

ON THE MECHANICAL EQUILIBRIUM BETWEEN A FILM OF FINITE THICKNESS AND THE EXTERNAL MENISCUS

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A variational procedure for deriving the conditions for mechanical equilibrium between a planar film of finite thickness and the external meniscus is formulated. It is shown that the normal condition can be satisfied only if a new "transversal" tension is introduced.

In this work we use Gibbs' theory of capillarity [1] and its recent extension to linear and point phases [2] in order to derive the force balance equations at the periphery of a thin liquid film of finite thickness. For clarity we give a brief outline of the Gibbs approach. A detailed and rigorous treatment can be found in refs. [1,3-5]. The transition regions between the phases in real non-homogeneous systems have finite thickness or width and the forces acting in them (more precisely, the pressure tensor) are continuous functions of the position. In the Gibbs treatment the phases are considered as being homogeneous, the transition regions are replaced by sharp boundaries (surfaces, lines or points) and the integrals over the pressure tensor are replaced by forces acting on the surfaces (e.g. surface tension) the lines and the points. In order to make these idealized (model) systems equivalent to the real ones, excesses of the extensive properties are also introduced. The positions of the phase boundaries (surfaces, lines and points) in the model systems are fixed by the conditions for equivalence of the real and model systems both mechanically and with respect to the extensive properties. In some cases the positions of a few boundaries can be *chosen* arbitrarily. Some of the macroscopic parameters so defined can depend on the localization of the boundaries (e.g. the surface tension of a drop depends on the choice of the drop radius [1,3,4]), i.e. on the choice of the idealized system, but once this choice has been

made all parameters have well defined fixed values for a given physical state of the real system. For the line tension this problem was investigated by Navascues and Tarazona [6].

The macroscopic parameters so defined are amenable to experimental measurement. The connection between the measured thermodynamic macroscopic parameters (surface tension, disjoining pressure, film and line tensions, etc.) and the force distribution in the real non-homogeneous system can be established only via a *microscopic* theory, allowing the representation of the thermodynamic parameters as integrals over the pressure tensor or some other equivalent forces, defined locally. Such a microscopic theory is presented in the following paper [7].

Two equivalent approaches have been used in the macroscopic theory of thin films: we call them the "membrane approach" when the film is considered as a membrane of zero thickness and one tension γ acting along the surface of tension, and the "detailed approach" when the film is treated as a homogeneous liquid layer of thickness h and two film surface tensions, σ_1^f and σ_2^f (see refs. [4,8]). All phase boundaries are assumed to be the surfaces or lines of tension (see refs. [3,8,9]).

We will study now in the framework of the detailed approach the mechanical equilibrium of a symmetrical film ($\sigma_1^f = \sigma_2^f \equiv \sigma^f$) surrounded by a meniscus (of surface tension σ^b) in the absence of gravity — see fig. 1.

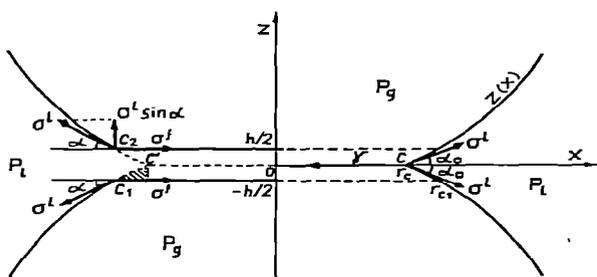


Fig. 1. The membrane and the detailed approaches (on the right- and left-hand side, respectively).

Such films may have translational [10] or cylindrical [11] symmetry. The right-hand side of fig. 1 illustrates the membrane approach. The extrapolated meniscus surfaces $z(x)$ (extrapolated at constant capillary pressure [9]), meeting at the contact line (at $x = r_c$) form an angle $2\alpha_0$. For translational symmetry the balance of the forces acting along the axis Ox at the contact line yields

$$\gamma = 2\sigma^l \cos \alpha_0. \quad (1)$$

The force balance along the axis Oz in this (membrane) approach is automatically satisfied. When the film has a cylindrical symmetry (when $z(x)$ is the generatrix of the meniscus surface), eq. (1) must include a term accounting for the line tension κ of the contact line C [12]:

$$\gamma + \kappa/r_c = 2\sigma^l \cos \alpha_0. \quad (2)$$

It was shown in ref. [9] that the contact line(s) defined by the extrapolation procedure described above is a line of tension, so that (2) does not contain the term $\partial\kappa/\partial r_c$ accounting for the virtual displacement of the contact line.

