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The Shape of the Disjoining Pressure Isotherm – its Effect on the Line Tension of Common Black (Emulsion and Foam) Films

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By the systematic direct numerical computation of the line tension of common black films it has been demonstrated that the value and sign of this line tension are very sensitive to the variation of the shape of the disjoining pressure isotherm and this finding may be used to obtain additional information on the surface forces acting in these films from the experimental values of the line tension.

When two drops of the fluid phase β are brought into mutual contact in the liquid phase α, a microscopic liquid film (MLF) is formed between them, Fig. 1(*a*). If the height of the coagulation barrier $\Pi_{\max}$ of the disjoining pressure isotherm $\Pi(H)$, Fig. 1(*c*), is high enough (high ζ potential, low electrolyte concentration) and is greater than the hydrostatic pressure difference $P = P_\beta - P_\alpha$ in the phases β and α, respectively, then only relatively thick stable common black films of thickness $H_f^c = 2z_f^c$, Fig. 1(*b*), may form in the region of the far coagulation minimum $_{\min 2}$ of the $\Pi(H)$-isotherm. On increasing the electrolyte concentration, the height of the coagulation barrier $\Pi_{\max}$ decreases, and so-called Newtonian black films, or bilayer membranes, of thickness $H_f^N = 2z_f^N$ may spontaneously appear in the near coagulation minimum $_{\min 1}$. Only the common black films are the object of our consideration in this paper.

