



Rapid Communication

Influence of the Disjoining Pressure on the Equilibrium Interfacial Profile in Transition Zone Between a Thin Film and a Capillary Meniscus

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ABSTRACT

The behaviour of liquid layers on solid substrates depends on a number of factors, the most important of which is the action of surface forces in the vicinity of the three phase contact line. The equilibrium interfacial (gas/liquid) profile in the transition zone between the thin flat film and the spherical part of a meniscus is determined by the combined action of the disjoining/conjoining and capillary pressures. The disjoining/conjoining pressure is considered to include the electrostatic, van der Waals and structural components. The Poisson–Boltzmann equation is also solved with various boundary conditions to calculate the electrostatic component of the disjoining/conjoining pressure. Wetting conditions are considered and the interfacial profile is determined for various parameters governing the surface interactions, as well as the ratio between the disjoining/conjoining and capillary pressures.

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1. Introduction

DCP¹ is a manifestation of the surface forces acting on thin liquid layers and this concept was introduced, and successfully investigated, in the pioneering works of Derjaguin [1,2]. The well-known DLVO (Derjaguin–Landau–Verwey–Overbeek) theory of colloidal stability is based on DCP acting between colloidal particles/droplets [1]. DCP also acts in the vicinity of the three-phase contact line in the case of wetting/spreading [3], and for historical reasons, the action of DCP under these conditions has received less attention. However, there are notable examples where the effect of surface forces on wetting and spreading phenomena of liquids on solid substrates are considered (see [4–7] and references therein).

Flat wetting films on solid substrates exist because the DCP inside the liquid film is balanced by CP² in the neighbouring meniscus or droplet. Within the spherical part of the meniscus or droplet, the separation between the liquid–vapour and solid–liquid interfaces is high and the DCP is negligible. Hence, the shape of the meniscus or droplet is determined by the action of CP only [3]. Therefore, a transition zone must

exist between the bulk meniscus or droplet and the flat film wherein DCP and CP act simultaneously [3,5,7]. Since measurements of equilibrium/hysteresis contact angles and surface curvature of bulk liquids are carried out outside the transition zone, its size and profile are of interest. The latter provide information on the DCP–isotherm for thin liquid films on a solid substrate. The transition profile of the meniscus was calculated in [3] for the case of complete wetting. The primary aim of this article is to determine the shape of the transition zone for various types of the DCP–isotherm. The exact numerical solutions for PW conditions and for complicated forms of the DCP–isotherm were obtained for the first time.

2. Model Description

2.1. Model Assumptions

The transition zone II (Fig. 1) under equilibrium conditions is located between a two dimensional capillary meniscus (I) and a flat wetting film (II). A rectangular coordinate system, (x_1, x_2) is used, in which x_1 and x_2 are the lateral and normal coordinates, respectively. The width of the capillary, $2H$, is assumed to be much larger than the thickness of the equilibrium flat film, h_e . In the case of CW³ (see Fig. 1,a), the

³ CW – complete wetting.

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¹ DCP – disjoining/conjoining pressure.

² CP – capillary pressure.

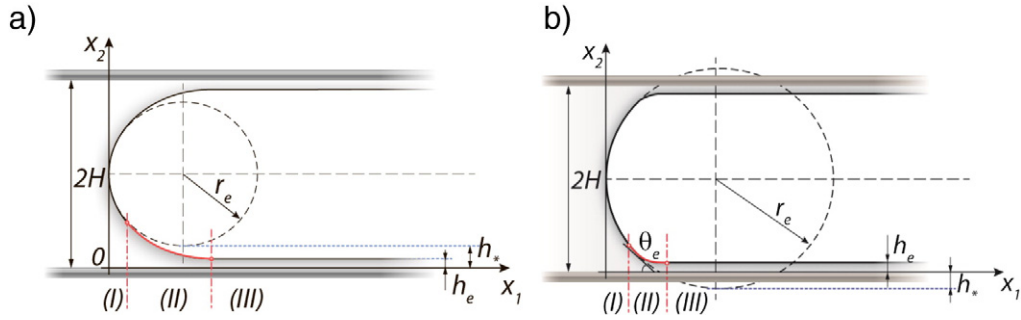


Fig. 1. Schematic presentation of a capillary meniscus under CW (a) and PW (b) conditions. I – spherical capillary meniscus; II – transition zone; III – flat wetting films. a) $\theta_e = 0, r_e < H, h^* = H - r_e > 0$; b) $\theta_e > 0, r_e > H, h^* = H - r_e < 0$.

continuation of the spherical meniscus (broken line) of radius r_e does not intersect either the solid walls of the capillary or the thin liquid film of thickness h_e . The case of PW⁴ is shown in Fig. 1,b; the continuation of the spherical meniscus intersects the boundary at the contact angle θ_e .

