

The statistical mechanics of wetting

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The wetting of a rigid solid by a simple fluid is studied. Using the methods of statistical mechanics an exact expression is obtained for the work of adhesion W_A (and hence the contact angle). It is found that W_A consists of two terms $W_A(1)$ and $W_A(2)$. $W_A(1)$ depends directly on the solid-fluid interaction potential and the fluid one-particle distribution function, and corresponds to the direct interaction between fluid and solid. $W_A(2)$ depends directly on the fluid-fluid interaction potential and the fluid two-particle distribution function, and corresponds to the relaxation of the fluid density profile to its free surface form when the liquid is pulled away from the solid. The existence of $W_A(2)$ is the novel feature of this theory. Comparisons with existing theories are made.

Calculations based on the theory are presented for the case of Lennard-Jones interactions and a flat smooth solid, using parameters corresponding to liquid methane on a variety of solids. The main result is that the new term $W_A(2)$ is comparable in magnitude to the term $W_A(1)$ to which previous studies have been confined.

1. INTRODUCTION

Wetting is a large subject ; it includes phenomena (adhesion, lubrication, immersion, flotation, . . .) in different branches of science ranging from biology to metallurgy [1-3]. Over the years much experimental work has been reported in the literature. In spite of this, and its practical importance, little progress has been made from the theoretical point of view. The theories available to date are those of Girifalco and Good [4], Fowkes [5], and Berry [6] (hereafter called GGT, FT and BT respectively).

The first two, GGT and FT, can be classified as semi-empirical, since they are not based on a rigorous fundamental analysis of the interfacial tension. In spite of their simplicity, however, these theories are able to correlate an impressive variety of properties [4, 7-10]. The basic result of these theories is the following expression for the solid-liquid interfacial tension :

$$\gamma_{SL} = \gamma_S + \gamma_{LV} - \gamma_I, \quad (1)$$

where γ_S and γ_{LV} are the surface tension of solid-vacuum and liquid-vapour respectively and γ_I is a term taking account of the interaction between the liquid and the solid. The work of adhesion (see equation (40)) in these theories is simply the interaction term γ_I , so that the thermodynamic equilibrium equation

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for wetting becomes (see equation (41))

$$\cos^2 \frac{\theta}{2} = \frac{\gamma_I}{2\gamma_{LV}}, \quad (2)$$

where θ is the contact angle. Extensions of these theories have been made [11], but the fundamental philosophy is the same.

The more recent BT, on the other hand, is firmly based on statistical mechanics; however, only with certain approximations can BT obtain an explicit expression for the contact angle; this is

$$\cos^2 \frac{\theta}{2} = (n_V - n_L) \int_{z_0}^{\infty} dz \Psi(z) / 2\gamma_F; \quad \Psi(z_0) \equiv 0, \quad (3)$$

where n_V and n_L are the vapour and liquid bulk densities, $\Psi(z)$ is the interaction potential between a liquid molecule and the whole solid and γ_F is the Fowler approximation for the liquid-vapour surface tension [12]. In BT, as in GGT and FT, the work of adhesion is given by a single solid-liquid interactive term.

In this paper we present a general theory for the solid-fluid interfacial tension which not only gives the exact form of the interactive term but also a new term associated with the relaxation of the fluid when it is separated from the solid. This theory is developed in § 2 from the microscopic statistical point of view, and in § 3 by the mechanical method; the identity of the results obtained by both methods shows the consistency of the theory. In doing this we have followed the procedure adopted by Evans [13] in developing a theory for the surface tension of liquid metals.

The interpretation of the theoretical results and a preliminary comparative study with previous theories are made in §§ 4 and 5 respectively. In § 6 a model calculation is made in order to understand the predictions of the theory over a wide range of conditions. The principal result is the discovery that the new term arising in the theory is often as large as the interactive term to which attention has previously been restricted.

2. MICROSCOPIC STATISTICAL THEORY

The exact statistical theory of the surface tension for a multicomponent fluid system was developed by Kirkwood and Buff [14] (see also Ono and Kondo [15]). Here we present a complementary theory for the interfacial tension of a fluid near a solid surface.

Consider a large two-phase solid-liquid system of N_T molecules in a total volume V at temperature T , both phases being separated by a plane surface of area A in the interface region. Let the number of molecules of the solid phase and fluid phase be N_s and N respectively ($N_s + N = N_T$). The solid will be supposed to be completely rigid; this restriction should be a good approximation in most cases.

The thermodynamic properties of such a system are given by the canonical partition function of the system

$$Q(T, V, A, N_s, N) = \Lambda \cdot Z(T, V, A, N_s, N), \quad (4)$$

$$Z(T, V, A, N_s, N) = \frac{1}{N!} \int \dots \int d\{\mathbf{r}\} \exp \left[-\frac{U_T(\{\mathbf{r}\})}{kT} \right], \quad (5)$$

where Z is the configurational partition function, U_T the total potential energy and Λ the kinetic part of the partition function. It should be noted that because of the rigidity of the solid the Gibbs factor for molecules in the solid does not appear in Z and the position variables $\{\mathbf{r}\}$ refer only to molecules in the fluid.