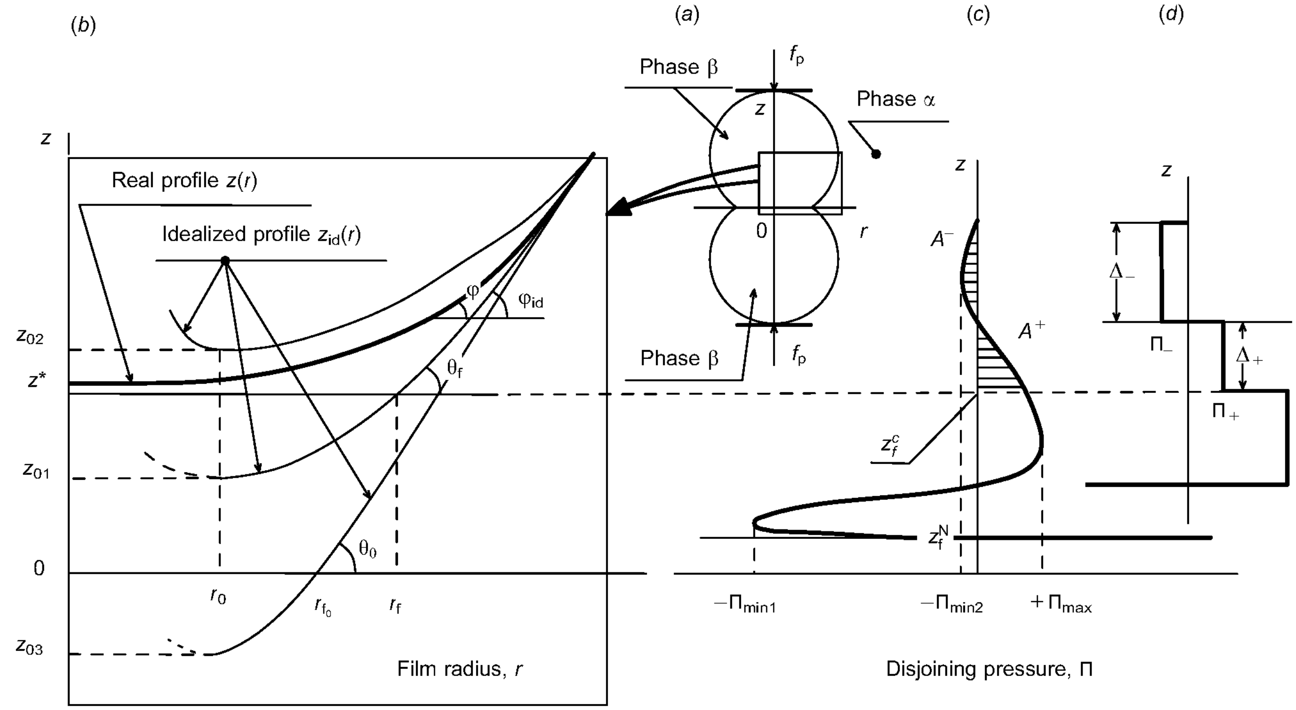

Fig. 1 When two fluid drops (phase β) are brought into mutual contact in the liquid phase α, a liquid film appears between them (*a*). The real profile $z(r)$ of this film differs from the idealized profile $z_{id}(r)$ (*b*) whose position with regard to $z(r)$ depends on the shape of the disjoining pressure isotherm (z) (*c*). Idealized step-wise (z)-isotherm is used for the numerical computation of the line tension of the liquid film (*d*).

The geometrical description of MLF is based on the consideration of the so-called idealized liquid film profile $z_{id}(r) = H_{id}(r)/2$, obtained by the extrapolation of the real profile $z(r) = H(r)/2$ from the region of the bulk meniscus, where $(H) = 0$ and the dividing surfaces of the film have a constant mean curvature k_0 and interfacial tension σ_0, into the transition region where by definition $(H) \neq 0$. When the drops are loaded by a joining force f_p, the idealized profile $z_{id}(r)$ is characterized by a minimum z_0, which may be localized above or below the plane $z = z_f = H_f/2$ depending on the sign of the interaction grand thermodynamic potential (H_f). The equilibrium liquid film thickness H_f [which does not necessarily coincide with the real thickness H^* in the centre of the circular film, see Fig. 1(*b*)] is defined by the equilibrium equation (1).

$$(H_f) = P = P_\beta - P_\alpha \tag{1}$$

The interaction grand thermodynamic potential $\Delta\Omega(H_f)$ in a film of thickness H_f is defined at constant temperature T and constant chemical potentials μ_i of the i-th component in the system by equation (2).

$$(H_f) = \int_{H_f}^{\infty} (H)\mathrm{d}H \tag{2}$$

If $\Delta\Omega(H_f)$ is positive, the minimum z_{02} is localized above the real profile $z(r)$ at $r = r_0$. In the case $\Delta\Omega(H_f) < 0$ the idealized profile $z_{id}(r)$ has minima z_{01} or z_{03} below the real profile $z(r)$ and intersects the plane $z = z_f$ under the contact angle θ_f at $r = r_f$, or intersects the plane $z = 0$ under the contact angle θ_0 at $r = r_{0f}$, if the absolute value of the negative $\Delta\Omega(H_f)$ is sufficiently great.

In our generalized line tension theory[1] we have obtained the strict analytical expression for the line tension τ, equation (3),

$$\frac{\tau}{r_f} = \int_{H_f}^{\infty} \frac{\sigma \sin\varphi}{r}\mathrm{d}H - \int_{H_f}^{\infty} \frac{\sigma_0 \sin\varphi_{id}}{r}\mathrm{d}H_{id} \tag{3}$$

defined within the framework of the so-called two dividing surfaces convention of the film as equation (4),

$$(H_f) + \frac{\tau}{r_f} = 2\sigma_0(\cos\theta_f - 1) \tag{4}$$

where the integration is carried out over real and idealized profiles in the first and the second integrals, respectively, r_f and H_f are radius and thickness of the circular liquid film, respectively, $\sigma(H)$ is the local interfacial tension in the transition region of the film with the local thickness H satisfying the relationship $(H) = 2\sigma(H) - 2\sigma_0$, and $\varphi(H)$ and $\varphi_{id}(H)$ are the local slope angles of the real and the idealized profiles, respectively.

