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LIQUID SURFACES

M. V. BERRY
 H.H. Wills Physics Laboratory,
 University of Bristol,
 Bristol,
 United Kingdom

Abstract

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1. LIQUID-VAPOUR INTERFACES — SURFACE TENSION

1.1. Macroscopic mechanical theory

Liquids are distinguished from other phases by the fact that they possess a mobile surface. Solids possess a surface, but it is not mobile, and gases are mobile but need possess no free surface. Macroscopically the mobile liquid surface is characterized by a single mechanical quantity — the surface tension γ . To understand this concept we consider the manner in which two important fluid-mechanical quantities change as we approach the surface of a liquid. Let the z axis be perpendicular to the liquid surface, pointing out into the vapour or air (Fig.1).

First consider the mass density $\rho(z)$. This will be a constant ρ_L within the liquid, whereas outside it will take a very low value ρ_v . $\rho(z)$ does not change discontinuously but falls from ρ_L to ρ_v (Fig.2) over a distance of about two intermolecular spacings. (In considering $\rho(z)$ as varying smoothly over such small distances, we are imagining looking at the surface with a microscope over periods of time long compared with atomic collision times, so that we observe quantities that are time-averaged but not spatially averaged; we call such quantities 'macroscopic'.)

The second quantity we consider is the stress tensor $\sigma_{ij}(z)$; σ_{ij} is defined as the force in direction j acting across an imaginary interface in the fluid perpendicular to direction i , on the fluid with the smaller value of the i co-ordinate (Fig.3). For any material, if classical mechanics applies, Newton's second law may be applied to an elementary cube at point \vec{r} and gives

$$\mathbf{F}_i(\vec{r}) \rho(\vec{r}) + \sum_{j=1}^3 \frac{\partial \sigma_{ji}(\vec{r})}{\partial x_j} = \rho(\vec{r}) \frac{du_i(\vec{r})}{dt} \quad (1)$$

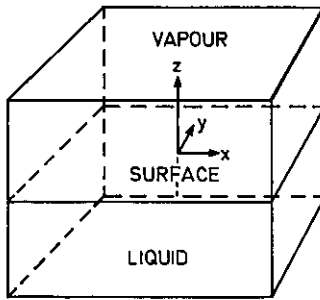


FIG. 1. Liquid-vapour system in a box.

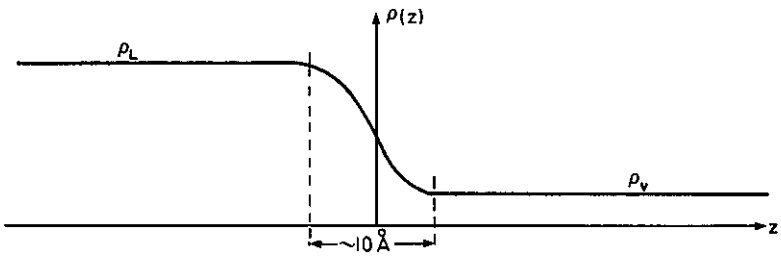


FIG. 2. Density profile.

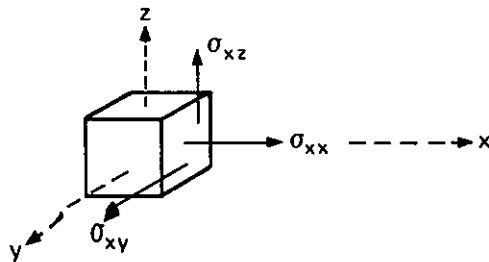


FIG. 3. Definition of stress tensor.

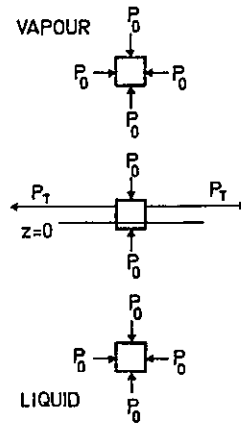


FIG. 4. Forces on fluid elements at different heights.

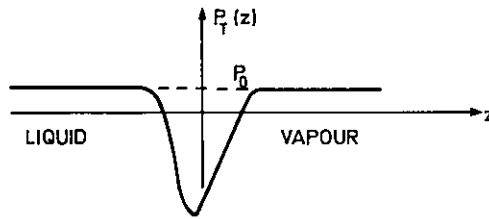


FIG. 5. Variation of tangential pressure through the interface.

The first term involves $F_1(\vec{r})$, the body force per unit mass, and describes effects such as gravitation; these affect the macroscopic shapes of — e.g. — liquid droplets, but are totally negligible in the surface region. The right-hand side involves $u_i(\vec{r})$, the fluid velocity at \vec{r} ; we are primarily interested in fluid statics, so we set $u_i = 0$. Thus Newton's law reduces to three equations of hydrostatic equilibrium:

$$\sum_{j=1}^3 \frac{\partial \sigma_{ji}(\vec{r})}{\partial x_j} = 0 \tag{2}$$

involving only the contact forces σ_{ij} between neighbouring elements of fluid. Within the bulk liquid and vapour, the stress tensor is

$$\sigma_{ij}^{(\text{bulk})} = \begin{pmatrix} -P_0 & 0 & 0 \\ 0 & -P_0 & 0 \\ 0 & 0 & -P_0 \end{pmatrix} \tag{3}$$

where P_0 is the pressure (atmospheric, say). (If we had included the effect of gravity, we would have $P_{\text{liq}} = P_0 - \rho_l gz$, but the extra term is unimportant near the surface.) This tensor contains no shear stresses $\sigma_{i \neq j}$ because it describes a fluid at rest. Equation (3) satisfies the equilibrium condition (2), but is not the most general tensor that does so. How is the actual stress tensor $\sigma_{ij}(\vec{r})$ restricted by (2)? By symmetry, σ_{ij} can depend only on z , so (2) reads:

$$\frac{\partial \sigma_{31}(z)}{\partial z} = 0, \quad \frac{\partial \sigma_{32}(z)}{\partial z} = 0, \quad \frac{\partial \sigma_{33}(z)}{\partial z} = 0 \quad (4)$$

Thus the shear stresses σ_{xz} and σ_{yz} are always zero, and the normal pressure $P_N(z) \equiv -\sigma_{33}$ is constant through the interface zone and equal to P_0 . A simple symmetry argument shows that the shear stresses σ_{xy} and σ_{yx} are always zero. This leaves only the possibility that the tangential pressure $P_T(z) \equiv -\sigma_{xx}(z) \equiv -\sigma_{yy}(z)$ could vary with z without upsetting hydrostatic equilibrium. Thus the most general tensor satisfying (2) is

$$\sigma_{ij}(z) = \begin{pmatrix} -P_T(z) & 0 & 0 \\ 0 & -P_T(z) & 0 \\ 0 & 0 & -P_N = -P_0 \end{pmatrix} \quad (5)$$

In particular, it is possible for $P_T(z)$ to decrease enormously in the surface layer, changing into a tension, and this is exactly what happens (Figs 4 and 5). The surface region is so thin that we can idealize this actual situation by imagining $z = 0$ to be a plane of discontinuity between liquid (ρ_l) and vapour (ρ_v), in which a tension acts, as follows: perpendicular to any line of unit length in the surface $z = 0$ (Fig.6) there acts a force γ with which the liquid surface on one side pulls the liquid surface on the other. To obtain γ it is necessary only to integrate the underpressure $P_0 - P_T(z)$ through the surface, to obtain the basic formula:

$$\gamma = \int_{-\infty}^{\infty} [P_N - P_T(z)] dz \quad (6)$$

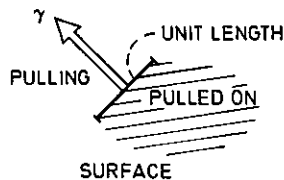
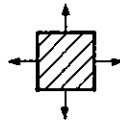


FIG. 6. Definition of surface tension.

Of course γ is simply the surface tension of the liquid; this is the basic quantity characterizing the surface from the point of view of mechanics, and it determines the form taken by the surfaces of liquid masses acted on by other forces such as gravity and interactions with solid surfaces (see Section 2).



TOTAL FORCE ZERO

FIG. 7. A surface element in equilibrium.

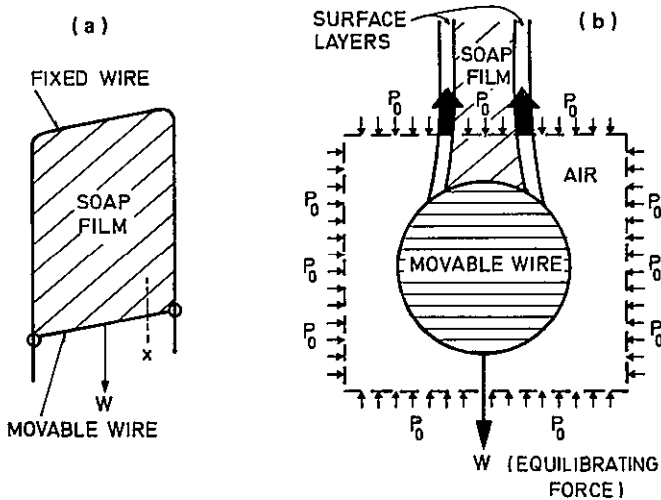


FIG. 8. Surface tension equilibrated by an external force: (a) experimental situation; (b) details of forces acting.

Provided that the radii of curvature of the surface are large compared with interatomic separations, and provided that any shear velocity differences between elements of the fluid separated by an interatomic distance are slow compared with the thermal velocities of the atoms, then γ may be treated as a constant for each liquid-vapour interface, depending only on the temperature T .

To detect the existence of γ there is no point in looking at a plane surface, since each element of it is in equilibrium (Fig. 7). But we can show that γ exists by employing a situation involving unbalanced forces. Consider a soap film stretched over a wire frame with a movable bottom (Fig. 8a), and look more closely at the cross-section at point x (Fig. 8b). The film is many thousands of layers thick, so the two surfaces act independently. We do not need to consider yet exactly what happens at the wire-soap-air boundary (see Section 2), since we can consider the equilibrium of the matter contained within the volume defined by unit length of the movable wire and the area inside the dashed rectangle in Fig. 8b. The bulk pressures P_0 act uniformly all round and cancel, while the surface tension gives a force 2γ acting to contract the film; to prevent this it is necessary to oppose the surface tension

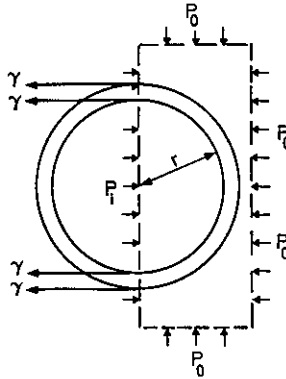


FIG.9. Forces keeping a bubble in equilibrium.

with an equal and opposite force — say a weight of magnitude 2γ /unit length of wire. Such experiments are easily carried out and prove very directly that γ exists.