It is possible, in principle, to derive the thermodynamic properties of the system from the partition function Q . In particular, the thermodynamic potential of the canonical ensemble, namely the Helmholtz free energy F , is related to Q by

$$F = -kT \ln Q. \tag{6}$$

On the other hand, the solid–fluid interfacial tension γ_{SF} is given by the thermodynamic relation

$$\gamma_{SF} = \left(\frac{\partial F}{\partial A} \right)_{T, V, N, N_s}. \tag{7}$$

From equations (4) to (7) we can express γ_{SF} as a function of Z (the only part of Q that depends on A):

$$\gamma_{SF} = -kT \frac{1}{Z} \left(\frac{\partial Z}{\partial A} \right)_{V, T, N, N_s}. \tag{8}$$

Before differentiating Z with respect to A we shall show that this configurational partition function can be factorized. Split the total potential energy U into three terms :

$$U = U_{SS} + U_{SF} + U_{FF}, \tag{9}$$

corresponding to the solid–solid, solid–fluid and fluid–fluid interactions. For convenience we denote by X^* that part of the physical property X which does not contain the solid–solid interactions ; then equation (9) becomes

$$U = U_{SS} + U^* \tag{10}$$

and Z becomes

$$Z = \frac{1}{N!} \int \dots \int d\{\mathbf{r}\} \exp \left[-\frac{1}{kT} (U_{SS} + U_T^*) \right]. \tag{11}$$

Because the position vectors for molecules in the solid do not appear in the integration, equation (11) can be written as

$$Z = Z_{SS} \cdot Z^*, \tag{12}$$

where

$$Z_{SS} = \exp \left[-\frac{1}{kT} U_{SS} \right] \tag{13}$$

and

$$Z^* = \frac{1}{N!} \int \dots \int d\{\mathbf{r}\} \exp \left[-\frac{1}{kT} U_T^* \right]. \tag{14}$$

Equation (12) expresses the factorization property of the configurational partition function ; the initial system is thus equivalent to two separate systems : the solid, which only depends on the solid properties, and the fluid, which consists of the fluid in interaction with an external potential U_{SF} . This result depends on the rigidity of the solid. Use of this property in equation (8) gives

$$\gamma_{SF} = \gamma_S + \gamma_{SF}^*, \tag{15}$$

where

$$\gamma_S = -kT \frac{1}{Z_{SS}} \left(\frac{\partial Z_{SS}}{\partial A} \right)_{T, V, N_s} = \left(\frac{\partial U_{SS}}{\partial A} \right)_{T, V, N_s} \quad (16)$$

and

$$\gamma_{SF}^* = -kT \frac{1}{Z^*} \left(\frac{\partial Z^*}{\partial A} \right)_{T, V, N} \quad (17)$$

We see that, as a consequence of the factorization of Z , the interfacial tension splits into two terms; the first comes just from the solid and the second is the *surface tension of the fluid interacting with an external potential*.

As we shall show later γ_S does not appear in the work of adhesion, which is the easily observable quantity; therefore from now on we limit our attention to γ_{SF}^* .

In the present paper we suppose that the fluid is *simple*, i.e. that the total fluid–fluid interaction potential can be expressed as

$$U_{FF} = \sum'_{i,j} \frac{1}{2} \phi_{LL}(|\mathbf{r}_i - \mathbf{r}_j|), \quad (18)$$

in which $\phi_{LL}(r)$ denotes the intermolecular potential between molecules in the fluid and the prime restricts the summation to $i < j$. Similarly the solid–fluid potential is supposed to be given by

$$U_{SF} = \sum_i^{N_s} \sum_j^N \phi_{SL}(|\mathbf{r}_i^S - \mathbf{r}_j|), \quad (19)$$

where $\phi_{SL}(|\mathbf{r}^S - \mathbf{r}|)$ is the interaction potential between molecules in the solid and fluid at \mathbf{r}^S and \mathbf{r} respectively.

Because of the rigidity of the solid equation (19) can be written as follows :

$$U_{SF} = \sum_j^N \Psi(\mathbf{r}_j), \quad (20)$$

with

$$\Psi(\mathbf{r}) = \sum_i^{N_s} \phi_{SL}(|\mathbf{r}_i^S - \mathbf{r}|), \quad (21)$$

in which Ψ is the interaction of a single molecule in the fluid with the whole solid. (Equation (20) is actually more general than (19), and could be used for *any* kind of solid in interaction with a simple fluid.) The interaction U^* becomes

$$U^* = \sum'_{i,j} \frac{1}{2} \phi_{LL}(r_{ij}) + \sum_j^N \Psi(\mathbf{r}_j). \quad (22)$$

We now have all the ingredients required to obtain an expression for γ_{SF}^* . However, as we need the derivative of Z^* with respect to the area in equation (17), the explicit function $Z^*(A)$ must be found. Bogoliubov [10] and Green [17] developed a convenient technique for this, consisting of a simple change of variables :

$$\mathbf{r} = (x, y, z) = \left(\sqrt{(A)}x', \sqrt{(A)}y', \frac{V}{A}z' \right), \quad (23)$$

transforms Z^* into

$$Z^* = \frac{V^N}{N!} \int_0^1 \dots \int_0^1 d\{\mathbf{r}'\} \exp \left[-\frac{U^*(\{\mathbf{r}'\}, A)}{kT} \right], \quad (24)$$

and these two relations follow :

$$\frac{\partial \mathbf{r}'}{\partial A} = \frac{\mathbf{r}^*}{A}; \quad \mathbf{r}^* \equiv \left(\frac{x}{2}, \frac{y}{2}, -z \right), \quad (25)$$

$$\frac{\partial r_{ij}'}{\partial A} = \frac{x_{ij}^2 + y_{ij}^2 - 2z_{ij}^2}{2Ar_{ij}}. \quad (26)$$

