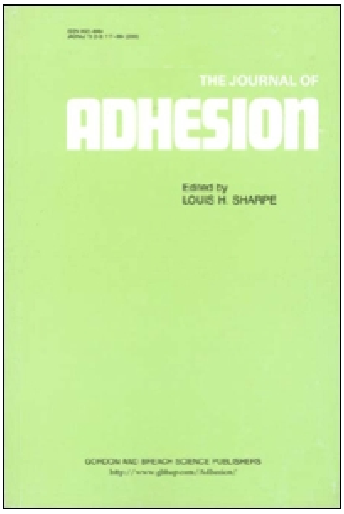
This article was downloaded by:
On: *22 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Contact Angle Equilibrium on Thin Elastic Solids

Martin E. R. Shanahan[a,b]
[a] Centre de Recherches sur la Physico-Chimie des, Mulhouse, France [b] Laboratoire de Recherches sur la Physico-Chimie, des Interfaces de l'Ecole Nationale Supirieure de Chimie, Mulhouse cedex, France

To cite this Article Shanahan, Martin E. R.(1985) 'Contact Angle Equilibrium on Thin Elastic Solids', The Journal of Adhesion, 18: 4, 247 — 267
To link to this Article: DOI: 10.1080/00218468508080461
URL: http://dx.doi.org/10.1080/00218468508080461

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Adhesion, 1985, Vol. 18, pp. 247–267
0021-8464/85/1804-0247 $18.50/0
© 1985 Gordon and Breach, Science Publishers, Inc. and OPA Ltd
Printed in the United Kingdom

Contact Angle Equilibrium on Thin Elastic Solids

MARTIN E. R. SHANAHAN

Centre de Recherches sur la Physico-Chimie des Surfaces Solides
24, Avenue du Président Kennedy 68200 MULHOUSE—FRANCE

and

Laboratoire de Recherches sur la Physico-Chimie des Interfaces
de l'Ecole Nationale Supérieure de Chimie de Mulhouse
3, rue Alfred Werner 68093 MULHOUSE CEDEX—FRANCE

Downloaded At: 15:57 22 January 2011

(*Received November 26, 1984; in final form April 4, 1985*)

A theoretical analysis has been carried out on the system consisting of an axisymmetric sessile drop resting on a thin elastic solid in the presence of gravity. The solid is treated in one case as a thin plate and in the other case as a membrane. The consequences of the variational treatment employed are equations relating to contact angle equilibrium, drop and solid profiles. It is shown that contact angles are not intrinsic surface properties of the phases involved but invoke equally such characteristics as bulk properties of the solid and physical dimensions when the solid in question is deformable.

Key words: Contact angle, Drop profiles, Equilibrium, Theoretical analysis, Thin elastic solids, Young's equation.

INTRODUCTION

The equilibrium contact angle of a liquid (1) on a solid surface (S) in the presence of an immiscible second fluid phase (2) has generally been considered to be an intrinsic property of the three phases in question. When the solid is undeformable, Young's relationship† is usually adopted[1]

$$\gamma_{s2} = \gamma_{s1} + \gamma_{12} \cos \theta_0 \tag{1}$$

† In fact, in the original frequently quoted Reference 1, Young never actually expressed mathematically the equation named after him, *i.e.* equation (1).

where γ represents an interfacial tension or free energy and θ_0 is the equilibrium contact angle measured in liquid 1. Probably the best known and simplest derivation of equation (1) depends on the simple mechanistic approach of assuming the γ terms to be physical tensions and then resolving horizontally. This argument was vehemently disfavoured by Bikerman (*e.g.*, Refs. 2,3), who was a strong advocate of Young's equation being rejected on the grounds of an improper vertical force balance. Nevertheless, in the case of a strictly, mathematically undeformable solid, Young's equation can be derived quite rigorously using thermodynamic arguments. In this case, the γ terms are usually considered as interfacial free energies—whether these are defined as Helmholtz or Gibbs free energies is of little import.[4] Examples of such thermodynamic approaches are to be found in Refs. 5–10.

At various times, others have objected to Young's equation for various reasons. Pethica and Pethica[11] suggested that gravity should be taken into account but this seems to have been adequately refuted both by the thermodynamic arguments cited above and also by the comments made by Gray[12] suggesting an inexact appraisal of the net situation. Both Jameson and Del Cerro[13] and White[14] have conjectured that Young's equation may be correct macroscopically but microscopically, it cannot be valid. Another factor possibly perturbing Young's equation is the existence of the much discussed line tension (*e.g.*, Ref. 15). Although for what follows it could easily be incorporated, at present it is assumed not to exist.

The above relates to various work and points of view concerning liquids on *undeformable* substrates. However, as pointed out by Bikerman[2] when considering the vertical tension, in real solids there must presumably be some deformation or strain resulting from the force required to compensate $\gamma_{12} \sin \theta_0$. Nevertheless relatively little work seems to have been done in this field, although experimental evidence does strongly suggest that solid strains should not, under certain circumstances, be neglected.[16–19] From a theoretical point of view, apparently the first approach including the effects of strain was that by Lester.[20–22] Later work is given in Refs. 23 and 24, but probably the most significant contribution comes from Rusanov.[25,26] However, both Lester and Rusanov considered semi-infinite elastic solids in their analyses, and although there must surely be some strain involved when a sessile drop of liquid is placed on the surface of such a solid, this effect will normally be minute. The effects of surface strain should be much more marked if the solid in question is very thin, and free to be distorted.

Downloaded At: 15:57 22 January 2011

To the author's knowledge, there exists but one reference at present in the literature concerning such thin solids and that is the very recent paper of Fortes.[27] In this work, the equilibrium of thin elastic solids in contact with liquid drops is analysed theoretically using force balances. For certain cases, calculations are facilitated by considering weightless drops. Equilibrium is considered to depend on surface tension and elastic forces.

The purpose of the present study is related in the sense that axisymmetric sessile drops on thin elastic solids, modelled by thin plate and by membrane theory, are to be considered with an aim to understanding better the contact equilibrium when the solid is strained, and to getting some theoretical idea of what conformation the system adopts. However, instead of considering forces, the approach of minimising the total free energy of the system will be adopted. All the mathematics used assumes that all phases may be treated by a continuum approach. No consideration is given to molecular aspects.

THEORY

In the following derivations, the usual implicit assumptions of meniscus calculations are taken to hold (solid and fluid homogeneous as far as surface state is concerned, immiscibility of phases, etc ...).

