FARADAY LECTURE*

The Molecular Theory of Small Systems

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1 Systems Large and Small

We are surrounded by (and indeed composed of) small systems—surfaces, bubbles, drops, colloids, emulsions, cells, membranes *etc.*—yet statistical mechanics, our principal theoretical tool for understanding the physical properties of matter at a molecular level is almost entirely the theory of the behaviour of infinitely large systems. Thus from any elementary text-book of thermodynamics we learn that the isotherm that connects the orthobaric states of a liquid and its vapour is a straight horizontal line of constant pressure, equal to the saturated vapour pressure (Figure 1). This result is strictly true, however, only in an infinitely large, and therefore, as I shall argue, in an essentially uniform system. Clearly we need to extend our theoretical understanding if we are to explain at a molecular level the behaviour of the real finite world.

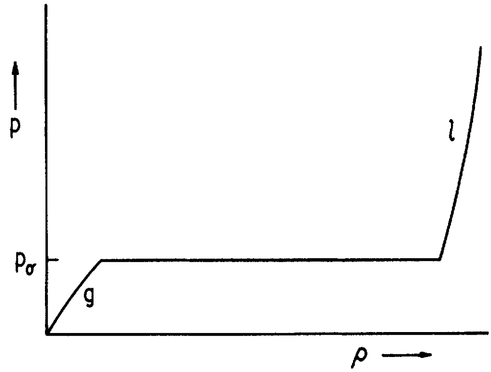

Figure 1 *The pressure as a function of density in a system at a fixed temperature. Only if the system is infinitely large is the central part of the isotherm,* p_σ*, truly horizontal, and the junctions at its ends sharp*

Progress towards this goal has been fitful. A key step was taken at the end of the nineteenth century by Rayleigh and van der Waals, but it is only recently that real progress has been made and the subject put on foundations which, although not entirely solid, are now sufficiently firm for many of our purposes.

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Let us start by looking more closely at the proposition that an arbitrarily large system is a uniform system, even if it comprises more than one phase. Consider a system (the grand-canonical ensemble of statistical mechanics) specified by its volume, to give it a scale, and by the two thermodynamic fields,[1] temperature and chemical potential, T and μ. (We assume for simplicity that the system has only one component.) If the temperature is not too high there will be some value of μ, say $\mu^{\mathrm{l,g}}$, at which the system changes from liquid to gas. If $\mu > \mu^{\mathrm{l,g}}$ the system will be entirely liquid. The number of molecules is not fixed but fluctuates about some average value, N, by an amount of order $N^{1/2}$. Thus if V, and hence N, become sufficiently large the relative fluctuations of N become negligibly small. Similarly if $\mu < \mu^{\mathrm{l,g}}$ the system is entirely gas, and the fluctuations are again negligibly small. If $\mu = \mu^{\mathrm{l,g}}$ exactly then the system contains either liquid or gas or an arbitrary mixture of them. The fluctuations in N are of order N, and so never small. The gas–liquid surface is entirely undefined in such a system which, although two-phase, is essentially uniform.

To produce a non-uniform system we must apply a non-uniform external field that has a potential $v(\boldsymbol{r})$ at point $\boldsymbol{r}$, for example a gravitational potential, $v(z) = mg(z - z_0)$ where m is the mass of a molecule and $z - z_0$ the height above some datum z_0. The state of equilibrium in the system is specified by the condition that the externally fixed potential μ is constant where

$$\mu = \mu(\boldsymbol{r}) + v(\boldsymbol{r}) \tag{1.1}$$

Here $\mu(\boldsymbol{r})$, which is defined by this equation as the difference of μ and $v(\boldsymbol{r})$, is the intrinsic chemical potential at point $\boldsymbol{r}$; a molecular interpretation of this is given below. To a first approximation in an inhomogeneous system it is just the potential of a homogeneous fluid of density equal to that prevailing at $\boldsymbol{r}$. That is

$$\mu(\boldsymbol{r}) = \mu[\rho(\boldsymbol{r}), T] \tag{1.2}$$

where $\rho(\boldsymbol{r})$ is the local density at $\boldsymbol{r}$. We can use this result to see that if $\mu = \mu^{\mathrm{l,g}}$ then the gravitational field separates the system into two distinct phases, liquid for $z < z_0$ and gas for $z > z_0$. At $z = z_0$ there is a planar interface between liquid and gas, and *in* that interface (1.2) is not an adequate approximation.

If $v(\boldsymbol{r})$ is not constant then we have a non-uniform system; formally it is a 'small' system since it is characterized by a finite scale of length determined by the variation of v with $\boldsymbol{r}$. This scale of length may, however, be so large that the system is hardly small in the conventional sense. Thus for nitrogen at 300 K the characteristic length, kT/mg, is 9.0 km, or rather more than the height of Everest. Such a length is long compared with ξ, the correlation length in a liquid which, except at the critical point, is equal to the range of the intermolecular forces, say 1 nm. Under these circumstances (1.2), which we may call the *point-thermodynamic*

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[1] For thermodynamics in terms of *fields* and *densities*, see R. B. Griffiths and J. C. Wheeler, *Phys. Rev.*, 1970, **A2**, 1047; L. Mistura, *Physica*, 1980, **104A**, 181; or, for an introduction, §4.7 of ref. 2, or Appendix 1 of ref. 3.

[2] J. S. Rowlinson and F. L. Swinton, 'Liquids and Liquid Mixtures', 3rd edn, Butterworth, London, 1982.

