Simple fluids near rigid solids: statistical mechanics of density and contact angle

Simple fluids near rigid solids: statistical mechanics of density and contact angle

M V Berry

H H Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK

Abstract. By making a simple approximation for the two-particle distribution function in a fluid, an approximate formula is obtained for the fluid density $n(r)$ throughout the liquid-vapour region near an arbitrary rigid solid which exerts forces on the fluid. The density formula is based on a 'surface of tension' Σ which curves in from infinity towards the solid. For a 'flat smooth solid', we show that only one asymptotic slope results in a surface Σ corresponding to stable contact with the solid. This gives simple formulae for the angle of contact and the work of adhesion, in terms of intermolecular potentials and the bulk liquid radial distribution function. Solids which are not flat or smooth are discussed. The effects of large and rapidly-varying curvatures of Σ are estimated, leading to the result that our formulae should become more accurate as the contact angle increases.

1. Introduction

The deportment of liquid–vapour interfaces near the surfaces of solids affects many technological and biological processes (Bikerman 1958), and its understanding is one of the main problems of surface science. The central concept is the angle of contact, θ, which describes the degree to which the liquid wets the solid, and also determines the shape of droplets on the surface; θ is a macroscopic quantity, determined by the microscopic interactions between fluid and solid molecules. In this paper we derive an approximate expression for the number density $n(r)$ of the molecules of the inhomogeneous fluid; if the solid surface is assumed microscopically flat, a formula for θ appears naturally, as the condition for stability of the surfaces of constant density.

Our treatment is based on an approximation for the correlations between fluid particles: we assume that $n_2(r_1, r_2)$, the two-particle distribution function between positions r_1 and r_2 in the fluid, may be written as

$$n_2(r_1, r_2) \simeq n(r_1)n(r_2)g(|r_2 - r_1|), \tag{1}$$

where $g(R)$ is the *bulk liquid radial distribution function*, and R denotes $|r_2 - r_1|$. This approximation, which was originally suggested by Green (1960), has been employed by Berry and Reznek (1971) to obtain a relation between the liquid density n_L and the vapour density n_V, and by Berry et al (1972) to study surface tension. Equation (1) is qualitatively correct, but has one obvious defect: it neglects the anisotropy of correlations in the liquid–vapour interface (in addition, the radial distribution function in the vapour is set equal to that of the liquid, but this will not lead to serious error except near the

critical temperature). More sophisticated discussions of the liquid–vapour interface have been published (Jouanin 1968, Toxvaerd 1971, 1972), but these methods cannot be applied easily to the more complicated situation resulting from the presence of a solid, whereas (1) can still be used, as we shall see. (This extension of (1) to curved surfaces can ultimately only be justified by experiment.)

We assume that the *fluid* is simple, that its molecules interact pairwise via a spherically symmetrical potential $\phi(R)$, which has the usual form (Egelstaff 1967), of a short range repulsive core and a long range part which is attractive for a non-metallic liquid and oscillatory for a liquid metal (March 1968). The effect of the *solid* is to produce an 'external field' $\psi(r)$ which is the potential energy of a fluid molecule at r, due to its inter-action with the solid. If the solid consists of molecules at r_i, which interact separately with the fluid molecules via pair potentials U_i (which may not be spherically symmetric), then we may write $\psi(r)$ in the form

$$\psi(r) = \sum_i U_i(r - r_i). \tag{2}$$

A useful expression for $\psi(r)$ can be obtained if the solid is composed of identical molecules with spherical potentials $U(R)$, if the centres of the solid surface molecules lie in the (flat) xy plane, if the effects of structure in the xy plane are averaged out, and if the solid molecules have number density n_S. Then $\psi(r)$ depends only on z, and is given by

$$\psi(z) = n_S \iiint_{z' < 0} dr' \, U(|r - r'|) = 2\pi n_S \int_z^{\infty} dR \, R(R - z) U(R), \tag{3}$$

after transforming to polar coordinates; $\psi(z)$ is similar to $U(R)$ in its general form. This is the 'flat smooth solid' approximation. However, we emphasize that $\psi(r)$ will be arbitrary for most of our treatment, so that the solid surface can have any degree of roughness from the molecular to the macroscopic, and may be composed of non-identical asymmetric molecules.

Like most previous workers we assume that the solid surface is *rigid*, that is, $\psi(r)$ does not depend on the fluid density $n(r)$. This assumption has been challenged by Lester (1967) who gives a careful analysis of possible deformation of the solid in the region of three-phase contact.

In several ways this paper is complementary to the work of Girifalco and Good (1957) (see also Good *et al* 1958, Good and Girifalco 1960, Good 1964). While we consider the potentials $\phi(R)$ and $\psi(r)$ as given functions, they show that the attractive forces between fluid molecules, and the attractive forces between fluid and solid molecules, satisfy an approximate relation, and this enables them to correlate an impressive variety of experimental results, including the measurements of Zisman (1964) of θ for a wide range of liquids and solids. On the other hand, Girifalco and Good neglect all position correlations between fluid molecules, whereas we include exactly at least the bulk liquid correlations embodied in the function $g(R)$. Further, they assume that $n(r)$ drops discontinuously from n_L to n_V, whereas we derive an approximation for the continuous variation of $n(r)$ throughout the fluid. Finally, Girifalco and Good start from statistical-mechanical expressions for liquid–vapour surface *energies* and the solid–liquid *work* of wetting, whereas we employ the alternative 'mechanical' procedure (Ono and Kondo 1960) to understand how the *forces* which act on the fluid cause the liquid–vapour interface to recede from the solid with the angle θ.

