MECHANICS AND THERMODYNAMICS OF INTERFACES, THIN LIQUID FILMS AND MEMBRANES

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ABSTRACT

First we review some recent studies devoted to the role of surface moments (torques) in the mechanics and thermodynamics of fluid interfaces of arbitrary shape. The presence of bending and torsion moments leads to a difference between the mechanical and thermodynamical surface tensions and shear stresses. Next we review recent results in the mechanics of thin liquid films and the transition region film-Plateau border. Line and transversal tensions are assigned as excesses on the contact line. The transversal tension accounts for the attractive forces in the transition zone. Experiments with floating bubbles show that the movement of the contact line can lead to non-equilibrium values of the line tension, which can be interpreted in terms of a plastic deformation.

INTRODUCTION

This article reviews some recent developments in the field of mechanics and thermodynamics of systems containing fluid interfaces, membranes and thin liquid films. The connection between the mechanical and thermodynamical approaches for description of arbitrarily shaped surfaces is investigated. The interfacial stresses and moments (torques) can be represented as *excesses*, in view of the Gibbs model which replaces the real transition region between two fluid phases with a mathematical surface. Such a treatment opens the possibility to invoke statistical mechanics in order to calculate the surface excesses after adopting certain model for the pressure distribution in the real system.

The thermodynamical theory considers the work associated with the four independent modes of interfacial deformation - dilatation, shear, bending and

torsion. The presence of moments leads to a difference between the mechanical surface tensions (isotropic and deviatoric scalar invariants of the surface stress tensor) and the thermodynamically defined interfacial dilatation and shear tensions (1). The bending and torsion moments are related to the isotropic and deviatoric part of the tensor of surface moments (1-3). Accounting for the subtle interrelation between the mechanical and thermodynamical lines of consideration can be very important for systems which exhibit low interfacial tension and/or high curvature, such as microemulsions and biological membranes, where the surface moments play a central role.

In thin liquid films two surfaces interact, and this constitutes the difference with the systems containing a single surface. The interactions affect both the pressure inside the film and the interfacial tensions on its surfaces. The smooth transition region between the film and the Plateau border is modelled as a sharp contact line, where the contact angle is defined. Line and transversal tensions are assigned as excesses on the contact line (4). In equilibrium the transversal tension can counterbalance the repulsive disjoining pressure and keep the surfaces attached to each other (5,6). The motion of the contact line was shown to substantially influence the properties of the film. The concept of dynamic line tension was introduced (6,7). Experimental measurements in dynamic conditions revealed that the line tension can deviate from its equilibrium value by orders of magnitude (7). The effect was obtained when the film surfaces detach (advancing meniscus), and not in the opposite case. Below we propose a physical explanation of this effect.

MECHANICS AND THERMODYNAMICS OF A SINGLE INTERFACE

Mechanical Approach

Two main routes, mechanical and thermodynamical, exist for the theoretical investigation of general curved interfaces of arbitrary shape. The first route originates from the classical theory of shells and plates, reviewed in Refs.(8, 9). The surface is regarded as a two-dimensional continuum whose deformation is described in terms of the rate-of-strain tensor and the tensor of curvature. The independent tensorial fields of the interfacial stresses, $\underline{\sigma}$, and moments (torques), $\underline{M}$, are supposed to be defined at each point. Fig. 1 shows the physical meaning of the components of the latter two tensors. Usually they are written in the form

$$\underline{\sigma} = a_\alpha a_\beta \sigma^{\alpha\beta} + a_\mu n \sigma^{\mu(n)} \quad ; \quad \underline{M} = a_\alpha a_\beta M^{\alpha\beta} \qquad [1]$$
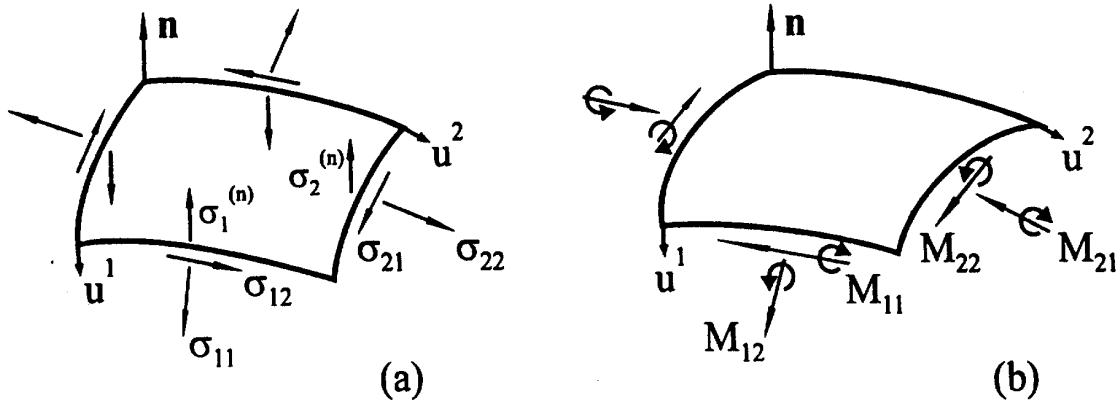
Fig. 1. Components of the tensors of surface stresses (a) and surface moments (b).

where Greek indices take values 1,2 (summation over repeated indices is implied); a_1, a_2 are surface covariant base vectors and n is the running unit normal to the surface. $\sigma^{\mu(n)}$ are called transversal shear stresses.

