THE TRANSITION REGION BETWEEN A THIN FILM AND THE CAPILLARY MENISCUS

Peter Atanassov KRALCHEVSKY and Ivan Boyanov IVANOV

Laboratory of Thermodynamics and Physico-chemical Hydrodynamics, Faculty of Chemistry, University of Sofia, 1126 Sofia, Bulgaria

Received 15 January 1985; in final form 14 August 1985

Generalized Laplace equations, accounting for the variations of the surface tension and the disjoining pressure in the transition region, are derived. They are used to obtain integral expressions for the line and transversal tensions.

1. Conditions for equilibrium of the transition region

We consider a symmetrical planar thin liquid film in the absence of external fields, encircled by a capillary meniscus of the same liquid (fig. 1). Close to the axis of symmetry Oz the film has constant thickness h (defined as the distance between the two surfaces of tension each of them with film surface tension σ^f).

Far from Oz (in the meniscus) the disjoining pressure $\Pi = 0$, the surface tension of the meniscus is a constant, σ^ℓ, and the generatix of the surface $z(x)$ satisfies the Laplace equation [1]. In the intermediate region the two surfaces interact and since the interaction energy depends on the distance between them, the surface tension in this region $\sigma(x)$ changes gradually from σ^f to σ^ℓ. The disjoining pressure Π is also a func-

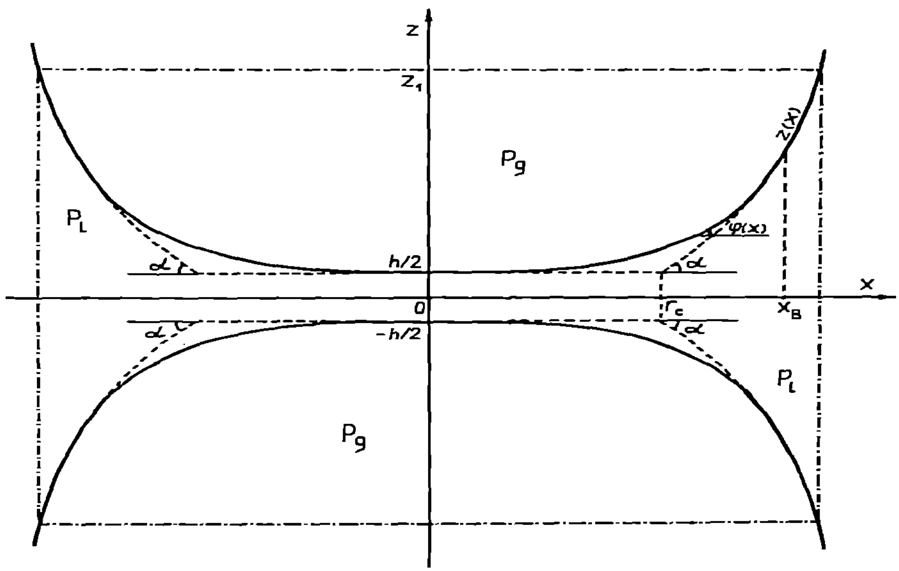

Fig. 1. The transition between a thin liquid film and the capillary meniscus is smooth. The solid and dashed lines represent the real and the extrapolated interfaces, respectively.

tion of x in this region. This (real) system is depicted in fig. 1 with continuous solid lines. It is customary to introduce an idealized system by extrapolating the meniscus and film surfaces (at constant surface tensions and capillary pressure [2]) until they intersect to form a contact angle α. The extrapolated surfaces are shown in fig. 1 with dashed lines.

According to Derjaguin [3], the profile of the transition region between the film and the meniscus (where $\sigma = \sigma(x)$ and $\Pi = \Pi(x)$) obeys

$$\sigma K(x, y, z) = P_c - \Pi(x)\,, \tag{1}$$

where $K(x, y, z)$ is the local curvature, P_c the capillary pressure of the meniscus and the surface tension σ is assumed constant (usually one assumes $\sigma \equiv \sigma^{\ell}$ [4–8]). De Feijter and Vrij [9] accounted for part of the variation of σ with x by making a local tangential (along Ox) force balance (see below) but in their calculations of the film profile they also used (1).

