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Line tension in the thermodynamics of thin liquid films

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ABSTRACT. **The results of theoretical and experimental studies of line tension in thin liquid films and three-phase systems in the last 20 years have been examined and generalised. The main theories of line tension, the reported measurements of its magnitude and sign, and the results of numerical calculations of the line tension on the basis of various thermodynamic models have been analysed. The results of this analysis are discussed in terms of the generalised theory of line tension.**

The bibliography contains 74 references.

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I. Introduction

Line tension manifests itself as a fundamental concept of the thermodynamics of surface phenomena in the description of the mechanical equilibrium and of the energy properties of thin liquid films and of three-phase systems of finite size. The line tension can be defined either as the force $æ(H)$ acting along the boundary line (or the three-phase contact line) of a thin liquid film and tending to shorten (for $æ > 0$) or to lengthen (for $æ < 0$) the contact line, or as the specific excess free energy (referred to unit length of the contact line) of the system, i.e. its grand thermodynamic potential æ, J m^{-1}. Being (by definition) an excess quantity the line tension can take different values, depending on the idealised thermodynamic model chosen to describe the real system including a film boundary or three-phase contact line.

The line tension concept is used in surface chemistry and in colloid chemistry to describe a variety of processes: the heterogeneous formation of a new phase,[1–3] the hydrodynamics of thin liquid films,[4] the breakdown of ordinary and of Newtonian black films,[5,6] bilayer membranes,[7] the adhesion of liquid particles,[8] etc.

According to theoretical calculations[9–15] the absolute numerical value of the line tension should be $10^{-11}-10^{-10}$ N. In spite of these low values the line tension makes a substantial contribution to the free energy and to the mechanical equilibrium of thin liquid films and of three-phase systems in highly dispersed and colloid systems. In particular, the lower work of formation of nuclei of a new phase (100 Å in diameter) on solid or liquid substrates than in homogeneous nucleation has been widely attributed[1,2,14,16–20] to negative line tension effects.

Positive line tension can explain the stability of Newtonian black films towards rupture in the theory of nucleational disintegration.[7,21–24] Positive line tension is associated with the stability of ordinary black films towards rupture or towards spontaneous conversion into Newtonian black films at the contact between air bubbles or microscopic solid spheres and the air–solution interface.[5,25] Allowance for the linear tension is necessary in calculations of the force of adhesion of solid particles to the air–water interface during flotation.[26] The observed dependence of the angle of contact in the region of the film meniscus on the radius of the film (r) is attributed to the existence of an excess two-dimensional pressure $æ/r$ (where r is the radius of curvature of the line of contact).[10,16,27–39]

However, we should note that no generally accepted experimental determinations of the line tension are available at present: data from various laboratories range between -10^{-7} and $+10^{-7}$ N, even for identical systems.[1,15,16,35]

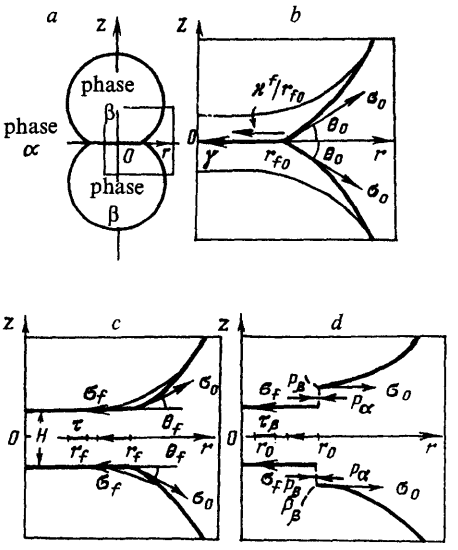


Figure 1. Different thermodynamic models of a thin liquid film used in the definition of the linear tension: *a*, contact of two identical fluid particles (phase β) in a liquid medium (phase α); *b*, membrane model of the liquid film; *c*, model of the liquid film which assumes two interfaces, used for a negative specific free energy of interaction in a film of thickness H_f; *d*, model of the liquid film for a positive specific free energy of interaction in a film of thickness H_f.

An analysis of experimental and of theoretical studies of line tension has shown[40–42] that different thermodynamic models are often used to define the line tension, and that this causes problems in comparing numerical values of æ.

The aim of this review is to analyse published work on the line tension problem in the thermodynamics of thin liquid films on the basis of the generalised theory of line tension developed by the writer.[40,42]

II. Different definitions of the line tension

All the reports on the line tension problem known to the writer can be arbitrarily divided into two groups. To the first we assign studies which have relied on the membrane approach to the thermodynamics of thin liquid films formulated by Deryagin and his co-workers.[43,44] In this approach the thermodynamic model of the thin liquid film is the interface (as defined by Gibbs,[45] i.e. a membrane of zero thickness) with respect to which the excess thermodynamic quantities are calculated (Fig. 1*b*).

Studies in which the film is treated as a layer of finite thickness H_f, bounded by two interfaces, are classified in the second group (Fig. 1*c*). This approach was proposed by Rusanov,[46–48] and has been further developed by the present writer and by others.[41,42,50–56]

In the membrane approach the condition of mechanical equilibrium of a symmetrical curved film of radius r_{f0} (see Fig. 1*b*) is defined as

$$\gamma + -\frac{æ^f}{r_{f0}} = 2\sigma_0 \cos\theta_0, \qquad (1)$$

where γ is the tension of the film, θ_0 is the contact angle corresponding to the radius of the film r_{f0}, σ_0 is the interfacial tension at the interface with the bulk phases, $æ^f$ is the line tension (in the symbols of Scheludko, et al.[1]). The term $æ^f/r_{f0}$ has the dimensions of N m^{-1} and can be interpreted as the two-dimensional pressure created by the curvature of the contact line (by analogy with the capillary pressure P_c created by the curvature of the interfacial surface). If the line of contact is straight (i.e. for $r_{f0}\to\infty$) the equilibrium equation of the film (or membrane) becomes

$$\gamma = 2\sigma_0 \cos\theta_{0\infty}, \qquad (2)$$

where $\theta_{0\infty}$ is the angle of contact corresponding to $r_{f0}\to\infty$. Ignoring the dependence of the film tension γ on its radius r_{f0} we obtain from Eqns. (1) and (2) the expression

$$æ^f = 2r_{f0}\sigma_0 (\cos\theta_0 - \cos\theta_{0\infty}), \qquad (3)$$

which is used as a basis for the experimental determination of the line tension $æ^f$ from the $\theta_0(r_{f0})$ relationship.

The line tension $æ^f$ defined in terms of the membrane approach is used, for example, by Scheludko, et al.[15,16] and by Churaev, et al.[57]

In the method of two interfaces the mechanical equilibrium condition of a symmetrical curved film is written (see Fig. 1*c*) as:[49]

$$2\sigma_f + \frac{\tau}{r_f} = 2\sigma_0 \cos\theta_f, \qquad (4)$$

where σ_f is the interfacial tension in a film of thickness H_f, which differs from the interfacial tension σ_0 and is related to it by the expression

$$2\sigma_f = 2\sigma_0 + \Delta\Omega(H_f), \qquad (5)$$

where $\Delta\Omega(H_f)$ is the specific free energy of the interaction between the interfaces in a film of thickness H_f, so that the condition for a finite angle of contact is $\Delta\Omega(H_f) < 0$; θ_f and r_f are the angle of contact and the radius of the film (note that $\theta_f \neq \theta_0$ and $r_f \neq r_{f0}$ for $H_f \neq 0$); τ is the line tension (in de Feijter and Vrij's symbols[49]).

If the thickness of the film H_f is unaffected by changes in the radius r_f we can write the expression [analogous to Eqn. (3)]

$$\tau = 2r_f\sigma_0 (\cos\theta_f - \cos\theta_{f\infty}), \qquad (6)$$

where $\theta_{f\infty}$ is the angle of contact for cylindrical films (i.e. for $r_f\to\infty$), which satisfies the condition

$$\sigma_f = \sigma_0 \cos\theta_f. \qquad (7)$$

Eqn. (6) is the basis of the experimental determination of the line tension τ from measurements of the $\theta_f(r_f)$ dependence.

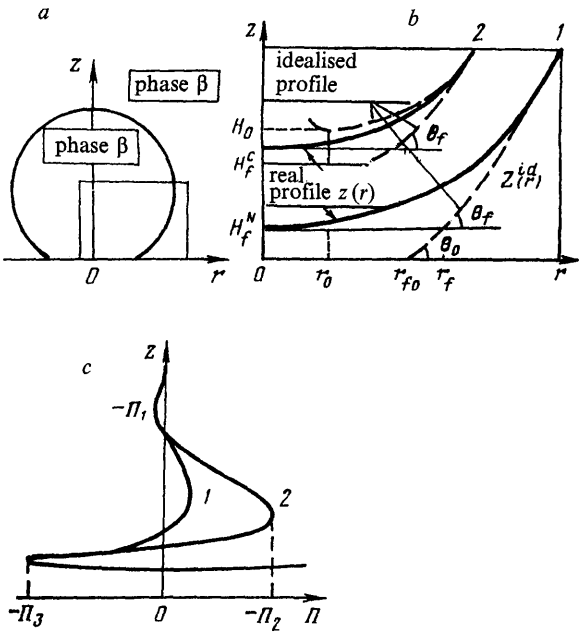


Figure 2. Definition of the parameters which characterise the profile of thin liquid films (see text).

We should stress the fact that the line tensions $æ^f$ and τ are different quantities, defined in terms of different thermodynamic models. As has been pointed out,[40,42] the difference between $æ^f/r_{f0}$ and τ/r_f is of the order of $\Delta P H_f$ (where $\Delta P = P_\beta - P_\alpha$, and P_α and

P_β are the hydrostatic pressures in the phases α and β respectively (see Fig. 1*a*), corresponding to $\sim 5 \times 10^{-6}$ N m^{-1} with $\Delta P \simeq 100$ Pa for films of thickness $H_f \sim 50$ nm thick. The error caused by identifying τ with $æ^f$ is $\sim 5 \times 10^{-10}$ N for films of radius $r_f \cong 100$ μm, and the relative error of the line tension $\tau \cong 10^{-12}$ N[49] is of the order of $\Delta P H_f/\tau = 500$. Thus failing to distinguish between the line tensions τ and $æ^f$ (as is often done in published work) can lead to serious errors in the determination of their numerical values for $H_f \neq 0$: the greater the product $\Delta P H_f$, the greater is the error.