Another way of showing the existence of surface tension is to employ curved surfaces. The soap bubble (Fig.9) is a simple example; it has been blown up to a radius r and to an internal pressure P_1 which exceeds the outside pressure P_0 . Consider the equilibrium of the matter inside the dashed rectangle in Fig.9. This requires:

Force to right = force to left

$$\text{i.e. } \pi r^2(P_1 - P_0) = 2(2\pi r\gamma)$$

$$\text{i.e. excess pressure} = P_1 - P_0 = \frac{4\gamma}{r} \quad (7)$$

This result can be generalized to give the excess pressure P_{ex} across a single surface (remember the soap bubble is a double surface) whose local radii of curvature are r_1 and r_2 :

$$P_{\text{ex}} = \gamma \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (8)$$

This is Laplace's equation, and is the basis for calculations of the forms of hanging, falling, spinning, vibrating or resting liquid masses.

Thus the properties of liquid surfaces differ from the bulk, and we can form the picture of a skin which is always stretched and trying to contract. This is not quite like an elastic skin (say a rubber balloon), because its tendency to contract (γ) is independent of how much it has already been

TABLE I. SURFACE TENSIONS
FOR SOME FAMILIAR LIQUIDS

Substance	Temperature (K)	γ (Nm ⁻¹)
H ₂	14	0.0028
N	26	0.0052
O ₂	90	0.013
H ₂ O	293	0.073
	373	0.059
Soap solution	293	~0.025
Hg	235	0.498
Fe	1810	1.872
Os	3283	2.5

stretched, whereas for an elastic skin the contractile (restoring) force increases with the stretching (Hooke's law). Surface tension is a force per unit length, so that the units of γ are Nm⁻¹; in terms of cgs units we have

$$1 \text{ Nm}^{-1} = 10^3 \text{ dyne/cm} \quad (9)$$

Surface tensions for some familiar liquids are shown in Table I. It can be seen that liquid metals have easily the largest values of γ . In terms of tangential stresses, these surface tensions are enormous; if we assume the stresses act uniformly over the 10-Å thickness of the surface layer, then the stresses are given by

$$\text{stress} = -P_T \approx \frac{\gamma}{10 \text{ \AA}} \sim 10^3 \text{ atm for water}$$

Although we employed soap films for illustrative purposes, their very existence depends on the fact that they consist of two components (soap and water), so that their composition can be, and is, different in the surface layer and the bulk. It is this capacity to adjust their composition that makes soap films stable against small disturbances. No single-component liquid can ever form a stable film — you cannot blow a water-bubble. It is the purpose of this paper to present the theoretical physics of surface tension in its simplest form, and from this point of view films represent a complication to be avoided; from now on, therefore, we consider only one-component ('pure') liquids.

1.2. Macroscopic thermodynamic theory

Now we show that the mechanical interpretation of surface tension is not the only one: γ is also a thermodynamic quantity characterizing the liquid surface. To see this, consider the system shown in Fig.1 and let the walls of

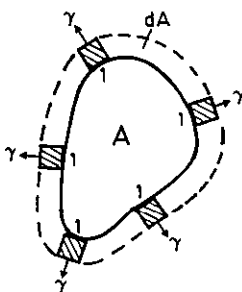


FIG. 10. Expanding a surface does work:

the container be moved in such a way that the area A of the liquid surface increases by dA , while the volume of the system and its temperature T remain constant. How much work dW will be done on the system in this process? It is easy to see (Fig.10) that

$$dW = \gamma dA \quad (10)$$

What about the internal energy U of the system? This will change by dU , where

$$dU = TdS + dW \quad (11)$$

dS being the change in entropy of the system. At this stage we do not know the value of TdS ; certainly it is not zero because the surface was expanded not adiabatically but isothermally. This suggests that we consider not U but the free energy F , defined by

$$F = U - TS \quad (12)$$

i.e.

$$dF = dU - TdS - SdT = -SdT + dW \quad (13)$$

In the process considered, dT was zero, so that (13) and (10) give $dF = \gamma dA$, i.e.

$$\gamma = \left(\frac{\partial F(T, V, A)}{\partial A} \right)_{T, V} \quad (14)$$

This gives a thermodynamic interpretation of γ , and may in fact be used to define this quantity instead of the mechanical equation (6). We emphasize, however, that both approaches are equally valid.

Since γ is independent of the area of the surface, we can integrate (14) to obtain

$$F(T, V, A) = \gamma(T)A + F_b(T, V) \equiv F_s(T, A) + F_b(T, V) \quad (15)$$

This expresses the total free energy as the sum of a contribution F_b from the bulk phases, and a contribution:

$$F_s(T, A) = \gamma(T)A \quad (16)$$

from the surface. This is equivalent to (14), and gives an interpretation of γ as surface free energy per unit area (there is no problem over units, since $\text{Jm}^{-2} = \text{Nm}^{-1}$ dimensionally). This interpretation easily explains the contractile tendency of liquid masses, and the spherical shape of falling droplets, for (13) states that for isothermal situations $dF = dW$, but dW is zero for a system in mechanical equilibrium (principle of virtual work), so that F is an extremum, which actually must be a minimum if the equilibrium is to be stable. For liquid masses V is essentially constant, so that only A changes and we have to minimize F_s ; from Eq.(16) this implies that A itself is minimized at constant V , hence the sphericity of raindrops.

It is also possible to define other thermodynamic 'surface functions'. From (13), the surface entropy S_s is defined as

$$S_s \equiv - \left(\frac{\partial F_s}{\partial T} \right)_A = - \frac{d\gamma(T)A}{dT} \quad (17)$$

while from (12) the surface energy U_s is defined as

$$U_s = F_s + TS_s = \left[\gamma(T) - T \frac{d\gamma(T)}{dT} \right] A \quad (18)$$

We conclude that the single function $\gamma(T)$ provides a complete mechanical and thermodynamic description of liquid surfaces. What is the form of this function? Clearly it is never negative – if it were, stable droplets would have the maximum area for a given volume, corresponding to an infinitely puckered and convoluted surface, and this is never observed. Furthermore, we expect γ to vanish at the critical temperature T_c , where the distinction between liquid and vapour disappears. Thus $\gamma(T)$ should decrease to zero at T_c , and this is indeed observed. To compare results for different substances it is convenient to employ the reduced surface tension γ_r , a dimensionless quantity defined by

$$\gamma_r \left(\frac{T}{T_c} \right) \equiv \frac{\gamma(T) v_c^{2/3}}{kT_c} \quad (19)$$

where v_c is the critical volume per molecule and k is Boltzmann's constant. The results (Fig.11 and Table II) show that γ_r is almost a universal function of T/T_c , i.e. there is a 'principle of corresponding states' for surface tension, in terms of which $\gamma(T)$ for one liquid can be calculated quite accurately from measurements of $\gamma(T)$ on another liquid, provided v_c and T_c are known. The experimental data are well described over a large range by the empirical equation:

$$\gamma(T) = \gamma_0 \left(1 - \frac{T}{T_c} \right)^f \quad (20)$$

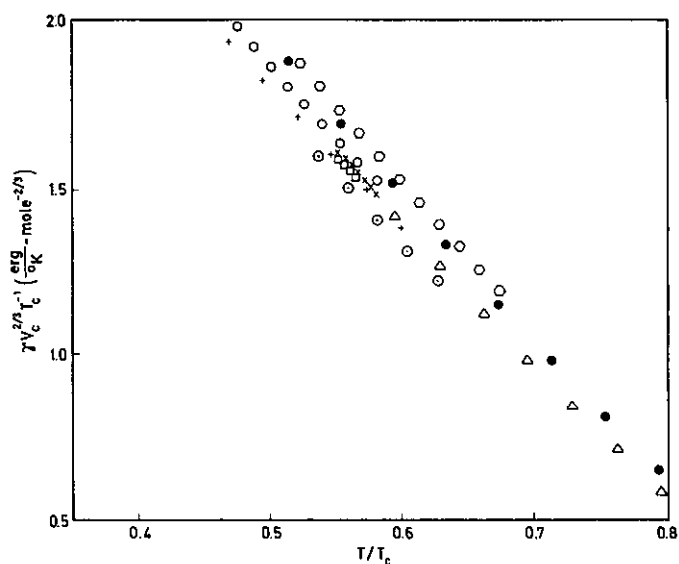


FIG.11. $\gamma(T) V_c^{2/3} T_c^{-1}$ plotted versus T/T_c . \odot : neon; Δ : argon; \times : krypton; \square : xenon; \bullet : nitrogen; \ominus : carbon monoxide; $+$: methane; \circ : oxygen. (From Buff and Lovett (1968).)

TABLE II. VALUES OF $\gamma_R = V_c^{2/3} T_c^{-1} \gamma(T)$ AT $T = 0.56 T_c$
(From Buff and Lovett (1968))

Substance	γ (dyne-cm ⁻¹)	γ_R (erg / K mole ^{-2/3})	$\gamma_R/\gamma_R(\text{Ar})$
Ne	5.55	1.500	0.955
CH ₄	13.790	1.548	0.986
Kr	16.081	1.568	1.000
Ar	13.28	1.570	1.000
Xe	18.98	1.583	1.008
O ₂	14.04	1.605	1.022
N ₂	10.42	1.662	0.059
CO	11.05	1.704	1.085

where the 'critical exponent' r is given by

$$r = 1.27 \pm 0.02 \quad (21)$$

For pure liquids, γ always decreases with T , but for liquids with more than one component it is possible for $d\gamma/dT$ to be positive in some temperature regions.

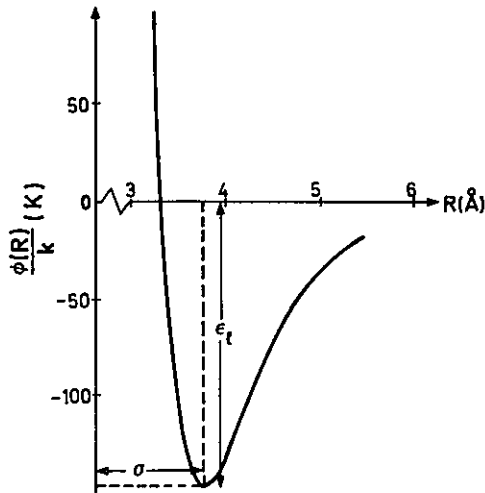


FIG.12. Typical interatomic potential (from Toxvaerd (1972 b)).