Tensor analysis and differential geometry can be applied in a straightforward manner to derive the interfacial balances of linear and angular momentum. General considerations can be found in Refs.(3, 8, 9). Here we will only mention the results for the case of quasistatic processes (negligible angular acceleration), when $\sigma_{\alpha\beta}$ and $M_{\alpha\beta}$ are symmetric surface tensors which are both diagonal in the basis of principal curvatures. In these conditions the normal projection of the angular momentum balance is identically satisfied (3), and the tangential projection reads (3, 8-10):

$$\sigma^{\alpha(n)} = -M^{\alpha\beta}{}_{,\beta} \qquad [2]$$

(the comma denotes covariant derivative). Obviously, the transversal shear resultants are connected with the presence of moments which are not constant along the surface. As discussed in Ref.(3), specific kind of viscous friction in the surface can also provide a contribution in $\sigma^{\alpha(n)}$. The normal and tangential projections of the linear momentum balance have the following form (3, 8-10):

$$b_{\alpha\beta} \, \sigma^{\alpha\beta} - M^{\alpha\beta}{}_{,\alpha\beta} = P_{II} - P_I \qquad [3]$$

$$\sigma^{\alpha\beta}{}_{,\beta} + b_{\beta}^{\alpha} \, M^{\beta\gamma}{}_{,\gamma} = 0 \qquad [4]$$

Here $b_{\alpha\beta}$ is the curvature tensor, and $P_{II}-P_I$ is the pressure difference across the interface. Eq.[3] is the generalised Laplace equation, valid in the presence of moments. On spherical fluid interfaces $M^{\alpha\beta}{}_{,\alpha\beta} = 0$, due to the symmetry ; the

curvature tensor is isotropic, $b_{\alpha\beta} = Ha_{\alpha\beta}$ ($a_{\alpha\beta}$ are components of the metric tensor, and H is the mean curvature, $H = \frac{1}{2} a^{\mu\nu} b_{\mu\nu}$). Then Eq.[3] reduces to

$$2H \sigma = P_{II} - P_{I} \qquad\qquad [5]$$

with σ being the scalar isotropic tension, $\sigma = \frac{1}{2} a_{\mu\nu} \sigma^{\mu\nu}$.

For a complete mechanical description of the surface one needs to specify expressions for the stresses and moments. This is usually done by postulating some constitutive relations between stress and strain, which pertain to a particular model for the rheological behaviour of the interface. For example, Scriven (11) proposed that the phase boundary between two liquids be treated as a two-dimensional fluid with intrinsic dilatational and shear viscosities. His constitutive relation for the surface stress tensor, $\underline{\sigma}$, is complemented in Ref. (3) with a constitutive relation for the tensor of the surface moments, $\underline{M}$.

Thermodynamical Approach and Its Connection with Mechanics

The general thermodynamics of systems containing surfaces (and lines) originates from Gibbs (12). The bulk phases in the idealised system are considered homogeneous up to the sharp mathematical boundaries. Excesses of all extensive properties (such are the internal energy, U, the free energy, F, the entropy, S, the number of molecules of the i-th component, N_i, etc.) are ascribed to those boundaries. The latter are considered as separate phases and fundamental equations are formulated for them. The work for mechanical deformation is also taken into account. As far as the surface rate-of-strain tensor and the curvature tensor are two-dimensional, each of them has two independent scalar invariants. Therefore, one may distinguish exactly four independent modes of surface deformation: dilatation, shear, bending and torsion provide separate contributions to the mechanical work per unit area, δw^s (1, 2):

$$\delta w^S = \gamma \, \delta\alpha + \zeta \, \delta\beta + B \, \delta H + \Theta \, \delta D \qquad\qquad [6]$$

This equation is valid locally, at each point of the surface. $\delta\alpha$ is the relative dilatation of an element dA, $\delta\alpha = \delta(dA)/dA$; $\delta\beta$ is connected with the deviatoric part of the rate-of-strain tensor (2) and characterises shear. H and D are the mean and deviatoric curvatures:

$$H = \frac{1}{2}(c_1 + c_2) \quad ; \quad D = \frac{1}{2}(c_1 - c_2)$$

with c_1, c_2 being the two principal curvatures at a certain point. The coefficients γ and ζ have the meaning of *thermodynamic* interfacial tension and shearing

tension, respectively. B and Θ represent the bending and torsion moments (2). The basic idea of the local thermodynamic description, which is due to Gibbs (12), is to apply the fundamental equation of a uniform surface phase *locally*, i.e. for each elementary portion, dA, of the curved interface:

$$\delta(dU^S) = T\delta(dS^S) + \sum_i \mu_i \, \delta(dN_i^S) + (\delta w^S)dA \qquad [7]$$

