

# 3. A Statistical Mechanical Theory for the Solid-Liquid Interface

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## ABSTRACT

A statistical mechanical theory for the solid-liquid interface is developed. The direct implications for wetting problems are analysed. Microscopic expressions for the interfacial tension, work of adhesion and contact angle are deduced. A brief discussion on previous theories is included.

## I. INTRODUCTION

Although much experimental work has been reported in the literature concerning the wetting problem little progress has been made from the theoretical point of view. The theories which are currently available for the contact angle fall into two classes. On the one hand there are those due to Girifalco and Good (1) and Fowkes (2) which are based on the following expression for the solid-liquid interfacial tension:

$$\gamma_{BL} = \gamma_{SS} + \gamma_{LV} - \gamma_1 \quad (1)$$

where  $\gamma_{SS}$  and  $\gamma_{LV}$  are the surface tensions of the solid-vacuum and liquid-vapour interfaces, respectively, and  $\gamma_1$  is a term which takes account of the interaction between the liquid and the solid. From Eq. (1) and the expression for the work of adhesion

$$W_A = \gamma_{LV} + \gamma_{SV} - \gamma_{SL} \quad (2)$$

It is found that if the spreading pressure ( $\gamma_{SS} - \gamma_{SV}$ ) is neglected,  $W_A$  reduces to  $\gamma_1$  and therefore the contact angle expression becomes

$$\cos^2(\theta/2) = W_A/(2\gamma_{LV}) \quad (3)$$

On the other hand, theoretical expressions for the interaction between molecules have been used (e.g. Padday and Uffindell (3)) to calculate the work of adhesion using the simple Hamaker (4) procedure. Extensions of these theories have been carried out by Dann (5) and Israelachvili (6), but the original philosophy is maintained.

More recently a statistical mechanical theory for the contact angle has been developed by Berry (7). However, in order to get an explicit expression for the contact angle in this theory, it is necessary to assume that the liquid density is constant up to the surface.

Here we present a general statistical mechanical theory for the solid-liquid interfacial tension. This theory gives the exact form of the interactive term in the work of adhesion and introduces a new contribution which is associated with the relaxation of the liquid when it is separated from the solid.

## II. MICROSCOPIC STATISTICAL THEORY

The exact statistical theory of the surface tension for a multicomponent fluid system was developed by Kirkwood and Buff (8) (see also Ono and Kondo (9)). Here we present a complementary theory for the interface tension of a fluid near a solid surface.

Let us consider a large two-phase solid-liquid system of  $N_r$  molecules in a total volume  $V$  at temperature  $T$ . We assume the phases are separated by a planar surface of area  $A$  which is sited somewhere in the interface region. Let the number of molecules of the solid phase and fluid phase be  $N_s$  and  $N$ , respectively ( $N_s + N = N_r$ ). For convenience the solid will be supposed to be completely rigid and it is thought that this restriction will be a good approximation in many cases. The thermodynamic properties of such a system are given in terms of the canonical partition function of the system

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

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

where  $Z$  is the configurational partition function,  $U_T$  the total potential energy and  $\Lambda$  the kinetic part of the partition function. It may be noted that, because of the rigidity of the solid, the Gibbs factor for the solid molecules does not appear in  $Z$  and that the position variables refer only to those of 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, the Helmholtz free energy  $F$ , is related to  $Q$  by the equation

$$F = -kT \ln Q. \quad (6)$$

On the other hand, the interfacial tension  $\gamma_{\text{SF}}$  (subscript F can denote liquid (L) or vapour (V)) is given by the thermodynamic relation

$$\gamma_{\text{SF}} = \left( \frac{\partial F}{\partial A} \right)_{T, V, N, N_{\text{S}}} \quad (7)$$

Using Eqs (4) to (7) we can express  $\gamma_{\text{SL}}$  as a function of  $Z$ , the sole part of  $Q$  that depends on  $A$ :

$$\gamma_{\text{SF}} = -kT \frac{1}{Z} \left( \frac{\partial Z}{\partial A} \right)_{T, V, N, N_{\text{S}}} \quad (8)$$