Figure 1 represents an axisymmetric drop of liquid 1 (radius r_0) resting in the centre of a thin, circular sheet of an elastic solid, S, of radius a, in the presence of a less dense fluid 2. The (conventional) contact angle, θ_0, is taken to be $<90°$ for simplicity. The system initially consisting of the flat solid alone has its free energy (F.E.) modified by the addition of the drop. This modification will be due to changes in

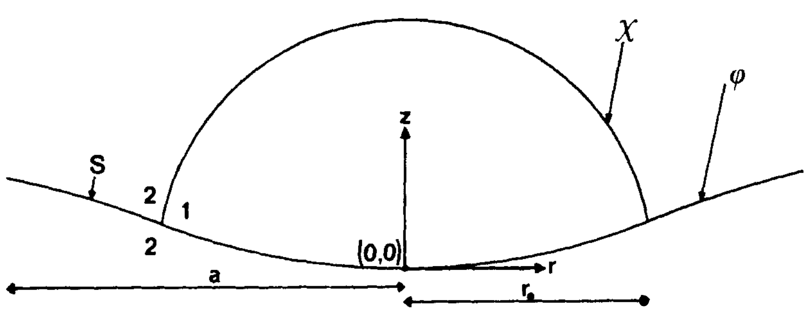


FIGURE 1 Drop of liquid (1) on solid surface (S) in presence of fluid (2) and coordinate system used (r,z). χ and ϕ represent respectively drop and solid profiles.

Downloaded At: 15:57 22 January 2011

interfacial F.E., gravitational F.E. both of the solid and the liquid, and the elastic energy of deformation of the solid. Since we consider here only a thin solid, it is assumed that the gravitational F.E. of the solid is negligible, although that of the liquid drop will not be. Under these conditions, we may define the change in F.E. of the system due to the presence of the drop, where the gravitational F.E. of the drop is taken with respect to the origin as shown in Figure 1.

$$E_T = 2\pi \int_0^{r_0} [(\gamma_{s1} + \gamma_{s2})r(1 + \phi_r^2)^{1/2} - 2\gamma_{s2}r + \gamma_{12}r(1 + \chi_r^2)^{1/2} + \frac{\rho g}{2} r (\chi^2 - \phi^2) + r E_e] \mathrm{d}r + 2\pi \int_{r_0}^{a} [2\gamma_{s2}r(1 + \phi_r^2)^{1/2} - 2\gamma_{s2}r + rE_e] \mathrm{d}r \tag{2}$$

In equation (2), γ_{s1}, γ_{s2} and γ_{12} represent the three interfacial free energies between the respective phases, ϕ (r) and χ (r) are the profiles respectively of the solid surface and liquid upper surface in cylindrical coordinates (r, z), the suffix r has its usual meaning of partial differentiation with respect to r, ρ is the (positive) density difference between the two fluids and g is gravitational acceleration. The term E_e may be interpreted as the elastic, stored energy density in the solid (per unit area) and, as will be seen below, may be a function of r, ϕ_r and ϕ_{rr}, depending on whether the solid is treated as a plate or as a membrane. It should be noted that in this simple geometry, it is assumed that the underside of the solid is only in contact with fluid 2—any supports are considered to touch at mathematical points or at most lines.

At equilibrium, E_T will be a minimum subject to the constraint of constant drop volume V.

$$V = 2\pi \int_0^{r_0} r(\chi - \phi) \, \mathrm{d}r \tag{3}$$

This is a problem of the calculus of variations. We define

$$J = E_T + \lambda V$$

Downloaded At: 15:57 22 January 2011

where λ is a constant, a Lagrange multiplier. Equations (2) and (3) can then be represented together in the following form.

$$J = \int_0^{r_0} F(r, \phi, \chi, \phi_r, \chi_r, \phi_{rr})\, \mathrm{d}r + \int_{r_0}^{a} H(r, \phi_r, \phi_{rr})\mathrm{d}r \tag{4}$$

where the ϕ_{rr} dependence of the two integrands may or may not exist. For the system to be at a minimum in F.E., any imposed infinitesimal changes in the system must result in a zero change in J, *i.e.* $\delta J = 0$. In the present case, we impose infinitesimal arbitrary changes $\delta\phi$ and $\delta\chi$ on the profile functions, ϕ and χ, accompanied by displacement of the three-phase line by δr_0. These changes are independent, except at $r = r_0$, where clearly $\delta\phi|_{r_0} = \delta\chi|_{r_0}$ and drop volume remains constant. Using the classical theory of the calculus of variations, as expounded, for example, by Smirnov,[28] we obtain after some algebra the general first variation, δJ, as

$$\begin{aligned}\delta J = &\int_0^{r_0} \left\{\frac{\partial F}{\partial \phi} - \frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{\partial F}{\partial \phi_r}\right) + \frac{\mathrm{d}^2}{\mathrm{d}r^2}\left(\frac{\partial F}{\partial \phi_{rr}}\right)\right\}\delta\phi \cdot \mathrm{d}r \\
&+ \int_{r_0}^{a} \left\{\frac{\mathrm{d}^2}{\mathrm{d}r^2}\left(\frac{\partial H}{\partial \phi_{rr}}\right) - \frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{\partial H}{\partial \phi_r}\right)\right\}\delta\phi \cdot \mathrm{d}r + \int_0^{r_0} \left\{\frac{\partial F}{\partial \chi} - \frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{\partial F}{\partial \chi_r}\right)\right\}\delta\chi \cdot \mathrm{d}r \\
&+ \left[\frac{\partial F}{\partial \chi_r} + \frac{\partial F}{\partial \phi_r} - \frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{\partial F}{\partial \phi_{rr}}\right) - \frac{\partial H}{\partial \phi_r} + \frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{\partial H}{\partial \phi_{rr}}\right)\right]_{r=r_0} \cdot \delta\phi|_{r_0} \\
&+ \left[F - \frac{\partial F}{\partial \chi_r}\cdot \chi_r - \frac{\partial F}{\partial \phi_r}\cdot \phi_r + \frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{\partial F}{\partial \phi_{rr}}\right)\cdot \phi_r - \frac{\partial F}{\partial \phi_{rr}}\cdot \phi_{rr}\right. \\
&\left. - H + \frac{\partial H}{\partial \phi_r}\cdot \phi_r - \frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{\partial H}{\partial \phi_{rr}}\right)\cdot \phi_r + \frac{\partial H}{\partial \phi_{rr}}\cdot \phi_{rr}\right]_{r=r_0} \cdot \delta r_0 \\
&+ \left[\frac{\partial F}{\partial \phi_{rr}} - \frac{\partial H}{\partial \phi_{rr}}\right]_{r=r_0} \cdot \delta\phi_r|_{r_0}\end{aligned} \tag{5}$$

Since $\delta J = 0$ and, in general, the infinitesimal changes leading to it are arbitrary and independent, the value of the coefficient of each is identically zero. We thus have 5 equations which apply to the drop/solid/fluid system at equilibrium, although one of them is useless (the term in $\delta\phi_r|_{r_0}$ is identically zero in what follows).