It should be noted that the contact angles θ_f or θ_0 are determined by the following procedure (Fig. 2*a*). Since the real profile $z(r)$ of the film in the transition region of the meniscus can seldom be determined experimentally to the required precision (because of the very small size of this region) the idealised profile $z_{id}(r)$ is usually employed. This is by definition identical to the real profile $z(r)$ in the region of the main bulk of the meniscus, where the disjoining pressure is zero (Fig. 2*b*), and it can be extrapolated to the transition region of the film on the assumption that the interfaces do not interact in that region. The idealised profile of the film $z_{id}(r)$ is determined with high precision by an interference method (called the topographic method[58]). We know that the following relationship applies[49] for negative values of the specific free energy of interaction $\Delta\Omega(H_f)$ in a film of thickness H_f:

$$\Delta\Omega(H_f) = \int_{H_f}^{\infty} \Pi(H)dH, \tag{8}$$

and the idealised profile $z_{id}(r)$ must intersect the plane $z = z_f = H_f/2$, forming an angle of contact θ_f such that the condition (7) applies for cylindrical films. On the other hand if $\Delta\Omega(H_f)$ is negative and has a high absolute value the idealised profile $z_{id}(r)$ can also intersect the plane $z = 0$ (with a contact angle θ_0), and for cylindrical films the relationship (2) applies.

When $\Delta\Omega(H_f) > 0$ the idealised profile $z_{id}(r)$ passes above the plane $z = z_f = H_f/2$ (see Fig. 2*b*), and is characterised by a minimum ($z = H_0/2$) at $r = r_0$.[59–61] If the contact line is straight, i.e. if $r_0 \to \infty$, we can write

$$\Delta\Omega(H_f) = \Delta P(H_{0\infty} - H_f), \tag{9}$$

where $H_{0\infty} = 2z_{0\infty}$, and $z_{0\infty}$ is the minimum in the profile of the film for $r_0 \to \infty$.

The expression (9) was first used to determine experimentally the specific free energy of interaction $\Delta\Omega(H_f)$ in water films stabilised by adsorbed layers of polyvinyl alcohol,[62] and it was shown that under these conditions $\Delta\Omega(H_f) = +2 \times 10^{-7}$ J m^{-2}. The expression (9) was also used[63] in an experimental determination of $\Delta\Omega(H_f)$ for wetting films of aqueous solutions of electrolytes on quartz. For these films the result was $\Delta\Omega(H_f) = +2 \times 10^{-5}$ J m^{-2}.

The line tension τ_B for films with a positive $\Delta\Omega(H_f)$ was first determined by the present writer[55,64,65] as

$$\Delta\Omega(H_f) + \frac{\tau_B}{r_0} = \Delta P(H_0 - H_f), \tag{10}$$

or, using (5),

$$2\sigma_f + \frac{\tau_B}{r_0} = 2\sigma_0 + \Delta P(H_0 - H_f). \tag{11}$$

Eqn. (10) reduces to (9) for $r_0 \to \infty$. If the film thickness H_f and the difference in hydrostatic pressures stay constant, $\Delta\Omega(H_f)$ is also unchanged, and by combining (9) with (10) we obtain

$$\tau_B = r_0 \Delta P[H_0(r_0) - H_{0\infty}], \tag{12}$$

where $H_0(r_0)$ is the minimum thickness of the idealised profile of a film of radius r_0. Eqn. (12) can be used as the basis of the experimental determination of the line tension τ_B from the $H_0(r_0)$ dependence, but only under conditions of constant H_f and ΔP for changes in r_0.

In Fig. 1*c* we show a scheme which illustrates the condition of mechanical equilibrium of liquid films for a positive value of $\Delta\Omega(H_f)$.

These considerations, and the formulae for the line tensions $æ^f$, τ, and τ_B of symmetrical liquid films, can be extended to asymmetrical liquid films and three-phase systems (Fig. 3).

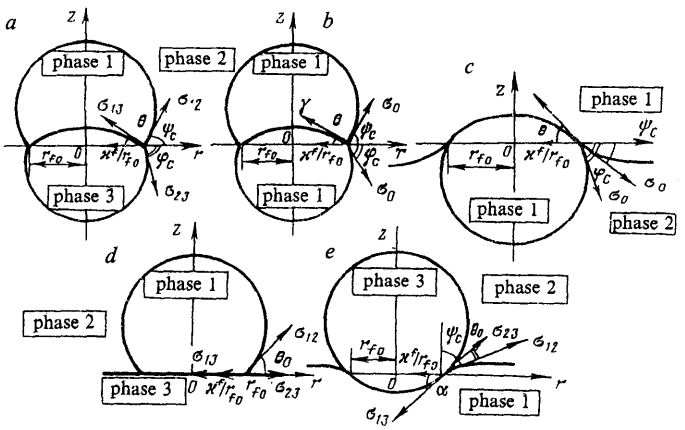


Figure 3. Definition of the line tension in asymmetric liquid films (see text).

At the contact of three fluid (liquid or gaseous) phases (Fig. 3*a*) the condition of mechanical equilibrium is

$$\sigma_{13}\cos\theta + \frac{æ^f}{r_{f0}} = \sigma_{12}\cos\psi_c + \sigma_{23}\cos\varphi_c. \tag{13}$$

If the inter-phase tensions σ_{12}, σ_{13}, and σ_{23} are known the line tension $æ^f$ can be determined by measuring the contact angles θ, ψ_c, and φ_c and the radius of the contact line r_{f0}.[18,31,39] If the interfacial tension σ_{13} is not known we must combine Eqn. (13) with the additional equilibrium equation

$$\sigma_{13}\sin\theta = \sigma_{23}\sin\varphi_c - \sigma_{12}\sin\psi_c. \tag{14}$$

When the phases 1 and 3 are identical we have $\sigma_{12} = \sigma_{23} = \sigma_0$, and $\sigma_{13} = \gamma$ (Fig. 3*b*), leading to a system of equations which describe the mechanical equilibrium of the phases and can be used to determine $æ^f$:[5,34,35]

$$\gamma\cos\theta_0 + \frac{æ^f}{r_{f0}} = \sigma_0(\cos\varphi_c + \cos\psi_c), \qquad (13')$$

$$\gamma\sin\theta_0 = \sigma_0(\sin\varphi_c - \sin\psi_c). \qquad (14')$$

If one of the phases is solid (Figs. 3*d* and 3*e*) the interfacial tensions σ_{13} and σ_{23} are unknown, and the condition of mechanical equilibrium of the three-phase line of contact of radius r_{f0} is written as follows (see Fig. 3*d* for a flat solid surface):

$$\sigma_{13} - \sigma_{23} + \frac{æ^f}{r_{f0}} = \sigma_{12}\cos\theta_0. \qquad (15)$$

On the assumption that the difference $\Delta\sigma = \sigma_{13} - \sigma_{23}$ stays constant during changes in the radius r_{f0} of the contact line we can write an expression analogous to (3):

$$æ^f = r_{f0}\sigma_{12}(\cos\theta_0 - \cos\theta_{0\infty}), \qquad (16)$$

which allows us to determine the line tension $æ^f$ from measurements of the $\theta_0(r_{f0})$ dependence.[32,38] In the case of a spherical solid surface (Fig. 3*e*) the mechanical equilibrium condition is

$$\sigma_{13} - \sigma_{23} + \frac{æ^f}{r_{f0}}\cos\alpha = \sigma_{12}\cos\theta_0. \qquad (15')$$

All these determinations of the line tension are based on the representation of the line tension as a force which stretches or compresses the line of contact. This approach to the determination of the line tension can nominally be called dynamic.

Another approach (arbitrarily termed the energy approach) depicts the line tension as the excess free energy æ referred to unit length of the contact line.[12,15,18,20] All these studies rely on the membrane model of liquid films and of three-phase systems. In particular, Rowlinson and Widom[12] determined the line tension æ by replacing the real system [including the three-phase contact line (Fig. 4*a*)], by an idealised model in which the surfaces A_{12}^{id}, A_{23}^{id}, and A_{13}^{id} have a constant average curvature and constant interfacial tensions σ_{12}, σ_{23}, and σ_{13} (up to the intersection of the surfaces with the contact line). Under these conditions the free energy (grand thermodynamic potential) of the idealised system Ω^{id} can be written

$$\Omega^{id} = -P_1V_1^{id} - P_2V_2^{id} - P_3V_3^{id} + \sigma_{12}A_{12}^{id} + \sigma_{23}A_{23}^{id} + \sigma_{13}A_{13}^{id} + æL, \qquad (17)$$

where L is the length of the contact line. The line tension æ is found from the condition of energy equivalence of the real and the idealised system, i.e. from the equality $\Omega = \Omega^{id}$, where Ω is the free energy of the real system, assumed to be known.

For the contact of a liquid drop (phase 1) with a solid surface (phase 3) in a gaseous medium (phase 2) the expression for the work of formation of the drop (assuming heterogeneous nucleation of water drops on a hydrophobic surface) can be written[1,15,20,66,67] (in our symbols) as

$$-W = \Delta\Omega = -\Delta PV_1^{id} + \sigma_{12}A_{12}^{id} + \Delta\sigma\pi r_{f0}^2 + 2\pi r_{f0}æ, \qquad (18)$$

where $\Delta\sigma = \sigma_{13} - \sigma_{23} - \sigma_{12}$; $\Delta P = P_1 - P_2$; V_1^{id} and A_{12}^{id} are the volume and surface area of the drop (for the idealised model of the drop, see above). All these workers determine the line tension æ on the basis of measurements of the work of heterogeneous nucleation of water drops from a supersaturated vapour onto hydrophobic (liquid or solid) substrates.

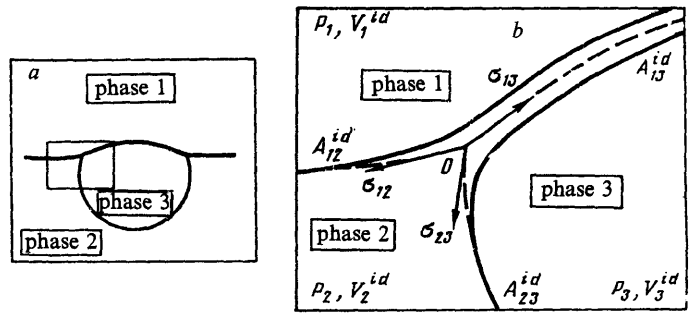


Figure 4. Definition of the line tension as the specific excess free energy of the system (referred to unit length of the contact line) which includes a thin liquid film (see text).