1.3. Microscopic mechanical theory (exact)

To calculate surface tension from the microscopic interactions between fluid molecules, we have to have a model. We choose the 'simple fluid' model, on which the molecules interact pairwise via a spherically symmetrical potential function $\phi(R)$, where \vec{R} is the vector joining the centres of the two interacting molecules. For real fluids, of course, there are triplet and higher-order interactions (i.e. the force between two molecules is modified by others in the neighbourhood) and, further, the interaction depends on the orientation of \vec{R} as well as its magnitude (i.e. on direction), and also on the relative velocity of the molecules (i.e. on temperature). If these complications are neglected, the resulting theory gives a very good description of bulk and interface properties of rare gases and liquids, and fluids with compact molecules, such as nitrogen, oxygen, carbon monoxide and methane; the theory does not work for liquid metals because of the electron gas, but it is possible to treat this separately. The potential $\phi(R)$ is attractive at large distances and repulsive at short distances, as shown in Fig.12 for argon; the attraction is responsible for the condensation of gases into liquids and solids, and the repulsion prevents interpenetration of molecules, so that in dense phases they act somewhat like 'hard spheres'. If we exclude the very lightest elements, we may use classical mechanics to describe the encounters between molecules, because their de Broglie wavelength is small in comparison with their size. Experimentally, $\phi(R)$ can be obtained from molecular scattering experiments or from the equation of state of nearly perfect gases.

In order to calculate γ from the mechanical definition (6) it is necessary to know the anisotropy $P_N - P_T(z)$ of the pressure in the interface. The pressure $P(\vec{\ell}, \vec{r})$ at a point \vec{r} acting in a direction specified by a unit vector $\vec{\ell}$ is defined as follows: imagine a plane at \vec{r} perpendicular to $\vec{\ell}$ (Fig.13), and consider an elementary area dS in this plane and containing \vec{r} . The plane divides the fluid

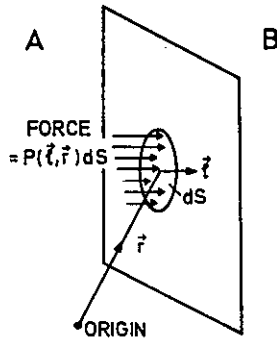


FIG.13. Definition of pressure.

into two regions, A and B, and the time average of the force exerted by the molecules in A on the molecules in B across dS is, by definition, $P(\vec{l}, \vec{r}) dS$. Now, it is most important to realize that while from a macroscopic point of view A and B are distinct portions of fluid, on the microscopic level they are constantly exchanging particles. The average momentum per unit time transferred in this way from A to B across dS gives a kinetic contribution $P^K(\vec{l}, \vec{r}) dS$ to the pressure at \vec{r} . In addition, there is a static force component $P^f(\vec{l}, \vec{r}) dS$, equal to the average total force arising from $\phi(R)$ that the molecules in A exert on those in B which can be joined to them by a straight line intersecting dS . Thus we have

$$P(\vec{l}, \vec{r}) = P^K(\vec{l}, \vec{r}) + P^f(\vec{l}, \vec{r}) \quad (22)$$

We calculate P^K first. Temporarily we say that \vec{l} points along the positive x axis. A molecule now in A, and moving with velocity \vec{v} with mass m will carry normal momentum $m v_x$ across dS into B in unit time if it lies in a region (Fig.14) whose volume is $v_x dS$, and if v_x is positive. The average number of molecules in this volume is $n(\vec{r}) v_x dS$, where $n(\vec{r})$ is the number density of molecules at \vec{r} , defined by

$$n(\vec{r}) \equiv \frac{\rho(\vec{r})}{m} \quad (23)$$

This includes molecules with all velocities \vec{v} ; the force due to molecules moving from A to B across dS is the average of $n(\vec{r}) v_x dS \times m v_x$ over the distribution of \vec{v} . This distribution is given by the Maxwell-Boltzmann law:

$$\mathcal{P}(\vec{v}) = \left(\frac{m}{2\pi kT} \right)^{3/2} \exp\left(-\frac{m v^2}{2kT} \right) \quad (24)$$

where $\mathcal{P}(\vec{v}) d\vec{v}$ is the fraction of molecules whose velocities lie between \vec{v} and $\vec{v} + d\vec{v}$. It is often thought, incorrectly, that this distribution only holds in an ideal gas, where molecular interactions embodied in $\phi(R)$ are infinitesimal,

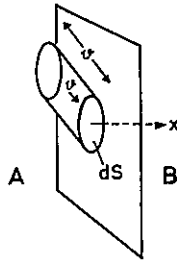


FIG. 14. Momentum transfer across a surface.

but Eq.(24) actually holds rigorously for any potential that is not velocity dependent. This result is a consequence of the fact that the kinetic energy part of the Hamiltonian for each particle does not involve $\phi(R)$. Denoting averages by $\langle \rangle$, we require

$$\begin{aligned} \langle n(\vec{r}) m v_x^2 dS \rangle &= n(\vec{r}) m dS \langle v_x^2 \rangle \\ &= n(\vec{r}) m dS \int_{-\infty}^{\infty} dv_y \int_{-\infty}^{\infty} dv_z \int_0^{\infty} dv_x \left(\frac{m}{2\pi kT} \right)^{3/2} v_x^2 \exp\left(-\frac{mv^2}{2kT}\right) \\ &= \frac{n(\vec{r}) kT dS}{2} \end{aligned} \tag{25}$$

This is the force from A onto B due to molecules carrying positive x-momentum into B. However, there will be, on the average, an equal number of molecules carrying negative x-momentum out of B into A. Therefore, the total kinetic pressure of A on B is

$$P^K(\vec{\ell}, \vec{r}) = n(\vec{r}) kT \tag{26}$$

This depends only on the density at \vec{r} and not on the direction $\vec{\ell}$ of the pressure. Therefore, P^K is isotropic, and cannot account for surface tension, which depends (Eq.6) on the anisotropy $P_N - P_T$. If the potential $\phi(R)$ is negligible there is no static force component P^f , so that $P = P^K$ and (26) is the well-known equation of state for an ideal gas (to see this, observe that $nk = \mathcal{N}k/V = R/V$, where \mathcal{N} is Avogadro's number, V is the molar volume, and R is the gas constant).

Now we must calculate $P^f(\vec{\ell}, \vec{r})$. The component along $\vec{\ell}$ of the force exerted by a molecule at \vec{r}_A in A on the molecule at \vec{r}_B in B is

$$-\nabla_{\vec{r}_B} \phi(|\vec{r}_B - \vec{r}_A|) \cdot \vec{\ell} = -\frac{\vec{R} \cdot \vec{\ell}}{R} \phi'(R) \tag{27}$$

where

$$\vec{R} \equiv \vec{r}_B - \vec{r}_A \tag{28}$$

The total force along $\vec{\ell}$ across dS is found by multiplying this expression by either member of (27) and integrating over all λ between 0 and 1 and all \vec{R} for which $\vec{\ell} \cdot \vec{R} > 0$; dropping the factor dS , we obtain

$$P^f(\vec{\ell}, \vec{r}) = - \iiint_{\vec{R} \cdot \vec{\ell} > 0} d\vec{R} \frac{(\vec{R} \cdot \vec{\ell})^2}{R} \phi'(R) \int_0^1 d\lambda n_2(\vec{r} - \lambda \vec{R}, \vec{r} - (\lambda - 1) \vec{R}) \quad (33)$$

We can rewrite this as an integral over all \vec{R} by realizing that (33) is unaltered if we reverse the $\vec{\ell}$ component of \vec{R} , replace λ by $1 - \lambda$ and use the fact that n_2 is a symmetric function of \vec{r}_A and \vec{r}_B . Thus we obtain

$$P^f(\vec{\ell}, \vec{r}) = -\frac{1}{2} \iiint d\vec{R} \frac{(\vec{R} \cdot \vec{\ell})^2}{R} \phi'(R) \int_0^1 d\lambda n_2(\vec{r} - \lambda \vec{R}, \vec{r} - (\lambda - 1) \vec{R}) \quad (34)$$

Combining this with (26) we find, for the pressure at \vec{r} in direction $\vec{\ell}$,

$$P(\vec{\ell}, \vec{r}) = n(\vec{r}) kT - \frac{1}{2} \iiint d\vec{R} \frac{(\vec{R} \cdot \vec{\ell})^2}{R} \phi'(R) \int_0^1 d\lambda n_2(\vec{r} - \lambda \vec{R}, \vec{r} - (\lambda - 1) \vec{R}) \quad (35)$$

For a bulk phase, where n is constant, I leave it as an exercise to show that this reduces to the more familiar expression:

$$P = nkT - \frac{2\pi n^2}{3} \int_0^\infty dR R^3 \phi'(R) g(R) \quad (36)$$

In the bulk vapour, n is small and the second term is negligible. In the bulk liquid, n is large and the second term almost cancels the first (the attractive forces, where ϕ' is positive, dominate); P^f is negative, in fact.

To calculate γ using (6), we must specialize the general expression (35) to obtain $P_T(z)$ and $P_N(z)$ when there is a plane interface perpendicular to Z . For P_N , $\vec{\ell}$ is parallel to the z axis, and for P_T , $\vec{\ell}$ may be taken as any line perpendicular to Z , and we choose the x axis. Then we have, if $\vec{R} \equiv (X, Y, Z)$:

$$P_N(z) = n(z) kT - \frac{1}{2} \iiint d\vec{R} \frac{Z^2}{R} \phi'(R) \int_0^1 d\lambda n_2(z - \lambda Z, \vec{R}) \quad (37)$$

$$P_T(z) = n(z) kT - \frac{1}{2} \iiint d\vec{R} \frac{X^2}{R} \phi'(R) \int_0^1 d\lambda n_2(z - \lambda Z, \vec{R})$$

Now we use (6), and notice that

$$\int_{-\infty}^\infty dz \int_0^1 d\lambda n_2(z - \lambda Z, \vec{R}) = \int_{-\infty}^\infty dz n_2(z, \vec{R}) \quad (38)$$

we obtain, as the final result,

$$\gamma = \frac{1}{2} \int_{-\infty}^{\infty} dz \iiint \frac{d\vec{R}}{R} (X^2 - Z^2) \phi'(R) n_2(z, \vec{R}) \quad (39)$$

This rigorous microscopic formula for γ involves not only the intermolecular potential $\phi(R)$, but also the function $n_2(\vec{r}_A, \vec{r}_B)$, whose form in the interface region is unknown. From (29), it is clear that this function will involve the 'density profile' $n(z)$ (cf. Fig.2), and the anisotropic surface correlations embodied in $g(z, \vec{R})$. A relation between these quantities, which does not, however, determine them completely, can be obtained by recalling that for hydrostatic equilibrium (Eq.(4)) $P_N(z)$ must be constant through the interface. Differentiating the first equation in (37) and using the symmetry of $n_2(\vec{r}_A, \vec{r}_B)$, we obtain

$$kT \frac{dn(z)}{dz} = \iiint d\vec{R} \frac{Z}{R} \phi'(R) n_2(z, \vec{R}) \quad (40)$$

(it helps to replace λ by a new integration variable $z - \lambda Z$). This expresses the fact that the total force on any element of fluid is zero, on the average. By performing more delicate averages, with one or more molecules held fixed, it is possible to obtain a hierarchy of equations, of which (40) is the first; the second equation in the series relates $n_2(\vec{r}_A, \vec{r}_B)$ to the triplet distribution function $n_3(\vec{r}_A, \vec{r}_B, \vec{r})$, and successive equations relate to higher-order distribution functions. A major problem in microscopic mechanics is the solution of this infinite hierarchy; it seems unfair of nature to make the relatively low-order correlations embodied in n_2 depend on the complicated higher-order distributions. However, simple approximations are possible, as will be seen in Section 1.5.