Here T and μ_i are temperature and chemical potentials; dU^s, dS^s and dN_i^s denote the excess surface internal energy, entropy and number of molecules of the i-th component, belonging to the elementary parcel dA; the symbol "δ" denotes infinitesimal variation due to the occurrence of a thermodynamic process in the system. Then one obtains (5)

$$\delta(dU^S) = \delta(u^S dA) = (\delta u^S + u^S \delta\alpha)dA \qquad [8]$$

where u^s is the surface density of U^s. Similarly, one can derive

$$\delta(dS^S) = (\delta s^S + s^S \delta\alpha)dA \quad ; \quad \delta(dN_i^S) = (\delta\Gamma_i + \Gamma_i \delta\alpha)dA \qquad [9]$$

with s^s and Γ_i being the surface densities of S^s and N_i^s. The substitution of Eqs. [6], [8] and [9] into Eq.[7], after some transformations, yields

$$\delta\omega^S = -s^S \delta T - \sum_i \Gamma_i \, \delta\mu_i + (\gamma - \omega^S)\delta\alpha + \zeta\delta\beta + B\delta H + \Theta\delta D \qquad [10]$$

where $\omega^S \equiv u^S - Ts^S - \sum_i \mu_i \Gamma_i$ is the density of the surface excess grand thermodynamic potential.

Let us consider now fluid interfaces composed of chemical components which are soluble in (and equilibrated with) the adjacent bulk phases. If a new piece of area is created at constant T, μ_i, β, H and D, this does not correspond to any change of the physical state of the interface. In such a case $(\partial\omega^S / \partial\alpha) = 0$ and from Eq.[10] one realises that $\gamma = \omega^s$. Then Eq.[10] reduces to a generalised form of the Gibbs adsorption equation. It is now evident that the bending and torsion moments, B and Θ, are connected with the curvature dependence of the interfacial tension.

The mechanical and thermodynamical approaches are two alternative (but complementary) routes for description of interfaces and membranes of arbitrary shape. It is very important to find the connection between them, that is, to establish relations between the thermodynamically defined tensions and moments, γ, ζ, B, Θ (Eq.[6]), and the mechanical tensors of stresses and moments, $\underline{\sigma}$, $\underline{M}$. This was done in Ref.(1) by direct calculation of δw^s in terms of purely mechanical quantities. The following results were obtained (1):

$$\gamma = \sigma + \frac{1}{2}BH + \frac{1}{2}\Theta D \quad ; \quad \zeta = \eta + \frac{1}{2}BD + \frac{1}{2}\Theta H \qquad [11]$$

$$\sigma = \frac{1}{2}(\sigma_1 + \sigma_2) \quad ; \quad \eta = \frac{1}{2}(\sigma_1 - \sigma_2) \qquad [12]$$

$$B = M_1 + M_2 \quad ; \quad \Theta = M_1 - M_2 \qquad [13]$$

In the basis of principal curvatures the scalars σ_1, σ_2, M_1, M_2 are the eigenvalues of the tensors $\underline{\sigma}$ and $\underline{M}$, respectively. Thus, σ and η are isotropic and deviatoric tensions; B and Θ are isotropic (bending) and deviatoric (torsion) moments.

What is remarkable in Eq.[11] is that the mechanical tensions, σ, η, do not coincide with the thermodynamical ones, γ and ζ. In particular, this leads to ambiguity in defining what is called "fluid interface". It could be either $\zeta = 0$ (no work for shear), or $\eta = 0$ (isotropic surface stresses) - see more extended discussion in Ref.(3). In the case of a spherical surface of radius a we have $B = 2M_1 = 2M_2$, $D = 0$, $H = -1/a$ and then Eqs.[5] and [11] yield

$$\gamma = \sigma - \frac{B}{2a} \quad ; \quad P_I - P_{II} = \frac{2\gamma}{a} + \frac{B}{a^2} \qquad [14]$$