There are two contact lines and two film surfaces in the detailed approach (see the left-hand side of fig. 1, where C_1 and C_2 are the points where the two contact lines pierce the plane of the drawing). For cylindrical symmetry the contact lines are circumferences with radii r_{c1} — see fig. 2. In the case of a film of finite thickness the contact angle $\alpha \neq \alpha_0$ — see fig. 1 and ref. [13]. The tangential condition for equilibrium (along Ox) in the detailed approach for translational symmetry was formulated by de Feijter and Vrij [14] and derived by a variational procedure by Toshev and Ivanov [15]:

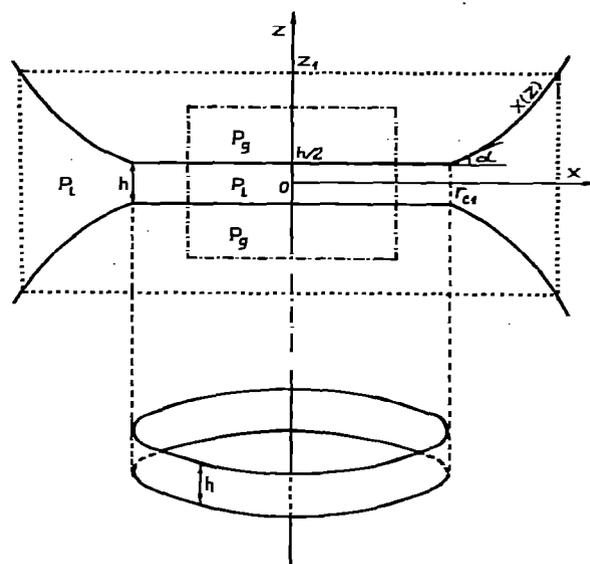


Fig. 2. A planar film in contact with a biconcave meniscus. In the case of an axially symmetric meniscus the contact lines are two equidistant circumferences (lower part of the figure).

$$\sigma^f = \sigma^l \cos \alpha. \quad (3)$$

For axially symmetric films one can write for each contact line (see [14]):

$$\sigma^f + \tilde{\kappa}/r_{c1} = \sigma^l \cos \alpha, \quad (4)$$

where $\tilde{\kappa} = \tilde{\kappa}_1 = \tilde{\kappa}_2$ is the line tension of the respective contact line C_1 or C_2 . There is a simple relationship between the two line tensions, κ and $\tilde{\kappa}$. Imagine that the plane of the paper in fig. 1 is a solid plate dividing the real film into two portions. Let us represent the film on the one side of the plate by the detailed approach and that on the other side by the membrane approach (the two models are depicted on the left-hand side of fig. 1 by solid and dashed lines respectively). Since the two models are mechanically equivalent (they refer to the same real system) one obtains

$$\kappa = 2\tilde{\kappa} + 2P_c \Delta A - 2\sigma^l \Delta l + 2\sigma^f \Delta r_c,$$

where $P_c = P_g - P_l$ is the capillary pressure, ΔA is the area of the dashed curvilinear triangle in fig. 1, Δl is the length of the arc $C_1 C'$, $\Delta r_c = r_{c1} - r_c$ and the relationship $\gamma = 2\sigma^f + P_c h$ [4] was used. If one sets $h = 0$, one obtains $\tilde{\kappa} = \kappa/2$.

The balance of the pressures, acting on the film surfaces, yields (see e.g. refs. [4,15]):

$$P_g = P_N = P_l + \Pi, \quad (5)$$

where Π is the disjoining pressure [16], P_g and P_l are the pressures in the bulk gaseous and liquid phases and P_N is the normal component of the pressure tensor in the film. The pressure difference $P_N - P_l$ can be considered as a mechanical definition of Π . Eq. (10) below is an equivalent thermodynamic definition.

Eqs. (3) (or (4)) and (5) do not form a complete set of equations describing the mechanical equilibrium between the film (in the detailed approach) and the surrounding phases, because there is no counterbalance to the normal force $\sigma^l \sin \alpha$ acting on *each* of the contact lines.

We will try to resolve this problem by using the variational method of Gibbs [1] as formulated and extended for linear phases by Boruvka and Neumann [2]. In the detailed approach (see fig. 2) one must ascribe to the film surfaces (superscript "f") and to the contact lines (superscript "L") excesses of the internal energy U , entropy S and the number of moles N_i of each component ($i = 1, 2, \dots, k$): U^f, S^f and N_i^f for the film surfaces and U^L, S^L and N_i^L for the contact lines. As Rusanov pointed out [4], since the two film surfaces interact, the excess surface internal energy U^f will depend not only on S^f, N_i^f and the film area A , but also on the thickness h , i.e.

$$dU^f = T dS^f + 2\sigma^f dA + \sum_i \mu_i dN_i^f + (\partial U^f / \partial h)_{S^f, A, (N_i^f)} dh. \quad (6)$$

The temperature T and the chemical potentials μ_i ($i = 1, 2, \dots, k$) have the same values for all phases at thermodynamic equilibrium.