Before differentiating  $Z$  with respect to the area in Eq. (8) we shall show that this configurational partition function can be factorized. To do this we divide the total potential energy  $U_{\text{T}}$  in three terms, namely

$$U_{\text{T}} = U_{\text{SS}} + U_{\text{SF}} + U_{\text{FF}} \quad (9)$$

corresponding to the solid–solid, solid–fluid and fluid–fluid interactions. For convenience we will denote by  $X^*$  that part of the physical property  $X$  which does not contain the solid–solid interactions: then Eq. (9) can be written as

$$U_{\text{T}} = U_{\text{SS}} + U^*_{\text{T}} \quad (10)$$

and  $Z$  as

$$Z = \frac{1}{N!} \int \dots \int d\{r\} \exp \left[ -\frac{1}{kT} (U_{\text{SS}} + U^*_{\text{T}}) \right] \quad (11)$$

and, because the vector positions of the solid molecules do not appear in the integration, Eq. (11) can be written as

$$Z = Z_{\text{SS}} Z^* \quad (12)$$

where

$$Z_{\text{SS}} = \exp \left[ -\frac{1}{kT} U_{\text{SS}} \right] \quad (13)$$

and

$$Z^* = \frac{1}{N!} \int \dots \int d\{r\} \exp \left[ -\frac{1}{kT} U^*_{\text{T}} \right]. \quad (14)$$

Equation (12) expresses the factorization property of our configurational partition function; our initial system is equivalent to two separated systems: the solid system, which only depends on the properties of the solid, and the fluid system, which consists of the fluid molecules interacting with an external potential  $U_{\text{SF}}$ . This result arises from the assumed rigidity of the solid. Using this property in Eq. (8) we get

$$\gamma_{\text{SF}} = \gamma_{\text{SS}} + \gamma_{\text{SF}}^* \quad (15)$$

where

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

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

We see that, as a consequence of the factorization of  $Z$ , the interfacial tension also separates 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  $\gamma_{\text{SS}}$  does not appear in the work of adhesion, which is the relevant quantity to our problem, and therefore from now on we focus our attention on  $\gamma_{\text{SF}}^*$ .

We suppose that the total fluid–fluid interaction potential is given by

$$U_{\text{FF}} = \sum_{ij}^N \frac{1}{2} \phi(|r_i - r_j|) \quad (18)$$

where  $\phi(r)$  denotes the intermolecular potential between fluid molecules. Similarly the solid–fluid potential is assumed to be given by

$$U_{\text{SF}} = \sum_i^{N_s} \sum_j^N \phi^{\text{SF}}(|r_i^s - r_j|) \quad (19)$$

where  $\phi^{\text{SF}}(|r_i^s - r_j|)$  is the interaction potential between a solid molecule and a fluid one sited at  $r_i^s$  and  $r_j$  respectively. Because of the rigidity of the solid Eq. (19) can be written as follows:

$$U_{\text{SF}} = \sum_j^N \psi(r_j) \quad (20)$$

with

$$\psi(r) = \sum_j^{N_s} \phi^{\text{SF}}(|r_i^s - r_j|) \quad (21)$$

in which  $\psi$  is the interaction potential of a fluid molecule with the solid. Equation (20) is somewhat more general than Eq. (19). From Eqs (18) and (20) the interaction  $U^*_{\tau}$  can be written as

$$U^*_{\tau} = \sum_{i,j}^N \frac{1}{2} \phi(r_{ij}) + \sum_j^N \psi(r_j). \quad (22)$$

We have now all the ingredients to obtain an expression for  $\gamma^*_{\text{SF}}$ ; however, as we need the derivative of  $Z^*$  with respect to area in Eq. (17), an explicit form for the function  $Z^*(A)$  must be found. Bogoliubov (10) (see Green (11)) developed a convenient technique for such problems. It consists of a simple change of variables:

$$r = (x, y, z) = [(\sqrt{A})x', (\sqrt{A})y', (V/A)z'] \quad (23)$$

so that  $Z^*$  becomes

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

and from which these two relations follow:

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

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

Using Eqs (22), (24), (25) and (26) in Eq. (17) the final expression for  $\gamma^*_{\text{SF}}$  is

$$\begin{aligned} \gamma^*_{\text{SF}} = & \frac{1}{2} \iiint \frac{d\mathbf{r}_1}{A} \iiint d\mathbf{r}_2 n^{(2)}_{\text{SF}}(\mathbf{r}_1, \mathbf{r}_2) \phi'(r_{12}) \frac{x_{12}^2 - z_{12}^2}{r_{12}} + \\ & \iiint \frac{d\mathbf{r}_1}{A} n_{\text{SF}}(\mathbf{r}_1) \mathbf{r}_1^* \cdot \nabla_{\mathbf{r}_1} \psi(r_1) \end{aligned} \quad (27)$$

where the pairwise distribution function  $n_{\text{SF}}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$  and the singlet function  $n_{\text{SF}}(\mathbf{r})$  have been introduced. For simplicity we shall refer to the first term of Eq. (27) as  $\gamma^*_{\text{SF}}(2)$  (since it depends on the 2-particle distribution function) and to the second as  $\gamma^*_{\text{SF}}(1)$  (as it depends on the 1-particle distribution function). With this notation the total interfacial tension Eq. (15) is written as

$$\gamma_{\text{SF}} = \gamma_{\text{SS}} + \gamma^*_{\text{SF}}(2) + \gamma^*_{\text{SF}}(1). \quad (28)$$

The first terms ( $\gamma_{ss}$  and  $\gamma_{sf}^*(2)$ ) are contributions to the interface tension of the excess of self-free energy of the two phases. The third term  $\gamma_{sf}^*(1)$  adds the *direct* interaction effect between the solid and the fluid. However, the equilibrium distribution functions  $n_{sf}(r_1)$  and  $n_{sf}^{(2)}(r_1, r_2)$  are not independent of each other, being connected by the first integrodifferential equation in the 'BBGKY hierarchy':

$$-kT \nabla \ln n(r_1) = n(r_1) \nabla \psi(r_1) + \frac{1}{2} \iint d r_2 n^{(2)}(r_1, r_2) \nabla \psi(r_2). \quad (29)$$

That means that an *indirect* contribution of the solid–fluid interactive potential appears in  $\gamma_{sf}^*(2)$  through  $n_{sf}^{(2)}$ . Similarly the fluid–liquid intermolecular potential is *indirectly* affecting  $\gamma_{sf}^*(1)$ . Because of the assumption that the solid is rigid this does not occur in  $\gamma_{ss}$ .

### III. WORK OF ADHESION AND CONTACT ANGLE

We can use our result of Eq. (28) to derive an expression for the work of adhesion  $W_A$ . From Eq. (2)

$$W_A = \gamma_{LV} + \gamma_{sv}^* - \gamma_{sl}^* \quad (30)$$

since the terms in  $\gamma_{ss}$  cancel when the solid is assumed to be rigid. Using Eq. (30) the Young–Dupré equation for the contact angle (Adamson (12))

$$\cos^2(\theta/2) = W_A/(2\gamma_{LV}) \quad (31)$$

becomes

$$\cos^2 \frac{\theta}{2} = \frac{\gamma_{sl} + \gamma_{sv}^* - \gamma_{sl}^*}{2 \gamma_{LV}}. \quad (32)$$

Now we proceed by assuming that the density of the vapour is negligible compared with the bulk liquid density and, since  $\gamma_{sl}^*(2)$  and  $\gamma_{sl}^*(1)$  in Eq. (27) are roughly proportional to the square of the liquid density and to the liquid density respectively, we might expect

$$|\gamma_{sl}^*(2)| \gg |\gamma_{sv}^*(2)| \text{ and } |\gamma_{sl}^*(1)| \gg |\gamma_{sv}^*(1)| \quad (33)$$

Equation (30) then reduces to

$$W_A = W_A(1) + W_A(2) \quad (34)$$

with

$$W_A(1) = -\gamma_{sl}^*(1) \quad (35)$$

and

$$W_A(2) = \gamma_{LV} - \gamma_{sl}^*(2). \quad (36)$$

Equation (32) can be written now as

$$\cos^2 \frac{\theta}{2} = \frac{W_A(1) + W_A(2)}{2\gamma_{LV}}. \quad (37)$$

We have artificially but deliberately divided  $W_A$  into two terms. This is because we can associate a different physical meaning to each. Let us imagine a process where the liquid is separated from the solid surface. We do it in two steps (see Fig. 1); the first one consists of the material

