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The prediction of wettability of curved surfaces on the basis of the isotherms of the disjoining pressure

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ABSTRACT

The generalization of Derjaguin–Frumkin approach for the description of wettability of curved interfaces is given. The equations for the calculations of the contact angle on concave and convex cylindrical and spherical surfaces based on the isotherms of the disjoining pressure are derived. Analysis performed has shown that for the radius of curvature comparable to the range of surface forces action increasing the surface curvature for convex surfaces results in the contact angle increasing, whereas for concave surfaces the wetting improves. It is shown that curving the substrate surface may cause philic/phobic or phobic/philic wettability transition.

1. Introduction

The dominant role of the long-range surface forces in wetting phenomena was stressed many years ago in the works of Derjaguin [1] and Frumkin [2]. Their consideration was based on the analysis of coexistence of bulk liquid (drop or concave meniscus) with a substrate. Such coexistence is quantified by contact angle, created by bulk liquid with substrate and characterizes the type of wetting in the three phase system under consideration. It was shown by Derjaguin and Frumkin that in the equilibrium the meniscus of bulk liquid coexists with the substrate which in general is not dry, but coated by wetting or adsorption film of liquid (Fig. 1). The thickness of above wetting film or monolayer coverage in the case of adsorption films is determined by surface force field. The latter is characterized by the isotherm of disjoining pressure for wetting films and by the isotherm of adsorption for adsorption films [3]. The first equation relating the equilibrium value of macroscopic contact angle θ_0 on the plane surface and the isotherm of disjoining pressure $\Pi(h)$:

$$\sigma_{LV} \cdot \cos\theta_0 = \sigma_{LV} + \Pi(h_0) \cdot h_0 + \int_{h_0}^{\infty} \Pi(h)dh \qquad (1)$$

was derived by Derjaguin [1] by consideration the conditions of equilibrium between the liquid meniscus and wetting films in a flat capillary. In this equation h_0 is the thickness of wetting film being in the equilibrium with the meniscus of bulk liquid or with the sessile drop, σ_{LV} the surface tension of liquid, $\Pi(h_0)$ the disjoining pressure in the wetting film, characterizing the combined action of different mechanisms [3–5] of surface forces. Since then numerous theoretical and experimental works have proved the predictability of wetting on the basis of long-range forces data [6–17]. In particular the equation of the same type has been derived for the equilibrium of a drop with the film on flat substrate and it was shown that Eq. (1) can also be applied to predict the quasi-equilibrium receding and advancing contact angles for the drop on the flat substrate [7,18]. The problem of equilibrium between the bulk liquid and wetting films on cylindrical surface through the analysis of the equilibrium shape of transition zone have been considered for convex surface (a drop on the fiber) in [11,19], and for concave surface (a meniscus inside the capillary) in [20,21]. All the approaches mentioned above allow one to calculate the contact angles on the basis of the isotherms of the disjoining pressure for the systems with plane or cylindrical geometry, and no general solution have been proposed in the literature for the systems with spherical or more complex geometries. Besides the influence of the curvature parameters on the wettability of curved substrates have to be discussed in more details. In the paper below we will present the thermodynamic approach allowing the calculation of the contact angles through the isotherms of the disjoining pressure on both plane and curved interfaces. The particular cases of substrates with spherical and cylindrical geometry will be considered in details and the influence of a sign and a magnitude of the curvature on the surface wettability will be discussed.

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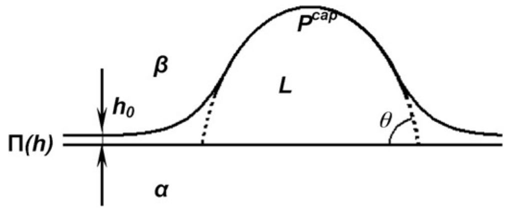

Fig. 1. For a wetting film on a flat surface being in the equilibrium with a sessile drop the disjoining pressure in the film, $\Pi(h)$, should be equal to the capillary pressure in the drop, P^{cap}.

2. Gibbs–Duhem equation for thin liquid film on curved substrate

Let us consider a system confined by a spatial angle ω and containing a wetting film of liquid f on curved substrate surface α, being in equilibrium with vapour phase β. The substrate is supposed to be non-deformable. In the present analysis we neglect effects of gravity, the film under consideration is one component and separates phases α and β. Following Guggenheim [22] and Defay et al. [23] we consider a wetting film as some surface phase, which is characterized by volume V_f and normal to the film boundaries component of pressure tensor P_f, being the same for any point inside the equilibrium film. As usual all the excesses for the interfaces αf and $f\beta$ associated with the variation of tangential component of pressure tensor across the film will be attributed to the interfacial tensions $\sigma_{\alpha f}$ and $\sigma_{f\beta}$. It is worthy of note that in general case $\sigma_{\alpha f}$ and $\sigma_{f\beta}$ differ from substrate/liquid σ_{SL} and liquid/vapour σ_{LV} tensions due to the deviations of physico-chemical properties of thin film from the corresponding properties of parent bulk liquid. The mechanical work, performed by the system to increase the spatial angle by $d\omega$ can be calculated as follows:

$$\delta W = P_\alpha\, dV_\alpha + P_\beta\, dV_\beta + P_f\, dV_f - d(\sigma_{\alpha f}A_{\alpha f}) - d(\sigma_{f\beta}A_{f\beta}), \qquad (2)$$

where $A_{\alpha f}$ and $A_{f\beta}$ are the areas of substrate/film and film/vapour interfaces.