III. Experimental determination of the line tension

The results of experimental determinations of the line tension $æ^f$ are shown in Table 1.

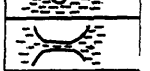
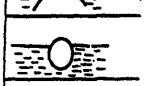
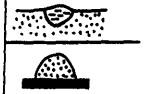
The lack of correlation between the magnitude and sign of the line tension (on the one hand) and other physicochemical parameters such as the angle of contact (on the other hand) is noteworthy. Furthermore the scatter of the $æ^f$ values measured by different workers for identical systems is 3–4 orders of magnitude.[33–35] Whereas Gaydos and Neumann,[38] and also Wallage and Schürch,[39] obtained positive values by measuring the dependence of the contact angle θ_0 on the radius of the contact line r_{f0} (i.e. they noted an increase in θ_0 upon decreasing r_{f0}), Good and Koo[32] found the opposite effect (i.e. they obtained a negative value of the line tension $æ^f$). However, the latter workers[32] attributed this $\theta_0(r_{f0})$ dependence to the roughness of their solid surface, and they called the measured $æ^f$ a pseudo-line tension.

The results of experimental determinations of the line tension $æ^f$ have led some workers[14–16,68] to the following conclusions on the effect of various physicochemical factors on $æ^f$.

For a relatively small coagulation barrier Π_2 (see curve *1* of Fig. 2*c*) very thin Newtonian black films (bilayer membranes) can be formed, with a thickness H_f^N less than 10 nm (curve *1* of Fig. 2*b*) and contact angles $\theta_0 \cong 10°$. These films are formed, for example, at the contact between air bubbles in an aqueous solution of sodium dodecyl sulphate containing NaCl ($c_{NaCl} > 0.36$ mol dm^{-3}).[5,26,34,36,68] In these films the line tension $æ^f$ is negative and equals $\sim 10^{-9}$ N. Upon raising the coagulation barrier Π_2 (curve *2* of Fig. 2*c*) by lowering the concentration of the NaCl electrolyte the contact angle θ_0 monotonically decreases, i.e. the negative specific free energy of the interaction $\Delta\Omega(H_f^N)$ decreases in absolute value. For example, for $c_{NaCl} = 0.32$ mol dm^{-3} the contact

angle is ~8°, and the line tension changes sign ($æ^f = +10^{-9}$ N) [5] (see Table 1).

Table 1. Results of experimental determinations of the magnitude and sign of the line tension æ.

æ, N	System	Experimental scheme	θ_0, deg	Refs.
$\pm 6\times10^{-8}$	Oil/aniline/water		> 10	[31]
-10^{-6} to -10^{-5}	Air/water/solid surface		> 10	[32]
$+1.25\times10^{-10}$	Air/solid surface/water		~ 25	[25]
$+10^{-10}$ to 10^{-9}	Air/water/air		~ 8	[5]
-1.7×10^{-11}	Air/water/air		< 1	[33]
-10^{-9} to 10^{-9}	ditto		~ 9	[34—36]
-1.9×10^{-10}	Gas/water/hexadecane		~ 50	[1, 20]
$+3\times10^{-6}$	Air/oil/Teflon		40—50	[38]
$+2.4\times10^{-8}$	Water/dibutyl phthalate/fluorocarbon		30—150	[39]

With an even higher coagulation barrier Π_2 (curve *2* of Fig. 2*c*), when the capillary pressure P_c in the film is less than Π_2, relatively thick ordinary black films are formed (of thickness $H_f^c > 10$ nm, see curve *2* of Fig. 2*b*). If $\Delta\Omega(H_f^c)$ is negative under these conditions the contact angle θ_f is formed. If the absolute value of $\Delta\Omega(H_f^c)$ is high enough we can find the contact angle θ_0, as in curve *1* of Fig. 2*b*. According to Kolarov and Zorin's measurements[33] the contact angle for $c_{NaCl} = 0.1$ mol dm^{-3} is $\theta_0 < 0.5°$. For ordinary black films Platikanov and Nedyalkov[68] found a positive value of $æ^f$, which is incompatible with Kolarov and Zorin's value:[33] a negative line tension $æ^f = -1.7 \times 10^{-11}$ N. This value of $æ^f$ agrees well with the numerical values of the line tension τ reported[49] for ordinary black films.

Let us examine some other methods of determining the line tension $æ^f$ experimentally.

Torza and Mason[31] measured the angles of contact formed by drops of silicone oil (phase 1) and aniline (phase 3) in water (phase 2) (see Fig. 3*a*), and calculated the line tension $æ^f$ by formula (13). The results lay in the range of $\pm 6 \times 10^{-8}$ N, denoting that the precision of the method was inadequate.

In the experiment reported by Mingins and Scheludko[25] glass microspheres (phase 1) of various diameters (< 50 μm) treated with an aqueous 0.01 M solution of octyltrimethylammonium bromide fell freely in water (phase 2) towards a water—air (phase 3) interface (see Fig. 3*e*). Spheres with a radius smaller than some critical value R_c formed ordinary black films with a relatively large thickness H_f^c (see curve *2* of Fig. 2*b*) because their mass was insufficient to overcome the coagulation barrier Π_2. According to those workers[25] a positive line tension $æ^f$ (tending to shorten the contact line) prevents the rupture of the liquid water film. Microspheres with a radius greater than R_c can overcome the line tension and fracture the black film, as can be seen in the microscope. The line tension was calculated by the formula[16,25]

$$æ^f = \frac{(2\rho g\sigma)^{1/2}}{3}(1-\cos\theta_0)R_c^2, \tag{19}$$

which gives $R = 20$ μm and $æ^f = +1.25 \times 10^{-10}$ N for the known values $\theta_0 = 25°$, $\sigma = 70$ mJ m^{-2}, and $\rho = 1.48$ g cm^{-3}.

In the experiment reported by Platikanov, et al.[5] a similar method[25] was used, but the glass spheres were replaced by microscopic gas bubbles (phase 3) which floated in an aqueous solution of sodium dodecyl sulphate (phase 2) and came into contact with a water—air (phase 1) interface (Fig. 3*c*). The diffusion of gas through the film decreased the radius of the bubble but increased the capillary pressure P_c, and for $P_c > \Pi_2$ (see Fig. 2*c*) the ordinary black films of thickness H_f^c (curve *2* of Fig. 2*b*) which had been formed initially were spontaneously converted into thin Newtonian black films of thickness H_f^N (curve *1* of Fig. 2*b*), as noted in the microscope by the sudden change in reflectance (the grey colour being replaced by black) and by the increase in the radius of the bubbles.

As reported,[5,25] the conversion of ordinary black films into Newtonian black films opposes the positive line tension tending to shorten the contact line and thus to suppress the increase in area of the film. Under these conditions the expression for the line tension $æ^f$ obtained from the mechanical equilibrium condition of the bubble becomes (in our symbols)

$$æ^f = 2\sqrt{\frac{2}{3}\rho g\sigma_0}(1-\cos\theta_{0\infty})R_{cr}^2, \tag{20}$$

where $\theta_{0\infty}$ is the angle of contact corresponding to infinitely large films (i.e. to a straight contact line), and R_{cr} is the critical radius of the gas bubble corresponding to the rupture of the ordinary black film.

The writer has pointed out[40] that this interpretation of the role of line tension in the stabilisation of ordinary black films is over-simplified and, in general, incorrect, because the same effect (i.e. the suppression of the increase in area of the film) is produced by negative line tension: it is the effect of bulk and surface forces contributing to the free energy, and not of line forces only, as could have been thought at first sight. An alternative explanation of the results, based on the theory of adhesion of liquid particles, has been suggested.[8]

Let us examine the results of measurements of the line tension æ through measurements of the work of heterogeneous nucleation of a water phase from the supersaturated vapour onto hydrophobic substrates.[1,15,20,66,67] The authors' interpretation of the results is based on the following arguments.

From measurements of the critical supersaturation S_0 of water vapour in the chamber the radius of curvature R of the surface of the nuclei is determined by the Thompson—Gibbs formula

$$P_c = \frac{kT}{\bar{v}}\ln S_0, \tag{21}$$

where $P_c = 2\sigma_0/R$ is the capillary pressure in the water nucleus, $\bar{v}$ is the molar volume of water, and k is Boltzmann's constant. Then, on the assumption that the heterogeneous creation of a new phase on reaching the critical supersaturation S_0 of water vapour is barrierless, i.e. that the work of formation W of the nuclei is zero, Eqn. (18) is re-written (for a solid hydrophobic surface, see Fig. 3*d*) as:

$$0 = W = \frac{2}{3}\sigma_{12}\pi R^2(1+\cos^3\theta_0) + \pi r_{f0}^2\Delta\sigma + 2\pi r_{f0}\text{æ}, \qquad (22)$$

where $r_{f0} = R\sin\theta_0$ is the radius of the contact between the nucleus and the solid substrate. Eqn. (22) establishes the relationship between the line tension æ and the parameters θ_0 (the angle of contact), R (the radius of the nucleus), and also σ_{12} and $\Delta\sigma$. Then, by using (15) (which relates the line tension æ^f to the contact angle θ_0) we can solve Eqn. (22) and obtain an expression for the line tension æ on the assumption that $\text{æ} = \text{æ}^f$.

The line tension can be obtained in a similar way from data on the heterogeneous nucleation on a liquid hydrophobic substrate (Fig. 4*a*).

Scheludko, et al.[1] give the results of one experiment ($S_0 = 41.9\%$ and $R \cong 3$ nm), and also the line tension calculated from them ($\text{æ} = -0.8 \times 10^{-10}$ N) by using the parameters $\sigma_{12} = 24.1$ mJ m^{-2}, $\sigma_{23} = 53.2$ mJ m^{-2}, $\sigma_{13} = 73$ mJ m^{-2}, $\theta_{0\infty} = 28.93°$, and $\varphi_{c\infty} = 41.59°$ (see Fig. 3*c*).

Scheludko, et al.[1] believe that ignoring the negative line tension (which lowers the work of heterogeneous nucleation) would make the critical supersaturation very much higher: for the example given it would be $S_0 = 105\%$, i.e. 2.5 times higher.

The reported line tension ($\text{æ} = -0.8 \times 10^{-10}$ N), and also the suggestion that this method can be used to determine the line tension, have attracted critical comments by the present writer.[40,42] The main objections to the determination of the line tension by this method are the following.