[3] J. S. Rowlinson and B. Widom, 'Molecular Theory of Capillarity', University Press, Oxford, 1982.

approximation, is valid; the properties of a substance in any phase are just those of that phase in the field-free homogeneous state appropriate to the prevailing density and temperature. The only condition in which (1.2) is invalid in an almost homogeneous system is near a gas–liquid critical point, where ξ is no longer determined by the range of the forces, but diverges to an infinite length.[4] A more important case of invalidity is in systems in which $\rho(\boldsymbol{r})$ is itself varying on the scale of length of the intermolecular forces, and the best example of this is at the boundary between two phases, when even a weak symmetry-breaking potential, such as gravitation, induces enormous changes of density. For a liquid in equilibrium with its vapour near the triple point the change of density over 1 nm can be from 3×10^4 mol m^{-3} to 30 mol m^{-3}. Thus a molecule in the interface at, say, a local density of 3×10^3 mol m^{-3} is influenced by the molecules in fluid at 10-times higher density on one side and 100-times lower on the other. Similarly, $v(\boldsymbol{r})$ arising from a solid phase, *e.g.* graphite or silica, has a range ξ, and so induces similar gradients of density. For convenience I shall, however, use liquid–gas surfaces as the principal example in this review.

What can we say of $\mu(\boldsymbol{r})$ in such a situation? There is, fortunately, a formally exact expression for this potential, which shows clearly its non-local character, and which is well-adapted for calculation by computer simulation. It follows from Widom's potential distribution theorem[5] that

$$\mu(\boldsymbol{r})/kT = \ln[\Lambda\rho(\boldsymbol{r})] - \ln\langle\exp[-u(\boldsymbol{r})/kT]\rangle \qquad (1.3)$$

where Λ is the de Broglie wave length. The first term is the kinetic part of $\mu(\boldsymbol{r})$ and is purely local. The second, the configurational part, is an unusual kind of canonical-ensemble average that can be described by the following thought-experiment. Take a system at equilibrium with a fixed number of molecules N in a fixed volume V, but which may have any degree of inhomogeneity. Clamp the molecules in a typical configuration, add a $(N + 1)^{\text{th}}$ molecule at $\boldsymbol{r}$, and measure $u(\boldsymbol{r})$, the increase in the configurational energy of the system. Withdraw the test molecule and let the system evolve to a new equilibrium molecular configuration. Clamp it again, and repeat the process. The average shown in (1.3) is the canonical average of the Boltzmann factors of the energies $u(\boldsymbol{r})$. This result is important because it is exact, operationally well-defined, and so computable, but it is an unusual form of statistical average and we consider later other approximate forms of this intrinsic potential. Note, however, that the construction of (1.3) implies that $\mu(\boldsymbol{r})$ is non-local in character; that is, it is determined by the state of the system both at point $\boldsymbol{r}$ and at all positions within a distance ξ of $\boldsymbol{r}$. In this respect it differs from the (1.2), to which it reduces if the gradients go to zero, or become negligible on the scale of length of ξ.

Let us see now if other thermodynamic functions can be ascribed to the fluid at point $\boldsymbol{r}$.

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[4] J. V. Sengers and J. M. J. van Leeuwen, *Physica*, 1982, **116A**, 345.

[5] B. Widom, *J. Chem. Phys.*, 1963, **39**, 2808; *J. Stat. Phys.*, 1978, **19**, 563; *J. Phys. Chem.*, 1982, **86**, 869.

2 The Quasi-thermodynamic Assumption

The assertion that it is possible to generate a unique or, at least, a useful and consistent set of thermodynamic functions for the material at a point in an inhomogeneous system is one that can be called the *quasi-thermodynamic assumption*. Ono and Kondo[6] use that description for (1.2), called here the *point-thermodynamic approximation*, but we have seen that this is inadequate. The functions in which we might be interested include the three fields,[1] pressure, temperature, and chemical potential;

$$p(\boldsymbol{r}), \qquad T(\boldsymbol{r}), \qquad \text{and} \qquad \mu(\boldsymbol{r})$$

and the three densities, number density, energy density, and either entropy or free-energy density (we choose the latter);

$$\rho(\boldsymbol{r}), \qquad \phi(\boldsymbol{r}), \qquad \text{and} \qquad \psi(\boldsymbol{r}).$$

The second group can be defined by describing about $\boldsymbol{r}$ a small volume δV, which contains δN molecules, has an energy δU and a free energy δF. The three densities are the limits of the ratios $\delta N/\delta V$, $\delta U/\delta V$, and $\delta F/\delta V$, as δV shrinks to zero around the point $\boldsymbol{r}$.

The simplest of these is $\rho(\boldsymbol{r})$ for there can be no doubt about whether or not the centre of a molecule is in δV. Number density is a one-body function and is always well-defined. (It is true that in some circumstances the fluctuations of $\rho(\boldsymbol{r})$ in an interface can be comparable with the function itself, but that is a problem of a different kind.[2,7]) Since $\rho(\boldsymbol{r})$ is well-defined, so is $T(\boldsymbol{r})$, since temperature is simply a measure of the local density of kinetic energy, and this is again a one-body function. In fact, $T(\boldsymbol{r}) = T$, a constant, in any system at equilibrium. We have seen that $\mu(\boldsymbol{r})$ is also well-defined, but note that it is μ of (1.1), not $\mu(\boldsymbol{r})$, that is constant throughout a system at equilibrium.

