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OP38. Thermodynamics of thin liquid film on a charged spherical particle

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Abstract

Vapor adsorption and condensation with formation a thin liquid film on electrically charged particle is a fundamental phenomenon with many scientific and technological applications. Here we will consider the thermodynamics of formation of a thin liquid film on charged solid nanoparticle in the cases when the electric charge is distributed uniformly over the particle surface (the case of a conducting particle) or located as adsorbed ion at the surface of the particle (the case of a dielectric particle). The key thermodynamic characteristics which have been found were the work of the film formation and the chemical potential of the condensate molecule in the film as functions of the number of molecules in the film, the radius of the particle, and the magnitude of electric charge of the particle.

Three years ago we have considered [1] the generalization of the classical J.J. Thomson and Tohmfor-Kelvin thermodynamic formulas in the case of thin spherical liquid film formed on conducting particle. This generalization was made within the Gibbs method of dividing surfaces and took into account the disjoining pressure of the thin liquid film in the central electric field of the charged particle. Next step has been done last year [2, 3] by thermodynamic consideration of the axisymmetric electric field of an ion attached to or absorbed in the particle surface, which acts on liquid film jointly with the disjoining pressure. New equations for the chemical potential of a condensate molecule in the liquid film around the particle, the work of the film formation and the film shape as functions of the number of condensate molecules in the film and the value of an electric charge have been derived analytically. The derived equations have been solved, and a deviation of the condensed film shape from the spherical one in the axisymmetric electric field of the discrete charge has been found numerically.

Being applied to the nucleation on the nanosized uniformly charged particles, the conventional Kelvin-Thomson formula predicts that the radius of the droplet corresponding to the maximum of the curve of the condensate chemical potential, as well as the radii of equilibrium droplets, can be smaller than the radius of the charged particle. It caused doubts in complete wetting of the particle and formation of an enveloping liquid film in this case, especially if the particle surface is not a lyophilic one. By contrast to the case of uniformly or centrally charged particles, the results for the case of adsorbed or absorbed ion at the particle surface showed the thermodynamic tendency to formation of non-spherical enveloping liquid film around a dielectric nanosized particle even in the case of one elementary electric charge at the particle surface. We have found that when the charge is near the surface of the particle and dielectric constant of the particle is low then that for the condensate, the maximum of the curve of the condensate chemical potential as a function of the number of condensate molecules in the film is located outside the particle as well as the branch of this curve corresponding to stable enveloping liquid shells.

However several questions still stay open for discussion. First question concerns with the right choice of the disjoining pressure isotherm for the film. The second question is related to the mutual influence of the disjoining pressure and the electric field. To find the answers to these questions is possible within the density functional approach by calculating the density and dielectric permittivity profiles in the film [4]. Consideration of these issues will be also given in the present report.

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