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Dependence of the condensate chemical potential on droplet size in thermodynamics of heterogeneous nucleation within the gradient DFT

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ABSTRACT

A scheme of computation of the condensate chemical potential per molecule as a function of the droplet equimolecular radius for stable and critical droplets on uncharged or charged spherical particle of molecular size at heterogeneous nucleation has been considered. The scheme is based of the gradient density functional theory (DFT) with the van der Waals (vdW) and Carnahan–Starling (CS) models for the hard-sphere contribution to intermolecular interaction in liquid and vapor phases and interfaces. The particle serving as a condensation center in the case of heterogeneous nucleation has been characterized by an attractive short-range molecular potential and the long-range electric Coulomb potential. The dielectric permittivities of the droplet–vapor systems have been taken as known functions of the local condensate density and temperature for polar and nonpolar fluids. Detailed numerical calculations of the density profiles in critical and stable equilibrium droplets at water or argon nucleation in presence of the capillary, electrostatic and molecular forces have been performed. Dependence of the condensate chemical potential in the droplet on the droplet equimolecular radius has been analyzed in the case of homogeneous and heterogeneous nucleation and compared for water and argon within the vdW and CS models for the hard-sphere part of the equation of state.

1. Introduction

Heterogeneous nucleation with adsorption and subsequent condensation of vapor on foreign particles is a fundamental natural phenomenon with many scientific and technological applications. We will be interested in this paper in thermodynamics of heterogeneous nucleation in vapor on charged and uncharged particles of molecular size. One needs to distinguish the case when nucleation on a particle initially occurs as formation of a spherical liquid droplet concentric with the particle [1,2] and the case of initial formation of a lens-like droplet [3]. The first case is realized for uniformly charged spherical [4,5] or uncharged wettable [1,2] particles, while the second case refers to particles with locally adsorbed ions [6,7] or uncharged partially wettable particles. Below we will restrict ourselves by the first case and will consider thermodynamics of a liquid droplet on a charged or uncharged conducting spherical particle of molecular size.

In thermodynamic theory of nucleation, the chemical potential per condensate molecule in the nucleating droplet is a quantity of first importance. If the dependence of the condensate chemical potential on the droplet size is known, then one can find, by integration, the work of droplet formation as a function of vapor supersaturation and droplet size [2]. The nucleation activation barrier and nucleation rate can be obtained as well. However, finding the condensate chemical potential is not an easy task, especially in the case of small particles serving as condensation nuclei. The droplets formed on such particles have essential nonuniform-in-density regions related to the particle–liquid and liquid–vapor interfaces which affect all droplet thermodynamic properties. In the case of ion-induced nucleation, a generalization of the classical J.J. Thomson [4] and Tohmfor–Volmer [3] thermodynamic formulas for the chemical potential per molecule and the corresponding work of droplet formation were given in Refs. [8–10] within the frameworks of the Gibbs method of dividing surfaces. Application of those formulas implies that there is a bulk liquid phase somewhere between the ion–liquid and the liquid–vapor interfaces in the droplet. Extension of this method to the case of overlapping interfaces within the droplet on a nanosized condensation nucleus had been done in Ref. [5]. The approach used in Ref. [5] was based on assumption of additivity of contributions to the condensate

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Nomenclature

Latin

a	specific mean-force parameter in the mean-field interaction term in the free energy density
C	parameter in the square-gradient term in the functional of the grand thermodynamic potential
d	hard sphere diameter
d_m	molecular dipole moment
e	the elementary charge
E	common energy term equal to $E = a_{vw}/\upsilon_0$ for the van der Waals model and $E = 6a_{cs}/\pi d^3$ for the Carnahan-Starling model
f	free energy density
g	the Kirkwood correlation factor
$\hbar$	the Planck constant
k_B	the Boltzmann constant
K	compressibility
L	distance from the center of the droplet where the local molecular density reaches the bulk value for the vapor phase
m	molecular mass (of the fluid)
p	bulk pressure
r	distance from the center of the droplet/spherical particle
R^{min}	a short-distance cutoff parameter if the potential of molecular interaction (of the particle) equal to $2^{1/6}\sigma$
R_e	radius of the equimolecular (with respect to the component of fluid) spherical dividing surface
T	temperature of the system
w	potential of molecular interaction (of the particle) with condensate molecules
z	coordinate normal to the interface
Z	electric charge ratio (electric charge in units of the elementary charge)