Our purpose now is to derive a self-consistent set of differential equations describing the hydrostatic equilibrium of the transition region. Following [10] we consider the film as divided by its surface of tension (in this case the surface $z = 0$) into two parts and will define the local disjoining pressure as

$$\Pi(x) = P_N^0(x) - P_{\ell}\,, \tag{2}$$

where P_{ℓ} is the pressure in the meniscus and $P_N^0(x)$ is the value of the component P_{zz} of the pressure tensor at the surface of tension. Eq. (2) connects Π directly with statistical mechanics, because P_{zz} can be expressed through integrals over the intermolecular potentials and the pair correlation functions — see e.g. ref. [11], eqs. (34.6)–(34.8). Let us consider a volume element (see fig. 2) whose lower base of area $x\,\mathrm{d}x\,\mathrm{d}\psi$ (ψ is the azimuthal angle) lies on the surface of tension and upper base is in the gas phase. According to the method of the local balance (see e.g. ref. [12]) we require that the local forces, acting on this volume along the axes Ox and Oz, are respectively zero. Setting equal the forces acting along the positive and negative direction of Oz we have

$$\begin{aligned}&[P_{\ell} + \Pi(x)]\, x\, \mathrm{d}\psi\, \mathrm{d}x \\ &\quad + (x + \mathrm{d}x)\, \sigma(x + \mathrm{d}x) \sin\phi(x + \mathrm{d}x)\, \mathrm{d}\psi \\ &\quad = P_g x\, \mathrm{d}\psi\, \mathrm{d}x + \sigma(x)\, x \sin\phi(x)\, \mathrm{d}\psi\,,\end{aligned} \tag{3}$$

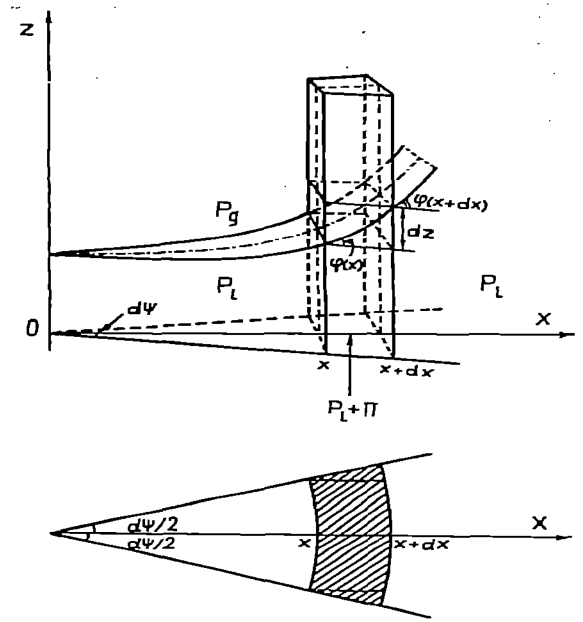

Fig. 2. A volume element in the transition region used for deriving the conditions for local mechanical equilibrium.

where P_g is the gas pressure and $\phi(x)$ is the running slope angle:

$$\tan\phi = \mathrm{d}z/\mathrm{d}x\,. \tag{4}$$

By taking the limit $\mathrm{d}\psi \to 0$ and $\mathrm{d}x \to 0$ we thus obtain

$$\mathrm{d}(\sigma \sin\phi)/\mathrm{d}x + \sigma(x) \sin\phi(x)/x = P_c - \Pi(x)\,, \tag{5}$$

where $P_c = P_g - P_{\ell}$. Setting equal the forces acting along the positive and negative directions of Oz, we similarly obtain

$$\begin{aligned}&P_g x\, \mathrm{d}\psi\, \mathrm{d}z + (x + \mathrm{d}x)\, \sigma(x + \mathrm{d}x) \cos\phi(x + \mathrm{d}x)\, \mathrm{d}\psi \\ &\quad = (x + \mathrm{d}x) P_g\, \mathrm{d}\psi\, \mathrm{d}z + \sigma(x) \cos\phi(x)\, x\, \mathrm{d}\psi \\ &\quad + 2\sigma(x) \frac{\mathrm{d}x}{\cos\phi(x)} \sin(\tfrac{1}{2}\mathrm{d}\psi)\,.\end{aligned}$$

The same limiting transition leads to

$$-\mathrm{d}(\sigma\cos\phi)/\mathrm{d}z + \sigma(x) \sin\phi(x)/x = P_c\,. \tag{6}$$

In a slightly different form eq. (6) was first derived in ref. [9]. The approximation $\sigma = \text{const.}$ reduces (5) to