With $p(\boldsymbol{r})$, $\phi(\boldsymbol{r})$, and $\psi(\boldsymbol{r})$ the position is more difficult. The difficulty is clearest with $\phi(\boldsymbol{r})$, for δU, the energy of a small sample of matter, is not uniquely defined. It is made up of the interactions of molecular pairs and larger groups, in which some of the molecules are within δV and some are not. There is no unique way of deciding how much of this energy is to be ascribed to δV and how much to the surroundings. There is a similar problem with $p(\boldsymbol{r})$ which is the mean value of the negative of the stress across an element of area. In an inhomogeneous system pressure is a tensor $\boldsymbol{p}(\boldsymbol{r})$ since the element can have different orientations with respect to the gradient of $\rho(\boldsymbol{r})$. The stress has two parts, an isotropic kinetic part due to the momentum carried by the molecules, $kT\rho(\boldsymbol{r})\mathbf{1}$, which is unambiguously defined, and a configurational or interaction part, which is not. As for $\phi(\boldsymbol{r})$, there is no unique way of deciding which intermolecular forces contribute to the stress across an element of area.

At a planar interface the tensor has only two components, one normal to the surface and one parallel or transverse to it; both are functions only of height z, and are denoted $p_N(z)$ and $p_T(z)$. Mechanical equilibrium requires that $p_N(z)$ is a

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[6] S. Ono and S. Kondo, in 'Encyclopedia of Physics', ed. S. Flügge, Vol. 10, Springer, Berlin, 1960, p. 134.

[7] R. Evans, *Mol. Phys.*, 1981, **42**, 1169.

constant; $p_N(z) = p^l = p^g$ at a liquid surface, where p^l and p^g are the pressures in the liquid and gaseous phases. The transverse component is also equal to p^l and p^g well away from the interface, but is large and negative, and not uniquely defined in the interface itself. The most commonly used forms of $p_T(z)$ are those associated with the names of Irving and Kirkwood, and Harasima,[8] but there are infinitely many other possibilities.[9] Figures 2 and 3 show the density profile $\rho(z)$ and the two

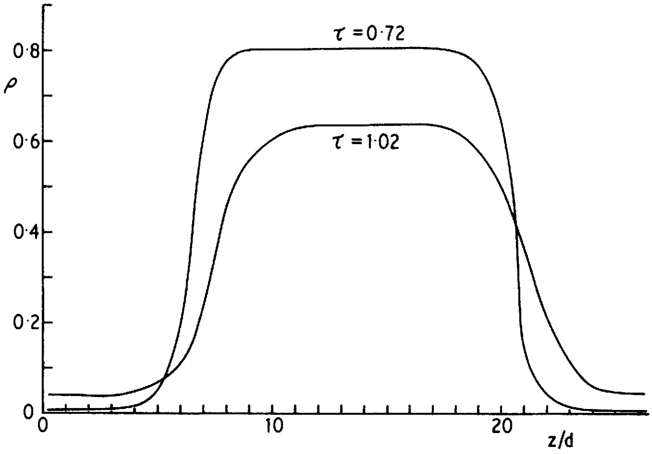

Figure 2 *The density $\rho = Nd^3/V$ as a function of distance z for a sheet of liquid between two gas phases,[10] at two temperatures, $\tau = kT/\varepsilon$. The parameters d and ε are the collision diameter and depth of a truncated Lennard-Jones* (12,6) *potential*

transverse components $[p_T(z)]_{IK}$ and $[p_T(z)]_H$ from a computer simulation of a film of a liquid about 15 molecular diameters thick.[10] The intermolecular potential is a truncated Lennard-Jones (12,6) potential. The difference between the two forms is small but has one interesting feature; on the gas side of the interface in the IK version there is a small layer of fluid that is in weak compression, not in tension, since $p_T(z) > p_N$. This feature cannot be seen in the H version. At higher temperatures it is seen in both, but is more prominent in the IK version.

Although the energy density and the pressure are not defined uniquely, they must satisfy certain constraints, since measurable physical properties cannot depend on how we choose to describe them. Thus the total energy, U, and the excess energy associated with a surface, ϕ^E, are measurable and so, whatever definition of $\phi(\mathbf{r})$ we choose,

$$\int \phi(\mathbf{r})\mathrm{d}\mathbf{r} = U \qquad (2.1)$$

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[8] J. H. Irving and J. G. Kirkwood, *J. Chem. Phys.*, 1950, **18**, 817; A. Harasima, *Adv. Chem. Phys.*, 1958, **1**, 203.

[9] P. Schofield and J. R. Henderson, *Proc. R. Soc. London, Ser. A*, 1982, **379**, 231; J. R. Henderson and P. Schofield, *ibid.* 1982, **382**, 211.

[10] J. P. R. B. Walton, D. J. Tildesley, and J. S. Rowlinson, *Mol. Phys.*, 1983, **48**, 1357.

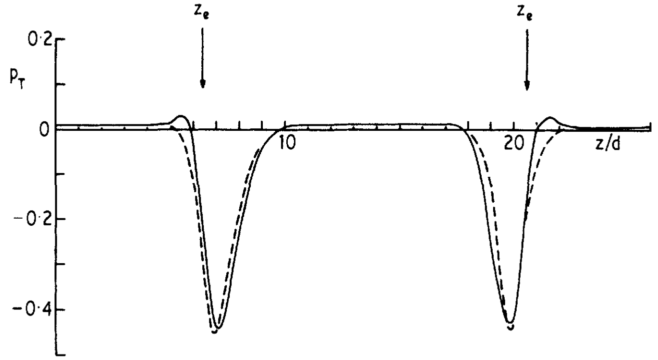

Figure 3 *The transverse component of the pressure tensor, in units of ε/d^3, for the sheet of liquid in Figure 2 ($\tau = 0.72$). The full line is p_T according to the recipe of Irving and Kirkwood, and the dashed line according to that of Harasima. The horizonal flat portions are in the homogeneous phases, where $p_T = p_N$. The distances marked z_e are the positions of the equimolar Gibbs surfaces, from Figure 2*