Using equations (22), (24), (25) and (26) in (17) the final expression for γ_{SF}^* is obtained :

$$\begin{aligned} \gamma_{SF}^* = & \frac{1}{2} \iiint \frac{d\mathbf{r}_1}{A} \iiint d\mathbf{r}_2 n_{SF}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \phi_{LL}(r_{12}) \frac{x_{12}^2 - z_{12}^2}{r_{12}} \\ & + \iiint \frac{d\mathbf{r}_1}{A} n_{SF}(\mathbf{r}_1) \mathbf{r}_1^* \cdot \nabla_{\mathbf{r}_1} \Psi(\mathbf{r}_1) \end{aligned} \quad (27)$$

where the doublet and singlet distribution functions $n^{(2)}(\mathbf{r}, \mathbf{r}')$ and $n(\mathbf{r})$ have been introduced. The first term of this expression will be denoted by $\gamma_{SF}^{*(2)}$ (it depends directly on the two-particle distribution function) and the second by $\gamma_{SF}^{*(1)}$ (it depends directly on the one-particle distribution function). The total interfacial tension (15) can now be written as

$$\gamma_{SF} = \gamma_S + \gamma_{SF}^{*(2)} + \gamma_{SF}^{*(1)}. \quad (28)$$

The first two terms correspond to the surface excess of self-free energy of the solid and the liquid. γ_S depends only on the properties of molecules in the solid. γ_{SF}^* , on the other hand, while depending explicitly on the fluid-fluid potential ϕ_{LL} , also depends implicitly on the fluid-solid potential Ψ via $n_{SF}^{(2)}$. The third term $\gamma_{SF}^{*(1)}$ in (28) represents the direct interaction between solid and fluid, but depends indirectly on the fluid-fluid potential ϕ_{LL} via n_{SF} .

It should be noted that in the absence of the solid (i.e. $\Psi = 0$) γ_S and $\gamma_{SF}^{*(1)}$ vanish and γ_{SF} reduces to the well-known equation for the surface tension (e.g. Ono and Kondo [15]) of a fluid in equilibrium with its vapour.

3. MECHANICAL THEORY

The mechanical method of deriving expressions for surface tension has been widely used in the literature since the original paper of Kirkwood and Buff [14]. Here we show that the fundamental result of our statistical analysis, equation (27), can also be deduced from the mechanical point of view. The agreement between the two methods strongly indicates the consistency of the theory.

To simplify the analysis we assume a flat smooth solid, so that by symmetry all properties will depend only on z , the normal distance from the interface. We shall also restrict ourselves to deriving the expression for γ_{SF}^* ; therefore the system considered is fluid in interaction with the external potential $\Psi(z)$.

The mechanical definition of the surface tension [18] is

$$\gamma_{SF}^* = \int_{-l_s}^{l_s} dz (\sigma_T(z) - \sigma_{\alpha\beta}) \quad (29)$$

with

$$\sigma_{\alpha\beta} = \sigma_{\alpha}(1 - \theta(z)) + \sigma_{\beta}\theta(z), \quad (30)$$

where $\theta(z)$ is the unit step function, σ_T is the tangential component of the fluid stress tensor and σ_{α} and σ_{β} its isotropic values inside the two bulk phases, i.e. for $z \leq -l_{\alpha}$ (solid bulk) and $z \geq l_{\beta}$ (fluid bulk) respectively. In the present case the bulk of the solid has no fluid, so that $\sigma_{\alpha} \equiv 0$; however, we shall retain it formally in order to have more symmetric expressions.

The fluid must satisfy the hydrostatic equilibrium equation; in the present geometry this is

$$n(z)\Psi'(z) - \frac{\partial\sigma_N(z)}{\partial z} = 0, \quad (31)$$

where $\sigma_N(z)$ is the normal component of the stress tensor, $n(z)$ the fluid local density and $-\Psi'(z)$ the external force per molecule. Integrating equation (31) gives

$$\sigma_N(z) - \sigma_{\alpha} = \int_{-l_{\alpha}}^z dz n(z)\Psi'(z) \quad (32)$$

and

$$\sigma_N(z) - \sigma_{\beta} = \int_{l_{\beta}}^z dz n(z)\Psi'(z). \quad (33)$$

Using equations (32) and (33) in (29) some elementary steps give the microscopic expression for the fluid in an external potential:

$$\gamma_{\text{SF}}^* = \int_{-\infty}^{\infty} dz [\sigma_T(z) - \sigma_N(z)] - \int_{-\infty}^{\infty} dz zn(z)\Psi'(z). \quad (34)$$

Equation (34) reduces to the more familiar expression for a free liquid interface when the external potential Ψ is zero.

The second term on the right hand side of equation (34) is precisely the term $\gamma_{\text{SF}}^*(1)$ (equation (28)) found by statistical mechanics if the flat smooth solid approximation is used. The first term can be identified as $\gamma_{\text{SF}}^*(2)$ with the help of the relations [19], [15]

$$\sigma_T(z) = -kTn(z) + \frac{1}{2} \int \int \int d\mathbf{r}_{12} \frac{x_{12}^2}{r_{12}} \phi_{\text{LL}}'(r_{12}) \int_0^1 d\eta n^{(2)}(z - \eta z_{12}, r_{12}) \quad (35)$$

and

$$\sigma_N(z) = -kTn(z) + \frac{1}{2} \int \int \int d\mathbf{r}_{12} \frac{z_{12}^2}{r_{12}} \phi_{\text{LL}}'(r_{12}) \int_0^1 d\eta n^{(2)}(z - \eta z_{12}, r_{12}). \quad (36)$$

Using equations (35) and (36) in (34) the isotropic parts of the stress tensor components cancel and we obtain

$$\gamma_{\text{SF}}^* = \frac{1}{2} \int_{-\infty}^{\infty} dz \int \int \int d\mathbf{r}_{12} n^{(2)}(z_1, r_{12}) \phi_{\text{LL}}'(r_{12}) \frac{x_{12}^2 - z_{12}^2}{r_{12}} - \int_{-\infty}^{\infty} dz zn(z)\Psi'(z), \quad (37)$$

which is identical to equation (27) for a flat smooth solid with interaction potential $\Psi(z)$. As pointed out by Evans [13] the consistency of the results

obtained by the statistical and mechanical methods shows that a system in thermodynamic equilibrium is also in hydrostatic equilibrium.

