

Small droplets at nucleation on a partially wettable substrate: effects of line tension and adsorption

Tatyanenko, Dmitry and Shchekin, Alexander

Department of Statistical Physics, Faculty of Physics, St. Petersburg State University
Ulyanovskaya 1, Petrodvorets, 198504, St. Petersburg, Russia

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Considering thermodynamics of heterogeneous nucleation of supersaturated vapours on a partially wettable surface, various effects have been taken into account (Gretz, 1966; Navascués & Tarazona, 1981; Scheludko, 1985). Particularly, it was shown that the effect of the three-phase contact line curvature on the contact angle is especially important. It may lead to intensive barrierless condensation at vapour supersaturations higher than a certain threshold value both on a planar substrate (Navascués & Tarazona, 1981) and on a spherical condensation nucleus (Scheludko, 1985). As an application, heterogeneous nucleation data can be used to estimate the line tension of condensate droplets (Hienola *et al.*, 2007).

Relation between the contact angle θ and the contact line radius r is given by the generalized Young equation (Rusanov *et al.*, 2004)

$$\sigma^{\alpha\beta} \cos \theta = \sigma^{\beta\gamma} - \sigma^{\alpha\gamma} - \kappa/r - \partial\kappa/\partial r, \quad (1)$$

where σ is the thermodynamic surface tension, κ is the thermodynamic line tension. Double Greek superscripts mark the interfaces; α , β and γ denote the liquid, vapour, and solid phases, respectively. This equation is compared with the “classical” Young equation

$$\sigma_0^{\alpha\beta} \cos \theta_0 = \sigma_0^{\beta\gamma} - \sigma_0^{\alpha\gamma}. \quad (2)$$

Here the subscript “0” marks the state where the liquid and the vapour phases coexist at the substrate forming the macroscopic contact angle θ_0 . Combining the equations (1) and (2) gives

$$\sigma_0^{\alpha\beta} \cos \theta_0 - \sigma^{\alpha\beta} \cos \theta = \sigma_0^{\beta\gamma} - \sigma_0^{\alpha\gamma} - (\sigma^{\beta\gamma} - \sigma^{\alpha\gamma}) + \kappa/r + \partial\kappa/\partial r. \quad (3)$$

The difference $\sigma_0^{\beta\gamma} - \sigma_0^{\alpha\gamma} - (\sigma^{\beta\gamma} - \sigma^{\alpha\gamma})$ is usually ignored as well as the dependence $\kappa(r)$. This leads to the simplified equation

$$\cos \theta_0 - \cos \theta = \kappa_0 / (\sigma_0^{\alpha\beta} r). \quad (4)$$

We employed a local interface displacement model (Dobbs & Indekeu, 1993) to calculate equilibrium shapes (interface displacement profiles $l(\mathbf{x})$) and characteristics of small sessile droplets. We showed that the nonzero term owing to adsorptions, $\sigma_0^{\beta\gamma} - \sigma_0^{\alpha\gamma} - (\sigma^{\beta\gamma} - \sigma^{\alpha\gamma})$, can be compared with the term κ_0/r even in the main order in $1/r$. For

smaller droplets, such as new phase embryos at nucleation, the term $\partial\kappa/\partial r$ is generally also important. A threshold vapour supersaturation for nucleation is shown to exist and to be determined by the surface spinodal. The scenario of nucleation and the properties of the new phase embryos are found to be qualitatively different from those obtained with use of Eq. (4) (see Figure 1).

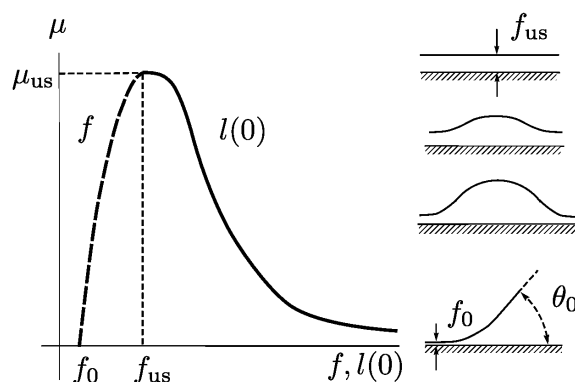


Figure 1. **Right:** Schematic droplet profiles $l(\mathbf{x})$ at different values of the condensate chemical potential μ . Droplets sit on precursor films of a certain thickness f varying from the value f_0 at bulk liquid-vapor coexistence to the value f_{us} at the surface spinodal. **Left:** The condensate chemical potential μ vs the “droplet height” $l(0)$ and the precursor film thickness f . Both interface displacements, $l(0)$ and f , meet at $\mu = \mu_{us}$ (at the surface spinodal).

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- Dobbs, H. T., and Indekeu, J. O. (1993). *Physica A*, 201, 457–481.
Gretz, R. D. (1966). *Surf. Sci.* 5, 239–251.
Hienola, A I, Winkler, P M, Wagner, P E, Vehkamäki, H, Lauri, A, Napari, I, Kulmala M. (2007). *J. Chem. Phys.* 126, 094705.
Navascués, G., Tarazona, P. (1981). *J. Chem. Phys.* 75, 2241–2246.
Rusanov, A. I., Shchekin, A. K., Tatyanenko, D. V. (2004). *Colloids Surf. A* 250, 263–268.
Scheludko, A. D. (1985). *J. Colloid Interface Sci.* 104, 471–476.