Greek

α_m	molecular polarizability (of condensate molecule)
γ	surface tension (of the liquid–vapor interface)
Δ	difference of the values
ε	dielectric permittivity
η	dimensionless molecular density ($\eta = (\pi/6)\, d^3\rho$)
λ_{th}	thermal de Broglie length
μ	chemical potential (per molecule)
ρ	number density of molecules (molecular density)
σ	molecular scale length parameter of the potentials
υ_0	excluded volume
Ω	grand thermodynamic potential

Common superscripts

A	refers to argon
cs	refers to the Carnahan–Starling model
vw	refers to the van der Waals model
W	refers to water
α	liquid phase
β	vapor phase

Common subscripts

∞	refers to the value corresponding to a flat liquid–vapor interface at bulk phase coexistence
b	refers to the bulk value of the quantity
c	refers to the value at the critical point
cap	refers to capillary contribution
cs	refers to the Carnahan–Starling model
el	refers to contributions from the electrostatic interaction
id	refers to ideal gas approximation
int	refers to mean-field interaction of molecules
hs	refers to hard-sphere contributions
vw	refers to the van der Waals model
p	refers to the solid particle
sp	refers to spinodal
T	refers to the value at a fixed temperature T
w	refers to molecular interaction of the particle with condensate molecules

In calculations, the electrostatic system of units (ESU) are used. The unit of electric charge is statcoulomb: $1\text{statC} = 1\text{g}^{1/2}\text{cm}^{3/2}\text{s}^{-1} = 1\text{erg}^{1/2}\text{cm}^{1/2} \simeq 3.33564 \cdot 10^{10}\text{C}$, Temperatures are given in Kelvins.

chemical potential originated from capillary forces, the Maxwell electric tensions and the simple model adsorption isotherms for condensate in presence of a particle. However, applicability of this approach for molecular condensation nuclei is under question.

The role of the density inhomogeneity in a small droplet on a more microscopical level had been intensively examined by methods of statistical physics for critical equilibrium droplets formed at homogeneous nucleation (see, for instance, [11–18]). The approaches of nonlocal and gradient density functional theory (DFT) had successfully been used for analysis of molecular density profiles, capillary contribution to the condensate chemical potential and curvature-dependent surface tension of a small droplet [11–15,17,18]. There were also several applications of nonlocal DFT to study of heterogeneous nucleation [19–21]. In particular, Kitamura and Onuki showed in Ref. [21] that the local dependence of the dielectric permittivity on density profile in the droplet may play an important role in thermodynamics of ion-induced nucleation in vapors of polar liquids. To describe effects of dependence of the dielectric permittivity on density profile in the case of water vapor nucleation, Kitamura and Onuki [21] used the gradient DFT for water described within the van der Waals (vdW) equation of state.

Being applied to nucleation on spherical conducting charged particles, the classical J.J. Thomson formula predicts existence of the barrierless threshold value of the degree of vapor supersaturation at charge-induced nucleation. All particles become centers of condensation in the vapor with the degree of supersaturation equal or above this threshold value. Decreasing the degree of vapor supersaturation below the threshold value (but keeping it positive) reveals two droplet sizes corresponding to thermodynamic equilibrium with the vapor. The smaller size refers to the droplet in stable equilibrium and the larger size belongs to a droplet in unstable (critical) equilibrium with the vapor. In fact, this is a general feature for not only charge-induced nucleation, but for any heterogeneous nucleation on wettable particles [1,2]. The nonlocal or local gradient DFT allows one to find the condensate density profiles around the uncharged and charged particle in the stable and unstable droplets in equilibrium with supersaturated vapor at a specified value of the condensate chemical potential. In this way,