1. The precision claimed for the determination of the angles of contact $\theta_{0\infty}$ and $\varphi_{c\infty}$ is unacceptably high. The error in the measurement of these angles is about 0.5° (the uncertainty in the sessile drop method), corresponding to an error in the determination of the line tension of the order of $\Delta\text{æ} \simeq \pm 10^{-10}$ N, i.e. of the same order as the measured quantity $\text{æ} = -0.8 \times 10^{-10}$ N.

2. For drops with a diameter of 3 nm the interfacial tension σ_{12}, σ_{23}, and σ_{13} differ from the corresponding macroscopic values since the drop size is comparable with the radius of action of the surface forces (molecular and ionic/electrostatic). In this case the drop cannot be treated as a substance in the thermodynamic sense, and the replacement of the interfacial tensions by their macroscopic values is equivalent to ascribing bulk and surface excess thermodynamic parameters to the contact line markedly different from the corresponding values for the reference phase 3 (see Fig. 4). In particular, the decrease in the critical supersaturation for nucleation S_0 can be more convincingly attributed to the decreased interfacial tension of droplets with a diameter as small as $R = 3$ nm than to the effect of the line tension.

In the case of wetting films only one attempt to determine experimentally the line tension τ_B has so far been reported [see Eqn. (11)].[63] Those workers used Eqn. (12) to calculate the line tension τ_B, and obtained $\tau_B = \pm 3 \times 10^{-11}$ N from the experimental $H_0(r_0)$ dependence (see Fig. 3*d*) by assuming a constant film thickness H_f (h_0 in Zorin's symbols[63]). We should stress that since the film thicknesses H_0 and H_f can be measured only to within ± 5 nm as a function of the radius r_0, and since H_f could decrease when r_0 increases (i.e. when the difference in hydrostatic pressure ΔP increases), Eqn. (12) should be replaced by

$$\frac{\tau_B}{r_0} = \Delta P[H_0(r_0) - H_0(\infty)] - 2\Delta\sigma_f(r_0), \qquad (23)$$

where $\Delta\sigma_f(r_0) = \sigma_f(r_0) - \sigma_f(\infty)$, and the following approximate relation applies;

$$2\Delta\sigma_f(r_0) \simeq \int_{H_f(r_0)}^{H_f(\infty)} \Pi(H)dH \simeq \Delta P[H_f(r_0) - H_f(\infty)]. \qquad (24)$$

We shall use Zorin's experimental results[63] to calculate the error in the measurement of the line tension ($\Delta\tau_\beta$) due to the failure to allow for the possible change in the actual thickness of the film ($\Delta H \simeq \pm 5$ nm). Assuming $\Delta P \simeq 150$ Pa we obtain, for a film of radius $r_0 = 50$ μm,

$$\Delta\tau_B \simeq r_0\Delta\sigma_f(r_0) \simeq (50\times10^{-6})\times 1.50\times(\pm 5\times10^{-9}) = \pm 3.7\times10^{-11}\text{H}.$$

Evidently, the error in the determination of the line tension is of the same order as the measured quantity.

IV. Theories of the line tension

We shall now examine existing theories of the line tension, which give a relationship between the line tension and physicochemical parameters such as the radius r and the thickness H of the liquid film, the capillary pressure P_c, and the interfacial tension σ_0, and also parameters which characterise the form of the disjoining pressure isotherm $\Pi(H)$ as a function of the local thickness of the film (H).

An analytical expression for the line tension τ [see Eqn. (4)] was first proposed by de Feijter and Vrij,[49] who used a thermodynamic model of the film based on the presence of two interfaces (Fig. 2*c*). They discussed the mechanical equilibrium of the element of volume *ABCDEFGL* of a symmetrical curved liquid film (Fig. 5*a*), and they wrote the fundamental equation for the equilibrium of this film by equating to zero the projection on the $0r$ axis of the resultant of all the surface and bulk forces acting on the element of volume:

$$\frac{d}{dr} = [2\sigma(H)r\cos\varphi(H) + \Delta PHr] - [2\frac{\sigma(H)}{\cos\varphi(H)} + \Delta PH] = 0, \qquad (25)$$

where $\sigma(H)$ is the local interfacial tension in a film of thickness H; $\varphi(H)$ is the local value of the angle of contact; $\Delta P = P_\beta - P_\alpha$ is the difference in hydrostatic pressure between the α and β phases respectively. Then, by invoking the mechanical equivalence (in the sense of mechanical equilibrium) of the real film (Fig. 5*b*) and of its idealised model (Fig. 5*c*) they arrived at Eqn. (4) and the following analytical expression for the line tension (see Fig. 2*c*):

$$\tau = \int_0^R \left[\frac{2\sigma(H)}{\cos\varphi(H)} + \Delta PH\right]dr - \int_{r_f}^R \left[\frac{2\sigma_0}{\cos\varphi_{id}(H)} + \Delta PH_{id}\right]dr_{id} -$$

$$-(2\sigma_f + \Delta PH_f)r_f, \qquad (26)$$

where R is the distance along the 0_r axis corresponding to a zero disjoining pressure, i.e. $\sigma(H) = \sigma_0$, where σ_0 is the interfacial tension of the noninteracting surfaces and *id* indicates a quantity

relating to the idealised profile. As we have pointed out,[41,42,55] Eqn. (26) (obtained[49] for curved films, i.e. for a curved contact line) is incorrect, though it approaches asymptotically the correct expression for a straight contact line (for $r_f \to \infty$):

$$\tau = \int_{H_f}^{\infty} \sigma(H)\sin\varphi(H)dH - \int_{H_f}^{\infty} \sigma_0 \sin\varphi_{id}(H)dH_{id}. \qquad (27)$$

For the case of a straight contact line the following expression relating the line tension τ to the specific free energy of the interaction $|\Delta\Omega(H_f)|$ [see Eqn. (8) in the limit of $\Delta\Omega(H_f) \ll \sigma_0$]:

$$\tau = \sigma_0^{1/2}\left\{\int_{H_f}^{\infty}\left[\Delta\Omega(H) - \Delta\Omega(H_f) + \Delta P(H - H_f)\right]^{1/2} dH - \right.$$
$$\left. - \int_{H_f}^{\infty}\left[-\Delta\Omega(H_f) + \Delta P(H_{id} - H_f)\right]^{1/2} dH_{id}\right\}, \qquad (28)$$

or for very small contact angles θ_f (ignoring the terms containing ΔP)

$$\tau = \sigma_0^{1/2}\left\{\int_{H_f}^{\infty}\left[\Delta\Omega(H) - \Delta\Omega(H_f)\right]^{1/2} - \left[-\Delta\Omega(H_f)\right]^{1/2}\right\}dH. \qquad (29)$$

The expressions (27) and (28) were used[49] for numerical calculations of the line tension in ordinary and in Newtonian black films.

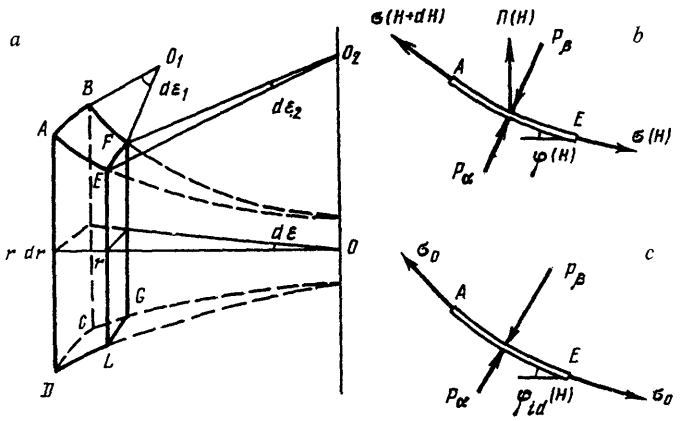


Figure 5. Formulation of the fundamental equilibrium equation of a thin liquid film [Eqn. (26)]: *a*, element of volume of a curved liquid film; *b*, equilibrium of the film surface in the transition region; *c*, equilibrium of the film surface in the Plateau region.

An approximate expression for τ, similar to Eqn. (26), was later obtained by other workers.[15,69,70]

The exact analytical expression (26) for the line tension τ was first obtained by Babak[55,64,65] in terms of the thermodynamics of the transition region of thin liquid films.[41] In particular, he showed[55] that the mechanical equilibrium of an element of volume of a thin liquid film (see Fig. 5*a*), like the element considered by de Feijter and Vrij,[49] is described by the system of equations:

$$\sigma(H)k(H) + \Pi(H)\cos\varphi(H) - \Delta P = 0, \qquad (30)$$

$$\Pi(H) = -\left.\frac{\partial\sigma(H)}{\partial H}\right|_{T,\mu_i,\Lambda} \qquad (31)$$

where $\Pi(H)$ is the disjoining pressure in the film as a function of the local thickness H, and $k(H)$ is the mean curvature of the film surface, which can be written (for a curved film)

$$k(H) = \frac{d\sin\varphi(H)}{dr} + \frac{\sin\varphi(H)}{r}. \qquad (32)$$

The Gibbs–Duhem equation (31) describes the equilibrium of the film surface in the direction of the tangent to this surface, since it can be rewritten [allowing for the fact that $dH = dl/2\sin\varphi(H)$, where dl is an element of length of the tangent] as

$$\Pi(H)\sin\varphi(H)dl = -2d\sigma(H). \qquad (33)$$

Eqn. (30) describes the equilibrium of the film surface in the direction normal to the surface (see Fig. 5*a*) in the presence of a gradient of interfacial tension in the transition region of the film.

Eqn. (30) reduces to the well known equation for the mechanical equilibrium of a plane-parallel film of thickness H_f (which is also a definition of the disjoining pressure, proposed by Deryagin and Churaev[72]):

$$\Pi(H_f) = \Delta P = P_\beta - P_\alpha, \qquad (34)$$

allowing for the fact that in this region $k(H_f) = 0$ and $\varphi(H_f) = 0$, and that in the Laplace equation for noninteracting tension surfaces

$$\sigma_0 k_0 = \Delta P = P_\beta - P_\alpha, \qquad (35)$$

since $\sigma(H) = \sigma_0$ and $\Pi(H) = 0$.