$$\int_{z_e}^{\infty}[\phi(z)-\phi^{g}]\mathrm{d}z + \int_{-\infty}^{z_e}[\phi(z)-\phi^{l}]\mathrm{d}z = \phi^{E} \tag{2.2}$$

where z_e is the equimolar Gibbs dividing surface,[3] and ϕ^g and ϕ^l are the unambiguous energy densities of gas and liquid. Similarly the zeroth moment of the difference $p_N - p_T$ is the surface tension, σ, and so is invariant:

$$\int_{-\infty}^{\infty}\mathrm{d}z[p_N(z)-p_T(z)] = \sigma \tag{2.3}$$

However the first moment, which describes where the tension acts, or the surface of tension, z_s, is not invariant to choice of pressure tensor:[9,10]

$$\int_{-\infty}^{\infty}z\mathrm{d}z[p_N(z)-p_T(z)] = \sigma z_s \tag{2.4}$$

but $(z_s)_{\mathrm{IK}} \neq (z_s)_{\mathrm{H}}$. The difference is small (Table 1), for the tension must act 'in' the

Table 1 *The surface of tension σ (in units of ε/d^2) and the surfaces of tension z_s (in units of d) for a truncated Lennard-Jones liquid of collision diameter d, and potential depth ε. The subscripts stand for Irving-Kirkwood and Harasima*[10]

$kT/\varepsilon = 0.723$

$\sigma_{\mathrm{IK}} = \sigma_{\mathrm{H}} = 0.680$
$(z_e - z_s)_{\mathrm{IK}} = 1.0$
$(z_e - z_s)_{\mathrm{H}} = 0.7$

$kT/\varepsilon = 1.013$

$\sigma_{\mathrm{IK}} = \sigma_{\mathrm{H}} = 0.237$
$(z_e - z_s)_{\mathrm{IK}} = 2.7$
$(z_e - z_s)_{\mathrm{H}} = 2.2$

interface and so the uncertainty in z_s is less than 0.5 molecular diameter, with $(z_s)_{IK}$ lying on the liquid side of $(z_s)_H$. This difference is smaller than the thickness of an interface, which is typically 3 molecular diameters or more. The conclusion is that z_s is neither definable nor measurable from the pressure tensor with a precision greater than ξ, which is the range of the intermolecular forces and also the thickness of the interface.

The two invariants σ and ϕ^E are related by a Gibbs–Helmholtz equation

$$\phi^E = \sigma - T(\mathrm{d}\sigma/\mathrm{d}T). \tag{2.5}$$

The remaining function is the free-energy density, $\psi(\boldsymbol{r})$, for which there is an apparently exact expression in terms of an infinite set of direct correlation functions,[11] each of which must be known as a function of density from zero to $\rho(\boldsymbol{r})$, a range which may include metastable states. An approximate but more accessible version of this is discussed below. The average Boltzmann factor in (1.3) can also be written in this form,[11] or in a more compact but still inaccessible form[12] in terms of the total pair correlation function at all densities up to $\rho(\boldsymbol{r})$. More useful approximations are again discussed later. Since ψ may or may not be well-defined, but ϕ is certainly not, it follows that there is no unique way of breaking ψ down into an energy density and an entropy density in an inhomogeneous system.

Let me close this section with a speculation on why $T(\boldsymbol{r})$ and $\mu(\boldsymbol{r})$ are uniquely defined, but the third field of classical thermodynamics, $p(\boldsymbol{r})$, is not. In uniform multi-phase systems, p, T, and μ enter symmetrically into the conditions of equilibrium. Any of them, or virtually any combination of them,[1] can be taken as the potential, the independent variable that can be expressed in terms of the other two fields. Thus we can write indifferently

$$\mathrm{d}\mu = -s\mathrm{d}T + v\mathrm{d}p$$

or

$$\mathrm{d}p = \eta\mathrm{d}T + \rho\mathrm{d}\mu \tag{2.6}$$

or

$$\mathrm{d}(p/T) = -\phi\mathrm{d}(1/T) + \rho\mathrm{d}(\mu/T) \quad etc.$$

where s and v are the entropy and volume per mole and η is the entropy density. Nevertheless in inhomogeneous systems p plays a different role from T and μ. The distinction is not between one-body and many-body functions, for T is one-body and p and μ are many-body. Possibly it is related to the different tensorial rank of the three properties. In a fluid of spherical molecules their collisions are characterized by three conserved properties—conservation of mass, of energy, and of momentum, which are, respectively, a scalar, a scalar, and a vector. Away from equilibrium the flow of these quantities is governed by the size of the gradients of μ (diffusion), of T (thermal conductivity), and of $\boldsymbol{p}$ (viscosity). Since momentum is a vector, $\boldsymbol{p}$ is a tensor, and there is more than one coefficient of viscosity.[13]

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[11] J. L. Lebowitz and J. K. Percus, *J. Math. Phys.*, 1963, **4**, 116, 248; A. J. M. Yang, P. D. Fleming, and J. H. Gibbs, *J. Chem. Phys.*, 1976, **64**, 3732; R. F. Kayser and H. J. Raveché, to be published.

[12] T. L. Hill, *J. Chem. Phys.*, 1959, **30**, 1521.

[13] S. Chapman and T. G. Cowling, 'The Mathematical Theory of Non-Uniform Gases', University Press, Cambridge, 1939; G. C. Maitland, M. Rigby, E. B. Smith, and W. A. Wakeham, 'Intermolecular Forces', University Press, Oxford, 1982.

