SOME THERMODYNAMIC ASPECTS OF WETTING AND ADHESION

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Abstract – A general formulation is given of the thermodynamics of systems
consisting of a solid in contact with two fluid phases. The treatment
is based on a general theorem concerning the geometry of fluid interfaces
constrained by a solid surface originally derived by Gauss. The Laplace,
Young and Kelvin equations emerge as equilibrium conditions in appropriate
cases. Special attention is given to the stability of the equilibrium
states and to the irreversible processes which accompany various capillary
phenomena. This analysis forms the basis for a thermodynamic discussion
of a number of particular problems, including immiscible displacement and
imbibition, contact angle hysteresis, capillary condensation, the wetta-
bility of porous and powdered media and the adhesive force between wetted
particles.

1.   INTRODUCTION

Most elementary discussions of wetting are based on a consideration of the free energy
changes which result from variations in the areas of solid/vapour (s/v) and solid/liquid
(s/ℓ) interfaces when a three-phase line of contact moves across the solid surface.
In this way familiar quantities such as spreading pressure, wetting tension, and work of
adhesion may be defined(1). However, these definitions refer to situations in which the
solid interface is planar and where changes in the area of the ℓ/v interface can be
ignored. In real systems, on the other hand, wetting processes – in, for example, a
porous body or packed powder – involve changes in the areas of all three types of interface,
and a more complete thermodynamic analysis is needed. Furthermore, the behaviour of real
systems is often determined by mechanistic factors which lead to irreversible transitions
whose influence must be taken properly into account.

In this paper a fundamental geometrical relation due to Gauss is employed, together with
a general thermodynamic argument, to establish the familiar equations of Laplace and Young.
The range of validity of these equations is then discussed and formulations presented of
the thermodynamics of liquid/liquid displacement and of capillary condensation leading to
Kelvin's equation. The possibility of using measurements of adsorption from solution to
predict the wettability of porous or powdered materials is examined.

2.   THE GAUSS EQUATION

The present discussion is based on the use of an equation derived by Gauss(2) and applied to
a system of two fluid phases α and β in contact with one another and with a rigid solid S
along a three-phase line of contact. The importance of this equation has only recently
been appreciated(3,4,5), but it provides a convenient and general approach to a thermodynamic
discussion of multiphase surface systems.

The changes in the α/β and α/S interfacial areas $(dA^{\alpha\beta}, dA^{\alpha S})$, and of the volume of phase α
(dV^{α}) accompanying the displacement of the line of contact, are related to the curvature,
$C^{\alpha\beta}$, of the α/β interface (defined by $C^{\alpha\beta} = 1/r_1 + 1/r_2$, where r_1 and r_2 are the principal
radii of curvature) by the equation

$$C^{\alpha\beta}dV^{\alpha} = dA^{\alpha\beta} - dA^{\alpha S} \cos \theta \ , \tag{1}$$

where θ is the contact angle, measured through phase α at the $\alpha/\beta/S$ line of contact. As
written, equation (1) applies only to α/β surfaces of constant curvature. For the present
purposes the equation needs to be expressed in a more general form, applicable when the
curvature varies from point to point on the surface.

This is readily done(6) by considering the contributions to $dA^{\alpha\beta}$ from the movement of
elements of surface remote from and immediately adjacent to the line of contact (Fig. 1).
For each element of surface away from the line of contact $\delta A_s^{\alpha\beta} = C^{\alpha\beta}\delta V^{\alpha}$, where $\delta A_s^{\alpha\beta}$ and δV^{α}

$A^{\alpha\beta} + \delta A^{\alpha\beta}$

$A^{\alpha\beta}$

(a)

r_2

r_1

$\delta A_s^{\alpha\beta} = C^{\alpha\beta} \delta V^{\alpha}$

(b)

$\delta A^{\alpha\beta}$

θ

$\delta A^{\alpha S}$

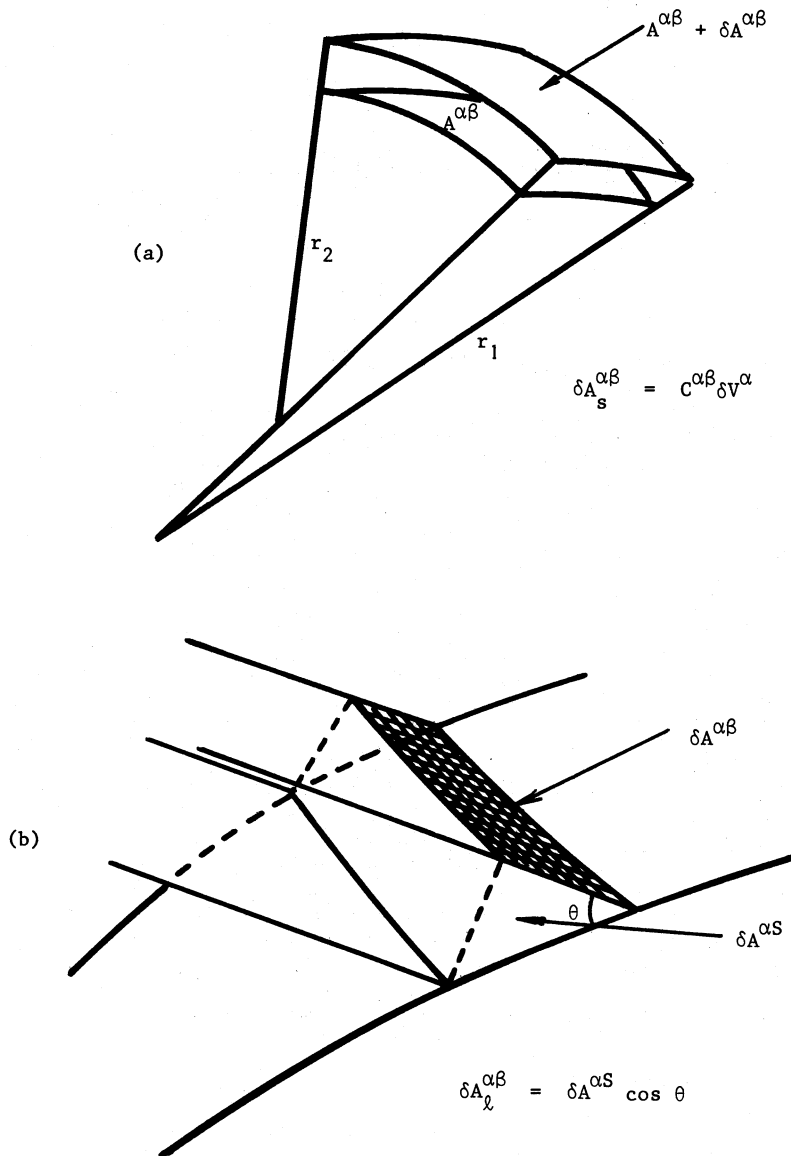$$\delta A_{\ell}^{\alpha\beta} = \delta A^{\alpha S} \cos \theta$$

Fig. 1   Contributions to changes in areas of α/β and α/S surfaces:
(a) at an $\alpha\beta$-interface;
(b) at the three-phase line of contact.