In principle, bending moment exists on any physical boundary between two phases (much as it is for the interfacial tension), and may depend on curvature. Theoretical studies were devoted to calculation of the contributions of different intermolecular interactions in B. In Ref.(13) the role of the van der Waals interactions between pure water and hydrocarbon phases was investigated. For a plane interface it was found that the van der Waals contribution in the bending moment, B^{vw}, is of the order of 5×10^{-11} N, and tends to bend around the phase which has larger Hamaker constant (the oil). Electrostatic effects, due to adsorption of ionic surfactants, were shown to influence the bending moment considerably (14). The Stern layer and the diffuse part of the double electric layer provide comparable contributions, both in the range $1-2 \times 10^{-11}$ N, having the same sign as B^{vw}. We can now estimate the order of magnitude of different terms in Eqs.[14]. Let us examine the particularly important case of microemulsions. Typical size of the microemulsion droplets is $a \approx 10 \div 20$ nm, and the interfacial tension is ultralow, $\gamma \approx 10^{-3}$ dyn/cm. Then, with $B \approx 5 \div 10 \times 10^{-11}$ N one obtains that $B/2a$ amounts up to several dynes/cm. In other words, $B/2a \gg \gamma$ and in the generalised Laplace equation [14] the leading term is that with the bending moment. In contrast to γ, σ is *not* small. We come to the conclusion that in systems of high curvature and low γ the distinction between the thermodynamical and the mechanical tension is of paramount significance. The biological membranes represent another example of such systems.

Recently, the bending moment and the two Helfrich curvature elastic constants have been connected with ΔV-potential across an interface (15). The charge distribution in the system was modelled to be as in a molecular capacitor; this is an appropriate model for zwitterionic surfactants or lipids as well as for electric double layer at high salt concentration or at low surface potential.

The effect of the interfacial bending moment (or the spontaneous curvature, $H_0 = -B/(4k_c)$, see Ref. 3 or 15) was found to be important for the interaction between integral proteins incorporated in lipid membranes (16). Kralchevsky et al. (16) have demonstrated that both the hydrocarbon interior of the lipid bilayer and its surfaces (the head regions) contribute to the bending elastic moduli. The role of the curvature energy for the stability of microemulsions was discussed in Ref.(17). It was established that the process of droplet fusion passes through a series of states in which the surfactant layer has to adopt high positive curvature (opposite to that on the spherical drop surface). This is associated with a free energy barrier, and consequently, the bending properties turn out to be directly related to the rate of coalescence (17). The flocculation of deformed emulsion drops is also influenced by the curvature effects. In Ref.(18) it was proven that the thin liquid film formation between two droplets of submicrometer size can be accompanied with energy changes of the order of dozens of kT due to flattening of the surfaces (bending deformation). Yet another case when the flexural properties and the moments are important is the case of a fluid interface of low tension (σ), corrugated by fluctuation capillary waves - see Ref.(3) for details.

COUPLE OF INTERACTING FLUID INTERFACES (THIN FILM)

A liquid film is designated as "thin" if the intermolecular interactions are significant, so as to modify the properties of the film interior and its surfaces, and render them different from those corresponding to a large (bulk) phase. Two model approaches, called "membrane" and "detailed", can be applied for description of such films - for reviews see e.g. Refs.(5, 6, 19). The models are illustrated in Fig. 2 for the case of plane-parallel geometry. In the membrane approach a single surface of zero thickness is thought to represent the whole film. The film tension, γ^f, is defined as the work for increase of the film area (19). In the detailed approach an *idealised* system comprises the two film surfaces and the liquid interior, regarded as separate phases (in a thermodynamical sense). The surface tensions of the film, σ^f, are in principle different from those referring to large (bulk) phases, σ^l. The *excess* pressure inside the *real* film, taken with
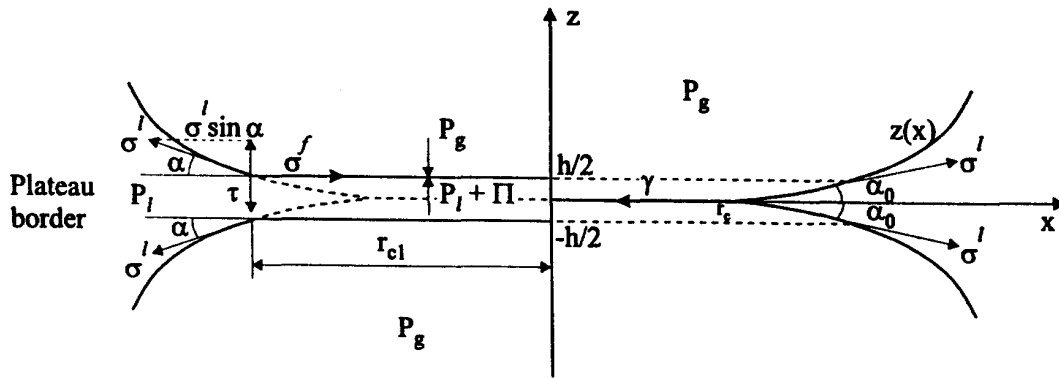
Fig. 2. Sketch of the membrane (right side) and detailed (left side) models of a thin liquid film.

respect to that in the meniscus, P_l, is called disjoining pressure, Π (20). In equilibrium, for flat films

$$\Pi = P_c = P_g - P_l \qquad [15]$$

where P_c is the capillary pressure - cf. Fig. 2. This equation follows from the fact that the pressure should be equal on both sides of a plane interface, i.e. $P_g = P_l + \Pi$. Physically, the disjoining pressure expresses the surface force per unit area. Depending on the specific system, surface forces of various origin can be operative: van der Waals, electrostatic, steric, oscillatory structural, hydrophobic, hydration, etc. (6, 20). It should be noted that two alternative and equivalent approaches exist for description of the surface forces in the thin films: "*disjoining pressure*" and "*body force*" approach, the latter being due to Felderhof (see Ref.(5) for discussion).