The exact analytical expression for the line tension τ_d is[55,64,65]

$$\tau_d = r_f\left\{\int_{H_f}^{\infty}\frac{\sigma(H)\sin\varphi(H)}{r}dH - \int_{H_f}^{\infty}\frac{\sigma_0\sin\varphi_{id}(H)}{r_{id}}dH_{id}\right\}, \qquad (36)$$

where τ_d is the dynamic line tension (see Fig. 2*c*), obtained from the mechanical equilibrium condition of the element of volume of the liquid film (see Fig. 5*a*), in contrast to the energy line tension τ_e which appears in Eqn. (17) for the free energy of the film.

The expression for τ_d was obtained as follows. The integration of the fundamental mechanical equilibrium equation (30) over the thickness $H(r)$ of the real profile between the local value H and the value H_p in the Plateau region of the meniscus [where $\varphi(H_p) = \varphi_p$ and $\Pi(H_p) = 0$] leads to an invariant expression, independent of the local thickness of the film:

$$2\sigma_0\cos\varphi(H) + \Delta PH + \Delta\Omega(H) + \tau_0(H) +$$
$$+ \int_{H}^{H_p}\frac{\sigma(H)\sin\varphi(H)}{r}dH = 2\sigma_0\cos\varphi_p + \Delta PH_p, \qquad (37)$$

where the function

$$\tau_0(H)=\int_H^{\infty}\left[\frac{1}{2}\Delta\Omega(H)\frac{d\sin\varphi(H)}{dr}-\Pi(H)(1-\cos\varphi(H))\right]dH, \quad (38)$$

is identically equal to zero.[42]

Similarly, the integration of the Laplace equation (35) (see Fig. 5*b*) over the thickness of the idealised profile $H_{id}(r)$ between the limits H_{id} and H_p also gives an invariant, independent of the thickness of the idealised profile:

$$2\sigma_0\cos\varphi_{id}(H)+\Delta PH_{id}+\int_{H_{id}}^{H_P}\frac{\sigma_0\sin\varphi_{id}(H)}{r_{id}}dH_{id}=2\sigma_0\cos\varphi_P+\Delta PH_P. \quad (39)$$

By equating the invariants (37) and (39) we obtain a fundamental equation which was first proposed by the present writer:[55,64]

$$2\sigma_0\cos\varphi(H)+\Delta PH+\Delta\Omega(H)+\int_H^{H_P}\frac{\sigma(H)\sin\varphi(H)}{r}dH=$$

$$=2\sigma_0\cos\varphi_{id}(H)+\Delta PH_{id}+\int_{H_{id}}^{H_P}\frac{\sigma_0\sin\varphi_{id}(H)}{r_{id}}dH_{id}, \quad (40)$$

and which is valid for any values of $H(r)$ and $H_{id}(r)$ in the range of interest. This equation is universal, and it can be used to obtain all the known film equilibrium equations which have been used as the basis of the various thermodynamic models as well as the corresponding expressions for the line tensions. We shall prove this assertion with a few examples.

By inserting $H = H_f$ and $\varphi(H_f) = 0$ into the left-hand side of Eqn. (40), and $H_{id} = H_f$ and $\varphi_{id}(H_f) = \theta_f$ into the right-hand side (see Fig. 2*c*), and using the equality $\Delta\Omega(H_f) = 2\sigma_f - 2\sigma_0$, we obtain

$$2\sigma_f+\frac{\tau_d}{r_f}=2\sigma_0\cos\theta_f,$$

which is equivalent to Eqn. (4) and defines the equilibrium of the film in terms of the model of two interfaces, while the line tension τ_d is given by the exact analytical expression (36).

On the other hand if we use the membrane model of the film (see Fig. 2*b*) we must insert into the left-hand side $H = H_f$ and $\varphi(H_f) = 0$, and into the right-hand side $H = 0$ and $\varphi_{id(0)} = \theta_0$. In this case, using the definition of the film tension

$$\gamma = 2\sigma_f + \Delta PH_f, \quad (41)$$

we obtain from Eqn. (40) the condition of mechanical equilibrium of the film

$$\gamma+\frac{æ_d}{r_{f0}}=2\sigma_0\cos\theta_0,$$

which coincides with Eqn. (1), while the corresponding line tension $æ_d \equiv æ^f$ is determined by the exact analytical expression[55]

$$æ_d=r_{f0}\left\{\int_{H_f}^{\infty}\frac{\sigma_0\sin\varphi(H)}{r}dH-\int_0^{\infty}\frac{\sigma_0\sin\varphi_{id}(H)}{r_{id}}dH_{id}\right\}. \quad (42)$$

From (36) and (42) we obtain a relationship between the line tensions $æ_d$ and τ_d:[55]

$$\frac{æ_d}{r_{f0}}=\frac{\tau_d}{r_f}-\int_0^{H_f}\frac{\sigma_0\sin\varphi_{id}(H)}{r_{id}}dH_{id}. \quad (43)$$

In the case of a straight contact line (i.e. for $r_f\to\infty$) we obtain from Eqns. (36) and (42) the following expressions for the corresponding line tensions τ_d^0 and $æ_d^0$:

$$\tau_d^0=\int_{H_f}^{\infty}\sigma(H)\sin\varphi(H)dH-\int_{H_f}^{\infty}\sigma_0\sin\varphi_{id}(H)dH_{id}, \quad (44)$$

$$æ_d^0=\int_{H_f}^{\infty}\sigma(H)\sin\varphi(H)dH-\int_0^{\infty}\sigma_0\sin\varphi_{id}(H)dH_{id}, \quad (45)$$

and the following expression also applies:[55]

$$æ_d^0=\tau_d^0-\int_0^{H_f}\sigma_0\sin\varphi_{id}(H)dH_{id}. \quad (46)$$

Thus the generalised line tension theory[55,64] allows us to reconcile the various definitions of the line tension, corresponding to different thermodynamic models of a thin liquid film. This is a very valuable attribute, especially since it has been stated[15,33,57] that the line tensions τ_d [defined by Eqn. (4)] and $æ_d$ [defined by Eqn. (1)] are identical, and a good agreement has been reported between the values of æ (measured, or calculated theoretically) and of τ_d (calculated by de Feijter and Vrij[49]). Nevertheless the line tension $æ_d$ for ordinary black films can be 10^3 times greater than the line tension τ_d.[55,71] We shall examine this difference more closely below.

The following conclusion on the properties of $æ_d$ and τ_d have been formulated:[40] 1) the line tensions $æ_d$ and τ_d are different quantities; 2) $æ_d$ (unlike τ_d) depends on the film thickness H_f and coincides with τ_d when $H_f = 0$; 3) $æ_d$ is more "negative" than τ_d, since the integrals in Eqns. (43) and (46) are positive.

The writer has obtained[55,64,65] a definition of the line tension $\tau_{Bd} \equiv \tau_B$ [see Eqn. (11)], corresponding to the case of a positive $\Delta\Omega(H_f)$, for which a contact angle is not formed, and has derived an expression for this line tension:

$$\tau_{Bd}=r_0\left[\int_{H_f}^{\infty}\frac{\sigma(H)\sin\varphi(H)}{r}dH-\int_{H_0}^{\infty}\frac{\sigma_0\sin\varphi_{id}(H)}{r_{id}}dH_{id}\right], \quad (47)$$

where r_0 is the radius of the film (see Fig. 2*d*). In the case of a straight contact line Eqn. (47) reduces to

$$\tau_{Bd}^0=\int_{H_f}^{\infty}\sigma(H)\sin\varphi(H)dH-\int_{H_0}^{\infty}\sigma_0\sin\varphi_{id}dH_{id}. \quad (48)$$

The generalised line tension theory[40,41,42] also yields expressions for the "energy" line tensions, which appear in the expressions for the free energy of systems which include a liquid film. For example, for the model of a liquid film which stipulates two interfaces, the expression for the grand thermodynamic potential of the system (see Fig. 2*c*) becomes

$$\Omega^{id}=-P_\alpha V_\alpha^{id}-P_\beta V_\beta^{id}+\int_{A^{id}}\sigma(H)dA^{id}+2\pi r_f\tau_e, \quad (49)$$

where the integration is carried out over the surface of the idealised model of the film, with $\sigma(H) = \sigma_0$ on the side surface and $\sigma(H) = \sigma_f$ on the plane parallel surface.

From the condition of energy equivalence of the real film and its idealised model we obtain an expression for the line tension corresponding to a negative specific free energy of interaction $\Delta\Omega(H_f)$ in the film:[42]

$$\tau_e = \frac{1}{r_f}\int_0^R \left[\frac{2\sigma(H)}{\cos\varphi(H)} + \Delta PH\right] rdr - \int_{r_f}^R \left[\frac{2\sigma_0}{\cos\varphi_{id}(H)} + \Delta PH_{id}\right] rdr - \\ -[2\sigma_f + \Delta PH_f]r_f. \qquad (50)$$

By comparing the exact expression for the line tension τ_e [Eqn. (50)] with the approximate expression (26) obtained by de Feijter and Vrij[49] for the dynamical line tension τ we find substantial differences in spite of their structural similarity. Thus, we conclude that the first exact expression for the line tension τ_e was published in the current year.[42]

On the other hand it is clear that the dynamical line tension τ_d [defined by the expression (36)] differs from the energy line tension τ_e [defined by the expression (50)] in the case of a curving contact line. For a straight contact line the dynamical (τ_d^0) and the energy line tension coincide and are defined by the relationship (44).

The first exact analytical expression[42] for the energy line tension $æ_e$, corresponding to the membrane model of the film for $\Delta\Omega(H_f) < 0$, and the expression for the energy line tension τ_{Be}, corresponding to $\Delta\Omega(H_f) < 0$, are shown below:

$$æ_e = \frac{1}{r_{f0}}\int_0^R \left[\frac{2\sigma(H)}{\cos\varphi(H)} + \Delta PH\right] rdr - \frac{1}{r_{f0}}\int_{r_0}^R \left[\frac{2\sigma_0}{\cos\varphi_{id}(H)} + \Delta PH_{id}\right] rdr - \gamma r_0, \qquad (51)$$

$$\tau_{Be} = \frac{1}{r_0}\int_0^R \left[\frac{2\sigma(H)}{\cos\varphi(H)} + \Delta PH\right] rdr - \frac{1}{r_0}\int_{r_0}^R \left[\frac{2\sigma_0}{\cos\varphi_{id}(H)} + \right. \\ \left. + \Delta PH_{id}\right] rdr - [2\sigma_f + \Delta PH_f]r_0. \qquad (52)$$

In particular we showed that the equalities $æ_d^0 = æ_e^0$ and $\tau_{Bd}^0 = \tau_{Be}^0$ apply for a straight line of contact [see Eqns. (45) and (48) respectively].