Downloaded At: 15:57 22 January 2011

Before going on to study the two cases of thin elastic solids, attention should briefly be paid to the third integral term in equ. (5), *i.e.* that involving $\delta\chi$.

It implies that

$$\frac{\partial F}{\partial \chi} - \frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{\partial F}{\partial \chi_r}\right) = 0 \tag{6}$$

and when equation (6) is evaluated using equation (2) and (3), we obtain

$$\frac{\mathrm{d}}{\mathrm{d}r}\left[\frac{\gamma_{12} r \chi_r}{(1+\chi_r^2)^{1/2}}\right] = \rho g r \chi + \lambda r \tag{7}$$

where λ is equal to $-\left(\dfrac{2\gamma_{12}}{b} + \rho g \chi(0)\right)$, b representing the radius of curvature at the drop apex.[10]

This is simply the standard capillary equation describing the profile of a sessile drop (*e.g.*, Refs. 29, 30). It may seem intuitively obvious but it is nevertheless interesting to show mathematically that the axisymmetric sessile drop profile equation is unaltered by what may happen "underneath". Clearly contact angles may be modified but this can be accounted for by the two constants of integration required to evaluate equation (7).

Downloaded At: 15:57 22 January 2011

Plates

In this analysis, we assume that the elastic solid behaves as a thin, flat plate which is bent under the effects of the sessile drop. All elastic strain energy is considered due to bending. Any elongation is taken to be negligible as far as elastic energy is concerned.

Such a thin plate under bending may be considered to be in plane stress, there being a strain but no stress component perpendicular to the plate. If in addition shear stresses are absent, it is easy to show, developing on Timoshenko and Goodier,[31] that the elastic strain energy/unit area of plate can be written as

$$\frac{Et^3}{24(1-\nu^2)}\left[\frac{1}{R_1^2} + \frac{1}{R_2^2} + \frac{2\nu}{R_1 R_2}\right]$$

where E and ν are respectively the Young's modulus and Poisson's coefficient of the solid, t is the plate thickness and R_1 and R_2 are the principal radii of curvature in bending. Given that these radii of curvature are given in the present coordinate system by

$$\frac{1}{R_1}=\frac{\phi_{rr}}{(1+\phi_r^2)^{3/2}}$$

and

$$\frac{1}{R_2}=\frac{\phi_r}{r(1+\phi_r^2)^{1/2}}$$

that the surface area of a thin hoop of plate at distance r from the origin is given by

$$2\pi r(1+\phi_r^2)^{1/2}\cdot\delta r$$

and that the flexural rigidity of the plate, D, is defined by

$$D=\frac{Et^3}{12(1-\nu^2)}$$

it is relatively simple to obtain an expression for the elastic, stored energy density, E_e, given in equation (2).

$$E_e=\frac{D}{2}\left[\frac{\phi_{rr}^2}{(1+\phi_r^2)^{5/2}}+\frac{\phi_r^2}{r^2(1+\phi_r^2)^{1/2}}+\frac{2\nu\phi_r\phi_{rr}}{r(1+\phi_r^2)^{3/2}}\right] \quad (8)$$

Using equation (8) in equation (2), and bearing in mind the definitions of F and H in equation (4), equation (5) may be applied and three relationships concerning the axisymmetric sessile drop on a plate emerge ($\delta\phi_r|_{r_0}$ and $\delta\chi$ are dealt with above).

Of these, the two concerning the terms δr_0 and $\delta\phi|_{r_0}$ are perhaps the more interesting concerning directly contact angle equilibrium. Equating the coefficient of δr_2 to zero, we obtain after evaluation at r_0 and some simplification

$$(\gamma_{s1}-\gamma_{s2})\cdot[1+\phi_r^2(r_0)]^{-1/2}+\gamma_{12}[1+\chi_r^2(r_0)]^{-1/2}=0 \quad (9)$$

In the derivation of equation (9), it is assumed that ϕ_r is continuous at r_0. This means physically that the plate is intact. A discontinuity in ϕ_r would imply infinitely sharp folding, or breaking of the material.

Considering Figure 2, it can be seen that at r_0, the angles of inclination with respect to the horizontal of the liquid, θ_0, and of the solid, α, are related to the profile derivatives such that $\chi_r\ (r_0)=-\tan\theta_0$ and $\phi_r\ (r_0)=\tan\alpha$.

Using simple trigonometrical formulae, it can be shown from equation (9) that:

Downloaded At: 15:57 22 January 2011

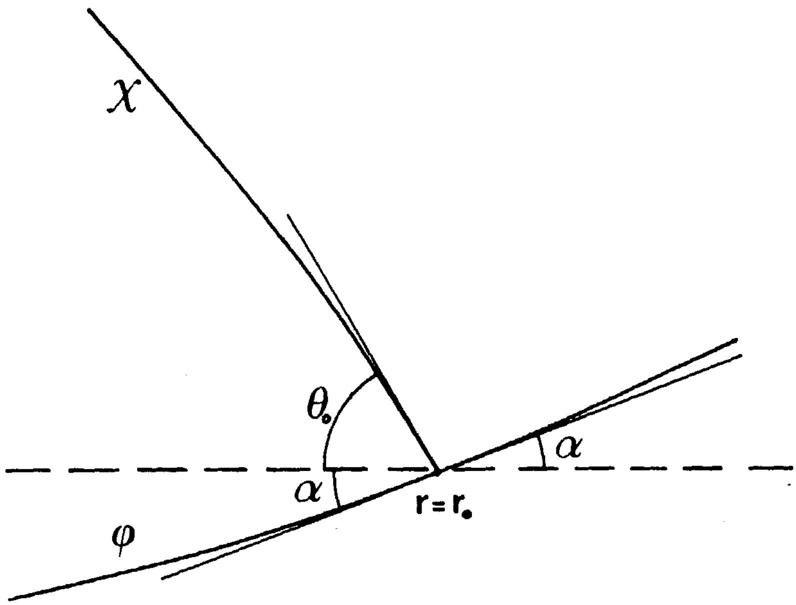


FIGURE 2 The contact region for a thin plate.

$$\gamma_{s2} = \gamma_{s1} + \gamma_{12}\frac{\cos\theta_0}{\cos\alpha} \tag{10}$$

Equation (10) may be taken as a modification of Young's equation for contact angle equilibrium when the strain energy of bending of the plate is to be taken into account. Clearly, unless the bending is significant, α is very small and in the limit of an undeformable solid as $\alpha \to 0$, equation (10) reduces to Young's equation.