Equilibrium is the state in which these gradients vanish;

$$\nabla\mu(\boldsymbol{r}) = 0 \qquad \nabla T(\boldsymbol{r}) = 0 \qquad \nabla \cdot \boldsymbol{p}(\boldsymbol{r}) = 0 \tag{2.7}$$

These equations imply that, even in a non-uniform system at equilibrium, μ and T are constant, but not that $\boldsymbol{p}$ is a constant, for the gradient of a tensor can vanish without all its components being constant, as we shall see below in the discussion of spherical drops of liquids. Thus μ and T are simpler and, as we have seen, less arbitrary functions than p. This line of thought could perhaps be followed further, for if the molecules are non-spherical then angular momentum is also conserved and the pressure becomes an even more complicated property.[14]

3 Local and Non-local Approximations to the Chemical Potential and Free-energy Density

The chemical potential $\mu(\boldsymbol{r})$ and the free-energy density $\psi(\boldsymbol{r})$ have formally exact expressions that are not practically useful. The crudest approximation to them, that of point-thermodynamics, (1.2), and its analogue $\psi(\boldsymbol{r}) = \psi[\rho(\boldsymbol{r}),T]$, are adequate only when the inhomogenity is weak on the scale of length of ξ. We need a better approximation to treat the interfaces between phases (the most important kind of small system), that is, to be able to describe accurately their structure and properties at a molecular level.

The first attempts in this direction, of which that of Rayleigh[15] is the most complete, started with $\phi(\boldsymbol{r})$, not $\psi(\boldsymbol{r})$. He argued that the departure of $\phi(\boldsymbol{r}_1)$ from the point-thermodynamic approximation depends on the density of molecules near but not at $\boldsymbol{r}_1$, that is on $\rho(\boldsymbol{r}_2)$, where $|\boldsymbol{r}_2 - \boldsymbol{r}_1| < \xi$. This density can be obtained from a Taylor expansion about $\boldsymbol{r}_1$;

$$\rho(\boldsymbol{r}_2) = \rho(\boldsymbol{r}_1) + (\boldsymbol{r}_{12}\cdot\nabla)\rho(\boldsymbol{r}_1) + \tfrac{1}{2}(\boldsymbol{r}_{12}\cdot\nabla)^2\rho(\boldsymbol{r}_1) + \cdots \tag{3.1}$$

The first derivative vanishes on integrating over $\boldsymbol{r}_2$, leaving only the second-order term. This line of argument led Rayleigh to an expression for σ of a planar liquid surface of the form

$$\sigma = m\int_{-\infty}^{\infty} \mathrm{d}z\rho'(z)^2 \tag{3.2}$$

where m is the second moment of the attractive part of the intermolecular potential, u_a,

$$m = -\tfrac{1}{6}\int_{d} r_{12}^2 u_a(r_{12})\mathrm{d}\boldsymbol{r}_{12} \tag{3.3}$$

However, the energy density is not an appropriate route to a surface tension, which is an excess free energy, *cf.* (2.5), and Rayleigh's calculation was repeated (apparently independently) by van der Waals[16] but with $\psi(\boldsymbol{r})$ in place of $\phi(\boldsymbol{r})$. He obtained the celebrated 'square-gradient' approximation to $\psi(\boldsymbol{r})$,

$$\psi(\boldsymbol{r}) = \psi[\rho(\boldsymbol{r}),T] + \tfrac{1}{2}m|\nabla\rho(\boldsymbol{r})|^2 + \cdots \tag{3.4}$$

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[14] D. J. Evans, *J. Stat. Phys.*, 1979, **20**, 547.

[15] Lord Rayleigh, *Phil. Mag.*, 1892, 33, 209.

[16] J. D. van der Waals, *Z. Phys. Chem.*, 1894, 13, 657; English translation in *J. Stat. Phys.*, 1979, **20**, 197.

where m and the surface tension are again given by (3.3) and (3.2). This result lay unused for many years until it was re-derived (again independently) by Cahn and Hilliard[17] in 1958, since when it has been used extensively by Cahn, Widom, Davis, Sullivan, Evans, and others, for tackling a wide range of problems such as surface wetting and phase transitions, critical and tricritical points, line tension, *etc.*[18] Its simplicity allows it to be used in situations that are complicated at the molecular level. The second-order terms on which it is based sometimes appear as second derivatives $\rho''(z)$, and sometimes as squares of first derivatives, $\rho'(z)^2$, but the two are often thermodynamically equivalent since macroscopic properties require an integration over z, after which the two are related by an integration by parts, since both derivatives are zero except in the interface,

$$\int \mathrm{d}z\rho(z)\rho''(z) = \int \mathrm{d}z\rho'(z)^2 \tag{3.5}$$

Let us call this square-gradient form a *local approximation* since it is less drastic than the point-thermodynamic approximation, but still expresses $\psi(\boldsymbol{r})$ in terms of $\rho(\boldsymbol{r})$ and its derivatives. The next stage is a *non-local approximation** in which the difference in properties over the range of the molecular correlations, ξ, is expressed explicitly. This can be generated from a functional expansion of the formally exact expression for $\psi(\boldsymbol{r})$ already mentioned:

$$\psi(\boldsymbol{r}_1) = \psi[\rho(\boldsymbol{r}_1)] - \tfrac{1}{2}kT\rho(\boldsymbol{r}_1)\int \mathrm{d}\boldsymbol{r}_2[\rho(\boldsymbol{r}_2) - \rho(\boldsymbol{r}_1)]c(\boldsymbol{r}_1,\boldsymbol{r}_2) \tag{3.6}$$

where $c(\boldsymbol{r}_1,\boldsymbol{r}_2)$ is the direct correlation function between points 1 and 2, which is related to the total correlation function $h(\boldsymbol{r}_1,\boldsymbol{r}_2) = g(\boldsymbol{r}_1,\boldsymbol{r}_2) - 1$ by the Ornstein-Zernike equation