Thus the first exact analytical expressions for the line tensions in terms of various thermodynamic models of thin liquid films have been derived from our generalised theory of line tension.[40,64] These expressions have been used[40–42,55,64,71] in numerical calculations of the line tension.

V. Calculation of the line tension by numerical methods

As was pointed out by de Feijter and Vrij,[49] the line tension τ_d^0 defined by Eqn. (27) can only be negative if the specific free energy of interaction $\Delta\Omega(H_f)$ in a film of thickness H_f is negative, i.e. when finite contact angles θ_f exist and the disjoining pressure isotherm is characterised by one coagulation minimum. This conclusion is self-evident, since in this case the product $\sigma(H)\sin\varphi$ is smaller than the product $\sigma_0 \sin\varphi_{id}$ over the whole integration range in Eqn. (27). We have shown[55,64] that under these conditions the line tension $æ_d^0$ determined in terms of the membrane model of the film [see Eqn. (1)] is even more negative if the sign of the integral in Eqn. (46) is taken to be positive. In the case of positive $\Delta\Omega(H_f)$ the line tension τ_{Bd}^0 defined by the expression (10) can only be positive[55,64] if the disjoining pressure $\Pi(H)$ is positive over the whole transition region. This obvious corollary follows from Eqn. (48) if we stipulate that the product $\sigma(H)\sin\varphi$ is greater than the product $\sigma_0 \sin\varphi_{id}$ over the whole integration region.

In the more complex disjoining pressure isotherms the sign of the line tension cannot be predicted from the form of Eqns. (44), (45), or (48). In this case the problem of the magnitude and sign of the line tensions determined on the basis of different thermodynamic models can be solved only by direct numerical calculations. The results of these calculations are examined in this section.

1. Choice of disjoining pressure isotherm for numerical calculations of the line tension

Figure 6 shows different types of disjoining pressure isotherm [$\Pi(H)$] used in line tension calculations.

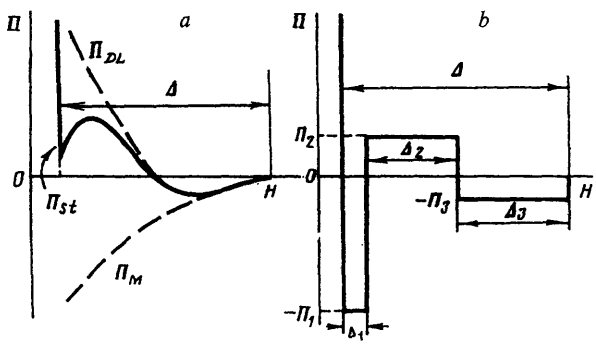


Figure 6. $\Pi(H)$ disjoining pressure isotherms used to calculate the line tension by de Feijter and Vrij[49] (*a*) and by Babak[40–42,55,64,65,71] (*b*).

De Feijter and Vrij[49] used a $\Pi(H)$ isotherm corresponding to the Deryagin–Landau–Verwey–Overbeek (DLVO) theory (see Fig. 6*a*), but including a very strong repulsion for $H \leqslant 4$ nm. This isotherm is thought to be characteristic of foam films stabilised by SAS and able to form stable Newtonian black films. The $\Pi(H)$ isotherm had the following analytical form:

$$\Pi(H) = -\frac{A}{6\pi H^3} + 1.59 \times 10^8 c \exp(-æH); \; H > 4 \text{ nm};$$

$$\Pi(H) = +\infty, \; H \leqslant 4 \text{ nm}, \qquad (53)$$

where A is the Hamaker constant, c is the concentration of electrolyte, and $æ = 3.28 \times 10^9$ s^{½} m^{-1} is the Debye length. The line tension τ was calculated by formula (29) for several values of the parameters: $A = (0.2-4) \times 10^{-19}$ J, $c = 10^{-3}-\infty$ mol dm^{-3}, and $\Delta P = 25-100$ Pa.

As can be seen from Table 2 the line tension depends on the difference in hydrostatic pressures, on the contact angle (or specific free energy of interaction in the film), on the equilibrium thickness of the film, and on the radius of action of the molecular forces. De Feijter and Vrij[49] concluded that in ordinary and in Newtonian black films the line tension τ has a negative sign if the contact angle θ_f is finite, because varying these parameters over their actual existence range did not change the sign of the line tension from negative to positive. This conclusion is inconsistent with the experimental results of Platikanov, et al.[5,34,37,68] and of Scheludko, et al.,[16] who obtained positive linear tensions for ordinary black films.

Table 2. Line tension τ calculated[49] by the approximate formula (29) for different values of the concentration of electrolyte c, of the difference in hydrostatic pressure ΔP, of the film thickness H_f, of the contact angle θ_f, and of the specific free energy of interaction $\Delta\Omega(H_f)$ in a film of thickness H_f and radius of action of the surface forces Δ (σ_0 = 30 mJ m^{-2}).

No.	c, mol dm^{-3}	ΔP, Pa	H_f, nm	θ_f, min	$10^{-6}\Delta\Omega(H_f)$, J m^{-2}	Δ, μm	$10^{-12}\tau$, N
1	0.001	25	81	5	-0.063	18.5	-2.1
2	0.002	25	60	13	-0.42	14.4	-3.1
3	0.01	25	26	34	-2.93	7.6	-4.8
4	0.05	25	10	87	-19.21	2.0	-5.6
5	∞	25	4	248	-256.1	1.0	-5.2
6	0.01	25	31	12	-0.37	11.5	-1.5
7	0.01	25	26	34	-2.93	7.6	-4.8
8	0.01	25	19	89	-20.1	3.8	-11.3
9	0.01	25	26	34	-2.93	7.6	-4.8
10	0.01	50	25.5	34	-2.93	6.0	-4.6
11	0.01	100	25	34	-2.93	4.7	-4.2

It follows from Table 2 that the effects of the parameters H_f, θ_f [or $\Delta\Omega(H_f)$], ΔP, and Δ on the line tension τ are inter-related: this prevents us from identifying the effects of the individual parameters on τ and from constructing the appropriate analytical expressions. In order to study the individual contribution of these parameters to the line tension the writer[55,64,71] has suggested using the idealised $\Pi(H)$ isotherm shown in Fig. 6*b*.

The main advantage of this isotherm over the DLVO isotherm of Fig. 6*a* is that in numerical calculations the equilibrium film thickness H_f can be kept constant, and the form parameters of the $\Pi(H)$ isotherm change in a way which keeps the angle of contact θ_f [or the parameter $\Delta\Omega(H_f)$] constant. Thus we are able to distinguish the effects of the contact angle θ_f on τ_d for constant values of the other parameters (H_f, ΔP, Δ_i, Π_i), and therefore we can establish the appropriate correlation dependences.

We should also note that the writer[64] used a $\Pi(H)$ isotherm which allows for the steric repulsion between adsorption layers of macromolecules in a liquid film, given by the Hesselink–Vrij–Overbeek (HVO) theory[73] as

$$\Pi(H) = a(1 - bH^2)H \exp(-cH^2), \qquad (54)$$

where a, b, and c are functions of the parameters which characterise the conformational state of macromolecules in the solution and their interactions.

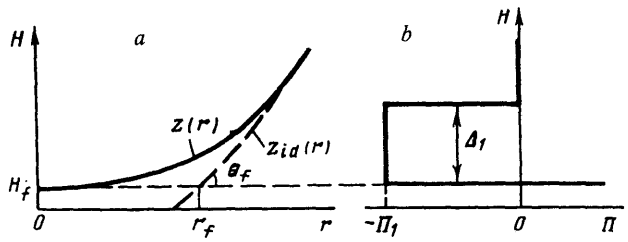


Figure 7. Idealised disjoining pressure isotherm $\Pi(H)$ with one coagulation minimum (see text).

Table 3. Line tension τ_d^0 calculated[79] by the exact formula (44) for different values of the parameters Δ_1 and Π_1 which describe the idealised disjoining pressure isotherm shown in Fig. 7, and also different values of the hydrostatic pressure ΔP, the contact angle θ_f, and of the specific free energy of interaction $\Delta\Omega(H_f)$ in a film of thickness H_f (σ_0 = 30 mJ m^{-2}).

ΔP, Pa	Δ_1, nm	Π_1, Pa	θ_f, min	$10^{-6}\Delta\Omega(H_f)$, J m^{-2}	$10^{-12}\tau_d^0$, N
10	10	10^2	49	-2	-0.92
10^2	10	10^2	49	-2	-0.78
10^3	10	10^2	49	-2	-0.44
10^4	10	10^2	49	-2	-0.17
10^5	10	10^2	49	-2	-0.06
10^3	10	10^3	154	-20	-2.45
10^3	10	10	16	-0.2	-0.02
10^3	1	10^3	49	-2	-0.08
10^3	100	10	49	-2	-1.71
10^2	10	10^3	154	-20	-29.10
10^2	10	10^4	482	-200	-94.00
10^2	1	10^5	482	-200	-9.43

2. Magnitude and sign of the line tension for a $\Pi(H)$ isotherm with one coagulation minimum

Let us first consider the $\Pi(H)$ disjoining pressure isotherm characterised by a single coagulation minimum (Fig. 7). It is obtained from the isotherm shown in Fig. 6*b* by the formal substitution $\Pi_2 = \Pi_3 = 0$, and it can describe Newtonian black films at relatively high concentrations of electrolyte (when the ionic–electrostatic repulsive forces in the electrical double layer are effectively suppressed and the coagulation barrier Π_2 disappears). Furthermore this disjoining pressure isotherm can describe ordinary black films (in which the radius of action of the molecular forces is much greater than the Debye length æ and the disjoining pressure Π_2 is greater than the capillary pressure in the film). The effect of the

height of the coagulation barrier on the magnitude and sign of the line tension will be discussed in depth below.