Since the shapes of the real surfaces in the transition region between the film and the meniscus depend on the surface-surface interaction, the excess linear internal energy U^L in the idealized system, depicted in fig. 2, will depend not only on S^L, N_i^L and the contact line length L but also on h . Therefore, by analogy with (6) one can write

$$dU^L = T dS^L + 2\bar{\kappa} dL + \sum_i \mu_i dN_i^L + (\partial U^L / \partial h)_{S^L, L, (N_i^L)} dh \quad (7)$$

Following Gibbs [1], let us imagine a box of fixed volume V (shown with dotted lines in fig. 2), containing the thin film and macroscopic portions of the phases environing the film. The box walls are permeable for the molecules of all components, i.e. all chemical potentials are fixed. Since the temperature is also fixed, the thermodynamic potential for the system in the box is the grand potential $\Omega = U - TS - \sum_{i=1}^k \mu_i N_i$ and the necessary condition for equilibrium reads

$$(\delta \Omega)_{T, V, (\mu)} = 0, \quad (8)$$

where $\delta \Omega$ is the first variation of Ω . The fundamental equation of the system in the box is obtained by summation of the fundamental equations of all phases (for the film surfaces and the contact lines see eqs. (6) and (7)).

Let us first consider a subsystem (shown in fig. 2 with dash-dotted lines) of fixed volume V' , temperature and chemical potentials. It contains only a portion of the film (of constant area A') *without* the contact lines. The variation of its grand potential Ω' corresponding to a variation of the film thickness in the subsystem with δh is (see eq. (6))

$$(\delta \Omega')_{T, V', A', (\mu)} = -P_g \delta V'_g - P_l \delta V'_l + (\partial U^f / \partial h) \delta h. \quad (9)$$

Since $\delta V'_l = -\delta V'_g = A' \delta h$ and at equilibrium $\delta \Omega' = 0$, from (9) one obtains

$$-A'^{-1} (\partial U^f / \partial h)_{T, A', (\mu)} \equiv \Pi = P_g - P_l; \quad (10)$$

obviously the left-hand side term is independent of A' . In fact, the variational derivation of (10) was first given by Rusanov [4].

We return now to the whole system. The volumes, areas and length involved in (8) are

$$V_g = 2\pi \int_{h/2}^{z_1} x^2(z) dz, \\ V_l = 4\pi \int_{h/2}^{z_1} x(1+x'^2)^{1/2} dz, \\ A = \pi r_{c1}^2, \quad L = 2\pi r_{c1}, \quad (11)$$

where $x' = dx/dz$.

Since the variation at fixed r_{c1} and h leads to a trivial result (it yields the Laplace equation for the meniscus) we take only the partial variations with respect to the independent variables r_{c1} and h . Then, from

$$(\delta\Omega)_{T, V, (\omega)} = -(P_g - P_l) \delta V_g + \sigma^l \delta A_l + 2\sigma^f \delta A + 2\tilde{\kappa} \delta L + (\partial U^f / \partial h + \partial U^L / \partial h) \delta h \quad (12)$$

along with (11) and the general equation for the variation of a functional with moving boundaries (see e.g. ref. [17], Chap. 7, §2) we get two transversality conditions:

$$-\partial\Phi/\partial x'|_{z=h/2} + 4\pi\sigma^f r_{c1} + 4\pi\tilde{\kappa} = 0, \quad (13)$$

$$(-\Phi + x' \partial\Phi/\partial x')|_{z=h/2} + 2(\partial U^f / \partial h + \partial U^L / \partial h) = 0, \quad (14)$$

where

$$\Phi(z, x, x') = 2\pi[-(P_g - P_l) x^2 + 2\sigma^l x(1 + x'^2)^{1/2}]. \quad (15)$$

Since $x'(z = h/2) = \text{ctg } \alpha$ (see fig. 2), from (10) and (15) we finally obtain

$$\sigma^f + \tilde{\kappa}/r_{c1} = \sigma^l \cos \alpha, \quad (16)$$

$$L^{-1}(\partial U^L / \partial h)_{L, S^L, (N^L)} \equiv \tau = \sigma^l \sin \alpha. \quad (17)$$

Eq. (16) coincides with (4), but eq. (17) is new and it is precisely the missing normal condition for equilibrium. One sees that the normal component of the surface tension force $\sigma^l \sin \alpha$ is counterbalanced by the tension τ , which is due to the interaction between

the two contact lines. The τ -tension is a vector, acting on the contact line and directed toward the film normally to its surfaces (see fig. 3). That is why it can be conveniently called "transversal tension". With a straight contact line $\tilde{\kappa}/r_{c1} \rightarrow 0$ and (16) reduces to (3), but (17) remains unaltered, i.e. as opposed to the line tension, the transversal tension is of importance even for large films.