$$h(\boldsymbol{r}_1,\boldsymbol{r}_2) = c(\boldsymbol{r}_1,\boldsymbol{r}_2) + \int \mathrm{d}\boldsymbol{r}_3\, c(\boldsymbol{r}_1,\boldsymbol{r}_3)\rho(\boldsymbol{r}_3)h(\boldsymbol{r}_3,\boldsymbol{r}_2) \tag{3.7}$$

and $g(\boldsymbol{r}_1,\boldsymbol{r}_2)$ is the two-body distribution function. A related non-local approximation can be obtained by a perturbation expansion and has been called by Abraham[21] a generalized van der Waals approximation:

$$\psi(\boldsymbol{r}_1) = \psi[\rho(\boldsymbol{r}_1)] + \tfrac{1}{2}\rho(\boldsymbol{r}_1)\int \mathrm{d}\boldsymbol{r}_2\, u_a(r_{12})g_0(r_{12},\rho(\boldsymbol{r}_1))[\rho(\boldsymbol{r}_2) - \rho(\boldsymbol{r}_1)] \tag{3.8}$$

where g_0 is the two-body distribution function in a hypothetical uniform fluid of density $\rho(\boldsymbol{r}_1)$, over which the attractive potential u_a is averaged. The exact expression for $\mu(\boldsymbol{r})$, (1.3), is also non-local, as is clear from its form.

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* This is the usual nomenclature,[3,19,20] but Sengers and van Leeuwen[4] call (1.2) *local* and (3.4) *non-local*. They do not use (3.6).

[17] J. W. Cahn and J. E. Hilliard, *J. Chem. Phys.*, 1958, **28**, 258.

[18] See ref. 3, Chap. 3, 8. and 9.

[19] J. A. Barker and J. R. Henderson, *J. Chem. Phys.*, 1982, **76**, 6303.

[20] J. K. Percus, in 'The Liquid State of Matter, Studies in Statistical Mechanics', Vol. 8, p. 31, ed. E. W. Montroll and J. L. Lebowitz, North-Holland, Amsterdam, 1982.

[21] F. F. Abraham, *J. Chem. Phys.*, 1975, **63**, 157, 163; *Phys. Rep.*, 1979, **53**, 93.

The non-local approximations are closer to the exact results but may contain correlation functions, such as $c(\boldsymbol{r}_1,\boldsymbol{r}_2)$ or $g(\boldsymbol{r}_1,\boldsymbol{r}_2)$, about which we know little. In a planar surface they are functions of three variables, say r_{12}, z_1, and z_2, and so much more difficult to estimate, even by computer simulation, than the corresponding function of one variable in a homogeneous fluid. A square-gradient expansion, or local approximation, can be derived from a non-local approximation by a Taylor expansion, but leads to a different expression for the coefficient, *m*, *e.g.*

$$m = -\frac{kT}{6}\int \mathrm{d}\boldsymbol{r}_{12}\, r_{12}^2\, c(r_{12}) \tag{3.9}$$

where $c(r_{12})$ is the direct correlation function of a uniform, but perhaps hypothetical, fluid. This expression and (3.3) are quite similar for a liquid since $kTc(r_{12}) \approx -u(r_{12})$ is the well-known mean-spherical approximation.

The distinction between local and non-local approximations is not merely one of numerical accuracy but can lead to qualitative differences in systems with attractive intermolecular forces that fall off only as an inverse power of r_{12}. If the potential were of strictly finite range, as for the square-well potential, or if it fell off exponentially rapidly with separation, then the gradient expansions such as (3.4) are convergent, and the coefficient *m* and its analogues in higher terms are convergent integrals (except at the gas–liquid critical point). The potential field outside a slab of a condensed phase, solid or liquid, would then also be of finite range or would fall off exponentially with distance from the surface. Hence the 'wings' of the profile of a liquid surface (Figure 2) would approach their asymptotic limits, ρ^{l} and ρ^{g}, exponentially. Real potentials, however, are neither finite nor exponential, but fall off as r_{12}^{-6} (or r_{12}^{-7} at extremely large distances that are not relevant here). For such potentials *m* is again finite (except at the critical point) but its higher analogues are divergent integrals. The gradient expansion (3.4) is thus, at best, an asymptotic expansion. Moreover the potential outside a slab of a condensed phase, and hence also the wings of a liquid–gas profile, now falls off only as z^{-3}, not exponentially. The non-local approximations avoid these divergent expansions and lead correctly to z^{-3} wings.[19,22] The difference between z^{-3} and an exponential fall off is small numerically, but it is conceptually important, and can lead to qualitative differences in the predicted thickness of wetting layers of a second liquid at a gas–liquid surface.[22–24]

This distinction between local and non-local expressions needs further exploration, since second-order differential equations can generally be converted into an integral form and *vice versa*. Nevertheless it is clear physically that (3.6) and (3.8) invoke the properties of the fluid-not-at-$\boldsymbol{r}_1$, in a way that (3.4) does not.

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[22] P. G. de Gennes, *Physique Lett.*, 1981, **42**, L-377.

[23] O'D. Kwon, D. Beaglehole, W. W. Webb, B. Widom, J. W. Schmidt, J. W. Cahn, M. R. Moldover, and B. Stephenson, *Phys. Rev. Lett.*, 1982, **48**, 125.

[24] P. Tarazona, M. M. Telo da Gama, and R. Evans, *Mol. Phys.*, 1983, **49**, 283, 301.

