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ORIGINAL CONTRIBUTION

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Return to de Feijter and Vrij's formula for line tension at thin liquid films

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Abstract A mechanical model description is presented of the transition zone between a thin soap (emulsion) film and its adjacent meniscus. The mechanical state of the system is described by introducing three surfaces of tension – two of them are at the surfaces of the film and the transition zone and constant surface tensions are attributed there; the central surface of tension divides the distance between the other two surfaces of tension in inverse ratio of their surface tensions. The disjoining pressure like the capillary pressure acts always normal to the phase surfaces of tension. This model is applied for calculating the line tension of the contact line film/meniscus. Thus a new way of deriving the formula of de Feijter and Vrij for line tension at thin liquid films is presented. The asymmetric case of emulsion films is also considered.

Key words Thin films – line tension – surface of tension

Introduction

There has been published a great variety of papers dealing with the thermodynamic properties of the contact line in which two or more surface phases meet. Both thermodynamics and statistical mechanics of the line tension have already been developed [1–3]. Attempts are made to clarify the role of line tension in such phenomena as flotation [4, 5], phase-formation [6], and wetting transition [7, 8].

By force balance in the transition region between a foam film and a bulk liquid, de Feijter and Vrij have derived a formula for the line tension κ that allows calculating x if the disjoining pressure isotherm Π vs. film thickness is available [9]. However, general agreement seems to be still lacking as regards the proper mechanical description of the transition region between the planar film and its meniscus [2]. As is known, two approaches could be applied: de Feijter and Vrij's approach with variable local surface tensions in the transition zone [9] and the method of Derjaguin [10] with a constant surface tension in the version of so-called "Derjaguin's plane-parallel film approximation".

The goal of the present paper is to describe a simple procedure for deriving a formula for line tension in the case of a circular flat film in contact with a bulk meniscus. The mechanical model of the transition zone between the film and its adjacent meniscus, described in ref. [11], is used. This method embraces the two seemingly different approaches mentioned above. Such a conclusion follows immediately after the recognition that the disjoining pressure like the capillary pressure [12] acts always normal to the phase surfaces of tension.

Mechanical model of the transition zone between a circular film and its adjacent meniscus

Figure 1 shows a symmetrical plane-parallel circular film in contact with a liquid meniscus. Three surfaces of tension are introduced [11, 13]: the basic surface of tension coincides with the plane of symmetry of the film (Fig. 1b); the other two surfaces of tension with constant surface tension σ_0 are at the surfaces of the film and they are symmetrically bent towards the meniscus. By rotating the generatrix of these two surfaces of tension around the axis z the volumes of the phases (film, transition zone and meniscus) and the areas of their interfaces could be readily obtained. The excess tension in x-direction, $\Delta\gamma^f$ in the film and $\Delta\gamma\cos\theta$ in the transition zone (θ is the slope angle), is considered to act in the basic surface of tension of the film. The disjoining pressure, Π_0 in the film and $\Pi(x)$ in the transition zone, acts *normal* to the other two surfaces of tension as the capillary pressure always does [12]. The liquid surfaces produce the other two components $\Delta\gamma\sin\theta$ which counterbalance each other at the basic surface of tension (Fig. 1a).

The capillary pressure is the pressure difference in two equilibrium coexisting phases. It is determined by Laplace's formula for any point of the interface identified as a surface of tension [12]. According to this formula the capillary pressure acts *normal* to the center of a curved phase surface of unit area. Thus at equilibrium of two bulk phases with pressures $P^\alpha > P^l$, in absence of gravity, the capillary pressure $P_{\alpha l}$ will be

$$P_{\alpha l} = P^\alpha - P^l = \sigma C = \text{const}\,, \tag{1}$$

where C is the local curvature of the interface surface of tension with a surface tension σ. If one of the phases is a small phase f, the capillary pressure $P_{\alpha f}$ is

$$P_{\alpha f} = P^\alpha - P_n\,, \tag{2}$$

where P_n is the normal component of the pressure tensor $\hat{P}$. Furthermore, the disjoining pressure Π can be introduced by the relationship

$$\Pi = P_n - P^l\,, \tag{3}$$

where P^l is the pressure of a bulk liquid phase which would be in equilibrium with the small phase f. So, it follows from Eqs. (1) – (3),

$$P_{\alpha f} + \Pi = P_{\alpha l} = \text{const}\,. \tag{4}$$

Equation (4) expresses the mechanical equilibrium in *normal* direction. It is also necessary that at the basic surface of tension, in x-direction, the overall film tension γ must everywhere have a constant value. From the simultaneous validity of both conditions the relationship between the excess tension $\Delta\gamma\cos\theta$ and the local disjoining pressure Π is readily obtained [11].