Connection between the membrane and detailed approaches (for plane-parallel films) is established by the relation (21)

$$\gamma^f = 2\sigma^f + \Pi h \qquad [16]$$

where h is the thickness. This can be readily obtained by making the balance of lateral forces acting on a plate of unit width and height h, placed normally to the film at $-h/2 < z < h/2$ (Fig. 2). A counterpart of Eq.[16] for spherically curved films was derived in Ref.(5).

From a macroscopic point of view, the actual smooth transition region between the film and the Plateau border is regarded as a sharp contact line. In Fig.2 this is the line of intersection of the film surfaces with the extrapolated

meniscus surfaces. The extrapolation means that the interaction between the two meniscus interfaces is neglected, i.e. a *model* system is considered in which Π is zero outside the film of thickness h. The *real* shape of the surfaces, with account for the continuous variations of Π and σ in the film-meniscus transition region, was investigated in Ref.(4). The contact angle, α, is defined (19) at the mathematical contact line in the idealised system (Fig.2). This approach of representing the transition zone film-meniscus as a sharp line requires introducing additional excess quantities in order to ensure that the conditions for equivalence between the real and idealised systems be satisfied. Such excess quantities are the line and transversal tensions, $\tilde{\kappa}$ and τ (4, 5). The tangential and normal projections of the force balance at each point of the contact line of radius r_{cl} (in a plane system of rotational symmetry, Fig. 2) read (4, 5)

$$\sigma^f + \frac{\tilde{\kappa}}{r_{cl}} = \sigma^l \cos\alpha \quad ; \quad \tau = \sigma^l \sin\alpha \qquad [17]$$

From Eq.[17] it is evident that due to line tension the contact angle, α, may depend on the film radius, r_{cl}. α and τ (Eq.[17]) originate from the integral effect of the long-range *attractive* surface forces acting in the transition region between the film and the Plateau border. Micromechanical expression for τ was proposed in Ref.(4),

$$\tau = \frac{1}{r_{cl}} \int_0^{x_B} \left[\Pi^{id} - \Pi(x)\right] x\, dx \qquad [18]$$

where Π^{id} corresponds to the idealised system, that is, $\Pi^{id} = P_c$ for $0 < x < r_{cl}$ and $\Pi^{id} \equiv 0$ for $x > r_{cl}$ (Fig. 2). The running radial coordinate is x, and $x = x_B$ at the point where the real profile coincides with the idealised one ($x_B > r_{cl}$). $\Pi(x)$ is the real continuous dependence of the disjoining pressure. Thus, τ takes into account the interaction between the two contact lines in the detailed model - Fig.2. Since at equilibrium Π is repulsive ($\Pi > 0$, Eq.[15]), there are only two reasons that can cause the film surfaces to stay attached to each other: (i) existence of external force, such as for example buoyancy, which presses a drop or bubble against a surface; (ii) positive τ, applied at the contact line, counterbalancing Π, see e.g. Ref. (6). Equation analogous to [18] was derived in Ref.(4) for the line tension:

$$\frac{\tilde{\kappa}}{r_{cl}} = \int_0^{x_B} \left\{ \left(\frac{\sigma \sin^2\varphi}{x\cos\varphi}\right)^{real} - \left(\frac{\sigma \sin^2\varphi}{x\cos\varphi}\right)^{model} \right\} dx \qquad [19]$$

Here φ is the running slope of the respective meniscus profiles. Eq.[19] was utilized in Ref.(22) to calculate $\tilde{\kappa}$ for emulsion films; negative $\tilde{\kappa}$ of the order of 10^{-13} N were obtained.

It should be noted that the width of the transition region between a thin liquid film and Plateau border is usually very small - below 1 μm (23). That is the reason why the optical measurements, e.g. by interferometric techniques (7), do not give information for the real transition zone. Instead, one obtains the meniscus profile away from the transition region and extrapolates to find the macroscopic contact angle, α, as mentioned above. Measurements of contact angle, film and line tension were presented in Refs.(7, 24) for the case of an air bubble sticking to a liquid/ air interface. A black thin liquid film formed at the top of the bubble. The system contained ionic surfactant (sodium dodecylsulfate) and inorganic electrolyte (NaCl). The experimental cell used in Ref.(7) allowed measurements with shrinking, expanding, and quiescent ("stopped") bubbles. Thus, the impact of the motion of the contact line was investigated. It was established that slowly shrinking bubbles exhibit non-equilibrium (dynamic) contact angles. This corresponds to detachment of the two film surfaces (advancing meniscus). On the other hand, the contact angle remains constant and equal to the equilibrium one in the case of receding meniscus (expanding bubble); in other words, a typical contact angle hysteresis is observed, see Ref. (25) for details. The data allowed independent calculation of the film tension, γ^f, and line tension, κ (in the membrane approach).