are defined for the displacement of an element of surface along normals to the surface (Fig. 1a); while adjacent to the line of contact (Fig. 1b), $\delta A_{\chi}^{\alpha\beta} = \delta A^{\alpha S} \cos \theta$. Thus in general when $C^{\alpha\beta}$ varies across the α/β surface and θ varies along the line of contact, $dA^{\alpha\beta} = \int \delta A_s^{\alpha\beta} + \int \delta A_{\chi}^{\alpha\beta}$ where the first integral is taken over all elements of surface and the second along the line of contact. Equation (1) can thus be written more generally:

$$\int_{\substack{\alpha/\beta \\ \text{surface}}} C^{\alpha\beta} \delta v^{\alpha} = dA^{\alpha\beta} - \int_{\substack{\alpha/\beta/S \\ \text{line of} \\ \text{contact}}} \cos \theta \, \delta A^{\alpha S} \; . \tag{2}$$

For reasons which will appear later it is convenient to introduce a quantity called the 'effective area', A^{eff}, defined by

$$dA^{eff} = \int_{\substack{\alpha/\beta \\ \text{surface}}} C^{\alpha\beta} \delta v^{\alpha} \; . \tag{3}$$

Integration of the right-hand-side of equation (2) gives

$$A^{eff} = A^{\alpha\beta} - \int_{A^{\alpha S}=0}^{A^{\alpha S}} \int_{\substack{\text{line of} \\ \text{contact}}} \cos \theta \, \delta A^{\alpha S} \tag{4}$$

If the contact angle is independent of the volume of liquid (and hence of $A^{\alpha S}$), and does not vary round the perimeter, this general definition reduces to the more usual form[7]

$$A^{eff} = A^{\alpha\beta} - A^{\alpha S} \cos \theta \; . \tag{4a}$$

An important feature of equation (2) is that it includes the case in which the shape of the α/β interface, and hence A^{eff}, varies at constant volume of α, i.e., $dv^{\alpha} = \int \delta v^{\alpha} = 0$. This is not true of the form of equation derived by Huang[6]:

$$dA^{\alpha\beta} = \langle C^{\alpha\beta} \rangle \, dv^{\alpha} + \langle \cos \theta \rangle \, dA^{\alpha S} \; , \tag{5}$$

where the average curvature $\langle C^{\alpha\beta} \rangle$ is defined as $\int C^{\alpha\beta} \delta v^{\alpha}/\int \delta v^{\alpha}$ which breaks down when $\int \delta v^{\alpha} = 0$.

The above demonstration of Gauss's equation does not constitute a rigorous mathematical proof and at first sight[4] might be thought to be inapplicable to the movement of an α/β interface past a mathematical discontinuity in the surface, during which the contact angle is indeterminate. The area of α/S contact remains constant however, and equation (2) still applies, the second term remaining zero during transit past the discontinuity. This may be illustrated simply by considering the movement of a spherical meniscus through a sharp-edged neck in a capillary (Fig. 2), for which during the hold-up of the movement of the $\alpha/\beta/S$ line of contact:

$$\left(\frac{\partial A^{\alpha\beta}}{\partial R}\right)_r = C^{\alpha\beta} \left(\frac{\partial v^{\ell}}{\partial R}\right)_r = -\frac{2\pi \, h^2}{(R-h)} \; . \tag{6}$$
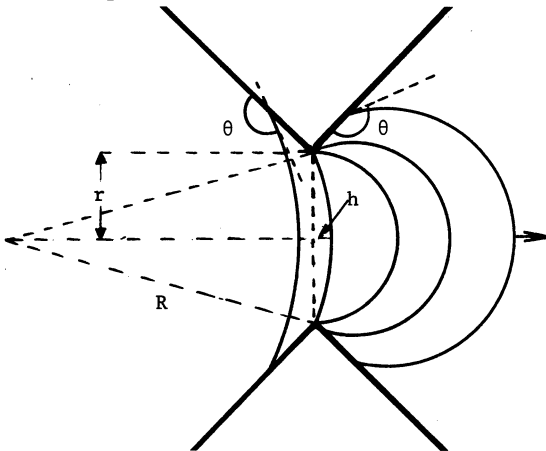

Fig. 2   Movement of a spherical meniscus through a circular sharp-edged neck, showing hold-up of line of contact during the readjustment of the angle of contact.

Finally, we stress that the general form of equation (2) is important in discussing the shapes of menisci in external fields such as gravity, and close to an adsorbing surface(5).

3.   THERMODYNAMICS OF IMMISCIBLE DISPLACEMENT

We consider first the case in which α and β are two immiscible one-component liquids as represented in Fig. 3.   Gravitational effects are excluded.   It is supposed that the α/β interface is distributed in some arbitrary, though continuous, fashion within the solid S.   If the fluids are incompressible, movement of the left-hand piston through a volume dV^A will be accompanied by an equal movement dV^B of the right-hand piston and of the α/β interface through the same volume $dV^{\alpha\beta} = -dV^\alpha = dV^\beta$.   The work done by the surroundings during such a displacement is

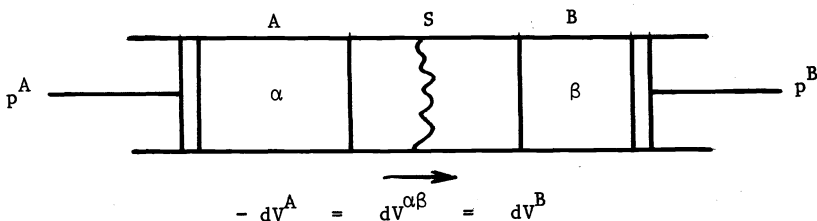$$dw = (p^A - p^B)dV^{\alpha\beta} \quad . \tag{7}$$

Fig. 3   Displacement of phase β by phase α in a porous solid S by application of a pressure difference $p^A - p^B$.

The total change of energy accompanying the process, which in general may involve irreversible displacement of at least some elements of the α/β interface, is thus given (using the second law of thermodynamics in the form $dS = dq/T + d_i S$) by

$$dU = TdS + (p^A - p^B)dV^{\alpha\beta} - Td_i S \quad , \tag{8}$$

where $d_i S \geqslant 0$ is the amount of entropy produced irreversibly during the movement of the interface.   The differential of the Helmholtz energy is thus

$$dF = - SdT + (p^A - p^B)dV^{\alpha\beta} - Td_i S \quad . \tag{9}$$

We now consider this total differential in terms of the internal variables upon which it depends.   In general

$$F = F(T, V^\alpha, V^\beta, A^{\alpha S}, A^{\beta S}, A^{\alpha\beta}, n^\alpha, n^\beta)$$

where n^α and n^β are the amounts of material in the two phases.   However, in this instance V^α, V^β, n^α and n^β are constant since there is no transport of material between phases.   For each surface the contribution to dF is assumed to be of the form $\int\sigma\delta A$, the integral being
taken over the element dA of the relevant surface.   The σ's (called interfacial tensions) are thus defined as the partial derivatives of the free energy with respect to the conjugate interfacial area.   By writing these contributions in the form of integrals over the surface regions, we allow the possibility that the interfacial tensions may vary across the surface. The dependence of F on the length of the line of three-phase contact is ignored, i.e., effects arising from line tensions are omitted.