4 Curved Surfaces

Two scales of length have been used so far, the gravitational length kT/mg which is so large as to be of no real interest, and the correlation length ξ, which is also a measure of the thickness of a liquid surface at all temperatures, and of the range of the intermolecular forces, say 1 nm, away from critical points. With curved surfaces a third length enters the physics of small systems, the radius of curvature,* R, and the length with which this can be most usefully compared is the capillary constant, a, defined as follows. The difference of mass density $\Delta^{\alpha\beta}$ between two phases, α and β, each composed of species 1, 2, ..., i, ..., of molecular mass $m_1, m_2, \ldots, m_i, \ldots$ is

$$\Delta^{\alpha\beta} = \sum_i \left| m_i^\alpha \rho_i^\alpha - m_i^\beta \rho_i^\beta \right| \tag{4.1}$$

The capillary constant $a^{\alpha\beta}$ is given by

$$(a^{\alpha\beta})^2 = 2\sigma^{\alpha\beta}/g\Delta^{\alpha\beta} \tag{4.2}$$

It is typically 10^{-3} m for a liquid–gas surface, *e.g.* 3.93 mm for water at 0 °C. If the radius of curvature R is large compared with a then the properties of a system are controlled by gravity and the surface tension can often be ignored. Thus waves on the sea have a wave-length, and so a curvature, large compared with a, and their propagation is entirely controlled by gravity. If R is comparable with a then both gravity and surface tension are important and from their interplay follow most of the conventional methods of measuring surface tension. If R is small compared with a then surface tension is dominant and gravity can be ignored. This is the case with very short waves, capillary waves, on the surface of a liquid.

The capillary constant can become large on a laboratory scale if either Δ or g tends to zero. The first limit is achieved in a Plateau tank when the density of two liquids is so closely matched that the form of the surface between them is controlled by surface tension alone. The second is achieved in free-fall or, for a longer time, in space flight where g is typically reduced to 10^{-5} or less of its value on the earth's surface.

The mechanical condition of equilibrium in the presence of an external field is

$$\nabla \cdot \boldsymbol{p}(\boldsymbol{r}) + \rho(\boldsymbol{r})v(\boldsymbol{r}) = 0 \tag{4.3}$$

which reduces to (2.7) if $R \ll a$, that is for very small drops and bubbles. At a spherical surface this condition reduces to[28]

$$\frac{\mathrm{d}}{\mathrm{d}r}[r^n p_N(r)] = r^{n-1}[(n-2)p_N(r) + 2p_T(r)] \tag{4.4}$$

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* For generality we should consider the two principal radii of a surface of arbitrary curvature, R_1 and R_2, but the discussion is restricted to spherical surfaces for which $R_1 = R_2 = R$, since the theory of surfaces of arbitrary curvature is, I believe, not yet fully developed.[25]

[25] Early work in terms of the pressure tensor is discussed in §4.8 of ref. 3. Recent work on the thermodynamics by L. Boruvka and A. W. Neumann, *J. Chem. Phys.*, 1977, **66**, 5464 and on the statistical mechanics by J. K. Percus (ref. 20) is critically discussed in refs. 26 and 27 respectively.

[26] J. S. Rowlinson, *J. Chem. Soc., Faraday Trans. 2*, 1983, **79**, 77.

[27] S. J. Hemingway, J. S. Rowlinson, and J. P. R. B. Walton, *J. Chem. Soc., Faraday Trans. 2*, 1983, in press.

[28] F. P. Buff, *J. Chem. Phys.*, 1955, **23**, 419; see also §4.8 of ref. 3. Mechanical equilibrium is implied by the condition of constant chemical potential; J. R. Henderson, *Mol. Phys.*, 1983, **48**, 715.

where $p_N(r)$ and $p_T(r)$ are the normal and transverse components at distance r from the centre, and n can have any value. By integration of this equation ($n = 0$) from a point R^α inside phase α to R^β in phase β, we have

$$p^\alpha - p^\beta = \int_{R^\alpha}^{R^\beta} r^{-1}\mathrm{d}r[p_N(r) - p_T(r)] \tag{4.5}$$

The excess pressure inside a drop of phase α, from obvious mechanical arguments that go back to Laplace, is related to the tension in the interface and to the radius R_s at which that tension acts;

$$p^\alpha - p^\beta = 2\sigma/R_s \tag{4.6}$$

Thus the surface of tension, or here, the radius of tension, plays a more important role in the properties of curved than it does for planar surfaces.

Since $(p^\alpha - p^\beta)$ is the difference between the (scalar) pressure in two homogeneous phases it is invariant to the choice of the form of the pressure tensor in the surface. Hence the ratio σ/R_s is also invariant, as is the equation of mechanical equilibrium (4.4) from which it is derived, and the integral in (4.5). Preliminary results for $(p_N)_{\mathrm{IK}}$ and $(p_T)_{\mathrm{IK}}$ by computer simulation are shown in Figure 4, but greater accuracy is needed before $(p_N)_{\mathrm{H}}$ and $(p_T)_{\mathrm{H}}$ can be found, and so it is too early to say much about the changes in the apparent values of R_s consequent upon changes in the choice of p.