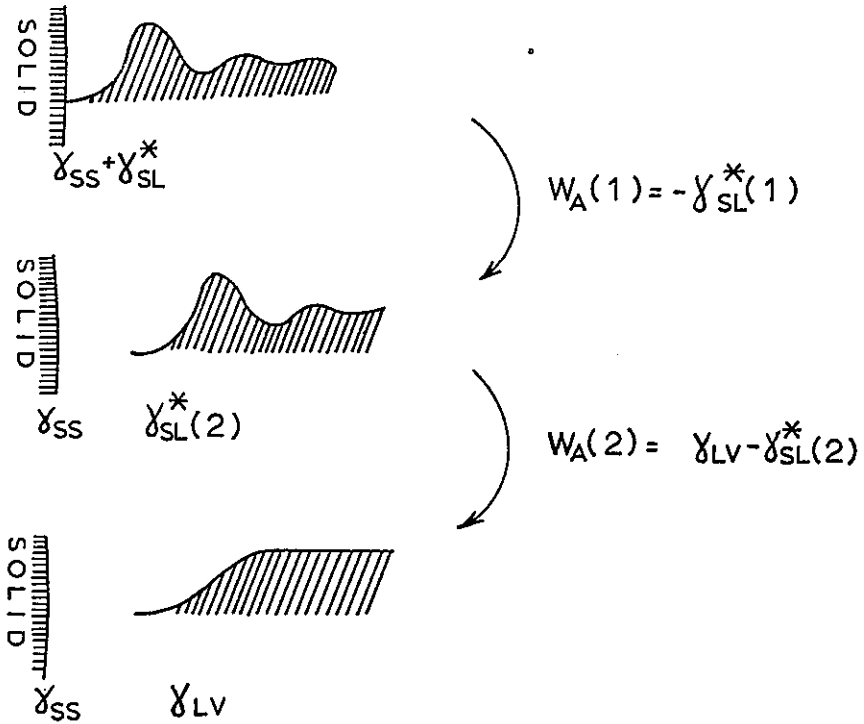


Fig. 1. Steps in the process of separating a liquid from a solid surface.

separation at the two phases keeping the local density of the liquid 'frozen', i.e. the final state consists of the solid (which because of its rigidity remains unperturbed) and the liquid with the density profile that corresponds to the solution of the exact solid liquid problem, i.e. the solution of Eq. (29) for this model. In the second step we allow the

liquid to relax to the final density profile of the free surface liquid. The work of adhesion involved in the first step is  $W_A(1)$  and it is work done against the *direct* solid-liquid interaction potential  $\psi(\underline{r})$ . The associated work in the second step is  $W_A(2)$ ; it is given by the difference of two surface tensions,  $\gamma_{LV} - \gamma_{sv}^*(2)$ , and corresponds to the work of relaxation as the liquid goes from the intermediate state to the equilibrium state.

We could interpret those terms of the work of adhesion which have been ignored by the use of approximation Eq. (33) in a similar way. Two slight differences should be noted: the term which we omitted has opposite sign because we destroy the solid-liquid interface but create the liquid-vapour interface in the work of adhesion (see Fig. 2). The other difference is that the term analogous to  $W_A(2)$  consists only of  $\gamma_{sv}^*(2)$ .