Thus

$$dF = - SdT + \int\sigma^{\alpha S}\delta A^{\alpha S} + \int\sigma^{\beta S}\delta A^{\beta S} + \int\sigma^{\alpha\beta}\delta A^{\alpha\beta} \quad . \tag{10}$$

If the solid is rigid, $\delta A^{\alpha S} = - \delta A^{\beta S}$ and $\delta A^{\alpha\beta}$ can be eliminated using Gauss's equation to give

$$dF = - SdT + \int\sigma^{\alpha\beta}C^{\alpha\beta}\delta V^{\alpha\beta} + \int\{\sigma^{\alpha S} - \sigma^{\beta S} + \sigma^{\alpha\beta}\cos\theta\}\delta A^{\alpha S} \quad . \tag{11}$$

The condition that the two equations (9) and (11) for dF shall be identical is thus

$$Td_i S = [(p^A - p^B)dV^{\alpha\beta} - \int\sigma^{\alpha\beta}C^{\alpha\beta}\delta V^{\alpha\beta}] - \int\{\sigma^{\alpha S} - \sigma^{\beta S} + \sigma^{\alpha\beta}\cos\theta\}\delta A^{\alpha S}. \tag{12}$$

If the system remains in equilibrium so that the change considered is reversible, then $d_i S = 0$ and both terms in (12) must separately be zero:

$$(p^A - p^B)dV^{\alpha\beta} - \int \sigma^{\alpha\beta} c^{\alpha\beta} \delta V^{\alpha\beta} = 0 \tag{13}$$

and, if $\delta A^{\alpha S} \neq 0$,

$$\sigma^{\alpha S} - \sigma^{\beta S} + \sigma^{\alpha\beta} \cos\theta = 0 . \tag{14}$$

In the particular case where $dA^{\alpha S} = 0$ (cf. Fig. 2) and θ is indeterminate, the condition (14) no longer applies. These equations refer, respectively, to the establishment of hydrostatic and contact angle equilibrium and will be discussed in turn.

4. THE LAPLACE EQUATION

The total change $dV^{\alpha\beta}$ in the volume of α is the sum of the contributions $\delta V^{\alpha\beta}$ from each element of surface so that the equilibrium condition (13) can be written in the 'local' form

$$(p^A - p^B)\delta V^{\alpha\beta} - \sigma^{\alpha\beta} c^{\alpha\beta} \delta V^{\alpha\beta} = 0 \tag{15}$$

whence

$$p^A - p^B = \sigma^{\alpha\beta} c^{\alpha\beta} . \tag{16}$$

This is Laplace's equation which is often taken as a starting point in the theory of capillarity: the present discussion shows how it follows from equation (2) and general thermodynamic considerations. In the form obtained here, equation (16) implies that since p^A and p^B are the external pressures exerted on the system, $\sigma^{\alpha\beta} c^{\alpha\beta}$ must be constant over all the α/β interface. If $\sigma^{\alpha\beta}$ is constant, then the equilibrium surface is one of constant curvature. However, if the system exhibits a dynamic surface tension different from its static value, the possibility exists that $c^{\alpha\beta}$ may vary with time as $\sigma^{\alpha\beta}$ relaxes to its static value. Thus, in principle, the present treatment can include Marangoni effects. However, since it is generally supposed that one-component fluids do not exhibit dynamic surface tension effects, we shall, for the present, assume constancy of $\sigma^{\alpha\beta}$ over the whole surface.

Since the molecular processes which establish the pressure difference across an element of surface are expected to occur much faster than the bulk viscous flow needed to change the curvature of the surface, we assume that equation (16) applies locally, p^A and p^B now being replaced by p^α and p^β, the hydrostatic pressures immediately adjacent to the element of surface under consideration, even though global hydrostatic equilibrium may not have been established. If the curvature varies from point to point on the α/β interface, a hydro-static driving force, acting from regions of high curvature to those of low curvature, will tend (in the absence of external fields) to produce a constant curvature interface.

It is to be noted that equation (16) applies to differences of hydrostatic pressure and therefore to regions sufficiently far from the surface that the stress tensor is isotropic. However, since in the interfacial region the deviations from a hydrostatic stress occur in tangential components whose mechanical effects are taken care of in the introduction of the concept of surface tension, in such regions equation (16) refers to the difference between the normal components of the stress tensor on either side of the surface of tension. Problems arise when the curvature is so high that in no part of the system is the stress hydrostatic. The following discussion becomes increasingly less valid when applied to menisci in micropores whose radii of curvature approach two or three times the molecular dimensions of the components of the fluid phases. We note also that this is the regime in which it may no longer be justifiable to neglect tensions in the three-phase line of contact, and in which the surface tension depends on the curvature.

5. THE YOUNG EQUATION

Equation (14) establishes that the condition for local contact angle equilibrium is

$$\sigma^{\beta S} - \sigma^{\alpha S} = \sigma^{\alpha\beta} \cos\theta , \tag{17}$$

which is Young's equation. The main assumptions upon which this derivation is based are that the solid is rigid and that line tension can be neglected. The effect of roughness can be taken account of by noting that Gauss's equation, when applied to a _finite_ displacement across a rough surface, becomes (Fig. 4)

$$c^{\alpha\beta}dV^{\alpha\beta} = dA^{\alpha\beta} - \frac{dA^{\alpha S}}{r} \cos\theta , \tag{18}$$

where $dA^{\alpha S}$ is the microscopic change in the surface area, θ is the apparent macroscopic contact angle, and r, the roughness factor, is the ratio of $dA^{\alpha S}$ to the change in the apparent macroscopic surface area.
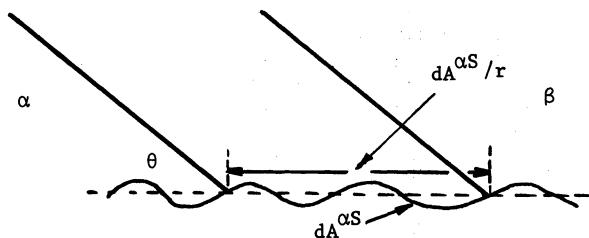
Fig. 4   Movement of an α/β interface across a rough solid surface.

This leads to Wenzel's modification(8) of Young's equation

$$\sigma^{\beta S} - \sigma^{\alpha S} = (\sigma^{\alpha\beta} \cos \theta)/r \quad . \tag{19}$$

This is, however, little more than a formal correction since, in effect, all that (19) does is to indicate that the interfacial tensions $\sigma^{\beta S}$ and $\sigma^{\alpha S}$ should be defined with respect to changes in the apparent macroscopic area rather than to the microscopic area change; and when they are, Young's equation holds.   Details of the local configuration of the $\alpha\beta$ surface close to a rough surface and for displacements small compared with the scale of roughness of the surface become important, however, in the discussion of contact angle hysteresis (see section 8).

6.   IRREVERSIBLE   PROCESSES   IN   IMBIBITION

We return to equation (12) and consider the case in which contact angle equilibrium is maintained so that the irreversibility arises only from the first term:

$$T d_i S = (p^A - p^B) dv^{\alpha\beta} - \sigma^{\alpha\beta} \int c^{\alpha\beta} \delta v^{\alpha\beta} \quad . \tag{20}$$

If the process occurs at constant volume, increases in $v^{\alpha\beta}$ associated with movements of some elements of surface being exactly cancelled by decreases elsewhere,

$$T d_i S = - \sigma^{\alpha\beta} \int c^{\alpha\beta} \delta v^{\alpha\beta} = - \sigma^{\alpha\beta} dA^{eff} \quad . \tag{21}$$

The interface thus adjusts itself spontaneously to a condition of minimum effective area consistent with the condition of constant volume.   This state of global Laplace equilibrium corresponds, as shown earlier, to constant curvature of the α/β interface.

Secondly, if the pressures on the two bulk phases are equal, equation (21) again applies and spontaneous flow of fluid occurs to a state of minimum effective area.