2. Formalism for fluid density

Our starting point is an exact equation, which can be derived from statistical mechanics, expressing the balance of forces on a volume element of an inhomogeneous fluid in an external potential $\psi(r)$, at temperature T:

$$kT\nabla n(r) + n(r)\nabla\psi(r) + \int\int\int dr' n_2(r, r')\nabla_r\phi(|r - r'|) = 0. \tag{4}$$

The first term represents the rate of net momentum transport into the element, the second term is the external force on the element from the solid, and the last term is the force on the element from the rest of the fluid. Equation (4) is the first in the 'BBGKY hierarchy' of equations (Hill 1956), for the molecular density distribution functions of increasing order.

As an elementary example of the use of equation (4), let $n(r)$ be so small that the effect of the interparticle fluid forces $\nabla\phi$ can be neglected; this would apply to the vapour–solid interaction far from the liquid region. Then (4) reduces to the Navier–Stokes equation for an 'atmosphere' of ideal gas, and the solution is simply the 'Boltzmann' expression

$$n(r) = n_V \exp(-\psi(r)/kT). \tag{5}$$

This has been used by Barker and Everett (1962) to describe vapour adsorption, in the case where ψ depends only on z (cf (3)).

In the general case, when forces within the fluid cannot be neglected, we employ in (4) the basic approximation (1) for n_2; this gives

$$\nabla(kT \ln n(r) + \psi(r)) + I(r) = 0, \tag{6}$$

where

$$I(r) \equiv \int\int\int dr' n(r') g(|r - r'|)\nabla_r\phi(|r - r'|). \tag{7}$$

The essential step is to express the vector function $I(r)$ as a gradient. We introduce the interparticle vector $R \equiv r' - r$, and denote differentiation of functions with respect to their arguments by primes, to obtain

$$I(r) = -\int\int\int dR \frac{R}{R} n(R + r) g(R)\phi'(R). \tag{8}$$

Now we define a function $S(R)$, which we shall employ frequently later:

$$S(R) \equiv -\int_R^\infty d\rho\, g(\rho)\phi'(\rho). \tag{9}$$

(When R is large, $g(R)$ is almost unity, and $S(R) \simeq \phi(R)$.) Equation (8) becomes

$$I(r) = -\int\int\int dR \frac{R}{R} n(R + r) S'(R) = -\int\int\int dR\, n(R + r)\nabla_R S(R). \tag{10}$$

Integrating by parts with respect to each of the variables, and noting the vanishing of the 'integrated' terms, we get

$$I(r) = \nabla_r \int\int\int dR\, n(R + r) S(R). \tag{11}$$

This has the required 'gradient' form, so that (6) becomes

$$\nabla\left(kT \ln n(r) + \psi(r) + \int\int\int dR\, n(r+R)S(R)\right) = 0, \tag{12}$$

which we can integrate immediately, to obtain

$$n(r) = C \exp\left[-\frac{1}{kT}\left(\psi(r) + \int\int\int dR\, S(R)n(r+R)\right)\right], \tag{13}$$

where C is a constant. This integral equation for $n(r)$ lies at the core of our treatment; it is the generalization of a result of Berry and Reznek (1971) to the case where there is an external field, and where the surfaces of constant n are not parallel planes.

3. Approximate determination of density

The first step in the solution of (13) is the determination of the constant C. We choose a point r within the bulk liquid, far from the solid and the vapour. Then $\psi(r)$ is zero and $n(r+R)$ equals the liquid density n_L, since $S(R)$ is strongly localized (equation (9)), and (13) becomes

$$n_L = C \exp\left(-\frac{n_L}{kT}\int\int\int dR\, S(R)\right). \tag{14}$$

The same argument can be applied if r lies well within the vapour, and since the value of C must be independent of r, we obtain the relation

$$n_L \exp\left(\frac{n_L}{kT}\int\int\int dR\, S(R)\right) = n_V \exp\left(\frac{n_V}{kT}\int\int\int dR\, S(R)\right), \tag{15}$$

which has been analysed by Berry and Reznek (1971) and shown to give physically sensible results, even near the critical temperature, provided it is not used to calculate pressures.

   Even in the 'flat smooth solid' approximation (3), the nonlinearity of (13), and the complicated geometry of the surfaces of constant n, preclude an exact analytical determination of the density. Therefore we regard equation (13) as a basis for iteration, any putative density distribution $n_0(r)$ being improved by substituting it into the integrand of the exponent and calculating the right-hand side of (13). To carry out this approximate procedure, we choose for $n_0(r)$ a 'macroscopic' distribution changing discontinuously from n_L to n_V across a 'surface of tension' Σ, as shown on figure 1 for a 'flat smooth solid' (the peculiar form adopted by Σ near the solid will be explained in § 4). Once Σ has been chosen, the first iteration of (13) gives the following 'smoothed' approximation for the fluid density:

$$n(r) \simeq n_L \exp\left[-\frac{1}{kT}\left(\psi(r) - n_L\int\int\int dR\, S(R) + \int\int\int dR\, S(R)n_0(r+R)\right)\right]. \tag{16}$$

   But how can we choose Σ? By requiring the iteration to be stable, in the following sense: Σ must remain a surface on which $n(r)$ (equation (16)) is constant, ie $\nabla n(r)$ must be directed perpendicular to Σ. This mathematically sensible condition, which will ensure
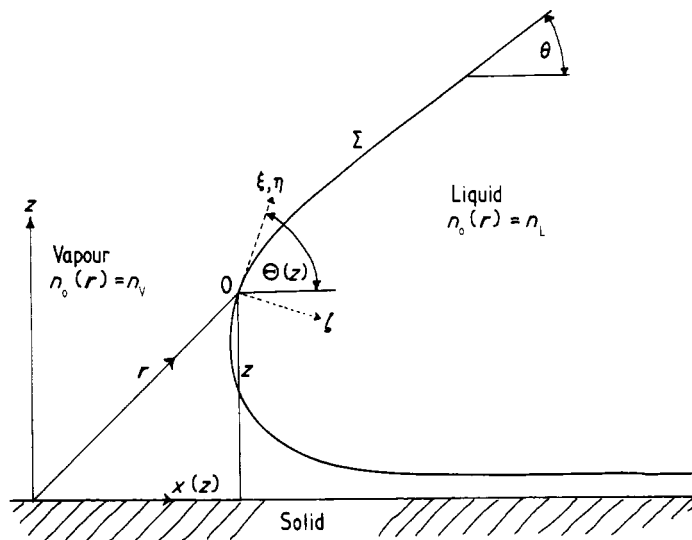
Figure 1. 'Macroscopic' fluid density $n_0(r)$, changing discontinuously across the 'surface of tension' Σ.

