EFFECTS OF ADSORPTION AND LINE TENSION ON CONTACT ANGLE OF LIQUID RIDGES AND SESSILE DROPLETS: THERMODYNAMICS AND AN INTERFACE DISPLACEMENT MODEL

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We consider a small axisymmetric sessile droplet and a narrow liquid ridge (an infinitely long "cylindrical droplet") formed on top of a precursor wetting / polymolecular adsorption film on a planar partially wettable solid substrate. Such axisymmetric sessile droplets are actively studied during last few decades in various contexts including heterogeneous nucleation, wetting, hydrophobic properties of solid surfaces etc. Modern scanning microscopy techniques allow to measure profiles and contact angles of even nanosized sessile droplets [1]. Liquid ridges became popular in molecular dynamics simulations since they require less calculation resources (due to use of periodic boundary conditions) and allow reducing line tension effect on the contact angle [2, 3].

The macroscopic contact angle in such a system is determined by equilibrium values of thermodynamic surface tensions σ — the specific surface excesses of the grand thermodynamic potential [4] and is given by the well-known Young relation:

$$\sigma_0^{\alpha\beta} \cos\theta_0 = \sigma_0^{\beta\gamma} - \sigma_0^{\alpha\gamma}. \tag{1}$$

Here and further, θ denotes the contact angle, Greek superscripts mark the phases, and double Greek superscripts mark the interfaces (see Fig. 1 for notations). The "0" subscript marks the value referring to the bulk liquid–vapor phase coexistence, i. e., the binodal. For small sessile droplets, the contact angle is affected also by the thermodynamic line tension κ — the specific line excess of the grand thermodynamic potential. Eq. (1) then changes to the generalized Young equation [5, 6]:

$$\sigma^{\alpha\beta} \cos\theta = \sigma^{\beta\gamma} - \sigma^{\alpha\gamma} - \kappa/r - \partial\kappa/\partial r. \tag{2}$$

Here the values of the thermodynamic quantities σ and κ refer to the current thermodynamic state of the system, different from the one in Eq. (1). The contact line (droplet base) radius r refers to the equilibrium/critical droplet at this thermodynamic state. Comparing Eqs. (1) and (2), we write

$$\sigma_0^{\alpha\beta} \cos\theta_0 - \sigma^{\alpha\beta} \cos\theta = \delta\Delta\sigma^\gamma + \kappa/r + \partial\kappa/\partial r \tag{3}$$

with $\delta\Delta\sigma^\gamma \equiv \Delta\sigma^\gamma - \Delta\sigma_0^\gamma$, $\Delta\sigma^\gamma \equiv \sigma^{\alpha\gamma} - \sigma^{\beta\gamma}$, $\Delta\sigma_0^\gamma \equiv \sigma_0^{\alpha\gamma} - \sigma_0^{\beta\gamma}$. The symbol "$\delta$" denotes the difference of the following thermodynamic quantity in the current thermodynamic state and its state at the binodal. For the sake of simplicity, we suppose the system to be isothermal, and containing the only mobile component constituting the fluid (liquid and vapor) phases.

In many cases, the difference between $\sigma^{\alpha\beta}$ and $\sigma_0^{\alpha\beta}$ can be neglected since the curvature radius of the $\alpha\beta$ interface of a sessile droplet/ridge is much larger than the Tolman length. Then Eq. (3) turns into an equation for correction to the [macroscopic] contact angle cosine. It clearly has three separate terms. With use of thermodynamic arguments, we show that $\delta\Delta\sigma^\gamma$ and κ/r, the first two corrections on the right-hand-side of Eq. (3), are $O(r^{-1})$, while the third one, $\partial\kappa/\partial r = O(r^{-2})$ [7]. The correction $\delta\Delta\sigma^\gamma$ can be estimated as $(\Gamma_0^{\beta\gamma} - \Gamma_0^{\alpha\gamma})\delta\mu$ with Γ the adsorption (the specific surface excess of matter), μ the chemical potential of the [single] component of the fluid phases, and thus is determined by adsorption effects. The correction $\partial\kappa/\partial r$ is due to an intrinsic dependence of the line tension on the three-phase contact line (droplet base) radius. The corrections $\delta\Delta\sigma^\gamma$ and $\partial\kappa/\partial r$ are usually ignored, and Eq. (3) is considered with the only correction term κ/r. Such a "simplified" form of the equation is widely used in contact-angle-based measurements of the line tension.

