Effect of contact line roughness on contact angle

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The generalized Young equation allowing for the roughness of the three-phase contact line has been derived and applied to an explanation of experimental results on the contact angle anisotropy of a sessile drop on deformed elastomers.

The contact angle of a drop placed on a solid substrate is the main and most commonly used characteristic of wetting. The classical Young equation relates the contact angle θ to the thermodynamic surface tensions (surface free energies in the case of one-component samples or, more generally, the specific surface grand potential with respect to liquids and the surface free energy with respect to solids) σ_{SV}, σ_{SL} and σ_{LV} at the interfaces solid/vapour, solid/liquid and liquid/vapour, respectively, as

$$\cos\theta = (\sigma_{SV} - \sigma_{SL})/\sigma_{LV} \tag{1}$$

Allowing also for the thermodynamic line tension κ (linear free energy in the case of one-component samples), equation (1) was generalized several times.[1–8] The most general formulation reads:[8]

$$\cos\theta = (\sigma_{SV} - \sigma_{SL})/\sigma_{LV} - (\kappa/r + \partial\kappa/\partial r)|\cos\varphi|/\sigma_{LV} \tag{2}$$

where r is the local curvature radius of the three-phase contact line and φ is the angle between the solid surface and the local plane of the three-phase contact line. The contribution of the line tension term is seen from equation (2) to depend on the curvature radius, so equation (2) may be written:

$$\cos\theta = \cos\theta_\infty - (\kappa/r + \partial\kappa/\partial r)|\cos\varphi|/\sigma_{LV} \tag{3}$$

where θ_∞ is the contact angle at an infinitely large radius corresponding to the Young equation (1).

Equation (3) allows for a macroscopic surface relief, but does not take into account a microscopic surface heterogeneity or roughness. If a solid surface is not smooth, surface and line roughness (the latter originating both because of surface roughness and surface heterogeneity) may be characterized by the surface roughness factor k_s and the line roughness factor k_l defined as

$$k_s \equiv A'_{SV}/A_{SV} = A'_{SL}/A_{SL},\; k_l \equiv L'/L \tag{4}$$

where A and L are the apparent visible surface area and the line length, respectively, and A' and L' are their true values. The microscopic surface roughness is known to have a significant influence on the contact angle, which is described by the Wenzel equation

$$\cos\theta = k_s\cos\theta_\infty \tag{5}$$

where we refer θ_∞ to a smooth surface. The surface roughness factor acts as a coefficient of σ_{SV} and σ_{SL} in equation (2). Similarly, the line roughness factor acts as a coefficient of κ, which changes equation (3) to the form:

$$\cos\theta = k_s\cos\theta_\infty - [k_l\kappa/r + \partial(k_l\kappa)/\partial r]|\cos\varphi|/\sigma_{LV} \tag{6}$$

Equation (6), the principal result of this paper, is the extension of the generalized Young equation (2) for the case of a rough line. For macroscopic radii, the thermodynamic line tension κ may be considered as independent of radius. In this case equation (6) is reduced to the form:

$$\cos\theta = k_s\cos\theta_\infty - \kappa(k_l/r + \partial k_l/\partial r)|\cos\varphi|/\sigma_{LV} \tag{7}$$

The dependence of the line roughness factor on radius is determined by the scale and geometry of roughness or/and microheterogeneity of a solid surface. Evidently, $\partial k_l/\partial r \to 0$ at $r \to \infty$, so that equation (7) produces a linear dependence of $\cos\theta$ on $1/r$ for sufficiently large drops (with radius much larger that the characteristic dimension of line roughness). Generally, however, the dependence of $\cos\theta$ on $1/r$ is not linear as is seen from equation (7) and was discovered by experiment indicating a negative value of κ.[9,10]

Equations (6) and (7) also predict that the thermodynamic line tension can contribute to the anisotropy of wetting which was observed on using one-dimensionally stretched elastomeric substrates. Stretching a substrate decreases the line roughness for those line parts with a line radius nearly perpendicular to the direction of stretching and increases the line roughness for the line parts with a line radius nearly parallel to the direction of stretching (Figure 1), so that $k_{l\parallel} > k_{l\perp}$.

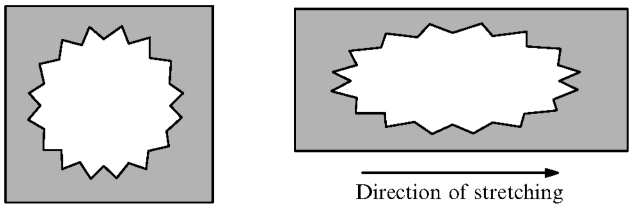

Figure 1 Changing the line roughness at surface stretching.

According to equation (7), we have

$$\cos\theta_\parallel - \cos\theta_\perp \equiv \cos\theta = -\kappa(k_l/r + \partial k_l/\partial r)|\cos\varphi|/\sigma_{LV} \tag{8}$$

where Δ symbolizes a difference in a quantity for directions $\parallel$ and $\perp$. For drops on a flat surface with radii larger than 1 mm exhibiting a linear dependence of $\cos\theta$ on the reverse drop radius,[13] equation (8) may be written as:

$$r\Delta\cos\theta = -\kappa k_l/\sigma_{LV} \tag{9}$$

At $\Delta k_l > 0$, equation (9) yields $\cos\theta_\parallel < \cos\theta_\perp$ and $\theta_\parallel > \theta_\perp$ if κ is positive or $\cos\theta_\parallel > \cos\theta_\perp$ and $\theta_\parallel < \theta_\perp$ if κ is negative. With a negative value of the thermodynamic line tension[9,10] we arrive at the conclusion that the contact angle along the direction of stretching should be smaller than along the other principal direction. Qualitatively, the same effect is observed due to the deformation of a substrate along the three-phase contact line caused by the surface tension of a drop.[14] For rubber substrates with microheterogeneity on the scale of 10 nm and roughness on a scale smaller than 500 nm, the effect of contact angle anisotropy was observed to be rather higher than that predicted from the elasticity modulus of substrates,[12] which may be explained by a contribution of the line roughness. At a three-fold elongation of a substrate by stretching,[13] the line roughness factor $k_{l\parallel}$ increases thrice and the line roughness factor $k_{1\perp}$ decreases thrice, which makes the magnitude of $\Delta(\kappa k_1)$ determined one order higher.[13] With this correction, the agreement between the theory of wetting of deformable solids[8,14] and experiment[12,13] becomes more satisfactory.

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