that $n(r)$ is similar to $n_0(r)$ in its gross features, will soon be shown to be physically sensible as well. Thus the 'surface of tension' is determined by the condition

$$\psi(r) + \iiint dR\, S(R)n_0(r+R) = \text{constant on } \Sigma. \tag{17}$$

To evaluate the integral we use local coordinates ξ, η, ζ for R (figure 1); the origin O lies at r, and Oζ is normal to Σ and is directed into the liquid, while ξ, η are coordinates in the tangent plane to Σ at r. In these local coordinates, let the surface Σ have the equation

$$\zeta = \zeta(\xi, \eta), \tag{18}$$

where, of course, $\zeta(0, 0)$ is zero. $\zeta(x, y)$ is positive if Σ is convex into the vapour. Then the integral in (17) is

$$\iiint dR\, S(R)n_0(r+R)$$

$$= \frac{n_L + n_V}{2} \iiint dR\, S(R) - (n_L - n_V) \int_{-\infty}^{\infty} d\xi \int_{-\infty}^{\infty} d\eta \int_0^{\zeta(\xi,\eta)} d\zeta$$

$$\times S((\xi^2 + \eta^2 + \zeta^2)^{1/2}). \tag{19}$$

The first term is independent of Σ, so that (17) becomes

$$\psi(r) - (n_L - n_V) \int_{-\infty}^{\infty} d\xi \int_{-\infty}^{\infty} d\eta \int_0^{\zeta(\xi,\eta)} d\zeta\, S((\xi^2 + \eta^2 + \zeta^2)^{1/2}) = \text{constant}. \tag{20}$$

Now we use the fact that $S(R)$ (equation (9)) is zero if R exceeds the range of the force between fluid molecules, to justify the assumption that $\zeta(\xi, \eta)$ is small and may be approximated by the leading terms of a power series. These approximations will

be analysed in § 5. If $O\xi$ and $O\eta$ are chosen as tangents to the lines of maximum and minimum curvature of Σ at r, these leading terms are

$$\zeta(\xi, \eta) = \frac{\xi^2}{2\rho_1(r)} + \frac{\eta^2}{2\rho_2(r)} + \ldots \tag{21}$$

where $\rho_1(r)$ and $\rho_2(r)$ are the principal radii of curvature at r. The integral in (20) therefore becomes

$$\int_{-\infty}^{\infty} d\xi \int_{-\infty}^{\infty} d\eta \int_{0}^{\zeta(\xi,\eta)} d\zeta \, S((\xi^2 + \eta^2 + \zeta^2)^{1/2})$$

$$\simeq \int_{-\infty}^{\infty} d\xi \int_{-\infty}^{\infty} d\eta \, S((\xi^2 + \eta^2)^{1/2})\left(\frac{\xi^2}{2\rho_1(r)} + \frac{\eta^2}{2\rho_2(r)}\right) \tag{22a}$$

$$= \frac{\pi}{2}\left(\frac{1}{\rho_1(r)} + \frac{1}{\rho_2(r)}\right) \int_{0}^{\infty} dR \, R^3 S(R)$$

$$= -\frac{\pi}{8}\left(\frac{1}{\rho_1(r)} + \frac{1}{\rho_2(r)}\right) \int_{0}^{\infty} dR \, R^4 g(R)\phi'(R), \tag{22}$$

where the third member follows from the symmetry of the integrand of the second in ξ and η, and the fourth member has been derived using the definition (9) and changing the order of integration.

It is natural to introduce the *total curvature* of Σ at r, denoted by $K(r)$ and defined as

$$K(r) \equiv \frac{1}{\rho_1(r)} + \frac{1}{\rho_2(r)}. \tag{23}$$

Also, we can write the last integral in (22) in terms of the *Fowler* (1937) *approximation to the liquid surface tension* γ^f, since

$$\gamma^f = \frac{\pi}{8}(n_L - n_V)^2 \int_{0}^{\infty} dR \, R^4 g(R)\phi'(R). \tag{24}$$

This formula follows from the exact theory of Kirkwood and Buff (1948), if (1.1) is assumed, and if the density falls discontinuously from n_L to n_V (see also Shoemaker *et al* 1970, Berry *et al* 1972). Thus, finally, the equation which determines the 'surface of tension' Σ is, from (26),

$$(n_L - n_V)\psi(r) + \gamma^f K(r) = \text{constant}. \tag{25}$$

This is a remarkable result, because it can be derived independently by considering $\psi(r)$ as an external field acting on a macroscopic fluid of density $n_0(r)$. For statical equilibrium, the pressure $p(r)$ must satisfy the equation

$$\nabla p(r) = \text{external force/unit volume on fluid} = -n_0(r)\nabla\psi(r). \tag{26}$$

If we assume that $p(r)$ is constant (eg atmospheric pressure) far from the solid, then (26) predicts that the liquid pressure $p_L(r)$ and the vapour pressure $p_V(r)$ are different, the discontinuity across the 'surface of tension' Σ being

$$p_L(r) - p_V(r) = -(n_L - n_V)\psi(r). \tag{27}$$

But by Laplace's equation this pressure difference is equilibrated by the liquid surface

tension γ, which acts by means of the curvature of Σ, according to the relation

$$p_L(r) - p_V(r) = \gamma K(r). \tag{28}$$

Taken together, these two relations give (25) with γ^f replaced by γ and the constant set equal to zero.