Under equilibrium conditions, there is no flow, and zero ion fluxes. The surface tension is assumed to be constant, which is valid in the absence of surfactants (and thermal gradients) [8].

2.2. Expression for the DCP Isotherm

The full DCP is a sum of electrostatic, van der Waals and structural components:

$$\Pi = \Pi_E + \Pi_W + \Pi_S. \quad (1)$$

The van der Waals component [1] is given by

$$\Pi_w = \frac{A}{6\pi h^3}. \quad (2)$$

Here $A = -A_H, A_H$ is the Hamaker constant; and h is a thickness of the liquid film. The influence of the structural component, Π_S , is discussed later (see [Effect of the structural component](#) section). An example of the graphic dependences of the DCP components will be given in Fig. 5,a.

To derive an expression for the electrostatic component, Π_E , the Poisson–Boltzmann equation in the small-slope approximation, $h'^2 \ll 1$, where the prime denotes differentiation with respect to x_1 , is used:

$$\frac{\partial^2 \varphi}{\partial x_2^2} = \frac{F^2 c_0}{RT \varepsilon \varepsilon_0} (\exp(\varphi) - \exp(-\varphi)) \quad (3)$$

where $\varphi = \Phi F / (RT)$ is a dimensionless potential in which the dimensional potential, Φ , is scaled on F/RT , wherein F is the Faraday constant, R is the gas constant, and T denotes the temperature, respectively; c_0 is the molar electrolyte concentration; ε and ε_0 are the dielectric constants of water and vacuum, respectively.

In the case of equilibrium, the momentum equations in the x_i directions ($i = 1, 2$) are expressed by the equations of electrohydrodynamics [9,10]:

$$-\frac{\partial p}{\partial x_i} - q \frac{RT}{F} \frac{\partial \varphi}{\partial x_i} = 0 \quad (4)$$

where $q = F c_0 (\exp(-\varphi) - \exp(\varphi))$ is a volume charge density; and p is the pressure in the liquid.

Eqs. (3) and (4) are used in the normal stress balance at gas–liquid interface in the transition zone [3]:

$$-p - \frac{1}{2} \varepsilon \varepsilon_0 E^2 + \varepsilon \varepsilon_0 E_2^2 = \frac{d}{dx_1} \frac{\gamma h'}{\sqrt{1+h'^2}}, \quad x_2 = h$$

where $E_i = -\frac{RT}{F} \frac{\partial \varphi}{\partial x_i}$ is the electric field; γ is the surface tension of solution.

Taking into account in the last equation that $\frac{\partial}{\partial x_1} \ll \frac{\partial}{\partial x_2}$, the following expression for the electrostatic component in the case of the small-slope profiles is obtained:

$$\Pi_E = RT c_0 (\exp(\varphi) + \exp(-\varphi)) - 2RT c_0 - \frac{(RT)^2 \varepsilon \varepsilon_0}{2F^2} \left(\frac{\partial \varphi}{\partial x_2} \right)^2. \quad (5)$$

The following boundary conditions are used here: $\Pi(h \rightarrow \infty) = 0$ and $\varphi(h \rightarrow \infty) = 0$, which correspond to the decay conditions for the DCP and the electric potential at long distances. The detailed description of the derivation of Eq. (5) and an analysis of the results for CW conditions are given in [11].

Eq. (5) coincides with Derjaguin's expression [1] for flat films. However, there is a substantial distinction of the expression (5) from that deduced in [1]: Eq. (5) is valid for non-flat thin liquid films in the case of small-slope approximation.

Two types of boundary conditions for Eq. (3) are used below to find the distribution of $\varphi(x_2)$ and $\partial \varphi / \partial x_2$ across the liquid film:

- (1) constant surface electrical potentials on both liquid–solid and liquid–vapour interfaces: $\varphi_s, \varphi_h = \text{const}$;
- (2) constant surface charge densities $\sigma_s, \sigma_h = \text{const}$.

The situations when $\varphi_s \neq \varphi_h$ or $\sigma_s \neq \sigma_h$ are rather common and will be studied below.

The equilibrium interfacial profile under the action of the surface forces is described by the augmented Young–Laplace equation [1,3]:

$$\frac{\gamma h''}{(1+h'^2)^{3/2}} + \Pi(h) = P_e. \quad (6)$$

Here P_e is the excess pressure equal to the capillary pressure for the spherical meniscus, $P_e = \gamma / (H - h^*)$.

Eq. (6) representing the normal stress balance, is solved for the case $\gamma = \text{const}$. The calculation results are discussed in the [Equilibrium interfacial profile in the transition zone](#) section. For the systems with the surface tension gradients, the significant tangential stress along

⁴ PW – partial wetting.

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