A second relationship concerning contact angle equilibrium can be obtained on considering the coefficient of $\delta\phi|_{r_0}$ in equation (5). Putting this coefficient equal to zero, evaluation at $r = r_0$ and simplification leads to

$$\gamma_{12}\cdot\chi_r(r_0)\cdot[1+\chi_r^2(r_0)]^{-1/2} + (\gamma_{s1}-\gamma_{s2})\cdot\phi_r(r_0)\cdot[1+\phi_r^2(r_0)]^{-1/2} = 0 \tag{11}$$

Again using the trigonometrical relations, this reduces to

$$\gamma_{12}\sin\theta_0 = (\chi_{s1} - \gamma_{s2})\sin\alpha \tag{12}$$

The last part of equation (5) to be considered involves the two integrals in $\delta\phi$. As they stand, these two terms should be taken together and equated to zero using standard variational arguments, but following

Courant and Hilbert,[32] we shall assume that each integral may be set to zero. This leads to

$$\frac{\partial F}{\partial \phi} - \frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{\partial F}{\partial \phi_r}\right) + \frac{\mathrm{d}^2}{\mathrm{d}r^2}\left(\frac{\partial F}{\partial \phi_{rr}}\right) = 0 \tag{13}$$

over the range $0 \leqslant r \leqslant r_0$ and

$$\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{\partial H}{\partial \phi_r}\right) - \frac{\mathrm{d}^2}{\mathrm{d}r^2}\left(\frac{\partial H}{\partial \phi_{rr}}\right) = 0 \tag{14}$$

in the range $r_0 \leqslant r \leqslant a$.

When equation (13) is evaluated, we obtain a differential equation describing the profile of the bent solid under the drop, *i.e.* ϕ. In equation (15), $\eta = (1 + \phi_r^2)^{1/2}$.

$$\frac{\mathrm{d}^2}{\mathrm{d}r^2}\left[D\left(\frac{r\phi_{rr}}{\eta^5} + \frac{\nu\phi_r}{\eta^3}\right)\right] - \frac{\mathrm{d}}{\mathrm{d}r}\left[\frac{r\phi_r}{\eta}(\gamma_{s1} + \gamma_{s2}) + \frac{D}{2}\left(\frac{2\phi_r}{r\eta} - \frac{\phi_r^3}{r\eta^3}\right.\right.$$
$$\left.\left. - \frac{2\nu\phi_{rr}}{\eta^3} - \frac{6\nu\phi_r^2\phi_{rr}}{\eta^5} - \frac{5r\phi_r\phi_{rr}^2}{\eta^7}\right)\right] - \rho g r\phi - \lambda r = 0 \tag{15}$$

This fourth-order equation is evidently rather complicated and therefore no attempt has been made to solve it analytically. However, an approximate perturbation type solution valid over a restricted range is suggested in the appendix to this paper.

Lastly, application of equation (14) leads to an equation describing the profile of the axisymmetric plate outside the drop. This may be written in the form

$$2r(1 + \phi_r^2)(r\phi_{rrr} + \phi_{rr}) - 5r^2\phi_r\phi_{rr}^2 - \phi_r(2 + 5\phi_r^2 + 4\phi_r^4 +$$
$$\phi_r^6) - 4\gamma_{s2}D^{-1}r^2\phi_r(1 + \phi_r^2)^3 = 0 \tag{16}$$

(Here the first integration has been performed and the physically reasonable boundary condition of all derivatives of ϕ tending to zero for large r employed.) Equation (16) is also solved approximately in the appendix.

It should be noted that both equations (15) and (16) require boundary conditions for their solutions. These may be obtained, in principle, by considering the methods of physical support of the system drop/plate (point contact of base of curved plate, clamping of plate outer edge, etc.), and the physical properties of the drop of liquid (volume, density, etc.), together with contact line equilibrium.

Downloaded At: 15:57 22 January 2011

Membranes

For the case of the elastic solid being considered as a membrane, it is assumed as is usual[33] that the elastic strain energy in the solid is due entirely to stretching. The energy is then proportional to change in area, and the constant of proportionality is the tension, T. Given the axial symmetry of the case in question, this corresponds to the term E_e in equation (2) being given by

$$E_e = T[(1 + \phi_r^2)^{1/2} - 1] \tag{17}$$

In the case of a membrane, no energy is associated with bending or folding. This means that, in contrast to the plate analysis, ϕ_r may become discontinuous although, of course, ϕ remains continuous. Of course, this is a mathematical model; the real situation will be more like that shown in Figure 3, line (b).

Downloaded At: 15:57 22 January 2011

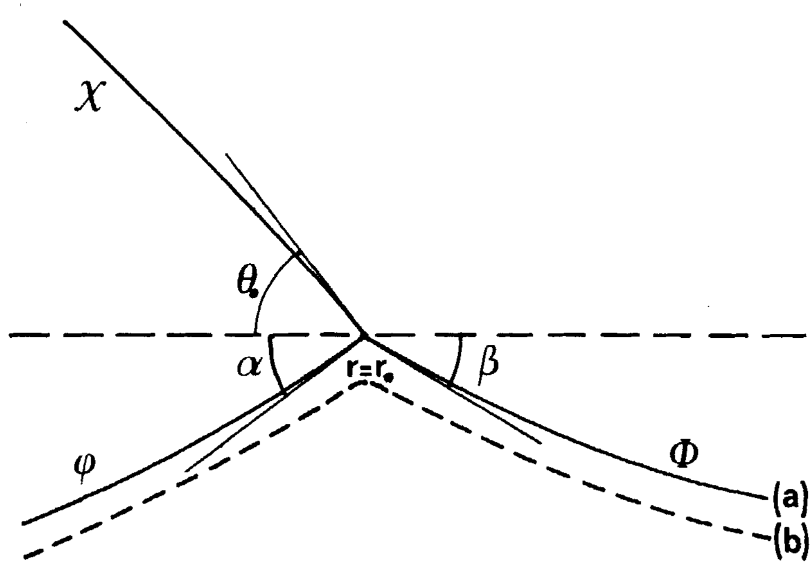


FIGURE 3 The contact region for a membrane: (a) mathematical model, (b) probable real situation.

As for the plate, we consider the relationships stemming from the coefficients of δr_0, $\delta\phi|_{r_0}$ and $\delta\phi$ being set to zero in equation (5) when applied to the functions defined by equation (2) and (3) and this time (17).