By regulation of the pressure inside the experimental cell initially shrinking bubbles were stopped at a fixed size. In those conditions both the film and the line tension, γ^f and κ, showed relaxation with time. γ^f finally reached its equilibrium value and κ tended to zero (within the experimental accuracy). Dynamic values of κ about $(-5) \div (-10) \times 10^{-8}$ N were measured. The equilibrium line tension, as predicted by the theory (22, 23, 26), is an extremely small quantity (of the order of $10^{-11} \div 10^{-13}$ N), so it usually turns out to be below the threshold of the experimental accuracy. On the other hand, the dynamic line tension can be several orders of magnitude larger. This finding clarifies the problem about the large values of κ determined experimentally (24), which brought about an ardent discussion in the literature, see Ref. (25) for a critical review.

Estimates of the viscous friction which accompanies the motion in the contact zone showed that *the viscous effects* can hardly be responsible for the observed non-equilibrium behaviour at such small flow rates. That is the reason why we will now check the possible role of *plastic effects* connected with the detachment of the film surfaces in the case of shrinking bubbles.

According to the concepts of rheology, an ideal plastic body is characterised by the following relationship between the rate of change, $\dot{x}$, of the dynamic variable, x, and the applied tension, τ (see Fig. 3a and Refs. (27), (28)):

$$\dot{x} = 0 \quad \text{for} \quad \tau < \tau^*, \qquad \tau = \tau^* = \text{const} \quad \text{for} \quad \dot{x} \neq 0 \qquad [20]$$

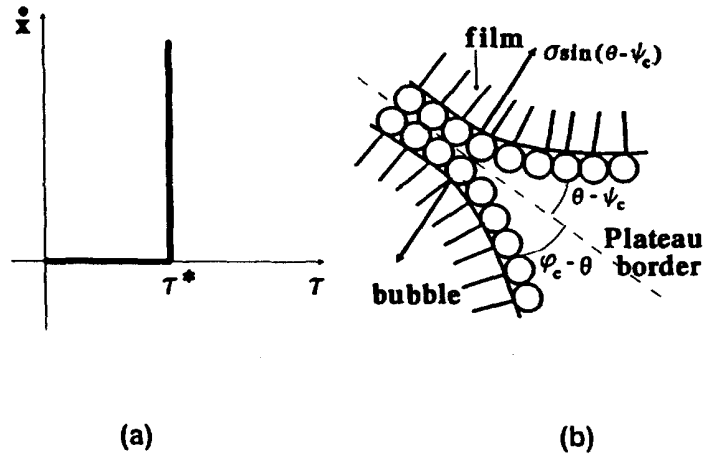(a)   (b)

Fig. 3. Shrinking of a contact line as a plastic deformation: (a) relation between the rate of strain, $\dot{x}$, and the applied stress, τ; (b) detachment of the two film surfaces in front of an advancing meniscus.

where τ^* is the "yield stress", i.e. the minimum applied tension needed for the plastic deformation to occur.

In our case the plastic deformation corresponds to the detachment of the two initially attached surfactant monolayers (the two film surfaces) during the advance of the contact line (Fig. 3b). The dynamic variable x can be chosen to be the number of surfactant molecules belonging to the two attached film surfaces; τ should be the transversal tension, which opposes the detachment of the film surfaces at the contact line. τ^* is to be identified with the constant value acquired by the transversal tension in the process of meniscus advance. To check whether the latter process can be really interpreted as a plastic deformation we consider the force balance along the normal to the film surface at the contact line (Fig 3b):

$$\sigma\sin(\theta - \psi_c) = \sigma\sin(\phi_c - \theta) + \frac{\kappa}{r_c}\sin\theta \qquad [21]$$

here θ, ϕ_c and ψ_c are angles measured experimentally in Ref.(24), Fig. 4 therein; r_c and κ are the contact line radius and the line tension in the membrane approach. In accordance with the hypothesis for *plastic* deformation, from Eqs.[20] and [21] one obtains that the following relationships should be satisfied in the case of advancing meniscus:

$$\sigma\sin(\theta - \psi_c) = \tau^* = \text{const} \qquad [22]$$

$$\sigma \sin(\varphi_c - \theta) + \frac{\kappa}{r_c} \sin\theta = \tau* = \text{const}$$ [23]

Eq.[22] predicts that $(\theta - \psi_c)$ must be constant. As demonstrated in Fig.4, the last prediction is very well satisfied by our experimental data from Ref.(24), Fig. 4 therein. The values of $\tau*$ determined from Fig. 4 are 3.6 and 4.4 mN/m for the SDS solutions with 0.25 and 0.32 M added NaCl.