More generally, writing $dv^{\alpha\beta} = \int \delta v^{\alpha\beta}$ and considering a local process

$$T \delta_i S = \left[(p^A - p^B) - \sigma^{\alpha\beta} c^{\alpha\beta} \right] \delta v^{\alpha\beta} \quad . \tag{22}$$

If $(p^A - p^B) - \sigma^{\alpha\beta} c^{\alpha\beta}$ is positive, then a spontaneous local increase $\delta v^{\alpha\beta}$ will occur. Equation (22) therefore defines the condition that, if the externally applied pressure difference is maintained constant, a local irreversible jump in the volume of imbibed α occurs (Haines jump(9) or rheon(10)).   Jumps of this kind occur, as is well known, in the displacement of a liquid from a capillary of varying cross-section (Fig. 5).
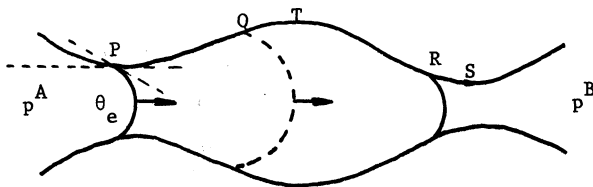

Fig. 5   Spontaneous motion of interface from P $\rightarrow$ R.

As the pressure difference $(p^A - p^B)$ is increased, the meniscus moves reversibly towards P, the curvature increasing to match the increasing pressure difference.   At P the α/β inter-face reaches a maximum curvature and the pressure difference a value $(p^A - p^B)_a$, consistent with the contact angle and geometry of the pore: further movement leads to a decrease in the local pressure difference and spontaneous imbibition occurs through unstable states such as Q until at R the equilibrium curvature is re-established.   The entropy production in this spontaneous jump is given by

$$T d_i S = (p^A - p^B)_a dV^{\alpha\beta} - \sigma^{\alpha\beta} \int_P^R c^{\alpha\beta} \delta V^{\alpha\beta} \tag{23}$$

and can be calculated from the pore geometry and contact angle.   A similar instability occurs during withdrawal of α when the retreating line of contact reaches a maximum in the pore diameter at T and a spontaneous jump occurs at $(p_A - p_B)_r$, see Fig. 7.   As is well known, these mechanisms provide a ready explanation of imbibition hysteresis.

Alternative forms of (20) are

$$T d_i S = (p^A - p^B) dV^{\alpha\beta} - \sigma^{\alpha\beta} dA^{eff} \quad , \tag{24}$$

and

$$T d_i S = \int (\mu^{\alpha,A} - \mu^\alpha) \delta n^\alpha + \int (\mu^{\beta,B} - \mu^\beta) \delta n^\beta \quad , \tag{25}$$

(where μ^α, μ^β are local chemical potentials and $\mu^{\alpha,A}$, $\mu^{\beta,B}$ those in the cylinders A and B). Equation (25) shows that equilibrium is achieved when the chemical potentials μ^α and μ^β are constant throughout phases α and β.

7.   IRREVERSIBLE MOVEMENT OF THE CONTACT LINE

The second term on the right of equation (12) refers to irreversibility associated with the movement of the three-phase contact line.   Considering a local process

$$T \delta_i S = \{\sigma^{\alpha S} - \sigma^{\beta S} + \sigma^{\alpha\beta} \cos \theta\} \delta A^{\alpha S} \quad . \tag{26}$$

Spontaneous movement leading to an increase in $A^{\alpha S}$ occurs if $\{\sigma^{\alpha S} - \sigma^{\beta S} + \sigma^{\alpha\beta} \cos \theta\}$ is negative, i.e., if

$$\sigma^{\beta S} - \sigma^{\alpha S} > \sigma^{\alpha\beta} \cos \theta \quad .$$

However, the equilibrium contact angle θ_e is given by $\cos \theta_e = (\sigma^{\beta S} - \sigma^{\alpha S})/\sigma^{\alpha\beta}$ so that for an advancing contact line $(\delta A^{\alpha S} > 0)$

$$\cos \theta_a = \cos \theta_e - \frac{T}{\sigma^{\alpha\beta}} \cdot \frac{\delta_i S}{\delta A^{\alpha S}} \quad , \tag{27}$$

i.e., $\theta_a > \theta_e$, and conversely, for receding contact line $(\delta A^{\alpha\beta} < 0)$,

$$\cos \theta_r = \cos \theta_e + \frac{T}{\sigma^{\alpha\beta}} \cdot \frac{\delta_i S}{\delta A^{\alpha S}} \quad , \tag{28}$$
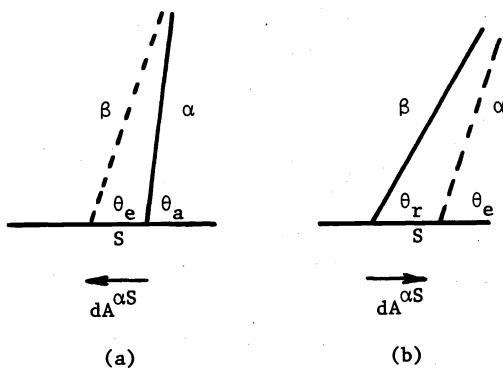
or $\theta_r < \theta_e$ (Fig. 6).

Fig. 6   Establishment of local contact angle equilibrium.

These equations refer to the establishment of local contact angle equilibrium, and show the tendency for a contact angle greater than the equilibrium value to decrease by increasing $\delta A^{\alpha S}$, and conversely. Since the distances which molecules have to move to change the contact angle are small, it is usually assumed that local equilibrium is achieved and that apparent contact angle hysteresis is to be attributed to other factors.