We shall discuss the solution of equation (25) in § 4, and show how the angle of contact θ emerges naturally in suitable circumstances. It is, however, evident from our derivation that (25) is not an exact equation. In arriving at (22) we have neglected all powers of the curvature higher than the first, and also ignored the effects of changes in the curvature near r; we shall estimate the 'curvature corrections' for equation (25) in § 5. Furthermore, the 'surface of tension' Σ which forms the basis of our initial density distribution $n_0(r)$ is a discontinuous approximation to a 'transition zone' in which n_L drops continuously to n_V, and which, moreover, has a thickness comparable with the range of the potential $\psi(r)$ due to the solid. The validity of (25) must therefore be related to the validity of the Fowler (1937) approximation for surface tension, and in any application it is consistent to use γ^f rather than the true surface tension γ (γ^f is usually a fair approximation to γ— see Shoemaker *et al* 1970).

The solution of equation (25) gives the surface Σ; this is the surface on which the fluid density $n(r)$ has the constant value n_Σ, given by

$$n_\Sigma = n_L \exp\left(-2\pi(n_L - n_V) \int_0^\infty dR\, R^3 g(R)\phi'(R)/3kT \right), \tag{29}$$

which follows from (16) and (9), together with the first term of the right-hand side of (19) (the working simplifies greatly if n_Σ is evaluated far from the solid, so that $\psi(r)$ vanishes). The form of the other constant-density surfaces, and in fact the complete fluid density $n(r)$ near and far from the three-phase region, can be found directly from equation (16). We expect the function $n(r)$ thus found to be about as accurate in comparison with the true fluid density as γ^f is in comparison with γ.

4. The 'surface of tension' and the angle of contact

The form of the 'surface of tension' Σ is determined by equation (25), which gives the local curvature $K(r)$. The 'constant' on the right-hand side is determined by global or asymptotic constraints on the fluid system. To see this, suppose we have a droplet resting on a horizontal solid surface at $z = 0$. Then the 'external field' $\psi(r)$ will contain a gravity term mgz (m is the mass of a fluid molecule), as well as the molecular term from the solid. It is gravity which causes the slow, macroscopic, curvature of the droplet allowing its volume to remain finite. Different 'constants' in (25) generate solutions corresponding to different droplet volumes. However, we are primarily interested in conditions 'near' the solid, so we assume the total liquid volume to be infinite, and ignore the effect of gravity (which will in any case be small near the solid unless its surface is macroscopically rough); then we have the asymptotic condition that the total curvature $K(r)$ vanishes far from the solid, where $\psi(r)$ is zero, so that the 'constant' in (25) is zero. We shall not introduce the angle of contact as an independent *boundary condition* restricting the inclination of droplet surfaces macroscopically close to the solid, but as a naturally-arising *asymptotic value* of the slope microscopically far from the solid.

The simplest case where an angle of contact θ can be defined is that of the 'flat smooth solid', which exerts a potential $\psi(z)$ (equation (3)). Let the surface Σ be represented by its lateral displacement

$$x = x(z) \tag{30}$$

at the point whose height above the surface is z, where Ox is a coordinate axis in the solid surface $z = 0$, as in figure 1 (we are assuming translational symmetry along Oy). Then the curvature K is given by

$$K(r) = \frac{x''(z)}{[1+(x'(z))^2]^{3/2}}, \tag{31}$$

and (25) becomes

$$(n_L - n_V)\psi(z) = \frac{-\gamma^f x''(z)}{[1+(x'(z))^2]^{3/2}} = -\gamma^f K(z). \tag{32}$$

The slope angle $\Theta(z)$ is defined by

$$\cot \Theta(z) \equiv x'(z), \tag{33}$$

and the *angle of contact* θ is the asymptotic value

$$\theta \equiv \lim_{z \to \infty} \Theta(z), \tag{34}$$

which will be determined presently.

To solve (32) we introduce the 'superpotential'

$$\chi(z) \equiv \int_z^\infty d\lambda \, \psi(\lambda), \tag{35}$$

which qualitatively resembles $\psi(z)$, and which is so named because $\psi(z)$ is related to $\chi(z)$ as the force is related to $\psi(z)$. Then (32) may be written in the form

$$\frac{d}{dz}\left(-(n_L - n_V)\chi(z) + \frac{\gamma^f x'(z)}{[1+(x'(z))^2]^{1/2}} \right) = 0, \tag{36}$$

which on integrating and using (34) becomes

$$\cos \Theta(z) = \cos \theta + \frac{n_L - n_V}{\gamma^f}\chi(z). \tag{37}$$

Given a value for θ, this equation may be integrated in towards the solid, the procedure being analogous to that involved in tracing light rays incident at an angle θ on the earth's atmosphere, whose refractive index (analogous to $\chi(z)$) varies with height. It is only for one value of θ that the surface Σ thus found is a physically acceptable liquid–vapour interface, and it is obvious that this will be the angle of contact.