It is commonly believed that the contact angle hysteresis originates predominantly from roughness or chemical heterogeneity of the substratum when the latter is solid. From theoretical point of view, the possibility for existence of hysteresis on smooth homogeneous surfaces was investigated in Refs.(29). The central result reported there was that the disjoining pressure isotherm in the thin liquid film explicitly determines not only the equilibrium value of the contact angle, but also the advancing and the receding angles. In other words, the hysteresis is explained solely in terms of the intermolecular interactions in the film. It was experimentally confirmed in Ref.(25) that hysteresis can actually take place in the case of liquid boundaries. In the present work this phenomenon is attributed to strong short-range attraction between the two film surfaces. It is operative with ionic surfactant at **high** electrolyte content, and can be due to the discreteness of the surface charges (30), and to ionic correlations (31). Grimson et al. (30) discuss the situation when the two opposing interfaces of the film bear a lattice mosaic configuration of positive and negative charges of equal number. Then, attractive electrostatic interaction was found to exist. Moreover, the energy associated with the charge discreteness had been shown to bring into agreement measured and calculated interaction energies of Newton black films stabilised by sodium dodecylsulfate (30). Results of other authors (31) have demonstrated that the interplay between the effects of the finite size of the ions and the electrostatic pair correlation also lead to attraction at small film thickness. In our case the attraction causes the two surfactant monolayers to stick firmly to each other. Their detachment is accompanied by significant local alterations of the interfacial shapes and tensions in the real dynamic transition zone, which contributes (cf. Eq.[19]) to large (10^{-8} N) values of the dynamic line tension.

The comparatively large values of the film tension, γ^f, measured with shrinking bubbles (7, 24), can be attributed to the stretching of the film at the first stage of the process, $\tau < \tau*$, when the detachment of the surfaces has not yet been started because the contact angle is still smaller than the advancing angle. The cause of this stretching is the fact that as the bubble diminishes the pressure inside increases and, correspondingly, the film curvature also increases at almost fixed contact line radius r_c. This process resembles the stretching of the interface in the
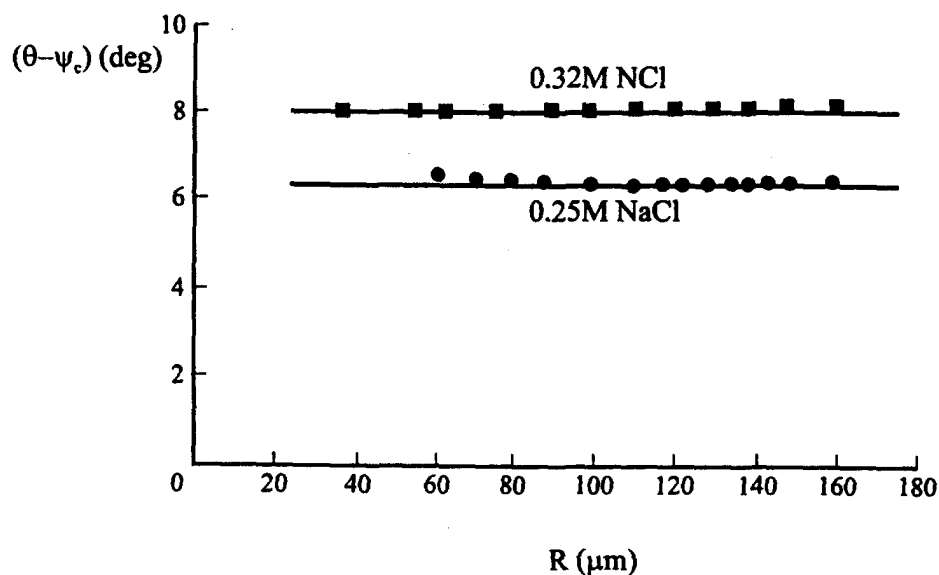
Fig. 4. Angle $(\theta - \psi_c)$ vs. the equatorial bubble radius, R, for shrinking bubbles formed in 0.05 wt.% aqueous solution of SDS with 0.25 and 0.32 M added NaCl.

known "maximum bubble pressure method" for dynamic surface tension measurement (32).

The above hypothesis about the origin of the measured large dynamic values of the film and line tension is supported also by the fact that the effect is observed only with advancing (but never with receding) menisci. Moreover, if one carries out the same experiment, but with a nonionic surfactant, rather than with SDS, no detectable line tension is found out (33). This is related to the absence of strong short-range attraction between the two nonionic surfactant adsorption monolayers, as indicated by the small contact angle which is not subjected to hysteresis in this case (33).

REFERENCES

1. Gurkov, T.D. and Kralchevsky, P.A., Colloids Surfaces, 47, 45 (1990).

2. Kralchevsky, P.A., J. Colloid Interface Sci., 137, 217 (1990).

3. Kralchevsky, P.A., Eriksson, J.C. and Ljunggren, S., Adv. Colloid Interface Sci., 48, 19 (1994).

4. Kralchevsky, P.A. and Ivanov, I.B., Chem. Phys. Lett., 121, 116 (1985).

5. Ivanov, I.B. and Kralchevsky, P.A., "Mechanics and Thermodynamics of Curved Thin Films", in "Thin Liquid Films", I.B. Ivanov, Ed., M. Dekker, New York, 1988, p. 49.