8. CONTACT ANGLE HYSTERESIS

Recent treatments of contact angle hysteresis(11,12,13) are based on models which depict real surfaces as either geometrically rough, or intrinsically heterogeneous. Thus the observed contact angle differs from that locally achieved either because the local tangent plane to the surface at the contact line lies at an angle to the macroscopic surface (e.g., Fig. 4), or because local variations in ($\sigma^{\alpha S} - \sigma^{\beta S}$) lead to variations in the intrinsic or local equilibrium value of θ depending on the particular patches of surface crossed by the line of contact. However, in discussing contact angle hysteresis it is essential to consider not only the local situations depicted in Figs. 4 and 6, but the constraints imposed upon them by the global geometry of the system considered. Thus detailed treatments must be presented in relation to a specific phenomenon such as the spreading of a sessile drop(11,13), capillary rise(12) or motion of a drop on an inclined plane(14). In particular, the stability of interfacial configurations has to be examined carefully to identify metastable states and to describe the spontaneous transitions which ensue when the metastability breaks down.
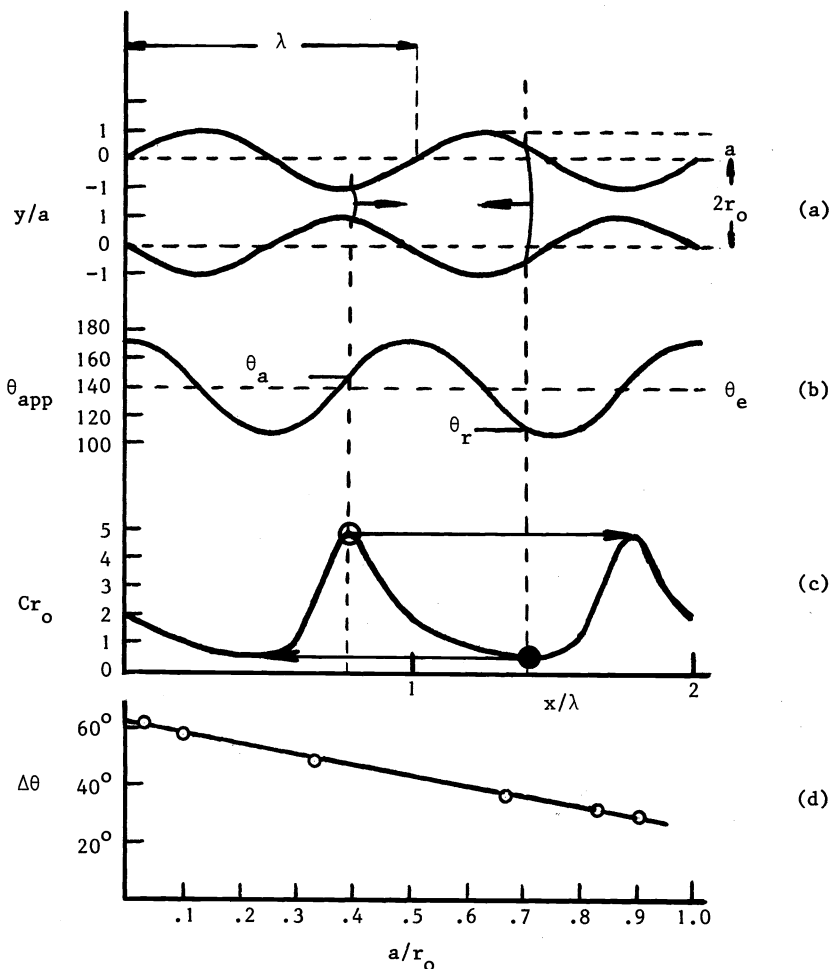

Fig. 7   (a) Sinusoidal capillary with $a/\lambda = 0.1$; $a/r_0 = 0.667$.
         (b) Apparent contact angle as function of position of contact line in capillary shown in (a), and for $\theta_e = 140°$, showing θ_a and θ_r corresponding to onset of spontaneous transitions.
         (c) Cr_0 ($\propto p^A - p^B$) as a function of position of contact line in capillary shown in (a), showing onset of metastability in imbibition (0) and retraction (●).
         (c) Dependence of contact angle hysteresis, $\Delta\theta = \theta_a - \theta_r$, on a/r_0 for case of $a/\lambda = 0.1$; $a/r_0 = 0.667$; $\theta_e = 140°$.

It is usually assumed that when contact angle hysteresis occurs the observed contact angle is the apparent contact angle at the point where, in an advancing or receding process, the system is about to undergo a spontaneous jump in the position of the line of contact.   The ensuing process depends on whether the pressure difference $p^A - p^B$ is maintained constant, $dv^{\alpha\beta}$ is constrained to zero, or $p^A - p^B$ may be allowed to relax in some predetermined way with $dv^{\alpha\beta}$.

As an example we consider the behaviour in a capillary whose radius varies sinusoidally with distance along the capillary (Fig. 7a), when $(p^A - p^B)$ is steadily increased (or decreased) until a spontaneous advancing (or receding) jump occurs at constant $(p^A - p^B)$: this depends on θ_e and on the ratios of the amplitude (a) of the radius variation to the wavelength (λ) and the mean capillary radius (r_o).   The apparent contact angle as a function of position of the contact line is shown in Fig. 7b, for $\theta_e = 140^o$, $a/\lambda = 0.1$, $a/r_o = 0.667$, while Fig. 7c shows the variation of curvature.   Since $p^A - p^B$ is proportional to $C^{\alpha\beta}$, the points of onset of instability in advancing (O) and receding (●) processes are given respectively by maxima and minima in curvature.   The observed advancing (θ_a) and receding (θ_r) angles corresponding to these extreme values of $C^{\alpha\beta}$ can be read from Fig. 7b.   The dependence of the contact angle hysteresis gap, $(\theta_a - \theta_r) = \Delta\theta$, is shown in Fig. 7d as a function of a/r_o

$\theta_e < 180^o - \alpha$

$\theta_{app} = \theta_e + \alpha$

(a)

$\theta_e = 180^o - \alpha$

$\theta_{app} = 180^o$

(b)

$\theta_e > 180^o - \alpha$

$\theta_{app} = 180^o$
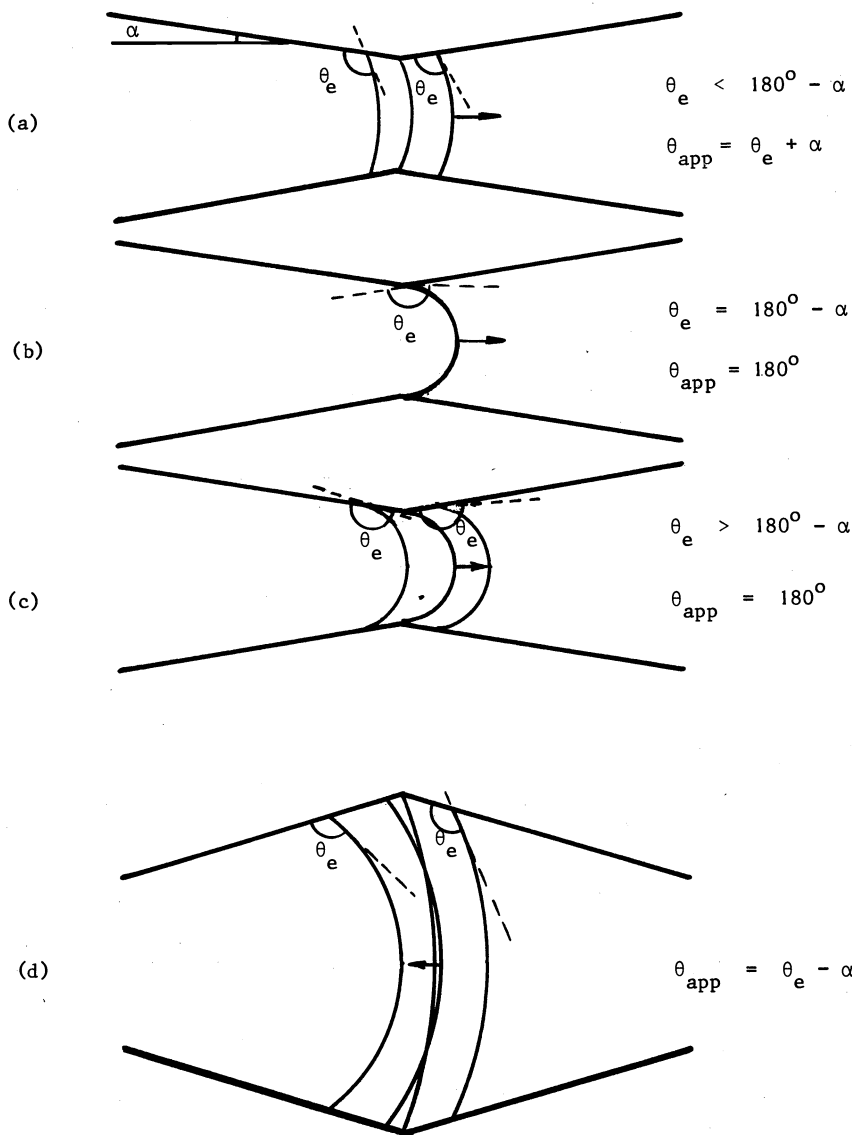
(c)

$\theta_{app} = \theta_e - \alpha$

(d)

Fig. 8   Motion of interface in capillary showing sharp discontinuities between cones of angle of taper $\pm \alpha$: (a) advancing, (b) receding menisci.

which is a rough measure of the 'degree of roughness'. Similar curves are obtained for other values of θ_e, and a/λ. If a/λ and a/r_o exceed certain limits for a given θ_e, a portion of phase β is trapped behind the advancing contact line and more complex phenomena result. When $a/r_o \to 0$, the situation approaches that in contact angle hysteresis in capillary rise in a rough tube.