To see qualitatively why γ is positive, we notice from (37) that it depends only on P_T^f and P_N^f . As we approach the interface from the liquid, $n(z)$ decreases and so, therefore, does the number of interacting molecular pairs. But this number decreases faster across the horizontal surface dS corresponding to P_N than for the vertical surface for P_T , so that $|P_N^f| < |P_T^f|$. But P^f is negative, so that, from (6), γ is positive.

1.4. Statistical-mechanical theory (exact)

Here we show that the exact microscopic formula (39) for γ can also be derived from the thermodynamic formula (14), employing the standard methods of Gibbsian statistical mechanics. Let the system (Fig.1) be closed, and contain N molecules with instantaneous positions $\{\vec{r}_i\} = \{\vec{r}_1 \dots \vec{r}_N\}$ and momenta $\{\vec{P}_i\} = \{\vec{P}_1 \dots \vec{P}_N\}$ in a volume V at temperature T . The Hamiltonian function H is just the instantaneous total energy:

$$H(\{\vec{r}_i\}, \{\vec{P}_i\}) = \sum_{i=1}^N \frac{P_i^2}{2m} + \frac{1}{2} \sum_{i \neq j=1}^N \sum_{j=1}^N \phi(|\vec{r}_i - \vec{r}_j|) \quad (41)$$

According to (14), we require the free energy F of the system: this is given by

$$F = -kT \log Z \quad (42)$$

where Z is the partition function of the system, defined as

$$Z = \iiint d\vec{P}_1 \dots \iiint d\vec{P}_N \iiint_V d\vec{r}_1 \dots \iiint_V d\vec{r}_N \exp \left[-\frac{H(\{\vec{r}_i\}, \{\vec{P}_i\})}{kT} \right] \quad (43)$$

The probability distribution of the particles is

$$\Pi(\{\vec{r}_i\}, \{\vec{P}_i\}) = \frac{\exp[-H(\{\vec{r}_i\}, \{\vec{P}_i\})/kT]}{Z} \quad (44)$$

where $\Pi(\{\vec{r}_i\}, \{\vec{P}_i\}) d\vec{r}_1 \dots d\vec{r}_N d\vec{P}_1 \dots d\vec{P}_N$ is the probability that any chosen instant molecule 1 will lie in the element $d\vec{r}_1$ about \vec{r}_1 with a momentum in the range $d\vec{P}_1$ about \vec{P}_1 , molecule 2 will lie in $d\vec{r}_2$, $d\vec{P}_2$, etc. These formulae apply even when the equilibrium system is inhomogeneous, as is the case here; in particular, the form (41) for the Hamiltonian means that the \vec{P}_i dependence factorizes out in (44), so that the particle velocities $\vec{v}_i = \vec{P}_i/M$ always have the Maxwell-Boltzmann distribution (25).

Using the relation:

$$\int_{-\infty}^{\infty} dp_x \exp\left(-\frac{p_x^2}{2mkT}\right) = \sqrt{2\pi mkT} \quad (45)$$

we can perform all the integrations over \vec{P}_i in (43), and we get

$$Z = (2\pi mkT)^{3N/2} \iiint d\vec{r}_1 \dots \iiint d\vec{r}_N \exp \left[-\frac{1}{2kT} \sum_{i \neq j=1}^N \phi(|\vec{r}_i - \vec{r}_j|) \right] \quad (46)$$

According to (14) and (42) we must differentiate Z with respect to the area A of the interface, keeping V (and T) constant. Referring to Fig.1, we let the container have unit length along the y direction, and let its x dimension be A and its z dimension V/A . Then define new variables x'_i and z'_i by

$$\vec{r}_i \equiv \left(A x'_i, y_i, \frac{V}{A} z'_i \right); \quad \iiint d\vec{r}_i = V \int_0^1 dx'_i \int_0^1 dy_i \int_0^1 dz'_i \quad (47)$$

With this transformation, the A dependence of Z occurs only in the arguments of the potential energy ϕ , since

$$|\vec{r}_i - \vec{r}_j| = \left[A^2(x'_i - x'_j)^2 + (y_i - y_j)^2 + \frac{V^2}{A^2}(z'_i - z'_j)^2 \right]^{1/2} \quad (48)$$

so that

$$\begin{aligned} \left(\frac{\partial}{\partial A} |\vec{r}_i - \vec{r}_j| \right)_V &= \frac{A(x_i' - x_j') - \frac{V^2}{A^3} (z_i' - z_j')^2}{|\vec{r}_i - \vec{r}_j|} \\ &= \frac{(x_i - x_j)^2 - (z_i - z_j)^2}{A |\vec{r}_i - \vec{r}_j|} \end{aligned} \quad (49)$$

Use of this result, together with (46), (42) and (14), gives for the surface tension

$$\begin{aligned} \gamma &= -\frac{kT}{Z} \left(\frac{\partial Z}{\partial A} \right)_{V, T} \\ &= \frac{\frac{1}{2} \iiint d\vec{r}_1 \dots \iiint d\vec{r}_N \sum_{i \neq j=1}^N \sum \frac{\phi'(|\vec{r}_i - \vec{r}_j|)}{|\vec{r}_i - \vec{r}_j|} \left\{ \frac{(x_i - x_j)^2 - (z_i - z_j)^2}{A} \right\} e^{-\frac{1}{2} \sum_{i \neq j} \phi(|\vec{r}_i - \vec{r}_j|)}}{\iiint d\vec{r}_1 \dots \iiint d\vec{r}_N e^{-\frac{1}{2} \sum \phi(|\vec{r}_i - \vec{r}_j|)}} \end{aligned} \quad (50)$$

To evaluate this expression, we can interchange the order of summation and integration, and realize that all of the $N(N-1)$ terms in the sum are the same, because of the indistinguishability of the molecules. Thus we can write

$$\begin{aligned} \gamma &= \frac{1}{2} \iiint d\vec{r}_1 \iiint d\vec{r}_2 \frac{\phi'(|\vec{r}_1 - \vec{r}_2|)}{|\vec{r}_1 - \vec{r}_2|} \left\{ \frac{(x_1 - x_2)^2 - (z_1 - z_2)^2}{A} \right\} \\ &\quad \times \left[\frac{N(N-1) \iiint d\vec{r}_3 \dots \iiint d\vec{r}_N \exp\left(-\frac{1}{2} \sum \phi(|\vec{r}_i - \vec{r}_j|)\right)}{\iiint d\vec{r}_1 \dots \iiint d\vec{r}_N \exp\left(-\frac{1}{2} \sum \phi(|\vec{r}_i - \vec{r}_j|)\right)} \right] \end{aligned} \quad (51)$$

Now it can be seen from (44) that the quantity in square brackets in (51), multiplied by $d\vec{r}_1 d\vec{r}_2$, is $N(N-1)$ times the probability that particle 1 will be found in $d\vec{r}_1$ and particle 2 in $d\vec{r}_2$, the position and momenta of the other particles being unspecified. However, there are $N(N-1)$ ways of choosing particles which go into $d\vec{r}_1$ and $d\vec{r}_2$, so that the quantity in [] is simply the familiar two-particle distribution function $n_2(\vec{r}_1, \vec{r}_2)$, involving particles whose identity is not specified. Thus (51) becomes

$$\gamma = \frac{1}{2} \iiint \frac{d\vec{r}_1}{A} \iiint d\vec{r}_2 \frac{\phi'(|\vec{r}_1 - \vec{r}_2|)}{|\vec{r}_1 - \vec{r}_2|} \left\{ (x_1 - x_2)^2 - (z_1 - z_2)^2 \right\} n_2(\vec{r}_1, \vec{r}_2) \quad (52)$$

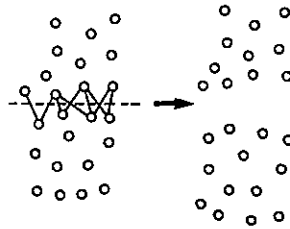


FIG.16. Surface tension is, approximately, work done in breaking 'bonds'.

Now we set $\vec{r}_2 - \vec{r}_1 \equiv \vec{R} \equiv (X, Y, Z)$ and integrate over \vec{R} instead of \vec{r}_2 . There is no dependence of the integrand on x_1 and y_1 , because of the symmetry of the problem, and $\iint dx_1 dy_1$ cancels out the A in the denominator; we are left with

$$\gamma = \frac{1}{2} \int_{-\infty}^{\infty} dz_1 \iiint d\vec{R} \frac{\phi'(R)}{R} (X^2 - Z^2) n_2(z_1, \vec{R}) \quad (53)$$

an expression identical with the result (39) obtained from microscopic mechanics. The regions of validity of the two derivations do not quite coincide, however: (39) holds even in non-equilibrium cases, but the derivation gives no method for calculating $n_2(\vec{r}_A, \vec{r}_B)$; (53) on the other hand, was derived using equilibrium statistical mechanics, but the derivation showed that in equilibrium $n_2(\vec{r}_A, \vec{r}_B)$ is given by the expression in [] in (51) — however, this involves N -fold integrations and so is hardly useful.

1.5. Some approximate methods

First we show that it is possible to obtain an order-of-magnitude estimate for γ without invoking any of the sophisticated theory of the last two sections. Imagine a column of liquid with cross-sectional area A . By breaking this column into two, new surface area $2A$ is created. If the operation is carried out isothermally, then (10) and (16) show that an amount of work $2\gamma A$ will be required. This work (Fig.16) comes from the breaking of molecular bonds in the interface. Most of these bonds are between pairs of molecules in each other's shell of nearest neighbours, where the bond strength is given by the depth ϵ_l of the intermolecular potential $\phi(R)$ (Fig.12). Thus we have

$$\gamma \approx \frac{\epsilon_l}{2} \times \text{number of bonds/unit area} \quad (54)$$

Each molecule is joined to Z_l nearest neighbours, where Z_l is the 'co-ordination number'. Of these Z_l bonds from one molecule, $Z_l/2$ are broken during the creation of new liquid. The number of molecules per unit area is roughly the

inverse square of the interparticle distance, i.e. about $n_L^{2/3}$. Thus our crude formula for γ is

$$\gamma \approx \frac{\epsilon_\ell Z_\ell n_L^{2/3}}{4} \quad (55)$$

For close-packed 'simple liquids', $Z_\ell \sim 8$. Values of γ calculated using this formula usually lie within a factor of two of the measured values. An order-of-magnitude value of ϵ — for use in emergencies only — is given by

$$\epsilon_\ell \sim kT_c \quad (56)$$

where T_c is the critical temperature. This formula is based on the idea that above T_c , where a close-packed phase cannot exist, the mean thermal energy kT exceeds ϵ_ℓ , all 'bonds' being broken. For all simple fluids (56) over-estimates ϵ_ℓ by about 40%.