6. Kralchevsky, P.A., Danov, K.D. and Ivanov, I.B., "Thin Liquid Film Physics", in "Foams: Theory, Measurements and Applications", R.K. Prud'homme and S.A. Khan, Eds., M. Dekker, New York, 1995, Chapter 1.

7. Dimitrov, A.S., Nikolov, A.D., Kralchevsky, P.A. and Ivanov, I.B., *J. Colloid Interface Sci.*, **151**, 462 (1992).

8. Naghdi, P.M., "The Theory of Shells and Plates", in "Handbuch der Physik", S. Flugge, Ed., Vol. VIa/2, Springer, Berlin, 1972, p. 425.

9. Podstrigach, Ya. S. and Povstenko, Yu. Z., "Introduction in Mechanics of Surface Phenomena in Deformable Solids", Naukova Dumka, Kiev, 1985 (in Russian).

10. Evans, E.A. and Skalak, R., "Mechanics and Thermodynamics of Bio-membranes", CRC Press, Boca Raton, Florida, 1979.

11. Scriven, L.E., *Chem. Eng. Sci.*, **12**, 98 (1960).

12. Gibbs, J.W., "The Scientific Papers of J. Willard Gibbs", Vol. 1, Dover, New York, 1961.

13. Kralchevsky, P.A. and Gurkov, T.D., *Colloids Surfaces*, **56**, 101 and 119 (1991).

14. Kralchevsky, P.A., Gurkov, T.D. and Ivanov, I.B., *Colloids Surfaces*, **56**, 149 (1991).

15. Kralchevsky, P.A., Gurkov, T.D. and Nagayama, K., "Electric Components of the Interfacial Bending Moment and Curvature Elastic Moduli", *J. Colloid Interface Sci.*, in press (1995).

16. Kralchevsky, P.A., Paunov, V.N., Denkov, N.D. and Nagayama, K., *J. Chem. Soc. Faraday Trans.*, **91**, 3415 (1995).

17. Fletcher, P.D.I., Howe, A.M. and Robinson, B.H., *J. Chem. Soc., Faraday Trans. I*, **83**, 985 (1987).

18. Petsev, D.N., Denkov, N.D. and Kralchevsky, P.A., *J. Colloid Interface Sci.*, **176**, 201 (1995).

19. de Feijter, J.A., "Thermodynamics of Thin Liquid Films", in "Thin Liquid Films", I.B. Ivanov, Ed., M. Dekker, New York, 1988, p. 1.

20. Derjaguin, B.V., "Theory of Stability of Colloids and Thin Films", Plenum Press, New York, 1989.

21. Toshev, B.V. and Ivanov, I.B., *Colloid Polymer Sci.*, **253**, 558 and 593 (1975).

22. Denkov, N.D., Petsev, D.N. and Danov, K.D., *J. Colloid Interface Sci.*, **176**, 189 (1995).

23. de Feijter, J.A. and Vrij, A., *J. Electroanal. Chem.*, **47**, 9 (1972).

24. Kralchevsky, P.A., Nikolov, A.D. and Ivanov, I.B., *J. Colloid Interface Sci.*, **112**, 132 (1986).

25. Ivanov, I.B., Dimitrov, A.S., Nikolov, A.D., Denkov, N.D. and Kralchevsky, P.A., *J. Colloid Interface Sci.*, **151**, 446 (1992).

26. Tarazona, P. and Navascues, G., *J. Chem. Phys.*, **75**, 3114 (1981).

27. Reiner, M., "Rheology", Springer-Verlag, Berlin, 1958.

28. Shchukin, E.D., Pertsov, A.V. and Amelina, E.A., "Colloid Chemistry", Moscow University Press, Moscow, 1982 (in Russian).

29. Martynov, G.A., Starov, V.M. and Churaev, N.V., *Kolloidn. Zh.*, **39**, 472 (1977); Starov, V.M., *Adv. Colloid Interface Sci.*, **39**, 147 (1992).

30. Grimson, M.J., Richmond, P. and Vassilieff, Ch.S., "Electrostatic Interactions in Thin Films", in "Thin Liquid Films", I.B. Ivanov, Ed., M. Dekker, New York, 1988, p. 275.

31. Kjellander, R. and Marcelja, S., *Chem. Phys. Lett.*, **112**, 49 (1984).

32. Mysels, K.J., *Colloids Surfaces*, **43**, 241 (1990).

33. Lobo, L.A., Nikolov, A.D., Dimitrov, A.S., Kralchevsky, P.A. and Wasan, D.T., *Langmuir*, **6**, 995 (1990).