To show this, consider figure 2, which shows the right-hand side of (37) for various possible values of $\cos \theta$ (which must of course lie between -1 and $+1$). All the curves have minima at the same point $z = z_0$, which is also (equation (35)) the height where the solid–fluid potential $\psi(z)$ vanishes (note that this is not the same as the *minimum* of $\psi(z)$, which is the height where the force on a fluid molecule is zero). A particular choice of θ selects a curve from the set on figure 2, and $\cos \Theta(z)$—and hence the slope of the 'surface of tension' Σ—may be found by following the curve inwards towards $z = 0$. If the curve
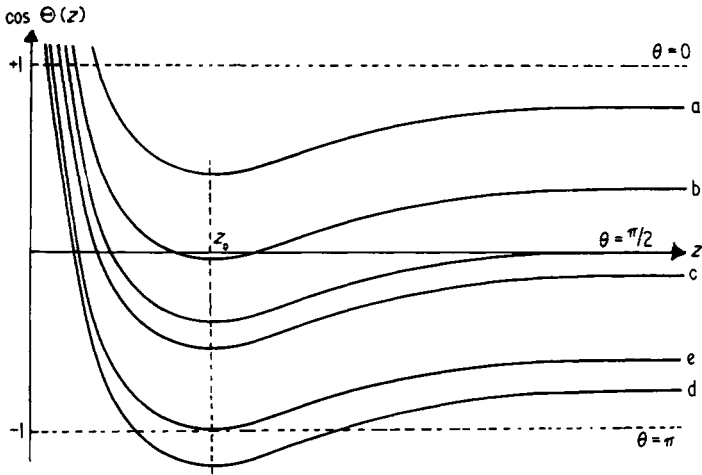
Figure 2. Sketch of cos $\Theta(z)$ (equation (37)) for various 'asymptotic angles' θ, drawn for a 'non-wetting' case where $(n_L - n_V)\chi(z_0)/\gamma^f > -1$.

crosses the abscissa, then $\Theta = \pi/2$ and Σ at that point is perpendicular to the solid surface. If the curve crosses either of the lines ± 1, Σ at that point is parallel to the solid surface. At the minima z_0 of the curves on figure 2, Σ has a point of inflection, where the curvature $K(z)$ (equation (32)) vanishes.

The surfaces Σ generated from figure 2 by four contact angles θ_a to θ_d are sketched on figure 3. It is clear that the surfaces corresponding to θ_a, θ_b and θ_d cannot represent a body of liquid in stable contact with a solid, while that corresponding to θ_c is impossible. The only case leading to a sensible surface Σ is generated by θ_e in figure 2, where the curve cos $\Theta(z)$ touches the line -1 at z_0. From equation (37), this requires that the angle of contact is given by

$$\cos\theta + \frac{n_L - n_V}{\gamma^f}\chi(z_0) = -1. \tag{38}$$

The resulting 'surface of tension' is sketched in figure 4(a). That Σ does indeed have the form shown is evident not only from the requirement that it must interpolate between the curves on figure 3 corresponding to θ_c and θ_d, but also from the analysis of equation (37) given in the appendix (this analysis also shows that, when (38) is not satisfied, x remains finite for all finite z, so that the curves of figure 3 are correctly drawn).
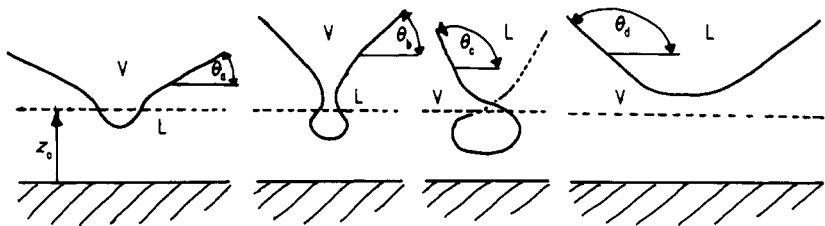

Figure 3. 'Surfaces of tension' generated by θ_a, θ_b, θ_c, θ_d on figure 2.
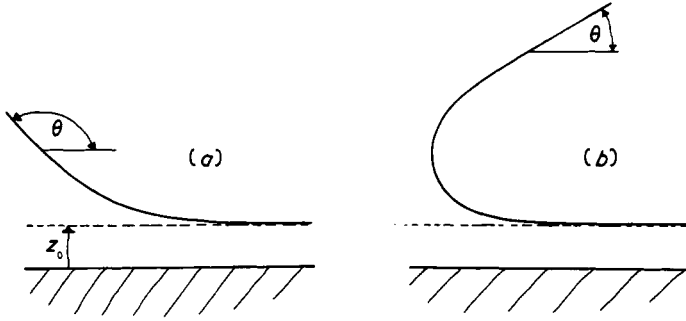
Figure 4. Stable 'surfaces of tension' for: (a) $(n_L - n_V)\chi(z_0)/\gamma^f > -1$ (non-wetting); (b) $-1 > (n_L - n_V)\chi(z_0)/\gamma^f > -2$ (wetting).

Figures 2, 3 and 4(a) are all drawn for a 'non-wetting case', where

$$(n_L - n_V)\chi(z_0)/\gamma^f > -1,$$

and θ is obtuse. If $(n_L - n_V)\chi(z_0)/\gamma^f$ lies between -1 and -2, the analysis leads to an acute angle θ; this is the 'wetting' case. Finally, if $(n_L - n_V)\chi(z_0)/\gamma^f < -2$, all curves of $\cos \Theta(z)$ cross the line -1, and no value of θ leads to stable contact; this is the case of 'spreading'.