After equating the coefficient of δr_0 to zero, evaluation at r_0 and simplification, we obtain

$$(\gamma_{s1} + \gamma_{s2} + T)[1 + \phi_r^2(r_0)]^{-1/2} + \gamma_{12}[1 + \chi_r^2(r_0)]^{-1/2} = (2\gamma_{s2} + T)\,[1 + \Phi_r^2(r_0)]^{-1/2} \tag{18}$$

where Φ represents the function ϕ for $r \geqslant r_0$ and ϕ is now reserved for $r \leqslant r_0$. Clearly $\phi(r_0) = \Phi(r_0)$ but $\phi_r(r_0) \neq \Phi_r(r_0)$ in the general case (cf. preceding paragraph). Considering Figure 3, line (a), it can be seen that $\tan\beta = |\Phi_r(r_0)|$, the sign depending on the orientation of the membrane beyond the drop (a boundary condition problem). Using the trigonometrical formulae referred to above, equation (18) reduces to

$$(\gamma_{s1} + \gamma_{s2} + T)\cos\alpha + \gamma_{12}\cos\theta_0 = (2\gamma_{s2} + T)\cos\beta \tag{19}$$

This then constitutes the modified Young equation for contact angle equilibrium when the solid is considered as a membrane, and should be compared to equation (10) for a plate. Again, if the membrane is sufficiently rigid or unbendable, α and β are small and in the limit of a rigid membrane, $\alpha \to 0$ and $\beta \to 0$, equation (19) becomes precisely Young's equation.

A similar analysis setting the coefficient of $\partial\phi|_{r_0}$ to zero in equation (5) leads to

$$(\gamma_{s1} + \gamma_{s2} + T)\sin\alpha - \gamma_{12}\sin\theta_0 = \pm(2\gamma_{s2} + T)\sin\beta \tag{20}$$

where the minus sign of $\pm$ should be taken with β as shown in Figure 3.

Equating the two integral coefficients of $\delta\phi$ in equation (5) separately to zero, *i.e.* assuming the validity of equation (13) and (14), leads respectively to equation (21) and (22).

$$\frac{d}{dr}\left[\frac{(\gamma_{s1} + \gamma_{s2} + T)r\phi_r}{(1 + \phi_r^2)^{1/2}}\right] + \rho g r\phi + \lambda r = 0 \tag{21}$$

$$\frac{d}{dr}\left[\frac{(2\gamma_{s2} + T)r\Phi_r}{(1 + \Phi_r^2)^{1/2}}\right] = 0 \tag{22}$$

It can be seen immediately that equation (21) is simply the capillary equation (*cf.* equation [7]), but this time there is a sign change accounting for the fact that we are considering the underside of the drop and the usual interfacial tension or free energy is replaced by $(\gamma_{s1} + \gamma_{s2} + T)$. This is to be expected if we consider the situation from the point of view of tension. Instead of the usual single interface, here we are considering a double-sided "interface" having γ_{s1} and γ_{s2} on the different sides, and in addition, there is an internal membrane tension, T.

Downloaded At: 15:57 22 January 2011

Equation (22) describes the membrane profile outside the drop. It is a standard, well-known differential equation having a general solution of the form

$$\Phi(r) = A \cosh^{-1}\left(\frac{r}{A}\right) + B \tag{23}$$

where A and B are constants. Clearly these constants, and those to be found in the solution of equation (21), depend on the boundary conditions.

DISCUSSION

The main aspect of this theoretical approach to sessile drops on thin, deformable, elastic substrates concerns the modifications to Young's equation for contact angle equilibrium. As pointed out above, both equation (10) and (19) representing contact angle equilibrium, respectively for thin plates and for membranes, reduce directly to Young's equation (1) when the solid is undeformable, *i.e.*, in the limit of angles α and $\beta \to 0$. This does tend to confirm that to all intents and purposes, in everyday contact angle evaluation on bulk solids for which solid strain is negligible, Young's equation will be so near to reality that any deviations may be totally ignored. It is only on very thin solids, of the order of microns thick, that physical deformation plays an important role.

Both equation (10) and (19) can, in fact, be derived directly from the simple mechanistic force balance. The horizontal components of the tensions γ_{s1}, γ_{s2} and γ_{12} are at equilibrium in equation (10). Although the liquid/fluid γ_{12} may be considered as a true tension, such treatment for the solid/fluid γ_{s1} and γ_{s2} is more dubious. As a result, the appealingly simple procedure of force resolution is best treated with care.

Nevertheless, the absence of elasticity terms in the overall equilibrium, in the case of the plate, may be construed as reflecting the fact that all stresses within the plate itself are self compensating. Although bending moments exist, the sum, in the direction parallel to the surface, of the tensile and compressive forces is zero. However, in the case of the membrane, forces due to the elastic tension T are present and must be allowed for in the mechanistic equilibrium equation when resolving horizontally. It should be noticed that, since in the general case of a membrane, the inclination of the solid takes on two distinct angles α and β on opposite sides of the contact line, the terms $\gamma_{s2} \cos \alpha$ and $\gamma_{s2} \cos \beta$

Downloaded At: 15:57 22 January 2011

corresponding to the underside of the membrane must also be allowed for in the equilibrium. Clearly in the case of an (intact) thin plate, the underside plays no role since only one angle of inclination, α, is involved and the forces cancel. Equation (19) indeed shows that the tension T may be considered in exactly the same context as the γ terms. This is also borne out by equation (21) describing the membrane profile under the drop. Equation (21) is simply the capillary equation where the total tension at the interface to be considered is the sum of the three effects, two interfacial tensions γ_{s1} and γ_{s2}, and the mechanical, elastic tension T.

Equation (10) was also derived by Lester for a bulk solid.[20] In the event of a membrane behaving such that the inclination is the same on each side of the contact line, *i.e.* $\alpha = \beta$, then equation (19) reduces to equation (10). Since in practice both α and β will usually be small, cos α and cos β will be virtually equal. As a result the contact equilibrium on both elastic plates and membranes can be described to a first approximation by equation (10). Fortes came to a similar conclusion[27] but also derived an equilibrium equation for the membrane involving the ratio γ_{12}/T (his equation [28] or [A7]). No direct comparison is really justified since he treated a weightless drop and ignored second-order terms in his derivation based on energy minimisation. Although, as stated above, too much importance should not be attached to mechanical arguments, the fact that equation (19) can be derived in this manner is satisfying. Fortes remarks that in the case of a weightless drop, which corresponds in the present nomenclature to angle $\beta = 0$, the mechanical approach of horizontal force resolution leads also to his equation (28). Nevertheless, he neglects the fact that the membrane has two sides in his force balance. Were this fact to be allowed for, equation (19) of this paper would result.

Considering equation (12) and (20), it can again be seen that the simple, mechanistic approach would have sufficed. Both of these may be considered as representing the equilibrium of forces when the vertical components are balanced, allowing still for the dubious assumption of γ_{s1} and γ_{s2} being treated as tensions. The reasons described above adequately explain why only γ terms come into play for the plate but the tension T cannot be neglected for the membrane. These equations may or may not have satisfied Bikerman's doubts[2] since his main contention was the lack of vertical equilibrium in Young's equation. Equation (19) and (20) for the membrane may be considered as modified expressions for Neumann's triangle[34] in which T is added.