In case of liquid ridges, the contact line is straight, Eqs. (2) and (3) then will not contain the line-tension term, while the derivative term $\partial\kappa/\partial r$ persists with r the half-width of the ridge base [5]:

$$\sigma^{\alpha\beta}\cos\theta = \sigma^{\beta\gamma} - \sigma^{\alpha\gamma} - \partial\kappa/\partial r, \tag{4}$$

$$\sigma_0^{\alpha\beta}\cos\theta_0 - \sigma^{\alpha\beta}\cos\theta = \delta\Delta\sigma^{\gamma} + \partial\kappa/\partial r. \tag{5}$$

With use of thermodynamic arguments, we show that in this case $\partial\kappa/\partial r = O\left(r^{-2}\right)$, even though the dependences $\kappa(r)$ in the two considered geometries are generally different for same physical system. Therefore, in the case of liquid ridges $\delta\Delta\sigma^{\gamma}$ remains the only first-order correction term.

To illustrate our results and compare sessile droplets and ridges in the same physical system, we have employed a local interface displacement model, allowing calculating the profiles of the sessile droplets and ridges, their contact angles and all the discussed correction terms for a model system. The grand thermodynamic potential of the system within the model is a functional of the interface displacement (local liquid film thickness) profile $l(\mathbf{x})$ and a function of the chemical potential μ:

$$\Omega^{(\mathrm{ID})}\left[l(\mathbf{x});\mu\right] = \int \mathrm{d}^2\,\mathbf{x}\left[-n^{\alpha}\delta\mu\, l(\mathbf{x}) + \sigma_0^{\alpha\gamma} + \sigma_0^{\alpha\beta}\sqrt{1+\left(\nabla l(\mathbf{x})\right)^2} + U\left(l(\mathbf{x})\right)\right] \tag{6}$$

with n^{α} the number density of molecules in the liquid phase. The effective interface potential $U(h) = \int_h^{\infty}\Pi(h')\,\mathrm{d}h'$ related to the disjoining pressure isotherm $\Pi(h)$ describes a thin-film-specific contribution. For interface potentials typical for partial wetting, two stationary profiles for the functional (6) have been found: a metastable precursor wetting film of a constant thickness f: $\Pi(f) = -n^{\alpha}\delta\mu$, representing an equilibrium (metastable) state of the solid surface in contact with vapor phase, and a hump-shaped sessile droplet/ridge (depending on geometry of the system) on top of the above-mentioned film. At $\delta\mu \to +0$, the main part of this profile has a shape of almost spherical segment for sessile droplets and almost right circular cylindrical segment for ridges.

Using a model interface potential $U(h)$ we find, for different values of the chemical potential μ, stationary interface displacement profiles $l(\mathbf{x})$, corresponding reference profiles (see Fig. 1) with values of r and θ, thickness f of the precursor film and calculate the correction terms on the right-hand-sides of Eqs. (3) and (5). Obtained numeric results support our thermodynamic estimations.
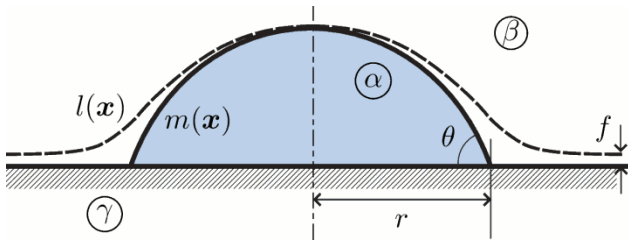
Figure 1. Cross-section of a liquid sessile droplet/ridge on the solid substrate. Dashed line shows the interface displacement profile $l(\mathbf{x})$ corresponding to droplet/ridge, solid line shows the corresponding "macroscopic" reference profile $m(\mathbf{x})$, forming a contact angle θ and the droplet/ridge base radius/half-width r. Circled Greek letters mark the phases: α is liquid, β is vapor, γ is solid.

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