Simple derivation of the formula of de Feijter and Vrij for line tension

We shall start from Eq. (4) expressed in Fortes' form [14, 15]. In accordance with our mechanical model the

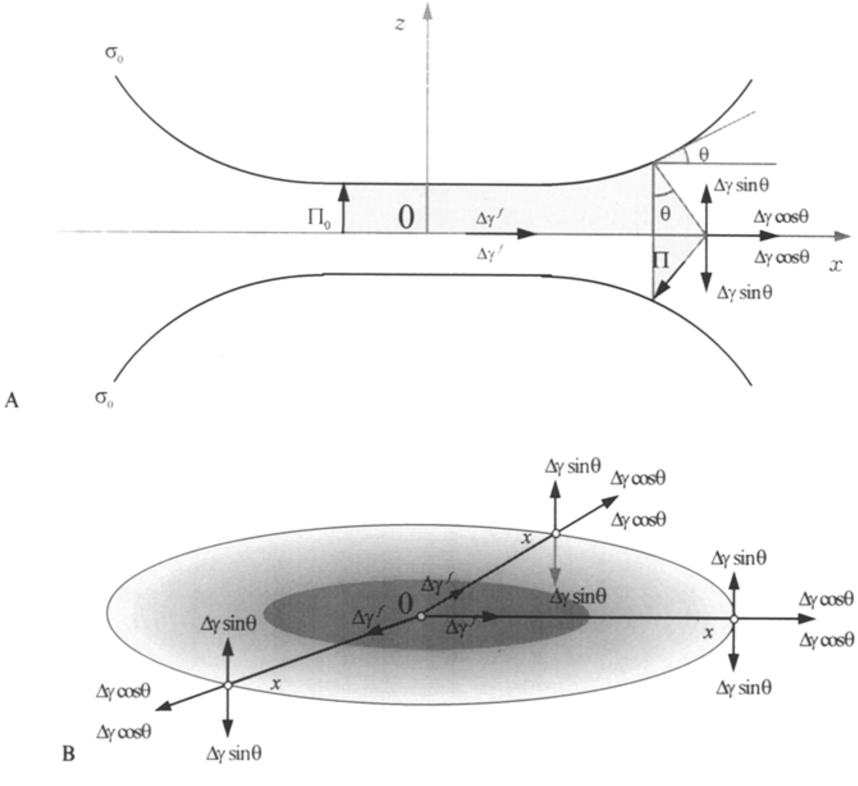

Fig. 1A The mechanical model of the thin film/transition region. The disjoining pressure acts normal to the surfaces of tension at the film surfaces. These symmetrically situated surfaces of tension are with a constant surface tension equal to the surface tension of the meniscus far from the film. The excess tensions $\Delta\gamma\cos\theta$ and $\Delta\gamma\sin\theta$ caused by the interaction between the film surface zones is assumed to act at the basic surface of tension where the overall tension of the film is applied **B** The excess tensions $\Delta\gamma^f/\Delta\gamma\cos\theta$ and $\Delta\gamma\sin\theta$ act at the basic surface of tension surface tension is split into two components, σ_0 at the two symmetrically situated surfaces of tension, and $\Delta\gamma\cos\theta$ $(\Delta\gamma^f)$, excess tensions, acting at the basic surface of tension, and then the Fortes' equation is written in the form

$$-\sigma_0\frac{d\cos\theta}{dz}-\frac{d\Delta\gamma\cos\theta}{dz}+\sigma_0\frac{\sin\theta}{x}+\frac{\Delta\gamma\sin\theta}{x}$$
$$=P_{\alpha l}=\text{const}\,. \tag{5}$$