Downloaded At: 15:57 22 January 2011

However, if the force balance for the plate is resolved perpendicularly to the surface of the plate, Bikerman's objection arises again—what balances $\gamma_{12} \sin(\theta_0 + \alpha)$? Here it becomes clear that the simple resolution of interfacial tensions is, in general, inadequate for deriving equilibrium conditions. In this case, the true, detailed force balance involves internal tensions and compressions within the plate. In addition, it should not be overlooked that the present derivation is itself somewhat simplistic in the sense that no real material will really behave exactly as a mathematically thin, elastic plate, or as a membrane, as described by linear elasticity theory. As for materials showing plasticity or hysteresis effects in viscoelasticity, the present treatment will be entirely inadequate and solution of the problem for a gel,[16] for example, would be a formidable task. In addition, apart from some probably small deviations from the "pure" theory when considering elastic solids, sight must not be lost of the molecular implications which cannot possibly be tackled using a continuum approach.

Probably the most important comment to make about equation (10) and (19) [or equation (12) and (20)] is that they show that the contact angle is *not* an intrinsic property of a given system liquid/solid/fluid (even if effects of a potential line tension are neglected). The true contact angle should now be defined as $(\theta_0 + \alpha)$, as opposed to the apparent, or conventional, contact angle θ_0. Now the γ terms are intrinsic to the surface characteristics of the three phases, but angles α (and β) also depend on several external factors such as the mechanical bulk properties of the solid, drop size and the physical support for the system. As a consequence, when α and/or β change, θ_0 must also change for the equilibrium equations to hold. Under usual conditions with bulk solids, both α and β are so small as to be negligible and as such θ_0 *can* be considered to be an intrinsic parameter related only to the surface properties. Nevertheless, from a fundamental point of view, apparent and real contact angles do depend on mechanical characteristics of the system as well as on free surface energies. Similarly contact angle does depend on gravity, but implicitly.

The boundary conditions required to solve equation (15), (16), (21) and (22) describing the profile of the solid will involve knowledge of the equilibrium at the contact line. With the present lack of experimental data providing physical values for the required boundary conditions, accurate solution of the profile equations would represent a fairly complex task (except of course in cases where α and β are sufficiently small to be negligible, but this would be begging the question). The

Downloaded At: 15:57 22 January 2011

calculations are feasible in principle, but it is felt that application to experimental data when available is preferable. Nevertheless, a brief account of approximate solutions for the plate profile together with a semi-quantitative representation of a hypothetical drop/plate system are to be found in the appendix to this paper. In addition, an order of magnitude calculation has been effected and briefly shows that typically, a drop of 1-bromonaphthalene of contact radius 0·1 cm can be expected to provoke a distortion amounting to the angle, α, being equal to 1°, when placed on a sheet of mica of ca. 7 μm thickness.

CONCLUSIONS

The conformation of a system consisting of a sessile drop of liquid lying on a thin elastic solid in the presence of a gravitational field has been studied with a principal aim of obtaining insight into contact equilibrium when elastic strain cannot be neglected. For the sake of simplicity, the axisymmetric case has been treated. Both solids modelled by thin elastic plates and by membranes have been considered. By minimising the free energy of the system due to interfacial free energies, potential energy and elastic strain energy within the solid using methods of the calculus of variations, several identities emerge which lead mathematically to relations concerning angle equilibrium and both drop and solid profiles. The essential conclusion is that, contrary to Young's equation in the case of an undeformable solid where the contact angle is a characteristic uniquely of the surface properties of the phases considered, when solid strains exist, contact equilibrium and the angles involved are dependent on other parameters such as the bulk properties of the solid, physical dimensions and methods of support for the system. (This is true whether or not effects of line tension are included.)

Of secondary importance in this study is the conclusion that the drop profile equation is unmodified by the behaviour of the elastic solid (except that boundary conditions are altered).

The profile of the solid under the drop obeys the classic capillary equation in the case of a membrane. This is perhaps to be expected since the elastic tension can be considered similar to interfacial tension. In the case of a thin plate, the profile equation is very complicated but a simple perturbation solution shows the first-order effect of flexural rigidity to be that of increasing the radius of curvature of an essentially circular profile. Given the complexity of the profile equations a full exploitation of them should await the availability of suitable experimental data,

Downloaded At: 15:57 22 January 2011

although an order of magnitude calculation has been effected (*cf.* appendix).

APPENDIX

Approximate solutions to the equations describing the profile of a thin plate supporting a sessile drop

In the case of the profile equations of a membrane both inside and outside an axisymmetric drop, no major problems occur in principle since for the former, the differential equation is the well-known capillary equation[29,30] which already has several numerical[35,36] and approximate[37–41] solutions to be found in the literature, and for the latter, an analytical solution exists, *viz.* equation (23). However, the profile equations are rather more complex for a plate. Consider first equation (15). This describes the profile of the plate under the drop when elasticity and gravity play a role, as well as surface effects. If both gravity and the flexural rigidity were zero, the profile would be circular *i.e.*

$$\phi = R - (R^2 - r^2)^{1/2} \tag{A1}$$

where R is the radius of curvature. (This solution assumes the origin to be at the base and in the centre of the plate). We now assume, in common with Ref. 39, that the profile is perturbed by these added effects. Defining

$$\varepsilon = \frac{\rho g}{(\gamma_{s1} + \gamma_{s2})} \tag{A2}$$

and

$$\omega = \frac{D}{(\gamma_{s1} + \gamma_{s2})} \tag{A3}$$

we may consider the true profile, $\phi(r, \varepsilon, \omega)$ to be a Maclaurin expansion about the circular solution without gravity or elastic effects, $\phi(r,0,0)$.

$$\phi(r,\varepsilon,\omega) = \phi(r, 0, 0) + \varepsilon \cdot \frac{\partial \phi}{\partial \varepsilon}\bigg|_{(r,0,0)} + \omega \cdot \frac{\partial \phi}{\partial \omega}\bigg|_{(r,0,0)} + O(\varepsilon^2, \varepsilon\omega, \omega^2) \tag{A4}$$

Equation (15) can be rearranged in the form

$$\frac{d^2}{dr^2}\left[\omega\left(\frac{r\phi_{rr}}{\eta^5} + \frac{\nu\phi_r}{\eta^3}\right)\right] - \frac{d}{dr}\left[\frac{r\phi_r}{\eta} + \frac{\omega}{2}\left(\frac{2\phi_r}{r\eta} - \frac{\phi_r^3}{r\eta^3}\right.\right.$$