The hydrostatic equation (31) shows that because of the presence of the external potential Ψ the normal component of the stress tensor changes with position z ; we can deduce the consequent modification of the first equation of the BBGKY hierarchy by differentiating the expression for $\sigma_N(z)$ (equation (36)) and using (31). After some algebra this gives the following relation between n and $n^{(2)}$

$$kTn'(z) + n(z)\Psi'(z) + \iiint d\mathbf{r}_{12} n^{(2)}(z_1, \mathbf{r}_{12}) \frac{z_{12}}{r_{12}} \phi_{LL}'(r_{12}) = 0. \quad (38)$$

4. WORK OF ADHESION AND CONTACT ANGLE

Now we consider the system consisting of solid, liquid and vapour. At constant temperature thermal equilibrium is determined by minimizing the Helmholtz free energy F with respect to the solid-liquid interfacial area A . This gives the well-known *Young equation* relating the three interfacial tensions of the solid-liquid-vapour system with the contact angle θ (figure 1), namely

$$\gamma_{SL} + \gamma_{LV} \cos \theta = \gamma_{SV}, \quad (39)$$

where γ_{SV} is the solid-vapour surface tension.

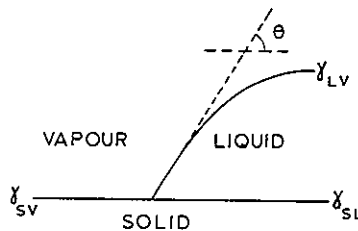


Figure 1. Three phase contact with contact angle θ .

The contact angle can be related to the work of adhesion W_A , defined as the work required to separate unit area of liquid from the solid. It is not difficult to see that W_A can be expressed as (figure 2) :

$$W_A = \gamma_{LV} + \gamma_{SV} - \gamma_{SL}. \quad (40)$$

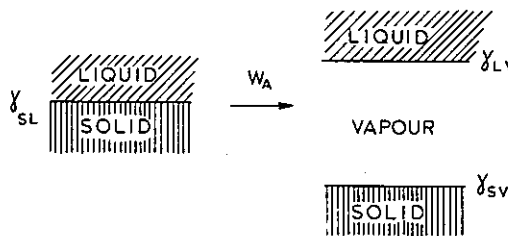


Figure 2. Separation process defining work of adhesion W_A .

Combining equations (39) and (40) gives the Young–Dupré equation

$$\cos^2 \frac{\theta}{2} = \frac{W_A}{2\gamma_{LV}}. \tag{41}$$

From now on our attention will be primarily focused on W_A .

The result (15) can be applied whether the fluid is vapour or liquid, and transforms equation (40) into

$$W_A = \gamma_{LV} + \gamma_{SV}^* - \gamma_{SL}^*, \tag{42}$$

i.e. the terms γ_S have cancelled (as a result of the rigidity of the solid). Now we proceed on the assumption that the vapour density is negligible compared with the liquid density; this will be an excellent approximation far from the fluid critical point. Then, observing that $\gamma_{SF}^*(2)$ and $\gamma_{SF}^*(1)$ (equation (27)) depend on the square of the density and the density respectively, the following approximations can be made

$$|\gamma_{SL}^*(2)| \gg |\gamma_{SV}^*(2)| \quad \text{and} \quad |\gamma_{SL}^*(1)| \gg |\gamma_{SV}^*(1)|. \tag{43}$$

With the earlier fundamental result (28), W_A now becomes

$$W_A = W_A(1) + W_A(2), \tag{44}$$

where

$$W_A(1) \equiv -\gamma_{SL}^*(1) \tag{45}$$

and

$$W_A(2) \equiv \gamma_{LV} - \gamma_{SL}^*(2). \tag{46}$$

We have deliberately divided W_A into two terms with clear physical interpretations, which will now be explained. The first term $-\gamma_{SL}^*(1)$ is the work necessary to remove the liquid from the solid without modifying its density profile (equation (27) and figure 3). (It should be noted that this work corresponds to free energy and not to total energy.) The second term $W_A(2)$ is the

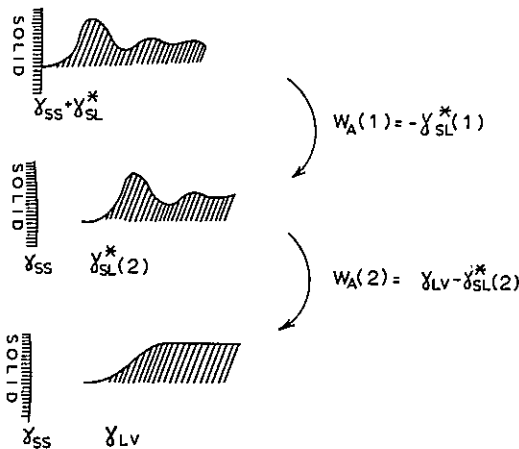


Figure 3. The two stages of separation, illustrating the physical meaning of the contributions $W_A(1)$ and $W_A(2)$.

difference $\gamma_{LV} - \gamma_{SL}^*(2)$; this is the work of relaxation of the liquid from the density profile corresponding to that near the solid into the equilibrium density profile of the liquid with free surface. γ_{LV} and $\gamma_{SL}^*(2)$ are identical in form but the density profiles correspond to two different situations. $W_A(2)$ is really the difference between the two surface tensions: the ordinary surface tension of the liquid, γ_{LV} , and the surface tension of the same liquid in an unstable state with density profile distorted by the force from the solid.