Similar considerations apply when sharp changes in contour occur: Fig. 8 illustrates a simple example of alternating conical segments. The behaviour now depends mainly on the relative magnitudes of θ_e and the angle of taper α of the cones. When the contact line reaches a constriction during imbibition, the contact line remains stationary while θ changes. When the contact angle with the exit cone reaches θ_e, a spontaneous jump commences. If this occurs before a hemispherical meniscus is achieved (case a, $\theta_e < 180^\circ - \alpha$), then $\theta_a = \theta_e + \alpha$. On the other hand if $\theta_e \leqslant 180^\circ - \alpha$, cases (b) and (c), the spontaneous jump occurs when a hemispherical meniscus just fills the constriction and $\theta_a = 180^\circ$. In the reverse process the contact line retreats along the expanding conical section until a maximum radius is reached (Fig. 8d). At this point a spontaneous increase in curvature occurs, first at constant volume to achieve local contact angle equilibrium with the contracting conical section, and then with expulsion of phase α by movement along the cone. The sequence of changes of $p^\alpha - p^\beta$ across the interface and θ_{app} are shown schematically in Fig. 9. Again if the angle α is large and the cones short, trapping of phase β can occur during imbibition.
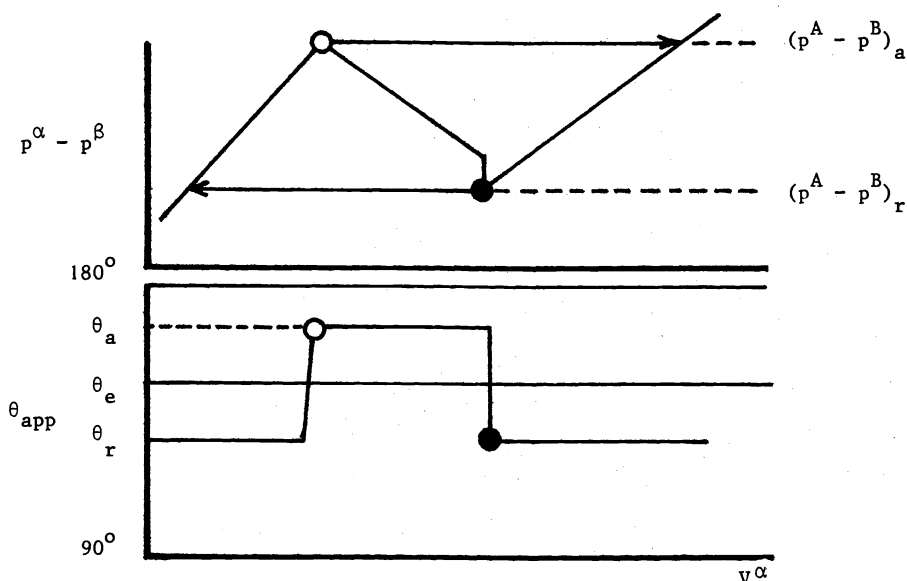

Fig. 9   Pressure differences and apparent contact angles in advancing and receding motion of interface in capillary showing sharp discontinuities between cones of angle of taper $\pm \alpha$. $\theta_e < (180^\circ - \alpha)$ (schematic).
O, ● points of onset of instability in advancing and receding respectively.

Similar considerations apply to the case of a heterogeneous capillary consisting of alternating bands of surfaces of different surface energies.

9.   THERMODYNAMICS OF LIQUID-VAPOUR DISPLACEMENT IN A ONE-COMPONENT SYSTEM

The discussion of this case follows that of section 3 except that the total volumes V^ℓ, V^g of liquid and vapour phases vary because of evaporation or condensation processes*.

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* The present treatment differs from that given previously(5) for capillary condensation only in that in the earlier discussion the Laplace equation was assumed _a priori_.
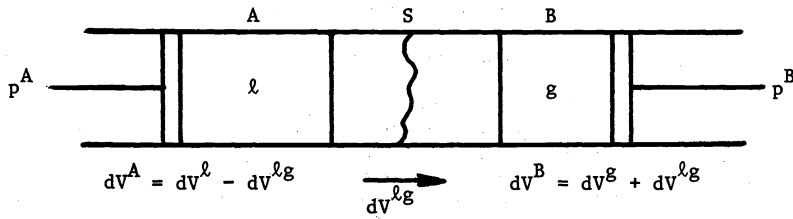
Fig. 10 Movement of liquid/vapour interface through porous solid by combined liquid flow and evaporation/condensation processes.

Denoting by dV^A and dV^B the volumes swept out by movement of the pistons, it follows that

$$dV^A = dV^\ell - dV^{\ell g} \quad ,$$

$$dV^B = dV^g + dV^{\ell g} \quad . \tag{29}$$

The work done in an infinitesimal displacement is

$$dw = - p^A dV^A - p^B dV^B$$

$$= - p^A dV^\ell - p^B dV^g + (p^A - p^B) dV^{\ell g} \quad , \tag{30}$$

whence

$$dF = - SdT - p^A dV^\ell - p^B dV^g + (p^A - p^B) dV^{\ell g} - Td_i S \quad . \tag{30a}$$

Now since

$$F = F(T, V^\ell, V^g, A^{\ell s}, A^{gs}, A^{\ell g}, n^g, n^\ell, n^\sigma) \quad ,$$

where n^σ is the amount of adsorbed material at the g/s interface,

$$dF = - SdT - p^A dV^\ell - p^B dV^g + \int \sigma^{\ell s} \delta A^{\ell s} + \int \sigma^{gs} \delta A^{gs}$$
$$+ \int \sigma^{\ell g} \delta A^{\ell g} + \int \mu^g \delta n^g + \int \mu^\ell \delta n^\ell + \int \mu^\sigma \delta n^\sigma \quad , \tag{31}$$

where the μ's are chemical potentials which in the general case may vary throughout each phase.

Using Gauss's equation, $\delta A^{\ell s} = -\delta A^{gs}$ and $\delta n^g + \delta n^\ell + \delta n^\sigma = 0$, leads to

$$dF = - SdT - p^A dV^\ell - p^B dV^g + \int \sigma^{\ell g} C^{\ell g} \delta V^{\ell g}$$
$$+ \int \{\sigma^{\ell s} - \sigma^{gs} + \sigma^{\ell g} \cos \theta\} \delta A^{\ell s}$$
$$+ \int (\mu^\ell - \mu^g) \delta n^\ell + \int (\mu^\sigma - \mu^g) \delta n^\sigma \quad . \tag{32}$$

The condition that (30) and (32) are identical is thus

$$Td_i S = (p^A - p^B) dV^{\ell g} - \int \sigma^{\ell g} C^{\ell g} \cos \theta \, \delta V^{\ell g}$$
$$- \int \{\sigma^{\ell s} - \sigma^{gs} + \sigma^{\ell g} \cos \theta\} \delta A^{\ell s}$$
$$+ \int (\mu^\ell - \mu^g) \delta n^\ell + \int (\mu^\sigma - \mu^g) \delta n^\sigma \quad . \tag{33}$$

Equation (33) is an extension of equation (12) and as before demonstrates that global equilibrium corresponds to Laplace's and Young's equations being satisfied and to $\mu^\ell = \mu^g = \mu^\sigma$.