Downloaded At: 15:57 22 January 2011

$$+\frac{2\nu\phi_{rr}}{\eta^3}-\frac{6\nu\phi_r^2\phi_{rr}}{\eta^5}-\frac{5r\phi_r\phi_{rr}^2}{\eta^7}\bigg)\bigg]-\varepsilon r\phi-\frac{\lambda r}{(\gamma_{s1}+\gamma_{s2})}=0 \quad \text{(A5)}$$

We define $$u(r)=\frac{\partial\phi}{\partial\varepsilon}\bigg|_{(r,0,0)},\quad v(r)=\frac{\partial\phi}{\partial\omega}\bigg|_{(r,0,0)}$$

whence $$u_r=\frac{\partial\phi_r}{\partial\varepsilon}\bigg|_{(r,0,0)} \quad \text{(A6)}$$

and $$v_r=\frac{\partial\phi_r}{\partial\omega}\bigg|_{(r,0,0)} \quad \text{(A7)}$$

We differentiate equation (A5) with respect to ε and evaluate at $\varepsilon=\omega=0$. A differential equation in u_r results which can be evaluated using equation (Ai), and its derivative with respect to r. The solution takes the form

$$u(r)=\frac{C_1R^3}{(R^2-r^2)^{1/2}}-\frac{R^3}{3}ln[R+(R^2-r^2)^{1/2}]+C_2 \quad \text{(A8)}$$

where C_1 and C_2 are constants to be obtained from the boundary conditions of the problem. (All the following C_n are constants).

A similar process may be applied to the elasticity dependence. Equation (A5) is differentiated with respect to ω and evaluated at $\omega=\varepsilon=0$. After considerable simplification and use being made of equation (A1) and its first two derivatives with respect to r, we obtain

$$\frac{d}{dr}\left[\frac{rv_r}{\eta^3}\right]+\frac{r}{(\gamma_{s1}+\gamma_{s2})}\cdot\frac{\partial\lambda}{\partial\omega}\bigg|_{\omega=\varepsilon=0}=0 \quad \text{(A9)}$$

This expression can be integrated simply to

$$v(r)=C_3R^3\left\{\frac{1}{R^2(R^2-r^2)^{1/2}}-\frac{1}{R^3}ln\left[\frac{R+(R^2-r^2)^{1/2}}{r}\right]\right\}$$
$$-\frac{R^3}{2(\gamma_{s1}+\gamma_{s2})}\cdot\frac{1}{(R^2-r^2)^{1/2}}\cdot\frac{\partial\lambda}{\partial\omega}\bigg|_{\omega=\varepsilon=o}+C_4 \quad \text{(A 10)}$$

Since v (0) must remain finite, the term in (ln r) must be removed and hence C_3 is zero. We thus have

$$v(r)=C_4+\frac{C_5R^3}{(R^2-r^2)^{1/2}} \quad \text{(A11)}$$

Downloaded At: 15:57 22 January 2011

as the simple perturbation term due to flexural rigidity, C_5 containing $\left.\frac{\partial \lambda}{\partial \omega}\right|_{\omega=\varepsilon=0}$.

The two perturbation terms, $u(r)$ and $v(r)$, contain four constants to be determined from the boundary conditions. By imposing, for example, the conditions of $u(0) = v(0) = 0$, which correspond physically to the drop/plate system resting on a flat, rigid, horizontal support, the number of constants is reduced to two. These two may then be evaluated, at least in principle, from $\phi(r_0)$ and $\phi_r(r_0)$, or other suitable values ($\phi(a), \phi_r(a)$, etc.).

Finally, the first-order perturbation solution is given by combining equation (A1), (A4), (A8) and (A11).

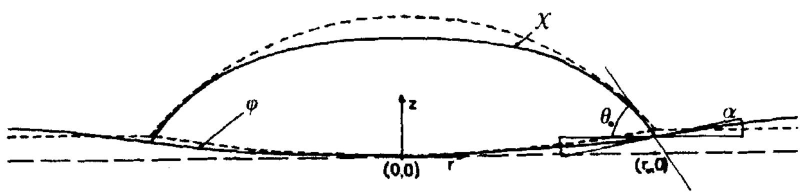


FIGURE A1 Semi-quantitative representation of an axisymmetric sessile drop on a deformed plate. The boundary condition corresponding to the value of $\chi(r_0) = \phi(r_0)$ is artificially exaggerated so that the general effect of plate bending may be seen.

Note that to first-order, the essential effect of flexural rigidity in the plate is to increase the radius of curvature of the spherical interface $S1$ with respect to its value on a hypothetical "soft" solid. This is evident on considering the Taylor expansion for a circle.

If $\phi(R) = (R^2 - r^2)^{1/2}$, then $\phi(R + \delta R)$ is given by

$$\phi(R + \delta R) = \phi(R) + \delta R . \phi_R(R) + O(\delta R^2) \quad \text{(A12)}$$

$$= (R^2 - r^2)^{1/2} + \frac{\delta R . R}{(R^2 - r^2)^{1/2}} + O(\delta R^2)$$

Comparison of the term in δR with equation (A11) makes the matter clear.

The last comment concerning this perturbation solution to equation (A5) concerns its range of validity. Clearly, it is never exact, but it will give a good approximation provided the perturbations are not too great. Using a homogeneity argument similar to that in Ref. 39, it can be shown that the approximation should be good provided both the

Downloaded At: 15:57 22 January 2011

dimensionless parameters εr_0^2 and ωr_0^{-2} are both sufficiently small, say less than about 1.

Equation (16) describes the plate profile for $r > r_0$. Since under normal circumstances, the degree of plate deformation will be relatively small, we shall assume that both ϕ_r and $r\phi_{rr} \ll 1$. In addition, since ϕ is missing we may pose $p = \phi_r$. We can therefore ignore terms of $O(p^2)$ or greater and $O(p_r^2)$. The term in $\gamma_{s2}D^{-1}$ will usually be negligible and equation (16) then reduces to

$$r^2 p_{rr} + r p_r - p = 0 \tag{A13}$$

This is a form of Euler's differential equation[42] and the general solution is

$$p = \frac{C_6}{r} + C_7 r \tag{A14}$$

Clearly it is reasonable physically to assume $p \to 0$ at large r and therefore we take C_7 to be zero. Solution of equation (A14) then gives simply

$$\phi(r) = C_6 \ln r + C_8 \tag{A15}$$

Determination of C_6 and C_8 should be considered within the context of the boundary conditions (*e.g.* continuity of ϕ_r at r_0, value of $\phi(r_0)$).