The simple result (55) takes no account of the effect on γ of (a) temperature, (b) the smooth change of density in the interface, (c) interactions between non-nearest-neighbours, (d) the existence of the vapour, and (e) correlations between molecular positions. Approximate methods taking some account of some or all of these effects fall into two groups. We start with the group of methods based on the exact formula (39). How can we find the two-body distribution function $n_2(\vec{r}_A, \vec{r}_B)$? According to (29), we need to know the density profile $n(z)$, and the pair correlation function $g(z, \vec{R})$. The simplest approximation is to treat the vapour as a vacuum (this will not cause serious error except near the critical point), assume the density falls suddenly from n_L to zero, and assume $g(z, \vec{R})$ to be the liquid pair correlation function $g_L(R)$. Thus this first model postulates that

$$\begin{aligned} n_2(\vec{r}_A, \vec{r}_B) &\approx n_L^2 g_L(R) \quad (z_A < 0 \text{ and } z_B < 0) \\ &= 0 \text{ otherwise} \end{aligned} \quad (57)$$

I leave it as an exercise to show that when used in (39) this leads to

$$\gamma \approx \frac{\pi n_L^2}{8} \int_0^\infty dR R^4 \phi'(R) g_L(R) \quad (58)$$

This simple formula was first derived (not from an exact theory) nearly forty years ago.

The result (58) is certainly an improvement on (55). It takes partial account of points (a), (c) and (e) at the beginning of the last paragraph, and can easily be modified to include point (d). It yields results that agree with experiment within about 20%. However, there are two points that must be made in this connection and they apply also to most of the later approximations we shall consider. The first is that $g_L(R)$ is not a microscopic quantity independent of $\phi(R)$; it can in principle be derived from $\phi(R)$ using bulk liquid statistical mechanics. But this is a vast subject and not strictly relevant here because we are concerned with those problems which specifically concern liquid surfaces. Therefore we shall treat $g_L(R)$ (and the corresponding

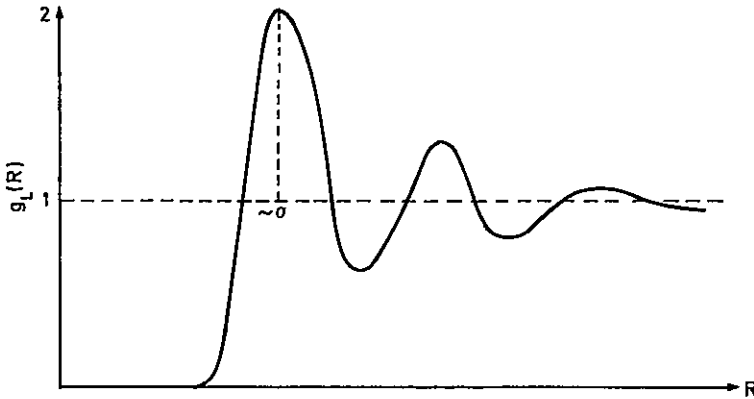


FIG. 17. Typical liquid pair correlation function.

vapour correlation function $g_V(R)$ as capable of being measured experimentally by X-ray or neutron scattering, for example. Figure 17 shows the typical oscillatory form of $g_L(R)$ far from the critical point.

The second point is that the integral in (58) is very sensitive to the relative positions of the maximum of $\phi'(R)$ and the first maximum of $g_L(R)$, so that great care must be taken to use 'compatible data', i.e. $g_L(R)$ and $\phi(R)$ must either be measured under exactly the same conditions (temperature, pressure), or $g_L(R)$ must be calculated from $\phi(R)$ by one of the methods of bulk statistical mechanics. It is usually the case that $\phi(R)$ is not in fact measured precisely, but fitted to the Lennard-Jones expression:

$$\phi(R) = \epsilon_f \left(\left(\frac{\sigma}{R} \right)^{12} - 2 \left(\frac{\sigma}{R} \right)^6 \right) \quad (59)$$

where ϵ_f is the depth and σ the radius of the minimum of $\phi(R)$ (Fig.12).

The formula (58), based on (57), violates the equation (40) for hydrostatic equilibrium; in other words, if (57) is used to calculate the normal pressure $P_N(z)$ (Eq.(37)), the result is not constant. This is because the simple form (57) does not take account of the smooth variation of the density through the interface. A better approximation for $n_2(\vec{r}_A, \vec{r}_B)$, which does take this into account, is

$$n_2(\vec{r}_A, \vec{r}_B) \approx n(\vec{r}_A) n(\vec{r}_B) g_L(R) \quad (60)$$

The only error here is to assume that the correlations between molecules in the interface and the vapour are the same as in the liquid. This is not so serious as might at first appear, because: (a) $n_V \ll n_L$, so that the nature of the vapour hardly affects γ (provided $T \ll T_c$); (b) in the vapour, close molecular encounters are rare and, for large R , g_L and g_V both tend to unity; (c) in the interface most of the interactions, which cause the correlations,

must occur with one molecule in bulk liquid. The approximation (60) leads to the following formula for γ :

$$\gamma \approx \frac{\pi}{2} \int_0^{\infty} dR g_L(R) \phi'(R) \left[- \int_{-R}^R dZ (R^2 Z - Z^3) \int_{-\infty}^{\infty} dz n(z) n(z+Z) \right] \quad (61)$$

Thus the surface tension can be calculated if the density profile $n(z)$ is known. However, $n(z)$ can be calculated self-consistently from the hydrostatic equation (40), which becomes, on using (60),

$$kT \frac{dn(z)}{dz} = 2\pi n(z) \int_0^{\infty} dR \phi'(R) g_L(R) \int_{-R}^R dZ Z n(z+Z) \quad (62)$$

The only unknown is $n(z)$. After a little transformation, (62) can be integrated once, to give

$$n(z) = n_L \exp \left[- \frac{4\pi n_L}{3kT} \int_0^{\infty} dR R^3 \phi'(R) g_L(R) \right. \\ \left. + \frac{\pi}{kT} \int_{-\infty}^{\infty} dZ n(z+Z) \int_{|z|}^{\infty} dR \phi'(R) g_L(R) (R^2 - Z^2) \right] \quad (63)$$

This exponentially non-linear integral equation has been solved by a form of iteration, but the numerical difficulties are great because the exponentiation tends to cancel the stabilizing effect of the integration. After each iteration, the density profile shifts bodily, but its form is stable after about 40 iterations. What we need is an analytical understanding of equations like (63). However, one result that can be derived from (63) by letting z tend to $+\infty$ is a relation between n_L and n_V . For a given n_L , the value of n_V is several times too large; nevertheless, considerable insight into the nature of liquid-vapour coexistence (especially near T_c) can be obtained in this way. To calculate γ at any given temperature, then, we start with n_L for that temperature, use (63) to calculate n_V and $n(z)$, and then employ (61). The resulting values of γ are accurate to a few per cent, which is comparable with the error introduced by using simple model potentials such as (59).

However, an improvement on (60) is the simplest pair correlation function which changes smoothly from its liquid to its vapour forms:

$$n_2(\vec{r}_A, \vec{r}_B) \approx \frac{n(\vec{r}_A) n(\vec{r}_B)}{n_L - n_V} \left\{ \frac{[n(\vec{r}_A) + n(\vec{r}_B)]}{2} [g_L(R) - g_V(R)] + n_L g_V(R) - n_V g_L(R) \right\} \quad (64)$$

This can be inserted into the hydrostatic equation (40), to give an equation similar to but more complicated than (63). The change from (60) to (64) is

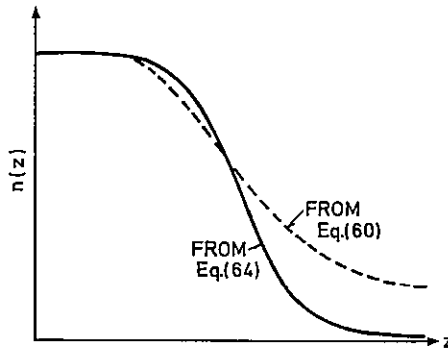


FIG.18. Calculated density profiles (from Toxvaerd (1972 a)).

said to affect the calculated value of γ by only a few parts in 10^5 (Toxvaerd, private communication), but this must surely be fortuitous. The density profiles differ considerably, however (Fig.18); that arising from (64) has the correct limiting values n_L and n_V .

For calculating γ it is probably unwise to use more sophisticated approximations of this type, because of the uncertainties in our knowledge of $\phi(R)$, $g_V(R)$, and $g_L(R)$.

The second major group of approximate methods is not based on the exact microscopic formula (39), but on a different idea. This is quasithermodynamics, in which the notion that pressure can be defined at any point in the interface is generalized to cover extensive thermodynamic functions. These can be expressed as quantities 'per particle'. Thus the volume per particle $v(z)$ is simply

$$v(z) \equiv \frac{1}{n(z)} \quad (65)$$

Likewise the free energy per particle, $f(z)$, exists; it can be defined rigorously and given exact statistical-mechanical expression in terms of $\phi(R)$ and $n_2(\vec{r}_A, \vec{r}_B)$.