Derjaguin's equation (1). For large distances between the meniscus surfaces $\sigma \equiv \sigma^{\ell} = \text{const.}$, $\Pi \equiv 0$ and both (5) and (6) lead to Laplace's equation in parametric form (see e.g. ref. [1]). However, when the meniscus surfaces interact, so that $\sigma = \sigma(x)$ and $\Pi(x) \neq 0$, eqs. (5) and (6) are no longer equivalent and their combination leads to an interesting equation, connecting σ and Π:

$$d\sigma/dx = -\Pi(x) \sin \phi(x) , \quad (7)$$

which shows that hydrostatic equilibrium in the transition region is ensured by simultaneous variation of σ and Π. In other words the assumptions $\Pi \neq 0$ and $\sigma = \text{const.}$ are incompatible. Therefore, all attempts to ascribe the interaction between the meniscus surfaces either to $\Pi(x)$ (with $\sigma = \text{const.}$) or to $\sigma(x)$ (with $\Pi = 0$) are inconsistent.

Eqs. (4), (5) (or (7)) and (6) form a full set allowing the calculation of $z(x)$, $\phi(x)$ and $\sigma(x)$ provided that $\Pi(x)$ is known from the microscopic theory. Generally speaking $\Pi(x)$ is a functional of the shape $z(x)$ of the meniscus surfaces so that eq. (5) (and (7)) is in fact an integro-differential equation. One way to solve it is to use an iterative procedure, starting with $\Pi(x)$ for the idealized system as zeroth approximation. Other forms of eqs. (5) and (6) which are convenient for the calculation of the line tension are:

$$d(\sigma \cos \phi) + P_c dz = (\sigma \sin^2\phi / x \cos \phi)\, dx , \quad (8)$$

$$d(x\sigma \cos \phi) + P_c d(xz) = (\sigma/\cos \phi + P_c z)\, dx , \quad (9)$$

$$d(x^2\sigma \cos \phi - xz\,\sigma \sin \phi) + P_c d(x^2 z)$$
$$= \{2\sigma \cos \phi + [P_c + \Pi(x)]\, z\}\, x\, dx . \quad (10)$$

The first two follow from (4) and (6) and the third from (4), (5) and (6).

Eqs. (6) and (7) can be derived also from the Gibbs variational principle, applied to the grand potential Ω for a system enclosed in a box depicted in fig. 1 with dash-dotted lines:

$$\Omega = 2\pi \int_{h/2}^{z_1} \Phi(z, x(z), x'(z), \sigma(z)) + \text{const.} ,$$

$$\Phi = -P_c x^2(z) + \Pi X^2(z) + 2\sigma(z)\, x(z)(1+x'^2)^{1/2}, \quad (11)$$

where $x' = dx/dz$ and $X(\sigma)$ is the inverse of the function $\sigma(x)$*. When taking the variation $\delta\Omega = 0$ we consider the variation of $\sigma(z)$ as independent from that of $x(z)$. In this way one obtains two Euler–Lagrange equations ($\sigma' = d\sigma/dz$)

$$\frac{\partial \Phi}{\partial x} - \frac{d}{dz}\left(\frac{\partial \Phi}{\partial x'}\right) = 0 , \quad \frac{\partial \Phi}{\partial \sigma} - \frac{d}{dz}\left(\frac{\partial \Phi}{\partial \sigma'}\right) = 0 .$$

By means of (4) and (11) it is easily shown that the first is equivalent to (6), and the second to (7). Fortes [13] used a somewhat similar approach (with $\sigma = \sigma(z)$) but he did not consider $\delta x(z)$ and $\delta\sigma(z)$ as being independent. Consequently, he obtained only one equation, i.e. he missed the second equation allowing the calculation of $\sigma(z)$.

2. Equations for the line and transversal tensions

The conditions for mechanical equilibrium between the film and the meniscus in the "membrane" and "detailed" approach (for definition of the two approaches see ref. [14]) read respectively:

$$\gamma + \kappa/r_c = 2\sigma^{\ell} \cos \alpha_0 , \quad (12)$$

$$\sigma^f + \tilde{\kappa}/r_{c1} = \sigma^{\ell} \cos \alpha , \quad (13a)$$

$$\tau = \sigma^{\ell} \sin \alpha , \quad (13b)$$

where γ is the film (membrane) tension and κ, r_c, α_0 respectively $\tilde{\kappa}$, r_{c1}, α are the line tension, the contact radius and contact angle in the membrane and detailed approaches (see fig. 3); we call τ the transversal tension [14]. We now derive expressions for κ, $\tilde{\kappa}$, and τ in terms of $\sigma(x)$, $\Pi(x)$ and the meniscus shape.