After integrating from z_f (the half of the film thickness h) to z, taking into account the existence of two symmetrically situated surface of tension, we get

$$\gamma=2\sigma_0+2\Delta\gamma^f+2P_{\alpha l}z_f=2(\sigma_0+\Delta\gamma)\cos\theta+2P_{\alpha l}z$$
$$-2\sigma_0\int_{z_f}^{z}\frac{\sin\theta}{x}dz\,. \tag{6}$$

If $z=z^*$ is chosen far enough from the film and its transition zone where $\Pi(x)=0$, then $\theta(z)=\theta^*(z)$, $\cos\theta=\cos\theta^*$, $\sin\theta=\sin\theta^*$, and the local angle θ^* corresponds to that profile of the surface which could be obtained by means of the equation

$$P_{\alpha l}=-\sigma_0\frac{d\cos\theta^*}{dz^*}+\sigma_0\frac{\sin\theta^*}{x^*}\,. \tag{7}$$

By extrapolating of the latter profile of the liquid surface (Eq. (7)) to the intersection with the extrapolated surface of the planar film at $z=z_f$, the radius of the film r and the macroscopic contact angle $\theta_h=\theta^*(x=r)$ are readily defined. Therefore, for the above condition $(z\gg z_f)$ it follows from Eq. (6)

$$\gamma=2\sigma_0\cos\theta+2P_{\alpha l}z-2\sigma_0\int_{z_f}^{z}\frac{\sin\theta}{x}dz\,. \tag{8}$$

However, if the term $2\sigma_0\int_{z_f}^{z}\frac{\sin\theta}{x}dz$ in Eq. (8) is replaced by $2\sigma_0\int_{z_f}^{z}\frac{\sin\theta^*}{x^*}dz$, determined by means of Eq. (7), then the mechanical equilibrium will obviously be violated. In order to keep it a correction term κ/r must be introduced:

$$\gamma=2\sigma_0\cos\theta+2P_{\alpha l}z-2\sigma_0\int_{z_f}^{z}\frac{\sin\theta^*}{x^*}dz-\frac{\kappa}{r}\,. \tag{9}$$

The comparison of Eqs. (8) and (9) results in an expression for the line tension κ

$$\kappa=2\sigma_0 r\int_{z_f}^{z}\left(\frac{\sin\theta}{x}-\frac{\sin\theta^*}{x^*}\right)dz\,. \tag{10}$$

If the contact line is straight, $r\to\infty$, then it follows from Eq. (10) that

$$\varkappa_\infty=2\sigma_0\int_{z_f}^{\infty}(\sin\theta-\sin\theta^*)dz\,. \tag{11}$$

This is the well known formula of de Feijter and Vrij for κ [9], written here in accordance to the transition region mechanical model used (the $\Delta\gamma\sin\theta$ – components, produced from both symmetrical liquid surfaces, counterbalance each other at any point of the basic surface of tension).

Asymmetric films

This is the case when the planar film, formed from the liquid phase l, is in contact with two different bulk phases α and β with pressures $P^\alpha=P^\beta$. At equilibrium there exist two equal capillary pressures $P_{\alpha l}=P^\alpha-P^l=P^\beta-P^l=P_{\beta l}$. The mechanical model used for the symmetrical case can here be applied without any difficulty. There are again three surfaces of tension; two of them are at the film surfaces and constant surface tensions are attributed there – $\sigma_0^{\alpha l}$ for the interface αl and $\sigma_0^{\beta l}$ for the interface βl. The tension components produced from these interfaces $(\Delta\gamma\cos\theta)^i$ ($i=\alpha l$ or βl) act at the basic surface of tension. At the basic surface of tension the components $(\Delta\gamma\sin\theta)^i$ ($i=\alpha l$ or βl) counterbalance each other.