Similar interpretations can be given of the terms in W_A that were dropped as a result of neglecting the vapour density (equation (43)), with two slight differences: first, the dropped terms have opposite signs because the solid-liquid interface is destroyed, whereas the solid-vapour interface is created (figure 2) in the process whose energy defines W_A ; second, the term analogous to $W_A(2)$ consists only of $\gamma_{SV}^*(2)$, since obviously $\gamma_{VV} \equiv 0$ ('vapour-vapour interfacial tension').

5. COMPARATIVE STUDY OF THE THEORIES

Two of the three previous theories of contact angle, GGT and FT, establish a theoretical expression for the solid-liquid interface tension, namely equation (1). The interaction term γ_I has the following explicit form on each theory:

$$\gamma_I(\text{GGT}) = 2\Phi\sqrt{(\gamma_S\gamma_{LV})} \tag{47}$$

and

$$\gamma_I(\text{FT}) = 2\sqrt{(\gamma_S' \gamma_{LV}')}. \tag{48}$$

In these expressions, v is the molar volume, Φ is defined by

$$\Phi \equiv \frac{4v_S^{1/3} v_L^{1/3}}{(v_S^{1/3} + v_L^{1/3})^2} \tag{49}$$

and γ' is that part of γ which contributes to the solid-liquid interaction. (It is assumed in writing γ' that if different kinds of forces—dispersion, polar, etc.—act between molecules, the surface tension can be expressed as a sum of terms separately taking account of these forces: $\gamma = \gamma^d + \gamma^p + \dots$)

Comparing equations (47) and (48) and (1) with our result, equation (28), we notice that there is a correspondence between the three terms of each theory. However, only the term γ_S (which does not contribute to the work of adhesion) is identical in the three equations. The interaction terms in GGT and FT are approximations to our term $\gamma_{SF}^*(1)$ in equation (28), but the degree of approximation is difficult to assess. It is harder to justify the second terms γ_{LV} in equation (1), since the exact form of these terms, namely $\gamma_{SL}^*(2)$, shows that although the formal expression is the same, the density profile is different. In GGT and FT this profile results from the free surface equilibrium while on our theory it is influenced by the forces from the solid. If the drastic approximation is made of using the step function for the density profile of the liquid near the solid, and the Fowler approximation for γ_{LV} , these differences disappear and the same numerical value is obtained from the three theories.

These approximate theories also give approximate expressions for the work of adhesion, namely:

$$W_A(\text{GGT}) = 2\Phi\sqrt{(\gamma_S\gamma_{LV})} \tag{50}$$

and

$$W_A(\text{FT}) = 2\sqrt{(\gamma_S' \gamma_{LV}')}. \quad (51)$$

In BT, W_A is given by the numerator of equation (3). Comparison of these approximate expressions with our exact result (44) shows the lack of the relaxation term $W_A(2)$ in all three of them. If the step function is used for the density profile everywhere in the equations of the present theory, $W_A(2)$ vanishes and the work of adhesion reduces to the interactive term $W_A(1)$, which becomes

$$W_A = n_L \int_{z_{\text{STEP}}}^{\infty} dz z \Psi'(z), \quad (52)$$

where z_{STEP} is the position of the step in the density profile. This distance, however, is not determined by the theory (which would give the exact density profile as the solution of the integro-differential equation (38)). It seems that the essential approximation made implicitly or explicitly in previous theories amounts to this oversimplification of the liquid density profile near the solid.

It should be noticed that equation (52) can be rewritten as

$$W_A = n_L z_{\text{STEP}} \Psi(z_{\text{STEP}}) - n_L \int_{z_{\text{STEP}}}^{\infty} dz \Psi(z), \quad (53)$$

which if $n_V \ll n_L$ and $z_{\text{STEP}} = z_0$ becomes identical to W_A on the BT (equation (3)). However, this identification is rather dangerous; the *free energy* should be minimized in order to get z_{STEP} in equations (52) or (53), and this would give a value different from z_0 which corresponds to minimizing W_A in the numerator of equation (3), a quantity that looks more like the *total interactive energy* than the free energy. It is not surprising that such 'paradoxes' arise when the essentially unstable step density profile is analysed in equilibrium terms.

6. NUMERICAL CALCULATIONS FOR A MODEL OF LIQUID METHANE

Experimental data on contact angles of simple liquids have not been reported in the literature, probably because rather sophisticated experimental techniques would be needed in order to measure θ at the low temperatures where simple liquids are stable. In the absence of such data we are obliged to introduce a model for the solid-liquid interface in order to understand the quantitative implications of the theory developed here.