In discussing capillary condensation we may assume that local Laplace equilibrium and local contact angle equilibrium are established; the latter also implies adsorption equilibrium, so that

$$Td_i S = \int (\mu^\ell - \mu^g) \delta n^\ell \quad . \tag{34}$$

The spontaneous processes contributing to $d_i S$ are (i) equalisation of μ^ℓ throughout the condensed phase by liquid flow to achieve global Laplace equilibrium, and (ii) equalisation of μ^ℓ and μ^g by condensation or evaporation processes leading to so-called Kelvin equilibrium. The application of these concepts to the problem of capillary condensation and capillary condensation hysteresis have been discussed previously and will not be repeated here(4,5). In particular, if global Laplace equilibrium is maintained, equation (34) leads immediately to Kelvin's equation:

$$c^{\ell g} = \frac{2}{r_m} = \frac{RT}{\sigma^{\ell g} v_2^\ell} \ln p^g/p^o \quad , \tag{35}$$

where $1/r_m$ is the mean radius of curvature. This equation can also be written in the form

$$dA^{eff} = \frac{RT}{\sigma^{\ell g}} \ln p^g/p^o \cdot dn_2^\ell \quad . \tag{36}$$

10.   WETTABILITY OF POROUS OR POWDERED MATERIALS

It is widely recognised that the interfacial tensions $\sigma^{\alpha S}$ and $\sigma^{\beta S}$ which appear in Young's equation are not separately measurable although the difference between them can be obtained from contact angle measurements. While in the absence of contact angle hysteresis this is possible for macroscopic surfaces, there is no simple method of obtaining this quantity for porous materials or packed powders: the Bartell tube method is essentially empirical(16).

The following method is in principle possible, but has so far not been tested experimentally. We consider three liquids A, B, C, of which A and B and A and C are miscible in all proportions while B and C are immiscible (for example, A = ethanol, B = benzene, C = water). If measurements are made of the adsorption by solid S from mixtures of A and B over the whole concentration range, then(17)

$$\sigma^{A,S} - \sigma^{B,S} = \int_{x_B=0}^{x_B=1} \frac{\Gamma_B^{(n)}}{(1 - x_B)} \tag{37}$$

where $\Gamma_B^{(n)}$ is the surface excess concentration of B which is related to the measured change Δx_B in mole fraction of B when a mixture of A and B containing n^o moles is equilibrated with a mass m of solid of specific surface area a_s:

$$\Gamma_B^{(n)} = \frac{n^o \Delta x_B}{m a_s} \quad . \tag{38}$$

Similarly $\sigma^{A,S} - \sigma^{C,S}$ can be obtained from adsorption measurements on A + C mixtures. From the difference between them, $\sigma^{B,S} - \sigma^{C,S}$, and hence (knowing σ^{BC}) $\cos \theta$ for the B/C/S interface. Thus a thermodynamic method is available for estimating the relative wettability of solid by liquids B and C.

11.   ADHESIVE FORCES BETWEEN PARTICLES WETTED BY A VOLATILE LIQUID

The procedures employed earlier may be extended to include other interactions with the surroundings, and in particular to a consideration of the forces between wetted particles.

Consider the arrangement shown in Fig. 11 in which two particles separated by a distance D have a volume V^ℓ of liquid condensed between them and in equilibrium with vapour at pressure p^g. A force f is required to maintain mechanical equilibrium.

In a process in which the total volume is changed by dV and the separation by dD, the work done on the system is

$$dw = - p^g dV - f dD \quad . \tag{39}$$

The first term can be written in terms of changes in volume of liquid and vapour: $dV = dV^\ell + dV^g$, and the local pressure in the liquid phase:

$$dw = - p^g dV^g - \int p^\ell \delta v^\ell + \int (p^\ell - p^g) \delta v^\ell - f dD \quad , \tag{40}$$

where the integrals are taken over the whole of the ℓ/g interface. We now assume that the local pressure p^ℓ is given by the Laplace equation so that the differential of the Helmholtz energy becomes:
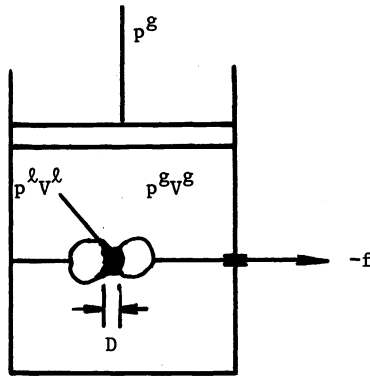
Fig. 11 Adhesion between two particles wetted with a volatile liquid.

$$dF = - SdT - p^g dV^g - \int p^\ell \delta V^\ell + \sigma^{\ell g} \int C^{\ell g} \delta V^\ell - fdD - Td_iS \ . \qquad (41)$$

For two particles of defined geometry and mutual orientation the Helmholtz energy will be a function of

$$T, \ V^g, \ V^\ell, \ A^{\ell s}, \ A^{gs}, \ A^{\ell g}, \ n^g \text{ and } n^\ell$$

so that

$$dF = - SdT - p^g dV^g - \int p^\ell dV^\ell + \int \sigma^{\ell s} \delta A^{\ell s} + \int \sigma \delta A^{gs} + \int \delta A^{\ell g}$$
$$+ \int \mu^g \delta n^g + \int \mu^\ell \delta n^\ell \ . \qquad (42)$$

If we assume that local contact angle equilibrium is achieved, and using the definition $A^{eff} = A^{\ell g} - A^{s\ell} \cos \theta$ the total differential of F may be written

$$dF = - SdT - p^g dV^g - \int p^\ell \delta V^\ell + \sigma^{\ell g} dA^{eff} + \int (\mu^\ell - \mu^g) \delta n^\ell \ . \qquad (43)$$

Comparing equations (41) and (43) we thus obtain

$$Td_iS = \sigma^{\ell g} \int C^{\ell g} \delta V^\ell - \sigma^{\ell g} dA^{eff} - \int (\mu^\ell - \mu^g) \delta n^\ell - fdD \ . \qquad (44)$$

It is important to note that Gauss's equation does not apply to the present case, since the positions of the solid boundary surfaces are not fixed. Consequently the first two terms on the right-hand-side of (44) do not cancel.

We now consider the condition of equilibrium ($d_iS = 0$) for two cases:

(i) at constant V^ℓ, hence also $dn^\ell = 0$

$$(f)_{V^\ell} = - \sigma^{\ell g} \left(\frac{\partial A^{eff}}{\partial D} \right)_{V^\ell} , \qquad (45)$$

while at constant $\mu^g = \mu^\ell$,

(ii) $$(f)_\mu = \sigma^{\ell g} \left[C^{\ell g} \left(\frac{\partial V^\ell}{\partial D} \right)_\mu - \left(\frac{\partial A^{eff}}{\partial D} \right)_\mu \right] \ . \qquad (46)$$

However, by considering A^{eff} and V^ℓ as functions of D and μ it is readily shown that

$$- \left(\frac{\partial A^{eff}}{\partial D} \right)_{V^\ell} = C^{\ell g} \left(\frac{\partial V^\ell}{\partial D} \right)_\mu - \left(\frac{\partial A^{eff}}{\partial D} \right)_\mu \qquad (47)$$

so that these two conditions are equivalent.