The expression (38) for the angle of contact on a 'flat smooth solid' may be rewritten in a particularly simple way, with the aid of equations (35), (3), (24) and the fact that $\chi'(z_0)$ vanishes; after some reduction, we obtain

$$\cos^2\frac{\theta}{2} = -\frac{(n_L - n_V)\chi(z_0)}{2\gamma^f} = \frac{n_S \int_{z_0}^{\infty} dR\,(R^2 - z_0^2)^2 U'(R)}{(n_L - n_V)\int_0^{\infty} dR\,R^4 g(R)\phi'(R)}, \qquad (39)$$

which involves the fluid–solid intermolecular force $U'(R)$, the fluid–fluid force $\phi'(R)$, and the bulk liquid radial distribution function $g(R)$. Alternatively we may use the exact Young–Dupré equation (Adam 1941), namely

$$\cos^2\frac{\theta}{2} = \frac{W}{2\gamma}, \qquad (40)$$

where W is the 'reversible work of adhesion', defined as the energy required to remove liquid from unit area of solid and replace it by vapour. We obtain for W the approximate formulae

$$W = \frac{\pi n_S(n_L - n_V)}{4}\int_{z_0}^{\infty} dR\,(R^2 - z_0^2)^2 U'(R) = -\pi n_S(n_L - n_V)\int_{z_0}^{\infty} dR\,R(R^2 - z_0^2)U(R). \qquad (41)$$

The first expression closely resembles the Fowler approximation (24) for the liquid surface tension, with the function $(R^2 - z^2)^2$ acting instead of $R^4 g(R)$ to 'cut off' the fluid density in response to the repulsion very near the solid. The second expression is a more direct representation for the work of adhesion, but the dependence on z_0 would have been difficult to foresee.

This discussion of the contact angle has been restricted to the case of a 'flat smooth solid', where the surfaces on which $\psi(r)$ is constant are parallel planes. What happens if the solid is rough? There are two limiting cases. In the first, the roughness is *macroscopic*; that is, the solid is smooth at the molecular level, and rough on a larger scale which is, however small in comparison with the droplets considered. Then the 'flat

smooth solid' approximation may be employed *locally*, and the contact angle θ is the same quantity that we have been discussing, except that it is now the angle made by the liquid–vapour interface with the local tangent plane on the solid, rather than with the horizontal. Near the perimeter of the droplet the liquid surface must be puckered and dimpled in a complicated way, in order to satisfy the local contact conditions. The analysis of equation (25) in these situations is very difficult; the main problem is to see whether an 'average contact angle' can be defined. This would be observed with instruments whose resolution is coarse in comparison with the roughness, but fine in comparison with the drop size. Some progress has been made, when the roughness is statistical in character (Wenzel 1949), and when the roughness is idealized to a simple sinusoidal form (Johnson and Dettre 1964); a large literature exists, which is reviewed by Blake and Haynes (1973).

In the second limiting case, the roughness is *microscopic*; that is, the solid surface is macroscopically flat, but no averaging of $\psi(r)$ across the surface is taken. Thus the surfaces of constant $\psi(r)$ undulate on an atomic scale (for a perfect crystal, the undulations will have the periodicity of the lattice). The arguments leading to formula (39) for the contact angle cannot now be applied, and a new analysis based on equation (25), is required. A preliminary study which takes account of the curvature of the ψ surfaces suggests that now there may be more than one stable 'surface of tension' Σ. If further analysis confirms this, then presumably equation (39) represents an average over the contact angles for the different possible surfaces Σ, whose existence may provide yet another explanation of contact-angle hysteresis (for the others, see Blake and Haynes 1973).

Of course many solid surfaces are both macroscopically and microscopically rough, and may also contain asperities on an intermediate scale. All such cases are covered by equation (25) if a gravity term is included in $\psi(r)$. A comprehensive mathematical study of this equation is therefore required, which would enable the form of 'surfaces of tension' (ie the shapes of droplets) to be understood even where it is difficult to define a contact angle.

5. Curvature corrections

In deriving the fundamental equation (25), which determines the 'surface of tension' Σ, we assumed that the curvatures of Σ were small and slowly varying. To examine these assumptions, we restrict ourselves to surfaces with translational symmetry, so that in the local coordinates of figure 1 we may write the equation of the surface near r as $\zeta(\xi)$. Then instead of (22a) we have, for the integral in (20)

$$
\begin{aligned}
J &\equiv \int_{-\infty}^{\infty} \mathrm{d}\xi \int_{-\infty}^{\infty} \mathrm{d}\eta \int_{0}^{\zeta(\xi)} \mathrm{d}\zeta \, S((\xi^2 + \eta^2 + \zeta^2)^{1/2}) \\
&\simeq \int_{-\infty}^{\infty} \mathrm{d}\xi \int_{-\infty}^{\infty} \mathrm{d}\eta \left(\zeta(\xi) S((\xi^2 + \eta^2)^{1/2}) + \frac{\zeta^3(\xi)}{6(\xi^2 + \eta^2)^{1/2}} S'((\xi^2 + \eta^2)^{1/2}) \right) \\
&= 2 \int_{-\infty}^{\infty} \mathrm{d}\xi \int_{|\xi|}^{\infty} \mathrm{d}R \frac{R}{(R^2 - \xi^2)^{1/2}} \left(\zeta(\xi) S(R) + \frac{\zeta^3(\xi) S'(R)}{6R} \right) \\
&= 2 \int_{0}^{\infty} \mathrm{d}R \int_{-R}^{R} \mathrm{d}\xi \left(\frac{\zeta(\xi) R S(R)}{(R^2 - \xi^2)^{1/2}} + \frac{\zeta^3(\xi) S'(R)}{6(R^2 - \xi^2)^{1/2}} \right),
\end{aligned}
\tag{42}
$$

where the first correction term in $\zeta(\xi)$ is now included; this will show the effect of large curvatures of Σ.