Since in the system under consideration the interfaces are curved, the surface tensions $\sigma_{\alpha f}$ and $\sigma_{f\beta}$ will be dependent on the position of dividing surfaces between the film and confining phases. However the choice of dividing surface coinciding with the surfaces of tension for each interface allows one to simplify further analysis [24,25]. It is not necessary to know exactly the real geometrical position of each dividing surface. Only the distance between them associated with the thermodynamic film thickness has a physical sense.

With the above choice of dividing surfaces Eq. (2) and equation for the differential of the Gibbs free energy read:

$$\delta W = P_\alpha\, dV_\alpha + P_\beta\, dV_\beta + P_f\, dV_f - \sigma_{\alpha f}\, dA_{\alpha f} - \sigma_{f\beta}\, dA_{f\beta}, \qquad (3)$$

$$dG = \sigma_{\alpha f}\, dA_{\alpha f} + \sigma_{f\beta}\, dA_{f\beta} + \sum_i V_i\, dP_i - \sum_i S_i\, dT + \sum_i \mu_i\, dn_i, \qquad (4)$$

where $i = \alpha, \beta, f$; S_i, n_i and μ_i are the entropy, number of molecules and chemical potential of molecules in corresponding phases, respectively.

By subtracting from Eq. (4) the corresponding equations for the energy of bulk phases α and β, for the differential of the Gibbs energy of the film we will have:

$$dG_f = \sigma_{\alpha f}\, dA_{\alpha f} + \sigma_{f\beta}\, dA_{f\beta} + V_f\, dP_f - S_f\, dT + \mu_f\, dn_f. \qquad (5)$$

From Eq. (5), the Gibbs–Duhem equation for thin wetting film on curved substrate is easily obtained by using the Euler theorem:

$$A_{\alpha f}\, d\sigma_{\alpha f} + A_{f\beta}\, d\sigma_{f\beta} - V_f\, dP_f + S_f\, dT + n_f\, d\mu_f = 0. \qquad (6)$$

For further analysis let us consider the bulk liquid phase (the drop or concave meniscus) which is in the equilibrium with thin wetting film, and is characterized by the chemical potential μ_b. In general case such equilibrium is possible when bulk liquid is confined by curved liquid/gas interface, characterized by capillary pressure P_b^{cap} and the following conditions are satisfied:

$$d\mu_b = d\mu_f, \; \mu_b = \mu_f \qquad (7)$$

Neglecting the compressibility of the liquid and thus supposing that molecular volume in the film is equal to that in the bulk, $v_f = v_b$, at T = const one can write the Gibbs–Duhem equation:

$$n_f\, d\mu_f = \frac{V_f}{v_f} d\mu_f = \frac{V_f}{v_b} d\mu_b = V_f\, dP_b \qquad (8)$$

The accounting for Eq. (8) simplifies Eq. (6) to the form:

$$A_{\alpha f}\, d\sigma_{\alpha f} + A_{f\beta}\, d\sigma_{f\beta} = V_f\, d\Pi \qquad (9)$$

where $\Pi = P_f - P_b$ is the disjoining pressure in the liquid film.

Eq. (9) is the main thermodynamic equation allowing one to relate the macroscopic contact angle θ_0 created by bulk liquid on the substrate of arbitrary geometry with the isotherm of disjoining pressure $\Pi(h)$. Let us demonstrate the way to derive such relations for different particular geometries.

3. Wetting of plane substrate

For the plane substrates we have $A_{\alpha f} = A_{f\beta}$ and $V_f/A_{f\beta} = h_f$. That allows one to rewrite Eq. (9) in the form, relating the film tension γ_f with the disjoining pressure:

$$d\sigma_{\alpha f} + d\sigma_{f\beta} = d\gamma_f = h_f\, d\Pi \qquad (10)$$

The integration of Eq. (10) over the film thickness from h_0, corresponding to the wetting film on the substrate in equilibrium with bulk liquid, characterized by the capillary pressure P_b^{cap}, till thick film h_∞ where the disjoining pressure is equal to zero and taking into account that:

$$\begin{aligned} &\sigma_{\alpha f}(h_0) + \sigma_{f\beta}(h_0) = \sigma_{SV} \\ &\sigma_{\alpha f}(h_\infty) + \sigma_{f\beta}(h_\infty) = \sigma_{SL} + \sigma_{LV} \end{aligned} \qquad (11)$$

leads to:

$$\sigma_{SL} + \sigma_{LV} - \sigma_{SV} = -\Pi_0 h_0 - \int_{h_0}^{h_\infty} \Pi dh. \qquad (12)$$

Here σ_{SV} is the surface tension for substrate/vapour interface, different from the substrate/vacuum surface tension due to the presence of wetting/adsorption film. If one takes into account that h_∞ can be replaced by ∞ without loss of accuracy and in the equilibrium between the bulk liquid and the substrate the surface tensions for all three interfaces are related by the Young equation:

$$\cos\theta_0 = \frac{\sigma_{SV} - \sigma_{SL}}{\sigma_{LV}}, \qquad (13)$$

Eq. (12) easily transforms to Eq. (1) derived earlier by Derjaguin [1,3]. In this paper we neglect the line tension effect on the contact angle and thus the conventional form of the Young equation has been used. The main features of Eq. (1) and the dependence of contact angle on the type of the isotherm of disjoining pressure were discussed in detail in [3,10,15]. Here we only will stress the points, which are important for further analysis of curved substrates. The equality of chemical potential of molecules of liquid in the bulk and in the film for flat substrates leads to the equality of the disjoining pressure in the film to the capillary pressure in the meniscus or in the drop. That indicates, that the value and sign of $\Pi(h_0)$ and the thickness of wetting film are determined by the bulk liquid being in the equilibrium with substrate. If contact angle