Table 3 shows the results of calculations of the line tension τ_d^0 by formula (44) as a function of the parameters Δ_1 and Π_1, which characterise the form of the idealised disjoining pressure isotherm $[\Delta P, \theta_f, \Delta\Omega(H_f)]$ for a constant interfacial tension.[40–42,55,64,71]

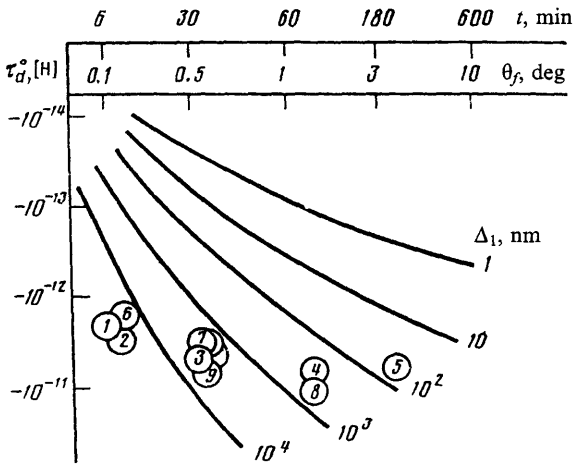


Figure 8. Plots of the line tension τ_d^0 against the contact angle θ_f for some values of the parameter Δ_1 which characterises the radius of action of the surface forces. The numbers by the curves denote the line tension value (τ) in Table 2 calculated by de Feijter and Vrij[49] by the approximate formula (29).

We note that the line tension τ_d^0 is negative for all forms of the $\Pi(H)$ isotherm, and also for the whole range of contact angles θ_f and of differences in hydrostatic pressure Δp examined. It is clear from the plots of the line tension τ_d^0 against the contact angle shown in Fig. 8 for constant values of the parameter Δ_1 (the action radius of the molecular forces) that the line tension tends towards zero as the angle of contact tends towards zero. Under these conditions the line tension is very sensitive to Δ_1, increasing as Δ_1 increases. We can see from Table 3 that the line tension τ_d^0 decreases as the difference in hydrostatic pressure ΔP increases while the other parameters stay constant.

Fundamental differences are revealed by comparing the dependences on the contact angle θ_f of the line tension τ obtained by de Feijter and Vrij,[49] and shown in Fig. 8, with the calculated $\tau_d^0(\theta_f)$ dependences.[42] For example, a change in the angle of contact from 0.5° to 3° is reported[49] to produce only a slight increase in the line tension (see the numbered points in Fig. 8). However, the line tensions in this range of θ_f actually increase by a factor of 30–100, depending on the parameter Δ_1 [see the corresponding $\tau_d^0(\theta_f)$ curves in Fig. 8]. The reason for this large difference between the calculated $\tau_d^0(\theta_f)$ dependences is self-evident when one notes that the disjoining pressure isotherm used in the calculations of de Feijter and Vrij (see Fig. 6*a*) cannot be used while keeping constant the film thickness, which decreases as the contact angle is increased (see Table 2), thus masking the true dependence of τ_d^0 on θ_f. The advantages of the $\Pi(H)$ isotherm used by the present writer[55,64,71] therefore seem obvious: it enables the film thickness H_f and the parameter Δ_1 to be held constant during changes in the contact angle θ_f, and it gives the true dependence of the line tension on θ_f.

We should also note that the use[49] of the approximate working formula (29) to calculate the line tension gives values at least 10 times too high, as can be seen by comparing the data in Table 2 with the numerical values of τ_d^0 calculated by the exact formula (44) (Table 3) for equal values of the parameters θ_f, ΔP, and Δ_1.

As was pointed out above, according to the generalised theory of the line tension[40] the tension $æ_d$, defined in terms of the membrane model of the film by Eqn. (1), differs from the line tension τ_d in the thermodynamic model, based on the assumption of a film with two interfaces [see Eqn. (4)]. The relationship between $æ_d^0$ and τ_d^0 in the case of a straight contact line is described by Eqn. (46). An analysis of the data in Table 4 leads to the important conclusion that the film thickness H_f has a marked influence on $æ_d^0$ but none on τ_d^0. Under these conditions the numerical value of the line tension $æ_d^0$ can exceed that of τ_d^0 by a factor of 10 or more.[55,71]

Table 4. Line tension $æ_d^0$ calculated[42] by the exact formula (45) as a function of the parameters Δ_1 and Π_1 which describe the idealised disjoining pressure isotherm shown in Fig. 7, and also for different hydrostatic pressures ΔP, contact angles θ_f, and specific energies of interaction $\Delta\Omega(H_f)$ in a film of thickness H_f and line tension τ_d^0 (σ_0 = 300 mJ m^{-2}).

ΔP, Pa	Δ_1, nm	Π_1, Pa	θ_f, min	$10^{-6}\Delta\Omega(H_f)$, J m^{-2}	$10^{-12}\tau_d^0$, N J m^{-2}	H_f, nm	θ_b, deg	$10^{-12}æ_d^0$, N
10	10	10^3	2.57	-20	-2.98	0.2	2.57	-3.06
10	10	10^3	2.57	-20	-2.98	2	2.57	-3.87
10	10	10^3	2.57	-20	-2.98	20	2.55	-11.9
10	10	10^3	2.57	-20	-2.98	200	2.43	-90.1
10^2	10	10^2	0.81	-2	-0.78	20	0.00	-2.67
10^2	10	10^3	2.57	-20	-2.91	20	2.43	-11.6
10^2	1	10^5	8.11	-200	-0.94	2	8.11	-2.35
10^2	10	10^4	8.11	-200	-9.40	20	8.07	-37.5
10^2	1	10^5	8.11	-200	-0.94	20	8.07	-29.1
10^3	10	10^3	2.57	-20	-2.45	20	0.00	-8.42

3. Magnitude and sign of the line tension for a $\Pi(H)$ isotherm without a coagulation minimum

As we have already noted, in the case of a positive specific free energy of interaction $\Delta\Omega(H_f)$ in a film of thickness H_f the idealised profile of the film lies above the real profile (see Fig. 2*b*), and the line tension τ_{Bd}^0 is defined by Eqn. (10).[55,64,65] Table 5 shows the results of calculations of the line tension τ_{Bd}^0 by the exact formula (48) for the idealised $\Pi(H)$ isotherm shown in Fig. 9. This $\Pi(H)$ isotherm, in the form of a step, allows us to keep constant the film thickness H_f and to identify the effects of the shape of the $\Pi(H)$ isotherm (the parameters Δ_2 and Π_2) and also of ΔP and $\Delta\Omega(H_f)$ on the line tension τ_{Bd}^0.

Table 5. Line tension τ^0_{Bd} calculated[42] by the exact formula (48) as a function of the parameters Δ_2 and Π_2 which characterise the idealised disjoining pressure isotherm shown in Fig. 9, and also of the difference in hydrostatic pressure ΔP, the difference in film thickness $\Delta H = H_0 - H_f$, and the specific free energy of interaction $\Delta\Omega(H_f)$ in a film of thickness H_f (σ_0 = 30 mJ m^{-2}).

ΔP, nm	Δ_2, nm	Π_2, Pa	ΔH, nm	$10^{-6}\Delta\Omega(H_f)$, J m^{-2}	$10^{-12}\tau^{\circ}_{Bd}$, N
10^2	100	10	20	+2.0	+5.66
10^2	20	50	20	+2.0	+1.89
10^2	2	50	2	+0.2	+0.06
10^2	10	10	2	+0.2	+0.18
20	10	10	10	+0.2	+0.30
10^3	10	10	0.2	+0.2	+0.06

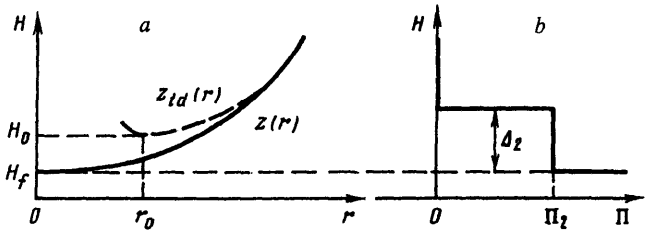


Figure 9. Idealised disjoining pressure isotherm $\Pi(H)$ without a coagulation minimum, used in calculations[41,42,71] of the line tension τ_{Bd} (see text).

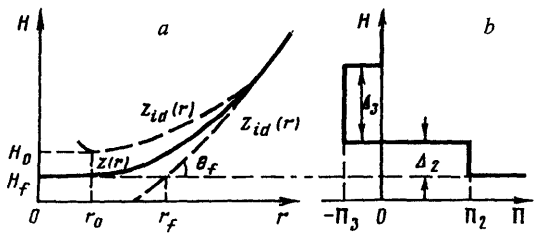


Figure 10. Idealised disjoining pressure isotherm $\Pi(H)$ with a long-range minimum and a coagulation barrier (see text).

The main conclusion from this analysis of the calculations is that the sign of the line tension τ^0_{Bd} is positive, i.e. it corresponds to the sign of $\Delta\Omega(H_f)$.[55,64] The line tension τ^0_{Bd} increases with Δ_2 and $\Delta\Omega(H_f)$, and as ΔP decreases.[55,64] More detailed results or the writer's calculations of τ^0_{Bd} as a function of these parameters have already been reported.[71]

4. Effect of the coagulation barrier on the magnitude and sign of the line tension

Let us first examine the idealised profile of the $\Pi(H)$ isotherm shown in Fig. 10, which can be used to model the change from wetting ordinary black films (which do not form a finite contact angle) to non-wetting ordinary black films (which form a finite contact angle θ_f). If the specific free energy of interaction in the film [which is equal, in our case of an idealised $\Pi(H)$ isotherm to $\Delta\Omega(H_f) = -2\Delta_3\Pi_3 + 2\Delta_2\Pi_2$] is less than zero the idealised profile $z_{id}(r)$ lies below the real profile $z(r)$ and forms the contact angle θ_f. If $\Delta\Omega(H_f) > 0$ the contact angle is not formed because $z_{id}(r)$ lies above $z(r)$. For $\Delta\Omega(H_f) = 0$ the contact angle θ_f is zero.

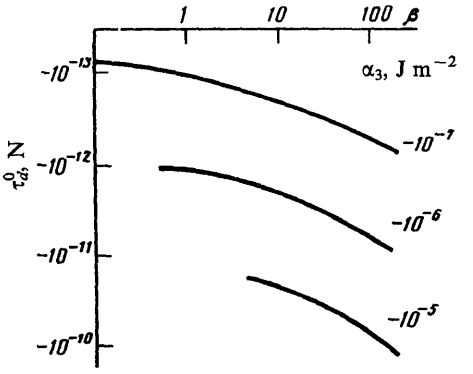


Figure 11. Dependence of the line tension τ^0_d on the parameter β for different values of the parameter α_3; ΔP = 100 Pa, σ_0 = 30 mJ m^{-2}, $\Delta\Omega(H_f) = 0$.