To describe the effect of varying curvature, we take for $\zeta(\xi)$ not (21) but

$$\zeta(\xi) = a\xi^2 + b\xi^3 + c\xi^4. \tag{43}$$

In terms of the curvature $K(0)$ of Σ at $\xi = 0$ (ie at r) and its rates of change $K'(0)$ and $K''(0)$ as Σ is traversed, we have

$$a = \tfrac{1}{2}K(0); \qquad b = \tfrac{1}{6}K'(0); \qquad c = \tfrac{1}{24}K''(0). \tag{44}$$

If we include the first four contributing powers of $\zeta(\xi)$ in (42) we obtain, after some reduction,

$$J \simeq \pi a \int_0^\infty \mathrm{d}R\, R^3 S(R) \left[1 + \frac{3R^2}{4}\left(\frac{c}{a} - \frac{5}{6}a^2\right) - \frac{35}{16}R^4(ac + b^2) \right]. \tag{45}$$

For the basic curvature equation (25) to be a good approximation, we require the terms in R^2 and R^4 in the square brackets in (45) to be small in comparison with the constant term. Let R_{max} be the largest value of R contributing significantly to the integral in (45); from (9), R_{max} is the range of the forces between fluid molecules. Then the validity conditions of (25) become

$$\left.\begin{array}{ll} \dfrac{5}{32}R_{max}^2 K^2(0) \ll 1 & (a) \\[3mm] \dfrac{R_{max}^2|K''(0)|}{16|K(0)|} \ll 1 & (b) \\[3mm] \dfrac{35R_{max}^4|K(0)K''(0)|}{768} \ll 1 & (c) \\[3mm] \dfrac{35}{576}R_{max}^4(K'(0))^2 \ll 1 & (d) \end{array}\right\}. \tag{46}$$

Condition (c) may be ignored: it is essentially the product of (a) and (b).

To estimate the curvature and its derivatives, we employ the analysis of §4, especially equations (32) and (33), and obtain

$$\left.\begin{array}{l} |K(0)| = \dfrac{n_L - n_V}{\gamma^f}|\psi(z)| \\[3mm] |K'(0)| = \left| \sin\Theta \dfrac{\mathrm{d}}{\mathrm{d}z}K(z) \right| = \dfrac{n_L - n_V}{\gamma^f}|\psi'(z)|\sin\Theta(z) \\[3mm] |K''(0)| = \left| \cos\Theta K\dfrac{\mathrm{d}K}{\mathrm{d}z} + \sin^2\Theta\dfrac{\mathrm{d}^2 K}{\mathrm{d}z^2} \right| \\[3mm] \qquad = \left| \dfrac{\cos\Theta}{\gamma^{f2}}(n_L - n_V)^2\psi(z)\psi'(z) + \dfrac{\sin^2\Theta}{\gamma^f}(n_L - n_V)\psi''(z) \right| \end{array}\right\}. \tag{47}$$

The first term in the expression for K'' may be ignored, since its use in (46b) simply

reproduces (46*d*). The conditions (46) may now be written approximately as

$$
\left.
\begin{aligned}
\frac{2R_{max}(n_L - n_V)|\psi(z)|}{5\gamma^f} &< 1 \qquad &(a) \\[2mm]
\frac{R_{max}^2 \sin^2\Theta(z)}{16}\left|\frac{\psi''(z)}{\psi(z)}\right| &\ll 1 \qquad &(b) \\[2mm]
\frac{R_{max}^2(n_L - n_V)}{4\gamma^f}\sin\Theta(z)|\psi'(z)| &< 1 \qquad &(d)
\end{aligned}
\right\}.
\tag{48}
$$

These conditions will apply most stringently when the angle of contact is zero, since then the forces from the solid are strongest and Σ is most strongly curved. Using (38) to eliminate $(n_L - n_V)/\gamma^f$, and (37) to eliminate $\Theta(z)$, we obtain conditions involving only the 'superpotential' $\chi(z)$, defined by (35):

$$
\left.
\begin{aligned}
\frac{4}{5}R_{max}\left|\frac{\chi'(z)}{\chi(z_0)}\right| &< 1 \qquad &(a) \\[2mm]
\frac{R_{max}^2}{4}\left(\left|\frac{\chi(z)}{\chi(z_0)}\right| - \left|\frac{\chi(z)}{\chi(z_0)}\right|^2\right)\frac{\chi'''(z)}{\chi'(z)} &\ll 1 \qquad &(b) \\[2mm]
R_{max}^2\left(\left|\frac{\chi(z)}{\chi(z_0)}\right| - \left|\frac{\chi(z)}{\chi(z_0)}\right|^2\right)^{1/2}\left|\frac{\chi''(z)}{\chi(z_0)}\right| &< 1 \qquad &(d)
\end{aligned}
\right\}.
\tag{49}
$$

The form of $\chi(z)$ is shown on figure 2; the minimum lies at z_0, and the 'surface of tension' Σ exists for z-values exceeding z_0.

To obtain definite estimates we approximate $\chi(z)$ by the following expression, which is qualitatively valid when $z \geqslant z_0$:

$$
\chi(z) \simeq \chi(z_0)\exp[-2(z-z_0)^2/R_{max}^2] \qquad (z \geqslant z_0)
\tag{50}
$$

(we have chosen this form to make $\chi(R_{max})$ small, bearing in mind the fact that z_0— roughly the 'hard-sphere radius'—is much less than R_{max}). This enables the functions on the left-hand side of (49) to be evaluated in dimensionless form, and their maxima determined. The approximate values are: condition (49*a*): 0·8; condition (49*b*): 0·4; condition (49*d*): 0·7. Thus all three conditions are only barely satisfied, to about the same degree.

These results by no means imply that the results of §4 are inapplicable, for we have taken the extreme case where the angle of contact is zero and the left-hand sides of (49) take their greatest values. For the case when θ is 90°, these 'greatest values' are approximately halved, and this means that our analysis based on (25) applies over almost all of the surface Σ. Even in 'wetting cases', when θ is small, the correction terms in (45) never diverge, so that the arguments of §4, and in particular the formulae (39) and (41) for θ and W, should still be quite accurate (the portion of the 'surface of tension' over which (49) is poorly satisfied is always limited).