Let x_B be chosen in such a way that at $x \geqslant x_B$ the shapes of the menisci of the real and the idealized systems coincide (see fig. 1) and $\sigma(x_B) = \sigma^{\ell}$. The integration of (8) from 0 to x_B yields:

$$\sigma(x_B) \cos \phi(x_B) - \sigma^f + P_c(z(x_B) - h/2)$$
$$= \int_0^{x_B} \frac{\sigma(x) \sin^2\phi(x)}{x \cos \phi(x)}\, dx . \quad (14)$$

By integrating (8) from r_c to x_B for the meniscus of the idealized system (set $\sigma \equiv \sigma^{\ell}$ in (8)) we obtain

* When writing down the functional (11) we imposed the requirement that with $\pi \equiv 0$ the variation of Ω leads to the Laplace equation.

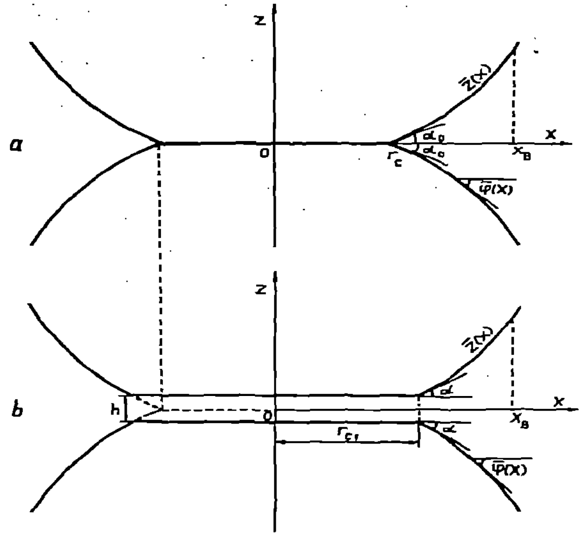

Fig. 3. The idealized system in the membrane (a) and the detailed (b) approaches.

$$\sigma^{\ell} \cos \bar{\phi}(x_B) - \sigma^{\ell} \cos \alpha_0 + P_c \bar{z}(x_B) = \int_{r_c}^{x_B} \frac{\sigma^{\ell} \sin^2 \bar{\phi}(x)}{x \cos \bar{\phi}(x)} \, dx \,, \tag{15}$$

where the barred quantities correspond to the idealized system.

Eqs. (14) and (15) along with (12) and $\gamma = 2\sigma^f + P_c h$ (see refs. [15,16]) lead to

$$\frac{\kappa}{r_c} = 2 \int_0^{x_B} \left[\left(\frac{\sigma \sin^2 \phi}{x \cos \phi} \right) - \left(\frac{\sigma \sin^2 \phi}{x \cos \phi} \right)_m^{\mathrm{id}} \right] dx \,, \tag{16}$$

where the superscript "id" refers to the idealized system and the subscript "m" denotes that the quantity in parentheses must be calculated in the membrane model – see fig. 3a. In a similar way from (9) and (10) two alternative expressions for κ can be derived:

$$\frac{\kappa}{r_c} = 2 \int_0^{x_B} \left[\left(\frac{\sigma}{\cos \phi} + P_c z \right) - \left(\frac{\sigma}{\cos \phi} + P_c z \right)_m^{\mathrm{id}} \right] \frac{dx}{r_c} \,, \tag{17}$$

$$\frac{\kappa}{r_c} = 2 \int_0^{x_B} \{ [2\sigma \cos \phi + (P_c + \Pi) z] - (2\sigma \cos \phi + P_c z)_m^{\mathrm{id}} \} \frac{x \, dx}{r_c^2} \,. \tag{18}$$

The same treatment of (8), (9), (10), and (13a) leads to three expressions for the line tension $\tilde{\kappa}$ in the detailed model i.e. film of finite thickness h (subscript "h") – see fig. 3b.

$$\frac{\tilde{\kappa}}{r_{c1}} = \int_0^{x_B} \left[\left(\frac{\sigma \sin^2 \phi}{x \cos \phi} \right) - \left(\frac{\sigma \sin^2 \phi}{x \cos \phi} \right)_h^{\mathrm{id}} \right] dx \,, \tag{19}$$

$$\frac{\tilde{\kappa}}{r_{c1}} = \int_0^{x_B} \left[\left(\frac{\sigma}{\cos \phi} + P_c z \right) - \left(\frac{\sigma}{\cos \phi} + P_c z \right)_h^{\mathrm{id}} \right] \frac{dx}{r_{c1}} \,, \tag{20}$$

$$\frac{\tilde{\kappa}}{r_{c1}} = \int_0^{x_B} \{ [2\sigma \cos \phi + P_c z + (z - h/2) \Pi] - (2\sigma \cos \phi + P_c z)_h^{\mathrm{id}} \} \frac{x \, dx}{r_{c1}^2} \,. \tag{21}$$

Eq. (20) was first derived by de Feijter and Vrij [9] by a different method. All eqs. (16)–(21) contain the film radii and the meniscus capillary pressure so that generally speaking κ (and $\tilde{\kappa}$) will depend on the geometrical parameters of the system. There are experimental indications that such a dependence exists [17, 18].