We now consider how the force depends on μ, and hence on the vapour pressure. From equation (46)

$$\left(\frac{\partial f}{\partial \mu} \right)_D = \sigma^{\ell g} \left[\left\{ \left(\frac{\partial C^{\ell g}}{\partial \mu} \right)_D \left(\frac{\partial V^\ell}{\partial D} \right)_\mu \right\} + \frac{\partial}{\partial D} \left\{ C^{\ell g} \left(\frac{\partial V^\ell}{\partial \mu} \right)_D - \left(\frac{\partial A^{eff}}{\partial \mu} \right)_D \right\} \right] \ . \qquad (48)$$

Now at constant D, $d\mu = v^\ell dp^\ell = \sigma^{\ell g} v^\ell dC^{\ell g}$ so that $(\partial C^{\ell g}/\partial \mu)_D = 1/(\sigma^{\ell g} v^\ell)$, while by Gauss's equation the second term in brackets on the right-hand-side is zero. Hence since $V^\ell/v^\ell = n^\ell$

$$\left(\frac{\partial f}{\partial \mu}\right)_D = \left(\frac{\partial n^{\ell}}{\partial D}\right)_{\mu} \quad, \tag{49}$$

where n^{ℓ} is the amount of liquid held between the particles. We note that this is an extension to the capillary condensation region of the equation previously derived by Ash, Everett and Radke[18] for the effect of adsorption on interparticle forces when

$$\left(\frac{\partial f}{\partial \mu}\right)_D = \left(\frac{\partial \Gamma A_s}{\partial D}\right)_{\mu} \quad, \tag{50}$$

when Γ is the surface excess concentration of adsorbed material and A_s the surface area of the solid particles. If the particles are of different materials (S_1, S_2), then the effective area may be defined as

$$A^{eff} = A^{\ell g} - A^{\ell S_1} \cos \theta_1 - A^{\ell S_2} \cos \theta_2 \quad, \tag{51}$$

and the same results are obtained.

If the particles are non-spherical, then their mutual orientation ϕ affects f, V^{ℓ}, etc., and the torque exerted by one particle on the other is

$$t = - \sigma^{\ell g} \left(\frac{\partial A^{eff}}{\partial \phi}\right)_{V^{\ell}, D} \quad. \tag{52}$$

The stability of the bridge between particles held apart by a force f may be investigated by considering

$$\left(\frac{\partial f}{\partial D}\right)_{V^{\ell}} = - \sigma^{\ell g} \left(\frac{\partial^2 A^{eff}}{\partial D^2}\right)_{V^{\ell}} \quad. \tag{53}$$

Instability, at constant applied f, occurs at the point where $(\partial^2 A^{eff} / \partial D^2)_{V^{\ell}} = 0$.

The equivalence between the thermodynamic formulation given here and the more conventional force analysis can be demonstrated in simple cases (e.g., the force between parallel wetted cylinders[19]). The use of a force analysis becomes more difficult when several particles are involved; here the thermodynamic method making use of the effective area may prove to be more convenient.

12. CONCLUSIONS

The objective of this paper has been to clarify, in a general thermodynamic context and with the minimum of mathematics, the status of the various equations employed to describe wetting, adhesion and capillary condensation phenomena. In broad terms the conclusions agree with those of earlier workers[20], but the discussion appears to be simplified by using an equation due to Gauss, and the concept of 'effective area'. In particular, the role of the assumption that the solid is rigid is confirmed. The importance of considering the stability of a given conformation of the fluid/fluid and fluid/solid interfaces is stressed since many important real phenomena are dependent on the persistence, and then the break-down, of metastable states. Brief discussions are given of immiscible displacement, contact angle hysteresis and liquid-vapour displacement in capillaries. In problems of adhesion, the relative positions of solid surfaces are not invariant but the treatment can be extended to include the capillarity contribution to adhesive forces, which is shown to have the same form as the equation previously derived for the effect of adsorption on interparticle forces.

REFERENCES

1. see, e.g., R. Defay, I. Prigogine, A. Bellemans and D.H. Everett, Surface Tension and Adsorption, Longman, London (1965), chap. 1.
2. C.F. Gauss, Comment.soc.reg.scient.Göttingen recent., 7 (1830); Theorie der Gestalt von Flüssigkeiten (trans. H. Weber), Ostwald's Klassiker der Exakten Wissenschaften No. 135, Engelmann, Leipzig (1903).
3. J.C. Melrose, A.I.Ch.E.Journal, 12, 986 (1966); J.Coll.Interface Sci., 38, 312 (1972).
4. D.H. Everett and J.M. Haynes, J.Coll.Interface Sci., 38, 125 (1972); Zeit.physik. Chem.(N.F.), 82, 36 (1972); ibid., 97, 301 (1975).
5. D.H. Everett, J.Coll.Interface Sci., 52, 189 (1975); in Characterisation of Porous Solids (S.J. Gregg, K.S.W. Sing and H.F. Stoeckli, eds.), Soc.Chem.Ind., London (1979).
6. S.-T. Hwang, Z.physik.Chem.(N.F.), 105, 225 (1977).
7. E.C. Sewell and E.W. Watson, RILEM Bull., 29, 125 (1965); cf. ref. 4.

8.   R.N. Wenzel, Ind.Eng.Chem., 28, 988 (1936).
9.   W.B. Haines, J.Agric.Sci., 20, 97 (1930).
10. J.C. Melrose, Can.J.Chem.Eng., 48, 638 (1970).
11. R.E. Johnson and R.H. Dettre, J.Phys.Chem., 68, 1744 (1964); Adv.Chem.Ser., 43, 112
       (1964).
12. A.W. Neumann, Adv.Colloid Interface Sci., 4, 105 (1974); in Wetting, Spreading and
       Adhesion (J.F. Padday, ed.), Academic Press, London (1978), p. 3.
13. C. Huh and S.G. Mason, J.Coll.Interface Sci., 60, 11 (1977).
14. E. Wolfram and R. Faust, in Wetting, Spreading and Adhesion (J.F. Padday, ed.),
       Academic Press, London (1978), p. 213.
15. J.F. Oliver, C. Huh and S.G. Mason, J.Coll.Interface Sci., 59, 568 (1977).
16. F.E. Bartell and H.J. Osterhof, Ind.Eng.Chem., 19, 1277 (1927); F.E. Bartell and
       H.Y. Jennings, J.Phys.Chem., 38, 495 (1934).
17. e.g., D.H. Everett, in Colloid Science, Specialist Periodical Reports (D.H. Everett, ed.)
       Chemical Society, London (1973), Vol. 1, p. 58; D.H. Everett and C.E. Brown, in
       Colloid Science, Specialist Periodical Reports (D.H. Everett, ed.) Chemical
       Society, London (1979), Vol. 3, p. 63.
18. S.G. Ash, D.H. Everett and C.J. Radke, J.Chem.Soc.Faraday II, 69, 1256 (1973);
       D.H. Everett, Pure and Applied Chem., 48, 419 (1976).
19. J.M. Haynes, private communication.
20. see, e.g., B.D. McLaughlin and P.L. de Bruyn, J.Coll.Interface Sci., 30, 21 (1969).