In the case $(H_f) > 0$, when the contact angle θ_f cannot be formed, we have suggested a new definition for the line tension τ_B,[2,3] equation (5),

$$(H_f) + \frac{\tau_B}{r_0} = P(H_0 - H_f) \tag{5}$$

and we have obtained the strict analytical expression for τ_B, equation (6),

$$\frac{\tau_B}{r_0} = \int_{H_f}^{\infty} \frac{\sigma \sin\varphi}{r}\mathrm{d}H - \int_{H_0}^{\infty} \frac{\sigma_0 \sin\varphi_{id}}{r}\mathrm{d}H_{id} \tag{6}$$

where $H_0 = 2z_0$.

The expressions (5) and (6) are valid also in the case $(H_f) < 0$, if instead of the contact angle θ_f and the film radius r_f one uses the parameters H_0 and r_0 (formally, the parameter H_0 may be negative when the contact angle θ_0 forms).

If the idealized liquid film profile forms a finite contact angle θ_0 with the plane $z = 0$, then one may use the so-called "membrane convention" of the liquid film and write the equilibrium equation in the form of equation (7),

$$\gamma + \frac{\varkappa}{r_{f_0}} = 2\sigma_0\cos\theta_0 \tag{7}$$

where γ is the film (membrane) tension and $\varkappa$ is the line tension relating to this convention of the film. The strict analytical expression for the line tension $\varkappa$, equation (8),

$$\frac{\varkappa}{r_{f_0}} = \int_{H_f}^{\infty} \frac{\sigma \sin \varphi}{r} \mathrm{d}H - \int_{0}^{\infty} \frac{\sigma_0 \sin \varphi_{id}}{r} \mathrm{d}H_{id} \qquad (8)$$

has been obtained in ref. 2.

The expressions (4) , (5) and (7) constitute the background for the experimental determination of the line tensions τ, τ_B and $\varkappa$ *via* measurement of the contact angles θ_f and θ_0, and also the thickness H_0, as functions of the liquid films radii r_f, r_{f_0} and r_0, respectively, at controlled values of other physicochemical parameters. The relationships between different types of line tensions τ, τ_B and $\varkappa$ follow from the expressions (3), (6) and (8). These expressions make it possible to realize the numerical computation of the corresponding line tensions values.

We have carried out a systematic investigation by the numerical computation method of the effect of different physicochemical parameters on the value and sign of the line tension for the case of common black films.[4] The variable and controlled parameters were: σ_0, k_0, H_f (or H_0), r_f (or r_0), $\Delta\Omega(H_f)$ (or the contact angles θ_f and θ_0), as well as the parameters characterizing the shape of the disjoining pressure isotherm $\Pi(H)$. We have chosen the step-wise isotherm $\Pi(H)$, see Fig. 1(*d*), with the effective parameters Δ_-, Δ_+, Π_- and Π_+, characterizing its shape and satisfying the relationship $\Delta\Omega(H_f) = 2(-_{-} - +_{+}+)$. Unlike the DLVO-type isotherm, the step-wise isotherm $\Pi(H)$ is characterized by more degrees of freedom in varying its shape and consequently gives the opportunity of obtaining detailed and comprehensive information concerning the effect of the $\Pi(H)$-isotherm shape on the line tension value and sign.

The main results of the numerical computations of differently-defined line tensions for the common black films may be summarized in the following conclusions.[4]