6. Conclusions

The methods of this paper led to the explicit approximation (16) for the density $n(r)$ in a liquid and vapour in contact with an arbitrary rigid solid. The calculation involves first finding the 'surface of tension' Σ, given by the solution of the semi-macroscopic

'curvature' equation (25). For a 'flat smooth solid', Σ can be calculated in detail, and from its slope far from the solid can be obtained the simple formulae (39) and (41) for the contact angle θ and work of adhesion W. The 'ingredients' of the method, which must be fed in *a priori*, are the bulk liquid radial distribution function $g(R)$, and the two potential functions: $\phi(R)$ between two fluid molecules, and $U(R)$ between a fluid and a solid molecule. These three quantities can be obtained in principle and often in practice by molecular-beam and neutron scattering experiments.

In future work we intend to apply the methods reported in at least three ways. First, we wish to test the formulae for θ and W for a range of fluid–solid systems. Second, we wish to examine the 'surface of tension' above a 'flat smooth solid' when the chief curvature correction term in § 5 is included. Third, we wish to study the behaviour of the 'curvature equation' for Σ above a solid that is neither flat nor smooth.

Acknowledgments

Appendix

Consider equation (37) for the surface of tension Σ above a 'flat smooth solid'; using (33), we get

$$\left|\frac{dz}{dx}\right| = \left(\frac{1}{\{\cos\theta + [(n_L - n_V)/\gamma^f]\chi(z)\}^2} - 1\right)^{1/2}. \tag{A.1}$$

Let the asymptotic angle θ made by Σ with the surface be less than the equilibrium contact angle defined by equation (38), which we shall now call θ_c. Then Σ has an inflexion point at z_0 (see curves c on figures 2 and 3), and (A.1) gives, for the horizontal distance $X(z)$ in which Σ climbs from z_0 to z,

$$X(z) = \int_{z_0}^{z} dz \left(\frac{1}{\{\cos\theta + [(n_L - n_V)/\gamma^f]\chi(z)\}^2} - 1\right)^{-1/2}. \tag{A.2}$$

We shall show that as $\theta \to \theta_c$, $X(z)$ diverges for any finite $z - z_0$, so that Σ does indeed take the limiting form shown on figure 4.

Expansion of $\chi(z)$ near its minimum using (38) gives

$$\frac{n_L - n_V}{\gamma^f}\chi(z) \simeq -1 - \cos\theta_c + A(z - z_0)^2, \tag{A.3}$$

so that (A.2) becomes

$$X(z) = \int_0^{z-z_0} dz \left(\frac{1}{[-1 + (\theta_c - \theta)\sin\theta_c + Az^2]^2} - 1\right)^{-1/2}$$

$$\underset{\substack{\theta \approx \theta_c \\ z \sim z_0}}{\simeq} \int_0^{z-z_0} dz \, \{2[Az^2 + (\theta_c - \theta)\sin\theta_c]\}^{-1/2}$$

$$= \frac{1}{(2A)^{1/2}} \sinh^{-1} \left[\frac{z - z_0}{(\theta_c - \theta)^{1/2}} \left(\frac{A}{\sin \theta_c} \right)^{1/2} \right]. \tag{A.4}$$

So long as $z - z_0$ is finite, then, as $\theta \to \theta_c$ we have

$$\chi(z) \xrightarrow[\theta \to \theta_c]{} \frac{1}{(2A)^{1/2}} \ln \left(\frac{(z - z_0) A^{1/2}}{(\theta - \theta_c)^{1/2}} \right), \tag{A.5}$$

which is infinite when $\theta = \theta_c$. QED.

References

Adam N K 1941 *The Physics and Chemistry of Surfaces* (London: Oxford University Press)
Barker J A and Everett D H 1962 *Trans. Faraday Soc.* **58** 1608–23
Berry M V, Durrans R F and Evans R 1972 *J. Phys.* A: *Gen. Phys.* **5** 166–70
Berry M V and Reznek S 1971 *J. Phys.* A: *Gen. Phys.* **4** 77–84
Bikerman J J 1958 *Surface Chemistry* 2nd edn (New York: Academic Press)
Blake T D and Haynes J M 1973 *Surface and Membrane Sci.* **6** in the Press
Egelstaff P A 1967 *An Introduction to the Liquid State* (New York: Academic Press)
Fowler R H 1937 *Proc. R. Soc.* A **159** 229–46
Girifalco L A and Good R J 1957 *J. phys. Chem.* **61** 904–9
Good R J 1964 *Adv. Chem.* **43** 74–87
Good R J and Girifalco L A 1960 *J. phys. Chem.* **64** 561–5
Good R J, Girifalco L A and Kraus G 1958 *J. phys. Chem.* **62** 1418–21
Green H S 1960 *Handb. Phys.* **10** 79 (Berlin: Springer-Verlag)
Hill T L 1956 *Statistical Mechanics* (New York: McGraw-Hill)
Johnson R E Jr and Dettre R H 1964 *Adv. Chem.* **43** 112–44
Jouanin C 1968 *C. R. Acad. Sci., Paris* B **268** 1597–600
Kirkwood J G and Buff F P 1948 *J. chem. Phys.* **17** 338–43
Lester G R 1967 *Wetting* (London: Society of Chemical Industry) pp 57–98
March N H 1968 *Liquid Metals* (Oxford: Pergamon)
Ono S and Kondo S 1960 *Handb. Phys.* **10** (Berlin: Springer-Verlag)
Shoemaker P D, Paul G W and de Chazal M L E 1970 *J. chem. Phys.* **52** 491–5
Toxvaerd S 1971 *J. chem. Phys.* **55** 3116–20
—— 1972 *J. chem. Phys.* **57** 4092–7
Wenzel R N 1949 *J. Phys. Coll. Chem.* **53** 1466–7
Zisman W A 1964 *Adv. Chem.* **43** 1–51