Thus, instead of Eq. (10), we get

$$\frac{\kappa}{r}=\left[\sigma_0\int_{z_f^\alpha}^{z}\left(\frac{\sin\theta}{x}-\frac{\sin\theta^*}{x^*}\right)dz\right]^{\alpha l}$$
$$+\left[\sigma_0\int_{z_f^\beta}^{z}\left(\frac{\sin\theta}{x}-\frac{\sin\theta^*}{x^*}\right)dz\right]^{\beta l}, \tag{12}$$

with

$$z_f^\alpha+z_f^\beta=h\,. \tag{13}$$

At $r\to\infty$, instead of Eq. (11), we write

$$\varkappa_\infty=\left[\sigma_0\int_{z_f^\alpha}^{z}(\sin\theta-\sin\theta^*)dz\right]^{\alpha l}+\left[\sigma_0\int_{z_f^\beta}^{z}(\sin\theta-\sin\theta^*)dz\right]^{\beta l} \tag{14}$$

The only problem here is the determination of the position of the basic surface of tension, i.e., the values of z_f^α and z_f^β at a given film thickness h. According to Gibbs [12; p. 306] the basic surface of tension "will divide the distance between the surfaces of tension for the two surfaces of the film taken separately, in the inverse ratio of their tensions". Actually, this Gibbs' statement is for the case of a thick film with a film interior having the properties of matter in mass. However, it evidently holds for the case of a thin film if the present mechanical model of the film and its adjacent meniscus could be applied. In accordance with this model the disjoining pressure as well as the capillary pressure both act everywhere *normal* to the surface of tension at the film surfaces and, consequently, the surfaces tensions associated with these surfaces of tension have kept their values constant and equal to the surface tensions of the phase boundaries in the meniscus far from the film. So, at a given film thickness h

$$\frac{\sigma_0^{\alpha l}}{\sigma_0^{\beta l}} = \frac{z_f^{\beta}}{z_f^{\alpha}} \tag{15}$$

(for more details cf. [16]).

Summary and conclusions

The system of a planar liquid film with the adjacent meniscus is considered and the line tension κ of the contact line with a radius r is determined. The disjoining pressure as well as the capillary pressure act everywhere along the phase surface *normal* to two surfaces of tension; the distance between these surfaces of tension in a plane-parallel part of the thin film determines the thickness of the film h. The surface tensions are assumed to be split into components: constant ones, equal respectively to the surface tensions far from the film, associated with the surfaces of tension for the two film surfaces taken separately, and excess components $\Delta\gamma \cos\theta$ and $\Delta\gamma \sin\theta$ acting at the basic surface of tension where the overall tension of the film γ is applied. Simple derivation of the formula of de Feijter and Vrij for the line tension κ, based on an application of Fortes' formula (5), is presented. The result is generalized for the asymmetric case with two bulk phases α and β separated by a planar liquid film in contact with a liquid meniscus.

Calculations of κ are carried out for the case of a thin soap film with a steep wall repulsion at $h = 4.0$ nm and a soft van der Waals attraction at $z > z_f$. Such type of disjoining pressure isotherm allows larger, and independent of $P_{\alpha l}$, contact angles θ_h to be obtained ($\theta_h = 3.71$ degrees for Hamaker's constant $K = 4 \cdot 10^{-21}$ J and $\theta_h = 11.71$ degrees for $K = 4 \cdot 10^{-20}$ J). The numerical results concerning the profiles of the phase boundaries are the same as those obtained by the method of de Feijter and Vrij with Derjaguin's plane-parallel film approximation [11] (three values of $P_{\alpha l}$ are used: 20 Pa, 25 Pa and 30 Pa). For these two cases ($K = 4 \cdot 10^{-21}$ J and $K = 4 \cdot 10^{-20}$ J) with $\sigma_0 = 30$ mN/m the line tensions κ are -4.41 pN and -13.8 pN, respectively.

For an example of the asymmetrical case, we choose $\sigma_0^{\alpha l} = 30$ mN/m, $\sigma_0^{\beta l} = 15$ mN/m, $h = 4.0$ nm and then $z_f^{\alpha} = 1.3$ nm, $z_f^{\beta} = 2.7$ nm, for $K = 4 \cdot 10^{-21}$ J $\theta_h^{\alpha} = 5.56$ degrees, $\theta_h^{\beta} = 3.89$ degrees, and $\kappa = -3.75$ pN.

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