The model consists of a simple liquid and a solid, both having interactions of the Lennard-Jones type:

$$\phi_{LL}(r) = 4\epsilon_{LL} \left[\left(\frac{\sigma_{LL}}{r} \right)^{12} - \left(\frac{\sigma_{LL}}{r} \right)^6 \right] \quad (54)$$

and

$$\phi_{SS}(r) = 4\epsilon_{SS} \left[\left(\frac{\sigma_{SS}}{r} \right)^{12} - \left(\frac{\sigma_{SS}}{r} \right)^6 \right]. \quad (55)$$

The same type of interaction is supposed to occur between molecules in the solid and liquid, with parameters

$$\sigma_{SL} = \frac{\sigma_{SS} + \sigma_{LL}}{2} \quad (56 a)$$

and

$$\epsilon_{\text{SL}} = \sqrt{(\epsilon_{\text{SS}}\epsilon_{\text{LL}})}. \tag{56 b}$$

To simplify the calculation we shall suppose that the solid is in fact a continuum with a constant density equal to σ_{SS}^{-3} molecules/Å³. This assumption gives a flat smooth external potential, namely

$$\Psi(z) = \frac{2\pi}{3} \epsilon_{\text{SL}} \left(\frac{\sigma_{\text{SL}}}{\sigma_{\text{SS}}}\right)^3 \left[\frac{2}{3} \left(\frac{\sigma_{\text{SL}}}{z}\right)^9 - \left(\frac{\sigma_{\text{SL}}}{z}\right)^3 \right], \tag{57}$$

between a liquid molecule and the semi-infinite solid.

The contact angle θ depends on γ_{LV} and W_{A} (equation (41)) and hence on γ_{SL}^* (equations (42) and (43)); γ_{SL}^* is given by equation (37). This involves $\Psi(z)$, which is given by equation (57). It also involves the liquid two-particle distribution function in the inhomogeneous liquid-vapour and liquid-solid interfaces. This function would be very difficult to calculate, and we employ the following approximation due to Green [20] in terms of the bulk liquid radial distribution function $g(r)$:

$$n^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = n(\mathbf{r}_1)n(\mathbf{r}_2)g(r_{12}). \tag{58}$$

The next ingredients of the calculation are the density profiles of the liquid in the solid-liquid and liquid-vapour interfaces. For the latter we use the exponential approximation [21] given by

$$n_{\text{LV}}(z) = \begin{cases} n_{\text{L}} \left[1 - \frac{1}{2} \exp\left(\frac{z_0 - z}{\sigma_{\text{LL}}}\right) \right], & z \geq z_0, \\ n_{\text{L}} \frac{1}{2} \exp\left(\frac{z - z_0}{\sigma_{\text{LL}}}\right), & z \leq z_0, \end{cases} \tag{59}$$

where we have supposed that the interface thickness is of the order σ_{LL} . It has been shown [6] that, when the approximation (58) is assumed, the density profile of the liquid near a solid is the solution of the following integral equation, arising from the BBGKY equation (38):

$$n_{\text{SL}}(z) = n_{\text{L}} \exp \left\{ -\frac{\Psi(z)}{kT} + \iiint d\mathbf{R} S(R)[n_{\text{L}} + n(z + Z)] \right\}, \tag{60}$$

where

$$S(R) = - \int_R^\infty d\rho g(\rho)\phi'(\rho).$$

We shall employ the first iteration of this equation for $n_{\text{SL}}(z)$, using the liquid-vapour density profile $n_{\text{LV}}(z)$ (equation (59)) as zeroth approximation. The advantages of this procedure are that the result obtained, namely

$$n_{\text{SL}}(z) = n_{\text{LV}}(z) \exp \left\{ -\frac{\Psi(z)}{kT} \right\}, \tag{61}$$

is very simple and moreover has the correct limit when the solid disappears. However, equation (61) does not define $n_{\text{SL}}(z)$ completely: a further condition

is necessary in order to determine the relative position z_0 of the zeroth approximation $n_{LV}(z)$ relative to the solid surface. The obvious condition is that mass is conserved during the iteration, i.e.

$$\int_{-\infty}^{\infty} dz n_{SL}(z) = \int_{-\infty}^{\infty} dz n_{LV}(z). \quad (62)$$

To make the model as realistic as possible we have used methane data to describe the liquid. Calculations were performed at three temperatures (96 K, 121 K and 168 K) for which g data for methane are available [22]. The Lennard-Jones parameters for methane at these temperatures were calculated by Shoemaker *et al.* [25] using the g data in the bulk expressions for the pressure and internal energy whose experimental values are known. The table shows σ_{LL} and ϵ_{LL}/k obtained at the three temperatures, along with other relevant values

T (K)	σ_{LL} (Å) (1)	ϵ_{LL}/k (K) (1)	γ_{LV} (exp) (2)	γ_{LV} (3)	γ_{LV} (4)	L (Å) (5)
96	3.579	181.25	16.0	15.83	10.81	1.20
121	3.325	236.85	11.3	14.62	9.69	2.45
168	3.464	175.01	—	7.97	5.24	—

(1) Lennard-Jones parameters for methane [25].

(2) Experimental values of methane surface tension in erg/cm² [26].

(3) Methane surface tension in erg/cm² calculated assuming a step function as density profile.

(4) Methane surface tension in erg/cm² calculated assuming the exponential form for $n_{LV}(z)$ with an interface thickness of σ_{LL} (see equation (59) in text).

(5) Thickness of the liquid-vapour interface calculated by Berry *et al.* [21] assuming the parameterized exponential form for $n_{LV}(z)$.