Now, according to (16), the surface tension is simply the free energy associated with unit area of the interface, i.e. the free energy in a column of fluid of unit area extending from bulk liquid into bulk vapour, minus the free energy that the same column would contain if the liquid changed abruptly to vapour at $z = 0$. Thus

$$\gamma = \int_{-\infty}^0 dz (n(z)f(z) - n_L f_L) + \int_0^{\infty} dz (n(z)f(z) - n_V f_V) \quad (66)$$

where f_L and f_V are the free energies per particle in bulk liquid and vapour. Of course the actual column and the idealized discontinuous column must

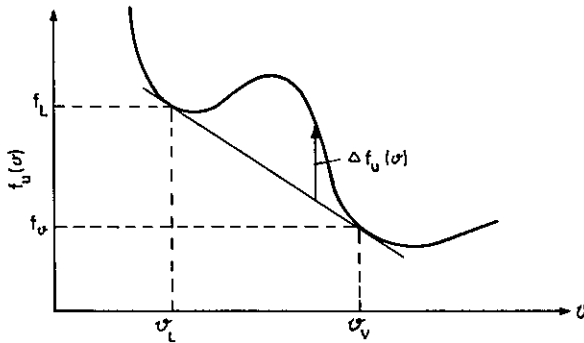


FIG.19. Analytic continuation of free energy between liquid and vapour phases.

contain the same number of particles, so that the location of the 'dividing surface' at $z = 0$ must satisfy

$$\int_{-\infty}^0 dz (n(z) - n_L) + \int_0^{\infty} dz (n(z) - n_V) = 0 \quad (67)$$

After a little algebra, these equations can be shown to imply that

$$\gamma = \int_{-\infty}^{\infty} dz n(z) \Delta f(z) \quad (68)$$

where

$$\Delta f(z) \equiv f(z) - \left\{ \frac{f_V \left(\frac{n_L n_V}{n(z)} - n_V \right) + f_L \left(n_L - \frac{n_L n_V}{n(z)} \right)}{n_L - n_V} \right\} \quad (69)$$

In these quasithermodynamic methods, approximate formulae for $f(z)$ are employed, which all involve $n(z)$. Then the principle is used that the system will adopt the density profile that minimizes γ as given by Eq.(68). When the exact formula for $f(z)$ is used, this method is identical to those discussed already: Eq.(68) becomes identical with Eq.(39), and the minimization condition simply gives again the condition (40) for hydrostatic equilibrium. (It is worth noting that an integrated form of (40) is sometimes used; this expresses the constancy of the 'chemical potential' across the surface.) When approximations are used for $f(z)$, however, then the quasithermodynamic method and those based on (39) need not give the same results. Nevertheless, with sophisticated approximations, analogous to (64), the two groups of methods begin to converge.

Of greater interest is a simple approximation for $f(z)$ which leads to a result that cannot obviously be obtained by any method based on (39). This is based on a major difference between $f(z)$ in an inhomogeneous system and

the free energies per particle f_L and f_V in the uniform bulk phases, namely that while f_L and f_V depend only on the densities n_L and n_V (and T), $f(z)$ cannot be expressed simply as a function of the local density $n(z)$, but depends on the density at all other levels in the fluid. An obvious approximation is to assume that $f(z)$ differs only slightly from $f_u(n(z))$, the free energy per particle of a hypothetical uniform fluid with density $n(z)$. Of course a uniform fluid with density lying between the coexistent densities n_L and n_V cannot exist, but we can obtain $f_u(n(z))$ by analytic continuation of the free energy $f(n)$ elsewhere on the same isotherm. The key assumption is that the difference between $f(z)$ and $f_u(n(z))$ depends only on $dn/dz(z)$, in the following way:

$$f(z) \approx f_u(n(z)) + K \left(\frac{dn(z)}{dz} \right)^2 \quad (70)$$

where K is a constant. Thus (68) becomes

$$\gamma \approx \int_{-\infty}^{\infty} dz \left[\Delta f_u(n(z)) + K \left(\frac{dn(z)}{dz} \right)^2 \right] n(z) \quad (71)$$

where Δf_u is simply (69) with $f(z)$ replaced by f_u . (Symmetry forbids a term in (70) proportional to dn/dz , and any term proportional to d^2n/dz^2 would be equivalent to the term in $(dn/dz)^2$ so far as γ is concerned.)

Now (71) is an integral of the type which can be minimized by the methods of the calculus of variations: the unknown function is $n(z)$, and the integrand involves dn/dz . These methods give, for the condition on $n(z)$,

$$\left[\Delta f_u(n(z)) - K \left(\frac{dn(z)}{dz} \right)^2 \right] n(z) = \text{const} \quad (72)$$

The 'constant' is zero, because dn/dz and Δf_u both vanish in the bulk phases as $|z| \rightarrow \infty$. Therefore, the density profile is determined by

$$\frac{dn(z)}{dz} = \sqrt{\frac{\Delta f_u(n(z))}{K}} \quad (73)$$

and γ can be expressed very simply by transforming (71) into an integral over n :

$$\gamma \approx 2 \sqrt{K} \int_{n_V}^{n_L} dn n \sqrt{\Delta f_u(n)} \quad (74)$$

Thus to calculate γ we require the bulk function $\Delta f_u(n)$ and a value for the 'coupling constant' K .

Finding K requires another theory, but it is instructive to devise a simple model for $\Delta f_u(n)$. It is simpler to consider Δf_u and f_u as functions of

ν rather than n . Then $f_u(\nu)$ for a given T must have the form shown in Fig.(19). This follows from basic thermodynamics: We must have

$$P_L = - \frac{\partial f_u(\nu_L)}{\partial \nu} = P_V = - \frac{\partial f_u(\nu_V)}{\partial \nu} \quad (75)$$

In addition, thermal and mechanical stability of the whole system implies that the Gibbs' function is extremal, i.e. that

$$dG \equiv d(F + PV) = VdP - SdT = 0 \quad (76)$$

If a fraction α is vapour, and $1-\alpha$ is liquid, then

$$G = N\alpha g_V + N(1-\alpha)g_L \quad (77)$$

For this to be stationary at all compositions α , $dG/d\alpha$ must vanish; therefore

$$g_V \equiv P\nu_V + f_V = g_L \equiv P\nu_L + f_L \quad (78)$$

i.e.

$$P = \frac{f_L - f_V}{\nu_V - \nu_L} \quad (79)$$

Taken together with (75), this implies the 'envelope' construction of Fig.(19). As $T \rightarrow T_c$, $\nu_L \rightarrow \nu_V$, and the curve representing Δf_u must become more and more symmetrical between its minima, both as a function of ν and of n . Therefore, we may take

$$\Delta f_u(n) \xrightarrow{T \rightarrow T_c} \beta(n - n_V)^2 (n_L - n)^2 = \beta \left[\left(\frac{n_L - n_V}{2} \right)^2 - \left\{ n - \frac{(n_L + n_V)}{2} \right\}^2 \right] \quad (80)$$

where β is a constant.

Now we can find γ , using (74); we obtain

$$\gamma \approx \frac{\sqrt{\beta K} n_c (n_L - n_V)^3}{3} \quad (81)$$

For the density profile, (73) gives

$$n(z) \approx \frac{n_L + n_V}{2} - \left(\frac{n_L - n_V}{2} \right) \tanh \left[\frac{z(n_L - n_V)}{2} \sqrt{\frac{\beta}{K}} \right] \quad (82)$$

This profile is physically sensible, because its 'width' is proportional to $(n_L - n_V)^{-1}$, and so diverges as $T \rightarrow T_c$ as we would expect. Finally, by assuming that the simple fluid is 'analytic', i.e. that thermodynamic functions can be

expanded in Taylor series about the critical point, we see that the dependence of (80) on $(n_L - n_V)^2$ suggests that

$$n_L - n_V \propto (T_c - T)^{1/2} \quad (83)$$

(van der Waal equation of state leads to the same result). Then (81) gives

$$\gamma \propto (T_c - T)^{3/2} \quad (84)$$

in fair agreement with the empirical results (21) and (22). Of course real fluids, even simple ones, are not analytic.

2. LIQUID-VAPOUR INTERFACES NEAR SOLIDS - CONTACT ANGLE

2.1. Exact macroscopic theories

A liquid-vapour interface meets a solid surface at what is, macroscopically, a line of three-phase contact. The angle θ_c (Fig.20) between the two surfaces, measured through the liquid and perpendicular to this contact line, is called the angle of contact. θ_c is the additional quantity needed in the application of Newtonian mechanics to the problem of determining the forms of the surfaces of liquid masses touching solids. For example, the shapes of droplets resting on solid surfaces can be calculated using Laplace's equation (8) to describe the joint action of gravity and surface tension in curving the liquid surface, but θ_c provides the necessary boundary condition at the three-phase line (Fig.21). It is conventional to call the case $\theta_c < \pi/2$ a wetting situation, and $\theta_c > \pi/2$ a non-wetting situation. If $\theta_c \leq 0$, we have a spreading situation; the liquid covers the whole solid, and there is no three-phase line. In practice, θ_c is found to be very sensitive to contamination of the solid surface, and even (if the droplet is moving) to whether the three-phase line is advancing or receding over the solid; this can be seen very clearly on rainswept window-panes (Fig.22). The concept of contact angle is central to a vast number of natural phenomena and technological processes involving wetting and waterproofing.

The contact angle is a basic mechanical and thermodynamic parameter of the three-phase line, and in Section 2.2 we shall show how it can be calculated directly from molecular interactions. We devote the remainder of this section to relating θ_c to other macroscopic parameters. First we adopt a mechanical approach. Consider the static equilibrium of a mass of liquid, solid and vapour containing unit length of the three-phase line (Fig.20). What forces act? A hydrostatic pressure P_0 acts all round the volume and may be ignored (cf. Fig.8b). Then there are surface tension forces at the intersections of the three interfaces with the volume. The surface tension in the liquid-vapour interface we now call γ_{lv} , that in the solid-liquid interface we call γ_{ls} , and that in the solid-vapour interface we call γ_{sv} . The possibility of the existence of γ_{ls} and γ_{sv} follows from theoretical arguments similar to those in Sections 1.1 and 1.2. Experimentally, it is difficult to detect effects of surface tensions involving solids, because solid surfaces are not mobile — the bulk static stress tensor can contain shear components giving rigidity to the solid. However, thin wires of gold near its melting point shrink unless a

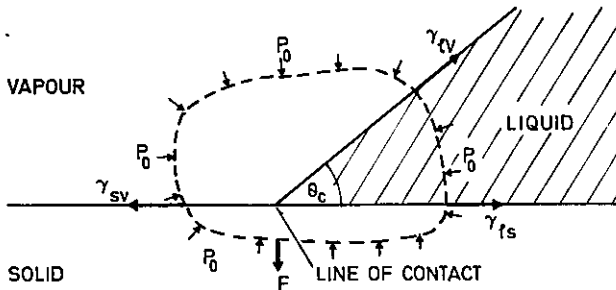


FIG. 20. Forces on matter near line of three-phase contact.

weight is applied (Fig.23), and X-ray diffraction indicates that the lattice spacing in tiny crystals is smaller than in large ones, suggesting that the material is under a high pressure similar in origin to that inside a bubble (Fig.9).

Now we consider the horizontal equilibrium of the forces on the matter shown in Fig.20; we must have

$$\gamma_{lv} \cos \theta_c + \gamma_{ls} = \gamma_{sv}$$

i.e.

$$\cos \theta_c = \frac{\gamma_{sv} - \gamma_{ls}}{\gamma_{lv}} \quad (85)$$

This is known as Young's equation, and expresses the three-phase parameter θ_c in terms of parameters characterizing the three surfaces separately. We must also consider the vertical equilibrium; this can only be achieved if there is a force F deep in the solid acting downwards (Fig.20), to counteract the tendency of the liquid surface tension to pull the solid upwards. We must have

$$F = \gamma_{lv} \sin \theta_c \quad (86)$$

For the solid to exert the force F , it cannot be perfectly rigid, but must strain a little near the line of contact; thus the perimeter of a droplet should lie on a ridge of solid, but the experimental evidence for this is slight and disputed. (For a liquid resting on a liquid, of course, the lack of rigidity leads to the formation of lens-shaped droplets, as with oil on soup.)

