for a spherical liquid film with the inner and outer radii R_n and R as (Rusanov and Shchekin, 2005)

$$\Pi \equiv p_N(R_n) - p_N^{\alpha}(R_n) \tag{2}$$

where p_N and p_N^{α} are the normal components of the film pressure tensor and the pressure tensor in the bulk liquid taken at the surface of the particle at the same value of the condensate chemical potential (in the absence of an external field p_N^{α} equals bulk pressure p^{α}) which depends on the thickness $h \equiv R - R_n$ of the film. The specific form of the isotherm $\Pi(h)$ for the disjoining pressure is determined by the characteristics of the film boundaries and the film mother phase, and $\Pi(h)$ tends to zero as $h \to \infty$. The disjoining pressure effects were intensively experimentally and theoretically investigated for flat thin liquid films (Derjaguin et al., 1987; Churaev, 1995, 2003; Henderson, 2005). Although the disjoining pressure for spherical films has been studied to a lesser extent, its role in heterogeneous nucleation has been analyzed thermodynamically (Kuni et al., 1996, 2001; Shchekin and Rusanov, 2008) and modeled for the films of nonpolar liquids around insoluble cores within the density functional approach (Bykov and Zeng, 2002, 2006; Napari and Laaksonen, 2003). Corresponding Kelvin's equation for the pressure p_R^{β} of vapor saturated over spherical liquid droplet with radius R and solid core of radius R_n can be written with account of the disjoining pressure as (Kuni et al., 1996, 2001; Shchekin and Rusanov, 2008)

$$k_B T n^{\alpha} \ln \frac{p_R^{\beta}}{p_{\infty}^{\beta}} = \frac{2\gamma^{\alpha\beta}}{R} - \frac{R_n^2}{R^2}\Pi. \tag{3}$$

The first attempt to reconcile the ideas of ion-induced nucleation and heterogeneous nucleation on wettable solid particles in thermodynamics of nucleation on charged solid particles was undertaken 13 years ago (Shchekin et al., 1996). Recently the similar approach was also formulated by J. Mitrovic (Mitrovic, 2006). Here we propose a more systematic and detailed thermodynamic model for such reconciliation based on specific isotherms for the disjoining pressure at different film thicknesses (Derjaguin et al., 1987; Churaev, 1995, 2003; Shchekin et al., 1999; Tatyanenko et al., 2000) and some recent developments for the condition of mechanical equilibrium of a curved thin liquid film (Rusanov and Shchekin, 2005; Shchekin and Rusanov, 2008; Shchekin et al., 2008). As a result, we come to a modified Thomson equation where the contribution from the electrostatic Maxwell tension interplays with the contributions from the disjoining and capillary pressures. Our goal in this paper will be to analyze with the help of the modified Thomson equation how the threshold value of the vapor supersaturation for barrierless nucleation on charged solid particles depends on size, charge, and surface characteristics of the particles.

2. Thermodynamics of thin liquid film formed on a charged condensation nucleus

Let us consider a droplet in the form of a liquid (phase α) film around a charged spherical solid (phase γ) particle in the atmosphere of the condensate vapor (phase β) as shown in Fig. 1. The solid particle consists of insoluble neutral one-component matter and carries an adsorbed insoluble charged component with the total electric charge q. The surface roughness of the particle is neglected and the charged component is distributed uniformly around the surface. In absence of the charged component, the surface of the particle may be wettable or partly wettable.

The outer droplet radius is R, the inner radius is R_n, thus the thickness of the condensed film is $h = R - R_n$. The elementary charges (ions) distributed over the solid core surface are shown by small circles (minus is shown just for the definiteness sake). Fig. 1 illustrates the case of thin film with overlapping surface layers and the disjoining pressure Π. If $\Pi \neq 0$, there is no a bulk liquid phase within the film. The disjoining pressure depends on the film thickness and temperature.

The pressure in the system considered is a tensor with radially inhomogeneous tangential, p_T, and normal, p_N, diagonal components which are related at the arbitrary point r by the local condition of mechanical equilibrium

$$p_T(r) = d\left[p_N(r) r^2\right] / dr^2. \tag{4}$$