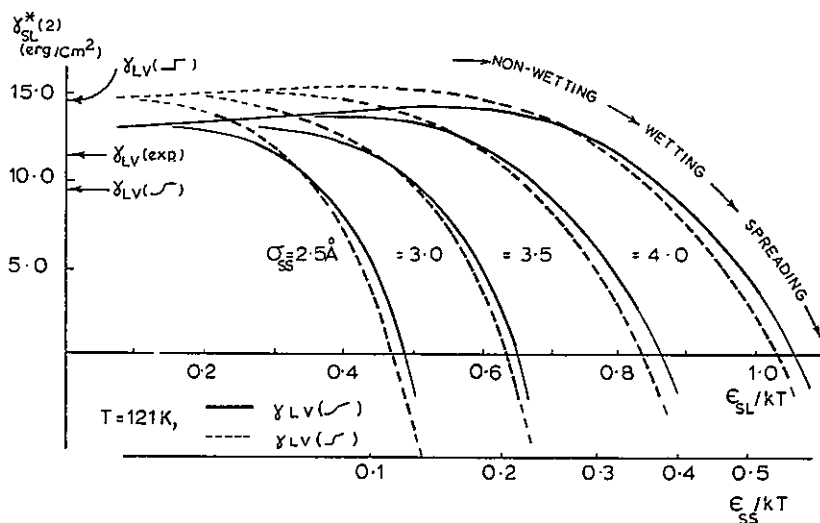


Figure 4. Contribution $\gamma_{SL}^*(2)$ to γ_{SL} plotted against ϵ_{SS}/kT (and ϵ_{SL}/kT) at $T=121$ K for several σ_{SS} values. Continuous and dashed lines correspond to the exponential (equation (59)) and step function approximations respectively for $n_{LV}(z)$.

connected with the present calculations. The calculations at 121 K were repeated using the step function for the density profile in the liquid-vapour interface.

We present calculations of $\gamma_{SL}^*(2)$ (figure 4), $W_A(2)$ and $W_A(1)$ (figure 5) and $\cos^2 \theta/2$ (figures 6 and 7) for different values of the two solid parameters σ_{SS} and ϵ_{SS} . For clarity we have used ϵ_{SL}/kT as abscissa in these figures, but the values of ϵ_{SS}/kT are also shown. The bold portions of each curve (full or dashed) correspond to the range of parameters ϵ_{SS} and σ_{SS} for which the contact angle is defined, i.e. for which $0 \leq \cos^2(\theta/2) \leq 1$. (When the attraction between solid and liquid is sufficiently strong the right-hand member of the Young-Dupré equation (41) exceeds unity, and spreading occurs; in the other extreme this quantity is negative, the work of adhesion is negative, indicating that the solid would repel the liquid which would presumably form spherical drops.)

The two families of curves in figure 4 correspond to the exponential and step function forms for the profile $n_{LV}(z)$, and $T = 121$ K. Berry *et al.* [21] fitted the Kirkwood-Buff theoretical value of γ_{LV} to its experimental value using the exponential density model with the interface thickness as parameter. The thickness was found to be 2.45 Å (see table). The thickness we have chosen for this density model (equation (59)), is $\sigma_{LL} (= 3.325 \text{ \AA})$, so the curves on figure 4 correspond to the extremes of reasonable density profiles n_{LV} . The curves show that the physically important quantity $\gamma_{SL}^*(2)$ behaves similarly on both models.

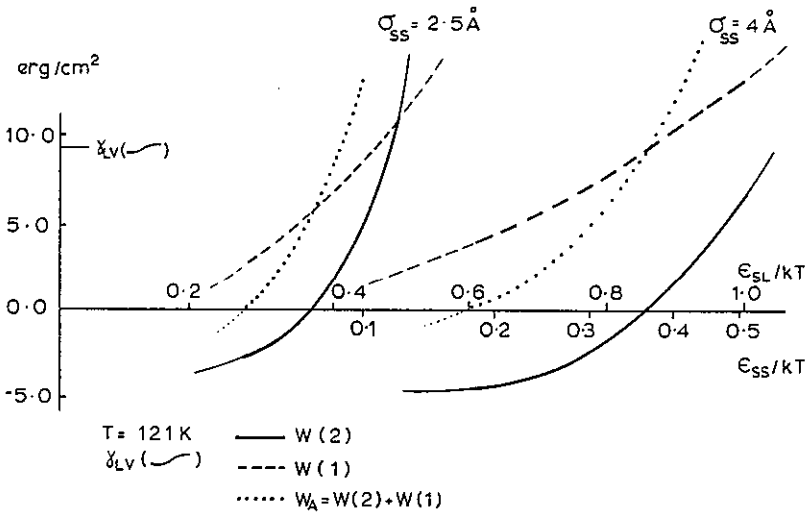


Figure 5. W_A , $W_A(1)$ and $W_A(2)$ plotted against ϵ_{SS}/kT (and ϵ_{SL}/kT) at $T = 121$ K for two values of σ_{SS} . The exponential approximation (equation (59)) has been used for $n_{LV}(z)$.

In figure 5 we compare the two terms in W_A (equation (44)) using the exponential model for n_{LV} and $T = 121$ K. The two groups of curves correspond to $\sigma_{SS} = 2.5 \text{ \AA}$ and $\sigma_{SS} = 4 \text{ \AA}$. It is clear that a considerable error could be made by omitting the relaxation term $W_A(2)$; in fact for the parameter ranges considered here this term that we have introduced is just as important as the previously studied interactive term $W_A(1)$.