Now we adopt a thermodynamic approach. For the liquid mass to be in equilibrium, θ_c must have a value such that no work would be done in an infinitesimal translation of the line of three-phase contact; we are simply applying the principle of virtual work to the static liquid. Let the line of contact move a distance dx in two steps, as shown in Fig. 24. The first step, from (a) to (b), requires the creation of new liquid-vapour interface with area $dx(1 + \cos \theta_c)$; this requires work dW_{ab} , given by

$$dW_{ab} = \gamma_{lv}(1 + \cos \theta_c) dx \quad (87)$$

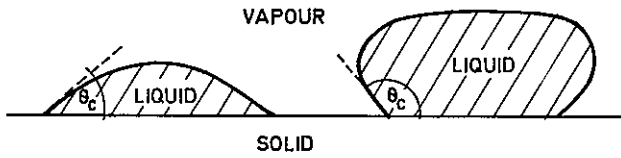


FIG. 21. Acute and obtuse contact angles.

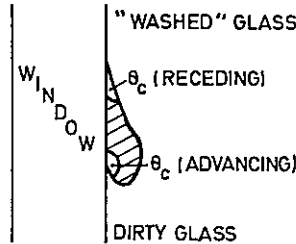


FIG. 22. Receding and advancing contact angles.

The step from (b) to (c) involves the destruction of solid-vapour area dx and liquid-vapour area dx and the creation of solid-liquid area dx , so that the required work dW_{bc} is

$$dW_{bc} = (-\gamma_{sv} - \gamma_{lv} + \gamma_{ls}) dx \tag{88}$$

The total work dW_{ac} is the sum of these quantities, and must be zero, so that

$$0 = \gamma_{lv}(1 + \cos \theta_c) - \gamma_{sv} - \gamma_{lv} + \gamma_{ls} \tag{89}$$

from which (85) follows, and, as expected, the thermodynamic and mechanical approaches yield the same result.

The quantity $-dW_{bc}/dx$ (Eq. 88) is called the work of adhesion, for obvious reasons. If we call it W_a , we have

$$W_a = \gamma_{sv} + \gamma_{lv} - \gamma_{ls} \tag{90}$$

It is a positive quantity, so that work is released in the process bc. Finally, combining (90) and (89), we obtain the useful relation:

$$1 + \cos \theta_c = 2 \cos^2 \frac{\theta_c}{2} = \frac{W_a}{\gamma_{lv}} \tag{91}$$

Because θ_c is so difficult to measure, there do not seem to be any graphs of its variation with temperature (cf. Fig. 11 for γ_{lv}). However, extensive measurements exist for particular solids of the variation of $\cos \theta_c$ with the

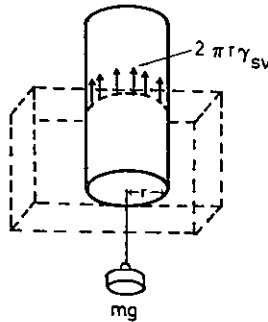


FIG. 23. Surface tension in a solid wire equilibrated by a weight (cf. Fig. 8).

surface tension of the liquid in contact with it (Fig. 25). The resulting 'wettability curves' all have similar forms: $\cos \theta_c$ decreases approximately linearly as $\gamma_{\ell v}$ increases from a value γ_c - the critical surface tension of wetting - which corresponds to $\theta_c = 0$. The limiting tension γ_c is a characteristic of the solid - it is the surface tension of the liquid that just wets the solid. From (85), we have, when $\cos \theta_c = 1$,

$$\gamma_{sv} = \gamma_c + \gamma_{\ell s} \quad (92)$$

where $\gamma_{\ell s}$ is the interfacial tension between the solid and this 'limiting liquid'. In the next section approximate microscopic arguments will be presented suggesting that in this case $\gamma_{\ell s}$ is zero; in actual cases, therefore, we might expect $\gamma_{\ell s}$ to be very small when $\theta_c = 0$, so that

$$\gamma_{sv} \approx \gamma_c \quad (93)$$

but we know of no rigorous macroscopic argument that would convert this approximate equality into an exact equation.

2.2. Approximate microscopic theories

The process (Fig. 24) used in defining contact angle involves no motion of molecules of the solid, so that θ_c cannot depend on the forces between solid molecules. However, the process does involve motion of the fluid molecules relative to one another and to the solid molecules. Therefore θ_c will depend not only on the potential $\phi(R)$ (Fig. 12) between two fluid molecules, but also on the potential $U(R)$ between a fluid and a solid molecule. $U(R)$ is qualitatively similar to $\phi(R)$; in particular, it has an attractive long-range part whose depth we call $\epsilon_{\ell s}$.

The simplest theory for θ_c is based on the idea of 'breaking of bonds', as was the simplest theory for $\gamma_{\ell v}$ which led to Eq. (55). According to (91), we require the work of adhesion W_a , which, looked at in another way, is the work required to pull unit area of liquid away from the solid. By analogy with (54) we may write

$$W_a \approx \epsilon_{\ell s} \times \text{number of liquid-solid bonds/unit area} \quad (94)$$

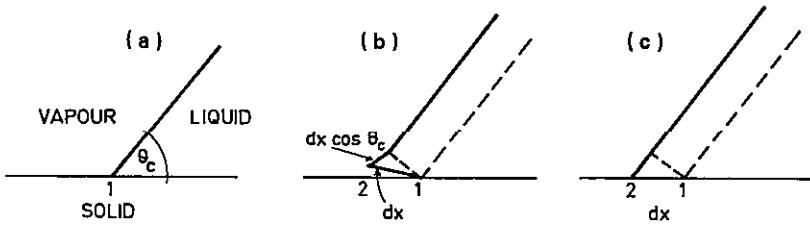


FIG. 24. Infinitesimal translation of contact line.

(there is no factor of $\frac{1}{2}$, because pulling liquid away from solid destroys only one liquid-solid interface, whereas breaking a column of liquid creates two liquid-vapour interfaces). If we now denote the solid co-ordination number and molecular number density by Z_s and n_s , then the number of bonds per unit area is about $\sqrt{Z_l Z_s} / 2 \times \sqrt{n_s^{2/3} n_l^{2/3}}$, so that (94) becomes

$$W_a \approx \frac{\epsilon_{ls}}{2} (Z_l Z_s)^{1/2} (n_s n_l)^{1/3} \tag{95}$$

Combining this with (55) and using (91), we get

$$\cos^2 \frac{\theta_c}{2} \approx \frac{\epsilon_{ls}}{\epsilon_l} \left(\frac{Z_s}{Z_l} \right)^{1/2} \left(\frac{n_s}{n_l} \right)^{1/3} \approx \frac{\epsilon_{ls}}{\epsilon_l} \tag{96}$$

the last member involving approximations that for most liquid-solid systems are unimportant in comparison with those underlying (54) and (94).

This formula for θ_c is crude, admittedly, but it does capture the essential elements of the physics of wetting. If $\epsilon_{ls} / \epsilon_l > 1$ the solid attracts the liquid more than the liquid attracts itself and $\cos^2 \theta_c / 2 > 1$, so that no contact angle exists and the liquid spreads over the solid. If $\frac{1}{2} < \epsilon_{ls} / \epsilon_l < 1$ then $0 < \theta_c < \pi / 2$ and we have the case of wetting. Finally, if $0 < \epsilon_{ls} / \epsilon_l < \frac{1}{2}$, then $\pi / 2 < \theta_c < \pi$ and we have the case of non-wetting, where liquid-liquid attraction considerably exceeds the liquid-solid attraction.

Now we simplify even further, and make a model which explains the qualitative form of the wettability curves of Fig. 25. It is probable that ϵ_{ls} will lie somewhere between ϵ_l and the depth ϵ_s of the solid-solid intermolecular potential function, i.e. that ϵ_{ls} is some mean value of ϵ_l and ϵ_s . There is some reasoning, based on the detailed origin of the intermolecular forces, suggesting that it is correct to take the geometric mean, so that

$$\epsilon_{ls} \approx (\epsilon_l \epsilon_s)^{1/2} \tag{97}$$

and

$$\cos \theta_c \approx 2 \sqrt{\frac{\epsilon_s}{\epsilon_l}} - 1 \approx 2 \sqrt{\frac{\gamma_{sv}}{\gamma_{lv}}} - 1 \tag{98}$$

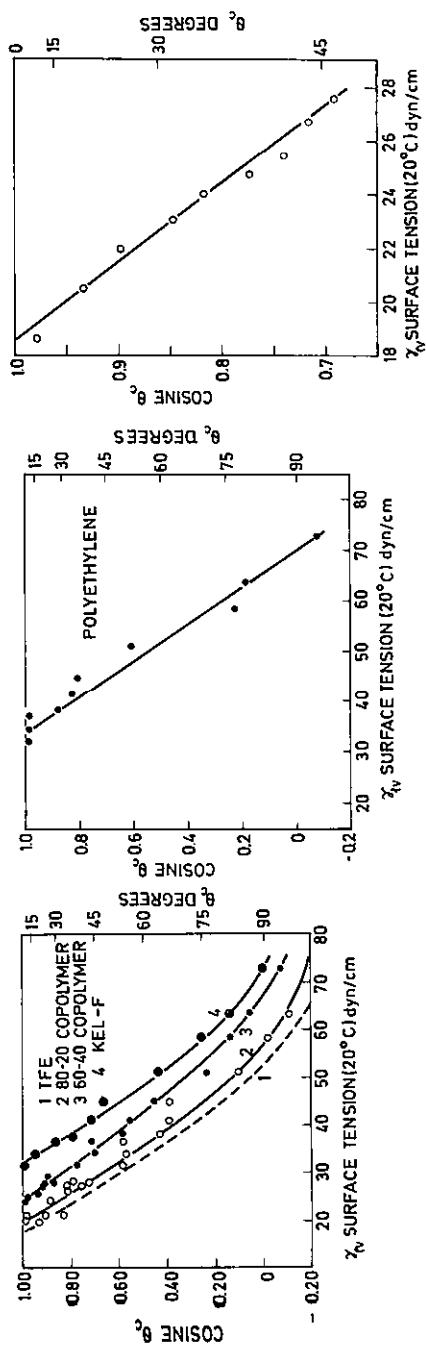


FIG. 25. (a) Wettability of copolymers of polytetrafluoroethylene and polychlorotrifluoroethylene. (b) Wettability of polyethylene; (c) Wettability of polytetrafluoroethylene by the n-alkanes. (From Zisman (1964).)