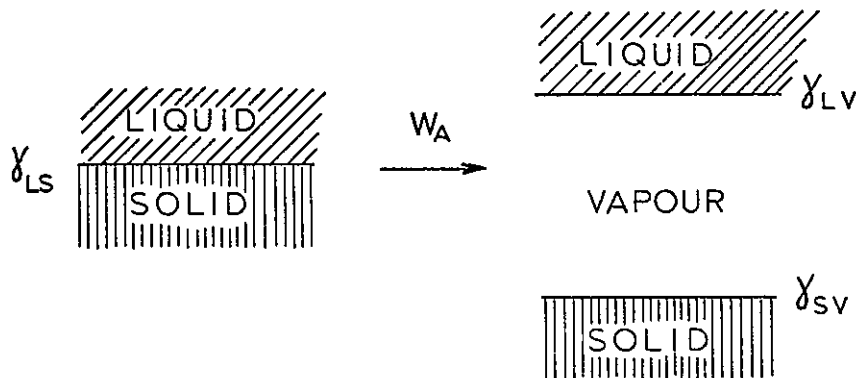


Fig. 2. Formation and destruction of surfaces in separating a solid from a liquid.

Previous theories implicitly or explicitly assume that the liquid density is constant up to the surface (hereafter referred to as the step density approximation (SDA)). In these theories (with the exception of Berry's work where the statistical mechanical analysis is formally correct) the role of the two particle distribution function is usually misunderstood. In fact this function does not appear explicitly in any of these models. The work of adhesion is usually expressed by a term that depends on the solid-liquid interaction potential which would correspond to our  $W_A(1)$ , and no contribution to  $W_A$  from the relaxation of the liquid



when removed from the solid appears. In order to compare our present theory with the earlier work we rewrite Eq. (34) more explicitly:

$$\begin{aligned}
 W_A = & \frac{1}{2} \int \int \int \frac{d\mathbf{r}_1}{A} n_{LV}(\mathbf{r}_1) \int \int \int d\mathbf{r}_2 n_{LV}(\mathbf{r}_2) g_{LV}(\mathbf{r}_1, \mathbf{r}_2) \phi(\mathbf{r}_{12}) \frac{x_{12}^2 - z_{12}^2}{r_{12}} \\
 & - \frac{1}{2} \int \int \int \frac{d\mathbf{r}_1}{A} n_{SL}(\mathbf{r}_1) \int \int \int d\mathbf{r}_2 n_{SL}(\mathbf{r}_2) g_{SL}(\mathbf{r}_1, \mathbf{r}_2) \phi^1(\mathbf{r}_{12}) \frac{x_{12}^2 - z_{12}^2}{r_{12}} - (38) \\
 & - \int \int \int d\mathbf{r}_1 n_{SL}(\mathbf{r}_1) \mathbf{r}_1 \cdot \nabla_{\mathbf{r}_1} \psi(\mathbf{r}_1).
 \end{aligned}$$

where we have introduced the radial distribution functions  $g_{LV}$  and  $g_{SL}$  which are defined by

$$n^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = n(\mathbf{r}_1) n(\mathbf{r}_2) g(\mathbf{r}_1, \mathbf{r}_2). \quad (39)$$

Frequently in calculating liquid-vapour surface tensions (Berry *et al.* (13)),  $g_{LV}(\mathbf{r}_1, \mathbf{r}_2)$  is approximated by the bulk radial distribution function of the liquid  $g_L(r_{12})$  and this can be reasonably well justified. It is less obvious that in any real fluid  $g_{SL}$  can be equal to  $g_L$  but clearly within the SDA it is rational to assume

$$g_{SL} \simeq g_{LV} \simeq g_L. \quad (40)$$

In these circumstances  $W_A$  reduces to  $W_A(1)$  which is then independent of the correlations in the liquid and only depends on the 'external potential',  $\psi$ , of the solid.

#### IV. CONCLUSION

The theory presented here gives a general picture of the solid-liquid interface, adhesion and contact angle based on a simple but exact statistical mechanical model.

With reference to the previous theories two points are revealed by our present work. The first concerns the description of the actual density profile of the liquid near the solid. This theory gives, in principle, a scheme (Hill (14)) for calculating this density. Although this is a complicated problem and some approximations and assumptions must be made in order to solve Eq. (29), it is clear that the SDA is too drastic an assumption. There is no sensible physical justification for the approximation and we have shown that its use erases completely the

relaxation contribution  $W_A(2)$  to the work of adhesion. This contribution is the second point that emerges from our theory. It is not obvious that this term is a small contribution and therefore it should be explicitly calculated in proper treatment of the work of adhesion.

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