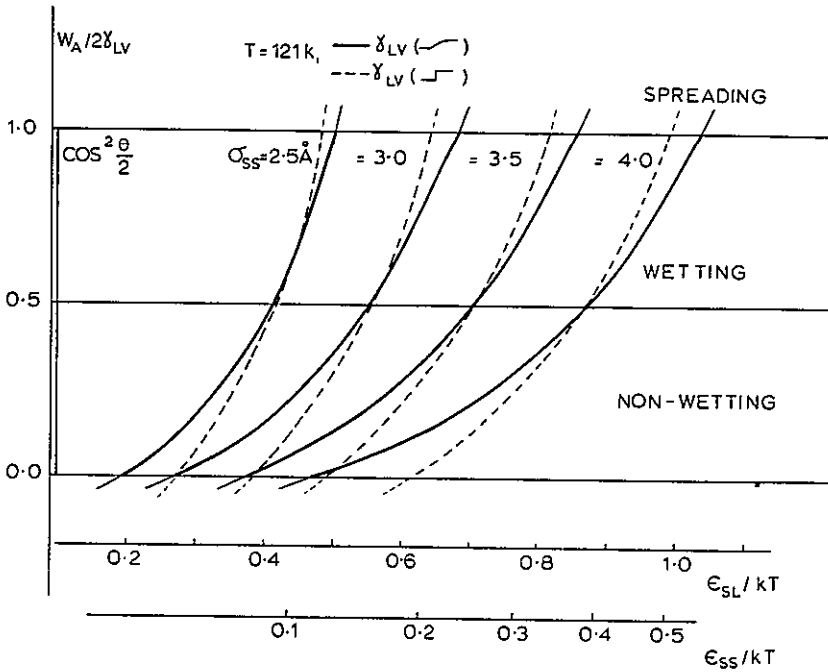


Figure 6. $W_A/2\gamma_{LV}$ and $\cos^2 \theta/2$ plotted against ϵ_{SS}/kT (and ϵ_{SL}/kT) at $T=121$ K for several σ_{SS} values. Continuous and dashed lines correspond to the exponential (equation (59)) and step function approximations respectively for $n_{LV}(z)$.

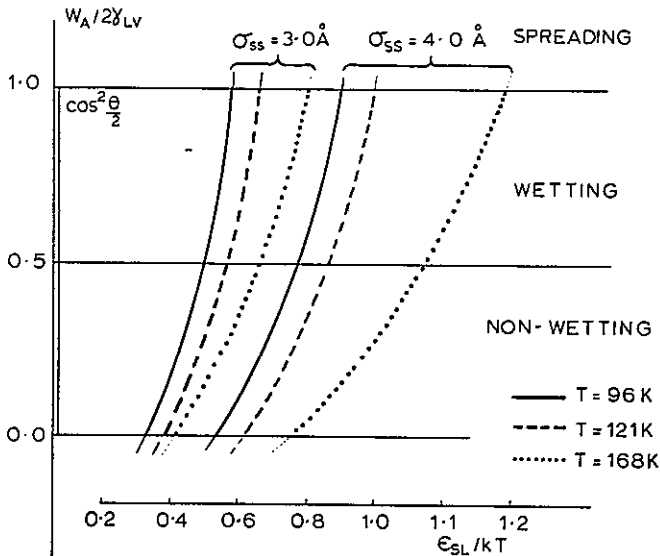


Figure 7. $W_A/2\gamma_{LV}$ and $\cos^2 \theta/2$ plotted against ϵ_{SS}/kT for two values of σ_{SS} at $T=96$ K (continuous line), $T=121$ K (dashed line) and $T=168$ K (dotted line). The exponential approximation (equation (59)) has been used for $n_{LV}(z)$.

The variation of $\cos^2 \theta/2$ with the solid parameters ϵ_{SS} and σ_{SS} is shown in figure 6 for the exponential and step profiles. As expected increasing interaction energy (i.e. increasing ϵ_{SS} and σ_{SS}^{-1}) gives increased wetting (smaller θ). Again we observe that the two models for $n_{LV}(z)$ give close agreement, particularly around the point ($\theta = 90^\circ$) which separates wetting from non-wetting.

Finally the effect of temperature on θ is shown in figure 7 for the exponential density profile. The obvious consequence of increasing T is that the liquid has more thermal energy so that effect of the attraction from the solid diminishes and the contact angle increases.

7. CONCLUSION

The new feature that emerges from the statistical-mechanical theory of wetting presented here is the existence of the term $W_A(2)$ (equation (46)) in the work of adhesion W_A . This term gives the contribution to W_A of the relaxation of the liquid density profile to its free surface form, and is comparable in magnitude with the term $W_A(1)$ that corresponds to the direct interaction between liquid and solid.

Nevertheless the theory is far from complete and should be extended in several directions. Most important from a practical point of view would be a removal of the restriction to simple liquids to enable polar liquids such as water to be studied. There is every reason to believe that the term $W_A(2)$ would retain its importance on such an extended theory.

Next the restriction to rigid solids should be removed, to allow for the consequences of wetting on 'soft' (i.e. deformable) solids to be understood (see Lester [23]).

Finally, while the numerical calculations of § 6 are based on the flat smooth solid approximation, the fundamental theory of §§ 2 and 4 is not. Therefore a detailed study of wetting on macroscopically and microscopically rough surfaces becomes possible. We have already made some progress in this direction: for macroscopic roughness both terms $W_A(1)$ and $W_A(2)$ contain contributions from the increase in surface area due to the undulations, and when these are carefully evaluated the well-known equation of Wenzel results.

It would be most desirable to test the theory, as it now stands, by experiment. This would involve the difficult problem of measuring contact angles at the low temperatures for which simple liquids exist. However, that effort now has theoretical motivation.

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