(In the last member we have used the fact that to this order of approximation γ_{sv} will be given by an approximation analogous to (54), but involving ϵ_s .) This formula does explain Fig.25, at least qualitatively, and moreover predicts that the critical surface tension of wetting γ_c satisfies (93) (any mean value of ϵ_l and ϵ_s yields the same result). For larger values of γ_l , $\cos \theta_c < 1$. However, the formula is quantitatively in error, because it predicts that the ratio of the value of γ_l when $\theta_c = \pi/2$ to the value γ_c should be 4, whereas from Fig.25 this ratio is more like 2.5. Finally, we make a very crude final approximation and assume by analogy with (56) that

$$\epsilon_s \sim kT_m \quad (99)$$

where T_m is the melting point of the solid. This gives

$$\cos^2 \frac{\theta_c}{2} \approx \left(\frac{T_m}{T_c} \right)^{1/2} \quad (100)$$

a formula which might give the general trend of θ_c across families of liquids and solids.

Now we turn to a method for calculating θ_c that is, in principle at least, much more firmly based on exact microscopic theory. We consider the statistical mechanics of the fluid molecules interacting via the potential $\phi(R)$ in an external field from all the solid molecules. If we consider the solid molecules as filling the half-space below the plane $z = 0$, then the potential $\psi(z)$ of this external field is

$$\psi(z) = 2\pi n_s \int_z^\infty dR (R-z) U(R) \quad (101)$$

where $U(R)$ is the fluid-solid molecular interaction potential, and we have averaged over the crystal structure of the solid — this is the 'flat smooth solid' approximation. For solids which are not flat or smooth, and may therefore undulate on all scales from the molecular to the macroscopic, and whose molecules may not be spherical, there will still exist a potential $\psi(\vec{r})$ describing the interaction of a single fluid molecule at \vec{r} with the whole solid, but it will not depend simply on z . We require the molecular number density $n(\vec{r})$ of the liquid-vapour system in the presence of the potential $\psi(\vec{r})$ from the solid. The function $n(\vec{r})$ should show how the liquid-vapour interface recedes from the solid, and for large z the surfaces of constant n should be parallel planes making an angle θ_c with the solid surface, where, of course, θ_c is the contact angle.

To find $n(\vec{r})$ we start from an exact equation that is a generalization of Eq.(40):

$$kT \nabla n(\vec{r}) + n(\vec{r}) \nabla \psi(\vec{r}) + \iiint d\vec{r}' n_2(\vec{r}, \vec{r}') \nabla_{\vec{r}} \phi(|\vec{r} - \vec{r}'|) = 0 \quad (102)$$

This expresses the balance of forces on a volume element of a static inhomogeneous fluid in an external potential. However, we cannot find $n(\vec{r})$ from this

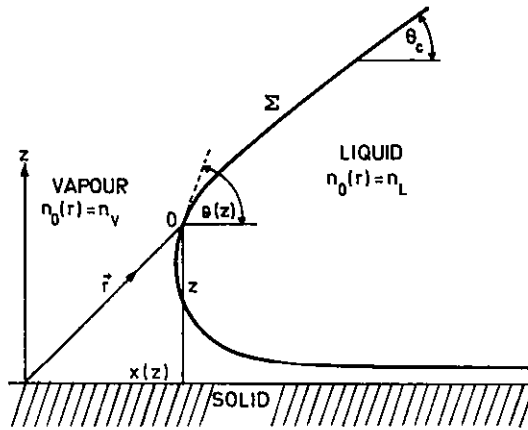


FIG. 26. Discontinuous approximate liquid-vapour interface curving near the solid.

equation, because we do not know the behaviour of $n_0(\vec{r}, \vec{r}')$ near the solid. Therefore we employ again the approximation (60), whereupon (102) gives, after some algebra, the following generalization of (63):

$$n(\vec{r}) \approx n_L \exp \left[-\frac{4\pi n_L}{3kT} \int_0^\infty dR R^3 \phi'(R) g_L(R) - \frac{\psi(\vec{r})}{kT} - \frac{1}{kT} \iiint d\vec{R} S(R) n(\vec{r} + \vec{R}) \right] \quad (103)$$

where

$$S(R) \equiv - \int_R^\infty d\rho g(\rho) \phi'(\rho) \quad (104)$$

Thus we have a non-linear integral equation in which $n(\vec{r})$ is the only unknown function. Any attempt to solve (103) numerically would probably run into great difficulties, since even the simpler but similar equation (40) is computationally barely tractable. Therefore we proceed analytically and investigate how (103) behaves under iteration.

Any 'trial' solution $n_0(\vec{r})$ can be inserted into the exponent on the right-hand side of (103), and this should yield an improved approximation. Let us take for $n_0(\vec{r})$ a density function (Fig. 26) changing discontinuously from n_L to n_v across a 'surface of tension' Σ whose form is initially unknown. After iteration, this will yield a 'smoothed' density function. Clearly the most stable iteration is one where the smoothed $n(\vec{r})$ most closely resembles $n_0(\vec{r})$. To achieve this, we choose the surface Σ in the following way: after iteration Σ must remain a surface on which n is constant. From (103) this implies that

$$\psi(\vec{r}) + \iiint d\vec{R} S(R) n_0(\vec{r} + \vec{R}) = \text{const for all } \vec{r} \text{ on } \Sigma \quad (105)$$

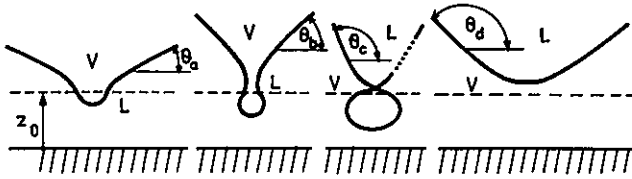


FIG. 27. Impossible liquid-vapour interfaces resulting from incorrect choice of contact angle.

We can expand the integral for small R , since $S(R)$ is a localized function (Eq.(104)). A careful analysis shows that only the lowest term is required; this involves the principal radii of curvature $r_1(\vec{r})$ and $r_2(\vec{r})$ of Σ at \vec{r} and (105) becomes eventually

$$(n_L - n_V) \psi(\vec{r}) + \gamma_{lv} \left(\frac{1}{r_1(\vec{r})} + \frac{1}{r_2(\vec{r})} \right) = \text{const} \tag{106}$$

where γ_{lv} is given by the approximation (58). This is a remarkable result, because it can be derived as follows, without using statistical mechanics: for statistical equilibrium, the pressure $P(\vec{r})$ must satisfy

$$\nabla P(\vec{r}) = \text{external force/unit volume of fluid} = -n_0(\vec{r}) \nabla \psi(\vec{r}) \tag{107}$$

If we assume that $P(\vec{r})$ is constant (e.g. atmospheric pressure) far from the solid, this predicts that the liquid pressure $P_L(\vec{r})$ and vapour pressure $P_V(\vec{r})$ are different at points \vec{r} on Σ , the excess pressure across Σ being

$$P_{ex}(\vec{r}) = P_L(\vec{r}) - P_V(\vec{r}) = -(n_L - n_V) \psi(\vec{r}) \tag{108}$$

But this excess pressure is equilibrated by the surface tension γ_{lv} acting via the curvature of Σ according to Laplace's equation (8) which when combined with (108) yields precisely (106).

To solve (106) and obtain a value for θ_c we treat a flat smooth solid, where $\psi(\vec{r}) = \psi(z)$. Let Σ be given by the curve $x(z)$ (Fig.26); then (106) becomes

$$(n_L - n_V) \psi(z) = - \frac{\gamma_{lv} x''(z)}{[1 + (x'(z))^2]^{3/2}} \tag{109}$$

This can be integrated once, to give

$$\cos \Theta(z) = \cos \theta_c + \frac{n_L - n_V}{\gamma_{lv}} \chi(z) \tag{110}$$

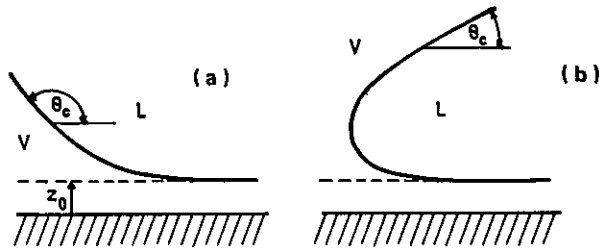


FIG. 28. Form of stable liquid-vapour interface for (a) θ_c obtuse, (b) θ_c acute.

where

$$\tan \Theta(z) \equiv \frac{1}{x'(z)}, \quad \Theta(\infty) = \theta_c \tag{111}$$

(see Fig.26), and

$$\chi(z) \equiv \int_z^\infty d\lambda \psi(\lambda) \tag{112}$$

Starting from any given θ_c , Eq.(110) can be integrated in towards the solid to find the stable form of Σ .

So far θ_c is arbitrary. But it is found that all values of θ_c except one yield surfaces Σ that are either impossible or do not correspond to a liquid resting on a solid (Fig.27). The exceptional value of θ_c is of course the required contact angle. Analysis of Eq.(110) shows that it is given by

$$\cos \frac{\theta_c}{2} \approx \frac{-(n_L - n_V)\chi(z_0)}{2\gamma_{lv}} \approx \frac{n_s \int_{z_0}^\infty dR (R^2 - z_0^2)^2 U'(R)}{(n_L - n_V) \int_0^\infty dR R^4 g_L(R) \phi'(R)} \tag{113}$$

where z_0 is the height at which $\psi(z)$ vanishes. We can regard (113) as a rather sophisticated version of (96), just as (58) was a sophisticated version of (55). To obtain a similar approximation for the work of adhesion W_a , we use (113) and (91), together with (58), to obtain

$$W_a \approx -\pi n_s (n_L - n_V) \int_{z_0}^\infty dR R (R^2 - z_0^2) U(R) \tag{114}$$

which is a sophisticated version of (95). The stable forms of surface Σ are shown in Fig.28 for (a) the non-wetting case and (b) the wetting case. At first sight the behaviour near the solid seems peculiar, but it must be remembered that $z = 0$ is the plane containing the centres of the surface solid molecules,

so we expect the density $n(\vec{r})$ of fluid atoms to be extremely small for \vec{z} smaller than about the hard-core radius of the solid molecules, and this hard-core radius is roughly at $R = z_0$.

With the approximate equations (113) and (114) for θ_c and W_a , we have reached the end of the formal theoretical development. However, it should be pointed out that our approach leads not only to a formula for θ_c , but also to an understanding of the mechanism by which the liquid-vapour interface recedes from the solid while making a definite angle with its surface; in fact, in this microscopic theory, θ_c appears not as a boundary condition (as in macroscopic theory) but as an asymptotic condition applying at distances (microscopically) far from the solid.

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