In conclusion, we add a few comments on the variations of Ω' and Ω with respect to h that have led us to eqs. (10) and (14) (respectively (17)). Because of the restriction imposed by us on the film shape (a planar film) we had to split the variational procedure into two steps and since each of them involves variation with respect to h it may seem that eqs. (10) and (14) are not independent. In fact, they are. We could have allowed the film thickness h and therefore, the film surface tension σ^f , to be functions of x , so that Ω would have been then a functional of h and σ . Then the variations with respect to $h(x)$ and $\sigma^f(x)$ at fixed film boundaries would have given Euler-Lagrange equations that would have led to generalized Laplace equations, of the kind of eqs. (5) and (6) in ref. [7]. By setting $h = \text{const.}$ and $\sigma^f = \text{const.}$ we would have again obtained (10) (cf. eq. (5) in ref. [7]). The variation of the film boundaries would have led us, within the framework of the model, considered here, again to (16) and (17). Therefore, the variation of Ω' is tantamount to deriving the Euler-Lagrange equation and the partial variation of Ω with respect to r_{c1} and h yields the transversality conditions, so that these variations are independent.

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References

- [1] J.W. Gibbs, The scientific papers of J. Willard Gibbs, Vol. 1. Thermodynamics (Dover, New York, 1961).
- [2] L. Boruvka and A.W. Neumann, J. Chem. Phys. 66 (1977) 5464.
- [3] S. Ono and S. Kondo, Molecular theory of surface tension in liquids. Handbuch der Physik, Vol. 10 (Springer, Berlin, 1960).

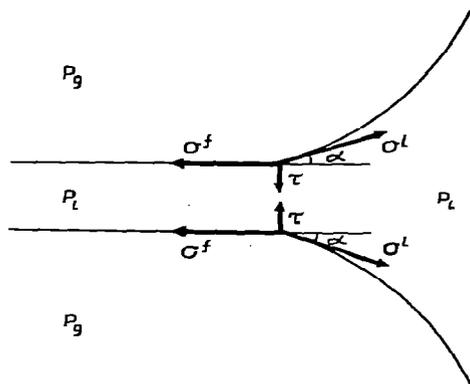


Fig. 3. The force balance in each point of a straight contact line.

- [4] A.I. Rusanov, Phase equilibria and surface phenomena (Khimia, Leningrad, 1967) [in Russian]; Phasengleichgewichte und Grenzflächenerscheinungen (Akademie-Verlag, Berlin, 1978).
- [5] A.I. Rusanov, in: The modern theory of capillarity, ed. F.C. Goodrich and A.I. Rusanov (Akademie-Verlag, Berlin, 1981).
- [6] G. Navascues and P. Tarazona, Chem. Phys. Letters 82 (1981) 586.
- [7] P.A. Kralchevsky and I.B. Ivanov, Chem. Phys. Letters 121 (1985) 116.
- [8] P.A. Kralchevsky and I.B. Ivanov, in: Surfactants in solution, ed. K.L. Mittal (Plenum Press, New York), to be published.
- [9] 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.
- [10] J.A. de Feijter and A. Vrij, J. Colloid Interface Sci. 64 (1978) 269.
- [11] B.V. Derjaguin and A.S. Titievskaja, Kolloidn. Zh. 15 (1953) 416.
- [12] G.A. Martynov, I.B. Ivanov and B.V. Toshev, Kolloidn. Zh. 38 (1976) 474.
- [13] I.B. Ivanov and B.V. Toshev, Colloid Polymer Sci. 253 (1975) 593.
- [14] J.A. de Feijter and A. Vrij, J. Electroanal. Chem. 37 (1972) 9.
- [15] B.V. Toshev and I.B. Ivanov, Colloid Polymer Sci. 253 (1975) 558.
- [16] B.V. Derjaguin, Kolloidn. Zh. 17 (1955) 207.
- [17] L.E. Elsgolz, Differential equations and variational calculus (Nauka, Moscow, 1969) [in Russian].