(1) The line tensions τ, τ_B and $\varkappa$ may only be negative if the specific interaction grand thermodynamic potential $\Delta\Omega(H_f)$ in the film of thickness H_f is negative, *i.e.* if the contact angles θ_f and θ_0 exist. These line tensions vary on varying the parameters $\Delta\Omega(H_f)$, ΔP and σ_0, and the corresponding dependences have been obtained in ref. 4. For example, the absolute value of the line tension τ increases approximately as a linear function of $|\Delta\Omega(H_f)|$ at constant ΔP and σ_0, being of the order of $\cong 10^{-13}$ N for $(H_f) = -10^{-7}$ J m^{-2}. At the same time, the line tensions τ and τ_B are revealed to be very sensitive to variation of the disjoining pressure isotherm shape, even if $\Delta\Omega(H_f)$ is maintained constant. We may point out that the condition for the constancy of $\Delta\Omega(H_f)$, and consequently of the approximate constancy of the contact angle θ_f, may be satisfied for different values and forms of the areas A^- and A^+ of the $\Pi(H)$-isotherm graph presented in Fig. 1(*c*), provided that the algebraic sum of these areas remains constant in the course of varying other parameters. For example, for the constant contact angle $\theta_f = 1°$ ($P = 25$ Pa, $\sigma_0 = 30$ mJ m^{-2}) we have determined that $\tau \cong -10^{-13}$ N at $_{-} = 1$ nm. On the other hand, if the parameters Δ_+ and Π_+ are kept constant and the parameters Δ_- and Π_- are varied in such a way that $\Delta\Omega(H_f)$ remains constant [see Fig. 1(*d*)], then the absolute value of the line tension increases with increasing the parameter Δ_- as $|\tau| \cong \sqrt{\ }$. We can point out that in the case of the DLVO-type disjoining pressure isotherm when one considers a given liquid film, the variation of the $\Pi(H)$-isotherm shape (for example, in the course of decreasing the height of the coagulation barrier, when one increases the electrolyte concentration in the system) is accompanied by a simultaneous increase in the contact angle θ_f and the effective "width" of the far coagulation minimum Δ_-. Therefore, one cannot differentiate the effect of θ_f and Δ_- on the line tension value. Nevertheless, if one considers another liquid film which is characterized by the greater Hamaker constant, and consequently by the greater "depth" Π_- of this coagulation minimum, then increasing the electolyte concentration as in the first case, one can achieve the same contact angle θ_f but with a more increasingly effective parameter Δ_-. So, according to the results obtained, the absolute value of the negative line tension τ will be greater in the second case in the proportion $|\tau| \cong \sqrt{_{-}}$ for an identical contact angle θ_f.

(2) If the contact angle θ_f is zero, *i.e.* $\Delta\Omega(H_f) = 0$, then for the invariable parameters ΔP and σ_0 the line tension τ being of the order of -10^{-13} N at $_{-} = 10$ nm, $_{-} = -2_{-} - = -10^{-7}$J m^{-2} and $\beta =_{+} /_{-} = 1$, increases by its absolute value as $|\tau| \cong |_{-}|$ at constant β and as $|\tau| \cong \sqrt{\beta}$ at constant $\Delta\Omega_-$.

(3) If the contact angle θ_f does not form, *i.e.* $\Delta\Omega(H_f) > 0$, then the line tension τ_B may be either negative or positive. The line tension τ_B may only be positive if the coagulation minimum on the $\Pi(H)$-isotherm disappears (this occurs in the case of so-called "wetting liquid films"). The appearance of the coagulation minimum on the $\Pi(H)$-isotherm has a drastic effect on the line tension τ_B, leading to a decrease in τ_B and even to the variation of its sign from positive to negative. This tendency increases with decreasing β, $\Delta\Omega(H_f)$ and ΔP with other parameters remaining constant. For example, at $\Delta P = 10$ Pa, $\sigma_o = 30$ mJ m^{-2} and $(H_f) = +10^{-6}$ J m^{-2} the line tension τ_B varies from $\cong +10^{-12}$ N to $\cong -10^{-12}$ N on decreasing the parameter β from 100 to 10.

The direct numerical computation of the differently-defined line tensions of common black (emulsion and foam) films shows that their value and sign are very sensitive to the variation of the shape of the disjoining pressure isotherm. This finding allows us to hope that new, additional information concerning the surface forces in thin liquid films, particularly concerning the $\Pi(H)$-isotherm shape, may be obtained based on the elaborated line tension theory,[1] from an experimental determination of the line tension *via* measurement of the contact angles θ_f or θ_0, and the minimum film thickness H_0 as a function of the thin liquid film size.

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