In practice, the deformation of the solid will be very small (unless the plate really is very thin, of the order of microns). However, to give some idea of the allure of an axisymmetric sessile drop on a flexible plate, the above equations have been used (in conjunction with the perturbation approach for drop profile[39]) to study an "artificial" or semi-quantitative example in which $\phi(r_0)$ is sufficiently large for the curvature of the solid to be noticeable. This semi-quantitative solution is shown in Figure A1. The dotted lines correspond to the zero-gravity, zero-flexural rigidity solution which was perturbed mathematically.

In order to estimate the order of magnitude of the plate distortion at the contact line, *i.e.* angle α, the above analysis was employed but for a small drop ($r_0 = 0{\cdot}1$ cm) for which the gravitational energy can be reasonably neglected. Equation (A11) and (A12) imply that ϕ is then approximately circular and it is known that χ is. Equation (2) may then be used to assess the approximate free energy of the drop/solid and this must be minimised with respect to the radii of ϕ and χ with the constraint of constant volume (Equation (3)). The problem is a fairly straightforward case of differential calculus in this simplified form and will

Downloaded At: 15:57 22 January 2011

therefore not be explained in detail. Suffice it to say that using typical values of the physical parameters in question, it was found that a drop of 1-bromonaphthalene ($\gamma_{12} = 44{\cdot}6$ $mJ.m^{-2}$) will provoke a value of α of ca. 1° on an unclamped mica sheet ($E \simeq 10$ GPa, $\nu \simeq \frac{1}{3}$, $\gamma_{s2} = 120$ $mJ.m^{-2}$ [43] of *ca.* 7 μm thickness, allowing for a value of θ_0 of *ca.* 50°. The effect of changing the overall radius of the plate, *a*, is small.

References

1. T. Young, *Phil. Trans. R. Soc. London* **95**, 65 (1805).
2. J. J. Bikerman, *J. Phys. Chem.* **63**, 1658 (1959).
3. J. J. Bikerman, *Physical Surfaces* (Academic Press, London), 1970, Ch. 6.
4. R. J. Good, *J. Colloid Interface Sci.* **59** (3), 416 (1977).
5. R. E. Johnson, *J. Phys. Chem.* **63**, 1655 (1959).
6. R. E. Collins and C. E. Cooke, *Trans. Faraday Soc.* **55**, 1602 (1959).
7. F. C. Goodrich, *Surface and Colloid Science, Vol 1* E. Matijević, Ed., (Wiley, New York, 1969), Ch. 1.
8. L. Boruvka and A. W. Neumann, *J. Phys. Chem.* **66**, 5464 (1977).
9. M. A. Fortes, *Phys. Chem. Liq.* **9**, 285 (1980).
10. M. E. R. Shanahan, *Adhesion 6*, (K. W. Allen, Ed.), (Applied Science Publishers, London, 1982), Ch. 5.
11. B. A. Pethica and T. J. P. Pethica, *Proc. Intern. Congr. Surface Activity, 2nd, London* **3**, 131 (1957).
12. V. R. Gray, *ibid.*, 191 (1957).
13. G. J. Jameson and M. C. G. Del Cerro, *J. Chem. Soc. Faraday Trans. 1*, **72**, 883 (1976).
14. L. R. White, *ibid.*, 390 (1977).
15. B. A. Pethica, *J. Colloid Interface Sci.* **62**, 567 (1977).
16. A. S. Michaels and S. W. Dean, *J. Phys. Chem., Ithaca* **66**, 1790 (1962).
17. J. Chappuis, *51st Colloid and Surface Symposium, Buffalo, New York*, p. 85 (1977).
18. J. D. Andrade, R. N. King, D. E. Gregoris and D. L. Coleman, *J. Polym. Sci.* **66**, 313 (1979).
19. D. Tabor, *Gases, Liquids and Solids*, (Penguin Books, 1969), p. 215).
20. G. R. Lester, *J. Colloid Sci.* **16**, 315 (1961).
21. G. R. Lester, *Nature* **209**, 1126 (1966).
22. G. R. Lester, *Soc. Chem. Ind. (London), Monograph No. 25*, 57 (1967).
23. E. E. Braudo, E. N. Michailow and W. B. Tolstogusow, *Z. Phys. Chemie, Leipzig* **253**, 369 (1973).
24. J. C. Eriksson, *Acta Chemica Scandinavica* **A31**, 235 (1977).
25. A. I. Rusanov, *J. Colloid J. USSR* **37**, 614 (1975); English translation of *Kolloidn Zh.* **37**, 687 (1975).
26. A. I. Rusanov, *J. Colloid Interface Sci.* **63**, 330 (1978).
27. M. A. Fortes, *J. Colloid Interface Sci.* **100**, 17 (1984).
28. V. I. Smirnov, *A Course of Higher Mathematics*, 3rd Ed., Vol. IV, translated D. E. Brown, (Pergamon, Oxford, 1964), pp. 239–242.
29. J. F. Padday, *Phil. Trans. Roy. Soc. (London)* **A269**, 265 (1971).
30. E. A. Boucher, *Rep. Prog. Phys.* **43**, 497 (1980).
31. S. P. Timoshenko and J. N. Goodier, *Theory of Elasticity*, 3rd Ed., (McGraw-Hill, New York, 1970), pp. 246–7, (1970).

Downloaded At: 15:57 22 January 2011

32. R. Courant and D. Hilbert, *Methods of Mathematical Physics*, (Vol. 1, Wiley New York, 1953), p. 233 (1953).
33. *Ibid, idem*, pp. 246–7.
34. F. Neumann, Vorlesungen über die Theorie der Capillarität, (B. G. Teubner, Leipzig, 1894).
35. J. F. Padday, *J. Electroanal. Chem.* **37**, 313 (1972).
36. S. Hartland and R. W. Hartley, *Axisymmetric Fluid-Liquid Interfaces*, (Elsevier, Amsterdam, 1976).
37. R. Ehrlich, *J. Colloid Interface Sci.* **28**, 5 (1968).
38. A. K. Chesters, *J. Fluid Mech.* **81**, 609 (1977).
39. M. E. R. Shanahan, *J. Chem. Soc., Faraday Trans 1* **78**, 2701 (1982).
40. *Ibid, idem*, **80**, 37 (1984).
41. P. G. Smith, T. G. M. Van De Ven, *J. Colloid Interface Sci.* **97**, 1 (1984).
42. E. Kamke, *Differentialgleichungen, Lösungsmethoden und Lösungen, I*, (Akademische Verlagsgesellshaft Geest und Portig K.-G., Leipzig, 1967), p. 436.
43. J. Schultz, K. Tsutsumi and J. B. Donnet, *J. Colloid Interface Sci.* **59**, 272 and 277 (1977).

Downloaded At: 15:57 22 January 2011