By multiplying (5) by $x \, dx$, integrating it and using (13b) one can derive an expression for the transversal tension:

$$\tau = r_{c1}^{-1} \int_0^{x_B} [(\Pi)^{\mathrm{id}} - \Pi(x)] \, x \, dx \,,$$

$$(\Pi)^{\mathrm{id}} = P_c \quad \text{for } 0 < x < r_{c1} \,;$$
$$= 0 \quad \text{for } x > r_{c1} \,.$$

One sees that τ is an integral effect of the difference of the disjoining pressures in the real and idealized systems whereas κ and $\tilde{\kappa}$ (see (16) and (19)) are also integral effects but determined by $\sigma(x)$ and the slope angle

$\phi(x)$ rather than by $\Pi(x)$. The fact that κ, $\widetilde{\kappa}$ and τ are represented as integrals over small differences suggests that they should be very sensitive with respect to minor variations of the functions in the integrands. In this respect the replacement of $\sigma(x)$ in ([illegible]) by σ^{ℓ} may substantially affect the result of the calculations.

Similar, although more complicated calculations, allowed us [19] to derive equations for the transition region, the line and transversal tensions of asymmetric planar and spherical films, which will be soon published.

Acknowledgement

We are indebted to Professor A.I. Rusanov for comments on the manuscript.

References

[1] H.M. Princen, in: surface and colloid science, Vol. 2, eds. E. Matijevic and F.R. Eirich (Wiley, New York, 1969) p. 1.
[2] I.B. Ivanov, B.V. Toshev and B.P. Radoev, in: Wetting, spreading and adhesion, ed. J.F. Padday (Academic Press, New York, 1978) p. 37.
[3] B.V. Derjaguin, Kolloidn. Zh. 17 (1955) 207.
[4] B.V. Derjaguin, V.M. Starov and N.V. Churaev, Kolloidn. Zh. 38 (1976) 875.
[5] G.A. Martynov, V.M. Starov and N.V. Churaev, Kolloidn. Zh. 39 (1977) 472.
[6] F. Renk, P.C. Wayner and G.M. Homsy, J. Colloid Interface Sci. 67 (1978) 408.
[7] A.V. Neimark and L.I. Heifets, Kolloidn. Zh. 43 (1981) 500.
[8] N.V. Churaev, V.M. Starov and B.V. Derjaguin, J. Colloid Interface Sci. 89 (1982) 16.
[9] J.A. de Feijter and A. Vrij, J. Electroanal. Chem. Interfacial Electrochem. 37 (1972) 9.
[10] P.A. Kralchevsky and I.B. Ivanov, in: Surfactants in solution, ed. K.L. Mittal (Plenum Press, New York), to be published.
[11] S. Ono and S. Kondo, Molecular theory of surface tension in liquids. Handbuch der Physik, Vol. 10 (Springer, Berlin, 1960).
[12] G.A. Martynov, I.B. Ivanov and B.V. Toshev, Kolloidn. Zh. 38 (1976) 474.
[13] M.A. Fortes, Phys. Chem. Liquids 9 (1980) 285.
[14] P.A. Kralchevsky and I.B. Ivanov, Chem. Phys. Letters 121 (1985) 111.
[15] A.I. Rusanov, Phase equilibria and surface phenomena (Khimia, Leningrad, 1967) [in Russian]; Phasengleichgewichte und Grenzflächenerscheinungen (Akademie-Verlag, Berlin, 1978).
[16] B.V. Toshev and I.B. Ivanov, Colloid Polymer Sci. 253 (1975) 558.
[17] A.D. Nikolov, P.A. Kralchevsky and I.B. Ivanov, in: Surfactants in solution, ed. K.L. Mittal (Plenum Press, New York), to be published.
[18] P.A. Kralchevsky, A.D. Nikolov and I.B. Ivanov, J. Colloid Interface Sci., to be published.
[19] P.A. Kralchevsky, Ph.D. Thesis, University of Sofia, Sofia (1984) p. 158.