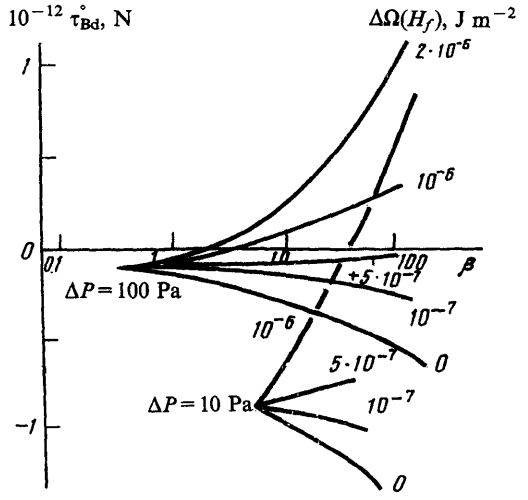


Figure 12. Dependence of the line tension τ^0_{Bd} on the parameter β for different positive values of the specific interaction energy $\Delta\Omega(H_f)$ in a film of thickness H_f and of the difference in hydrostatic pressure ΔP (σ_0 = 30 mJ m^{-2}, $\alpha_3 = -5 \times 10^{-7}$ J m^{-2}).

The latter case is illustrated in Fig. 11,[42] where the different $\tau^0_d(\beta)$ curves correspond to the condition $\Delta\Omega(H_f) = 0$ but to a different form of $\Pi(H)$ isotherm, characterised by the parameters $\beta = \Delta_2/\Delta_3$ and $\alpha_3 = -2\Delta_3\Pi_3$.

The most important conclusion suggested by the $\tau_d^0(\beta)$ curves of Fig. 11 is that the line tension τ_d^0 (and, even more, $æ_d^0$) is negative when the films have a finite angle of contact θ_f. This conclusion coincides with the results of numerical calculations of the line tension by de Feijter and Vij,[49] who obtained only negative values of τ_d^0 for ordinary black films, but is incompatible with the experimental results of Platikanov, et al.,[5,34] who obtained positive values of the line tension $æ_d$ for those films.

We also note that increasing the depth α_3 of the coagulation minimum (or the height of the coagulation barrier) for $\Delta\Omega(H_f) = 0$ (or $\theta_f = 0$) increases the absolute value of the (negative) line tension almost in proportion to the parameter α_3. This feature can be used as a criterion of the form of the $\Pi(H)$ isotherm under the conditions of a reliable experimental determination of both τ_d^0 and the contact angle θ_f.

When $\Delta\Omega(H_f) > 0$ the contact angle is not formed (see Fig. 10). In Fig. 12 we show the results of calculations of the line tension τ_{Bd}^0 as a function of the parameter $\beta = \Delta_2/\Delta_3$ for constant values of $\Delta\Omega(H_f)$ ($\alpha_3 = -5 \times 10^{-7}$ J m^{-2} in all the calculations). The upper family of curves corresponds to $\Delta P = 100$ Pa, the lower to $\Delta P = 10$ Pa.

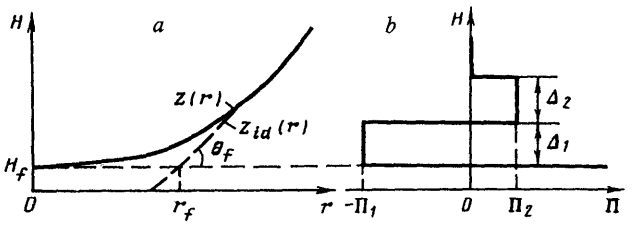


Figure 13. Idealised disjoining pressure isotherm $\Pi(H)$ with a coagulation barrier and a short-range coagulation minimum (see text).

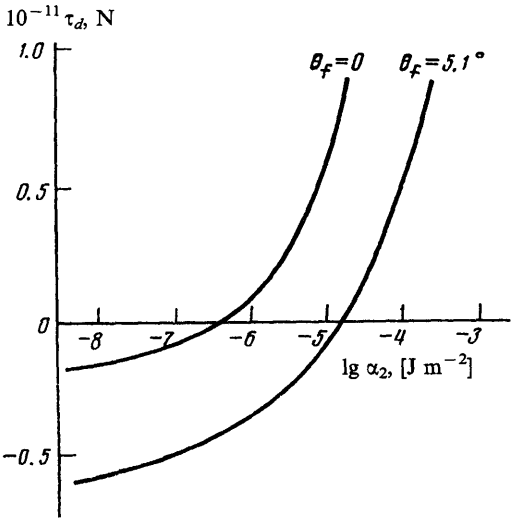


Figure 14. Dependence of the line tension τ_d^0 on the parameter α_2 for two values of the contact angle θ_f ($\Delta P = 100$ Pa, $\sigma_0 = 30$ mJ m^{-2}, $\Delta_1 = \Delta_2 = 10$ nm).

The line tension τ_{Bd}^0 determined according to Eqn. (48) can (in principle) have both negative and positive values.[42,74] However, since in ordinary black films the parameter β cannot be greater than 1 we may conclude that the line tension τ_{Bd}^0 is more likely to be negative than positive. The measured[63] positive value $\tau_{Bd}^0 = +3 \times 10^{-11}$ N for $\Delta\Omega(H_f) = 10^{-5}$ J m^{-2} and $\Delta P \simeq 100$ Pa is not incompatible with the numerical calculations of the line tension τ_{Bd}^0 shown in Fig. 12 provided that the films of aqueous solutions of electrolytes studied in that work[63] do not possess a long-range coagulation minimum, i.e. long-range molecular forces are entirely absent.

Let us now examine another generalised $\Pi(H)$ isotherm (Fig. 13), which models the Newtonian black films when the effect of the long-range coagulation barrier can be ignored. The dependence of the line tension $\tau_d^0(\alpha_2)$ on the parameter $\alpha_2 = 2\Delta_2\Pi_2$ for a constant $\Delta P = 100$ Pa is shown in Fig. 14 ($\Delta_2 = \Delta_1 = 10$ nm), where constant values of $\Delta\Omega(H_f)$ are also assumed (i.e. constant angles of contact θ_f).

We can see from Fig. 14 that upon increasing the height of the coagulation barrier Π_2 (i.e. upon increasing the parameter α_2) the line tension τ_d^0 passes from the negative into the positive region: this transition takes place at a higher value of α_2 when the contact angle θ_f is increased.

Lastly, if the effect of the long-range coagulation minimum cannot be ignored, the $\Pi(H)$ isotherm shown in Fig. 5*b* (characterised by two coagulation minima and a coagulation barrier) must be used in the calculation of the line tension.

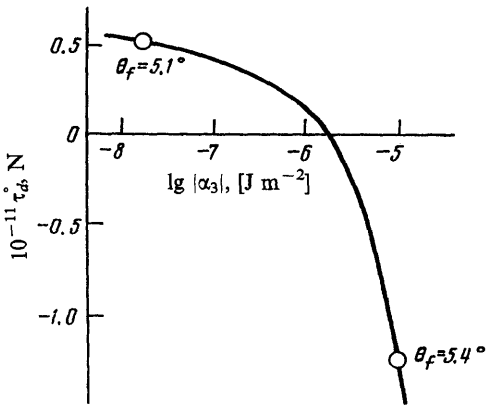


Figure 15. Dependence of the line tension τ_d^0 on the absolute value of the parameter α_3 ($\Delta P = 100$ Pa, $\sigma_0 = 30$ mJ m^{-2}, $\alpha_1 = -0.98 \times 10^{-4}$ J m^{-2}, $\alpha_2 = +1.8 \times 10^{-5}$ J m^{-2}, $\Delta_1 = \Delta_2 = \Delta_3 = 10$ nm).

In Fig. 15 we show the dependence of the line tension $\tau_d^0(\alpha_3)$ on the parameter $\alpha_3 = -2\Delta_3\Pi_3$ for constant $\Delta P = 10$ Pa, $\Delta_1 = \Delta_2 = \Delta_3 = 10$ nm, $\alpha_1 = -0.98 \times 10^{-4}$ J m^{-2}, and $\alpha_2 = +1.8 \times 10^{-5}$ J m^{-2}. Increasing the depth of the long-range coagulation minimum, i.e. increasing the absolute value of the parameter α_3, changes the sign of the line tension from positive to negative. Under these conditions the angle of contact θ_f is almost unaffected (at least,

any change in this angle is experimentally undetectable, since $\Delta\theta_f$ = 0.3° for an absolute value of $\theta_f \simeq 5°$).

Thus we may conclude that the most significant effects on the magnitude and sign of the line tension are produced by the form of the $\Pi(H)$ disjoining pressure isotherm rather than by the absolute value of the specific free energy of the interaction in the film, $\Delta\Omega(H_f)$, i.e. by the contact angle θ_f. This justifies the effort now being directed towards the experimental determination of the line tension, since a knowledge of the magnitude and sign of this parameter should provide new information on the form of the disjoining pressure isotherm.

As to the sign of the line tension τ_d^0 in Newtonian black films, in principle this parameter can be either positive or negative, depending on the form of the idealised $\Pi(H)$ isotherm. However, for real $\Pi(H)$ isotherms, for example those described by the DLVO theory, de Feijter and Vrij showed[49] that the line tension has only negative values in Newtonian black films, characterised by relatively large angles of contact. The same conclusion was reached by the present writer from the first calculations of the line tension τ_d of microscopic curved films[55] by the exact analytical formula (36).

VI. Conclusions

The following conclusions can be formulated from the analysis of the line tension problem in the thermodynamics of thin liquid films given in the present review.

Line tensions are defined by different workers in terms of different thermodynamic models of thin liquid films, and therefore they are physically different quantities. Identifying line tensions defined in different ways leads to incompatible numerical values and even signs of these parameters. The writer's generalised theory of the line tension[40] reconciles the different definitions and establishes their mutual relationships.

Exact analytical expressions for the line tension have been proposed.[40–42,55,64,65,71] In particular, it has been shown that the well known expression for the line tension [Eqn. (26)] obtained by de Feijter and Vrij,[49] which is widely used at present, is incorrect for the general case of a curved line of contact though it approaches asymptotically the correct expression as the radius of curvature of the contact line tends towards infinity.

The writer has reported[40–42,71] the first calculations of the line tension by numerical methods, and has obtained the dependence of the line tension on the form parameters of the disjoining pressure isotherm and on the capillary pressure in the film, the interfacial tension, the contact angle (the specific free energy of interaction in the film), and the film thickness. The numerical values of the line tension have been compared with known experimental results for this quantity.

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