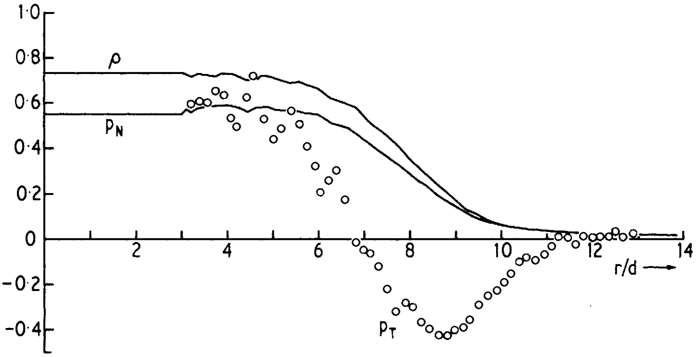

Figure 4 *The density, ρ, and the normal component of the pressure, $p_N(r)$ as obtained at $\tau = 0.83$ for a drop of liquid of 2048 molecules. The transverse component $p_T(r)$ is obtained from (4.4) with $n = 2$, and is shown by the points. Both p_N and p_T are for the Irving-Kirkwood convention*

The difficulty of obtaining R_s from mechanical arguments, *via* p_N and p_T, can be overcome by appealing to thermodynamic and statistical arguments.[29] Tolman[30]

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[29] S. J. Hemingway, J. R. Henderson, and J. S. Rowlinson, *Faraday Symp. Chem. Soc.*, 1981, **19**, 33.

[30] R. C. Tolman, *J. Chem. Phys.*, 1949, **17**, 118, 333.

showed that the change of σ with curvature can be expressed

$$\sigma = \sigma_\infty \left(1 - \frac{2\delta}{R_e}\right) \qquad \delta = R_e - R_s \tag{4.7}$$

where σ is the tension of a surface of equimolar radius R_e, and σ_∞ that of the planar surface. (Tolman, in fact, obtained also higher terms in $1/R_e^2$, *etc.*, but we have shown that these are without physical meaning.[9,29]) The tension of the curved surface can be expressed also in terms of an integral over the direct correlation function and so the consistency of (4.7) checked.[27,29] This route to R_s avoids the uncertainty of that *via* the pressure tensor, although the imprecision there is probably not very serious since $(z_s)_{IK} - (z_s)_H$ is only about 1/6 of δ.

Since δ is only of the order of the thickness of the surface, or of the range of the intermolecular forces, say 1 nm, it follows that σ differs from σ_∞ only for very small drops and bubbles; a radius of 10^{-7} m is needed to detect a change in σ of 1%. The measurements of Fisher and Israelachvili[31] come close to this size but have not yet revealed unambiguously any change from σ_∞.

5 Line Tension

If we place a trace of a light hydrocarbon on a clean water surface it spreads over it as a continuous film. A heavier hydrocarbon (C_8 and above[32]) does not spread but forms a set of liquid lenses on the water surface. A hydrocarbon of about the critical length can be made to go from the spreading or wetting regime to the non-wetting by lowering the temperature. Such transitions have been much studied lately, experimentally by ellipsometry,[33] and theoretically[34] with a square-gradient approximation for ψ, but it is the thermodynamics of the non-wetting regime that is the subject of this section, since it reveals a further type of inhomogenity and its consequence—namely a line tension.

The free-energy of two phases, α and β, separated by a $\alpha\beta$ interface is not $(V^\alpha\psi^\alpha + V^\beta\psi^\beta)$, where V^α and V^β are the volumes of the phases measured to the equimolar dividing surface, but differs from this sum by a term proportional to the interfacial area, $A^{\alpha\beta}\sigma^{\alpha\beta}$. Similarly if three phases meet in three surfaces, and if the three surfaces meet in a line, then the free-energy is not to be accounted for solely by the volume and surface terms but includes a term proportional to the length of three-phase contact $L^{\alpha\beta\gamma}$. That is, the line tension, $\tau^{\alpha\beta\gamma}$, is defined by

$$F = V^\alpha\psi^\alpha + V^\beta\psi^\beta + V^\gamma\psi^\gamma + A^{\alpha\beta}\sigma^{\alpha\beta} + A^{\alpha\gamma}\sigma^{\alpha\gamma} + A^{\beta\gamma}\sigma^{\beta\gamma} + L^{\alpha\beta\gamma}\tau^{\alpha\beta\gamma} \tag{5.1}$$

Unlike surface tension, which is always positive, the line tension[35] can have either sign.

In principle we could go one stage further, and envisage three lines of phase-contact meeting at a point, and giving rise to a point-contribution (it could scarcely

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[31] L. R. Fisher and J. N. Israelachvili, *Nature*, 1979, **277**, 548; *Chem. Phys. Lett.*, 1980, **76**, 325.

[32] F. Hauxwell and R. H. Ottewill, *J. Colloid Interface Sci.*, 1970, **34**, 473.

[33] D. Beaglehole, *J. Phys. Chem.*, in press.

[34] See, *e.g.* reference 3, §8.5.

[35] Reference 3, §8.6.

be called a tension) to the free energy. However, volume contributions to F are of order N, surface contributions of order $N^{2/3}$, line contributions of order $N^{1/3}$, and point contributions of order N^0. Such a size-independent contribution would be swamped by other terms arising from the finite size of a sytem,[36] *e.g.* restrictions on the phonon spectrum or its equivalent in a liquid, which contribute terms of the order of $\ln N$.

A further length of interest in the physics of small systems is therefore the ratio $|\tau/\sigma|$. For soap solutions σ is about $5.10^{-2}\,\mathrm{N\,m^{-1}}$, and experimental values[35,37] of τ range from $-10^{-9}\,\mathrm{N}$ to $+10^{-9}\,\mathrm{N}$. The ratio τ/σ is therefore 20 nm or less, according to the size of τ, and it is only for very small lenses or beads that the effects of line tension are important; $(\tau/\sigma R_s)$ is at most 1/20 for a lens of 1 μm diameter. Between 1 μm and 1 mm we can treat capillary problems by surface tension alone, ignoring gravity on the one hand, and line tension on the other. The general conclusion that (τ/σ) is of the order of ξ, the correlation length, is supported by arguments based on the structure of the pressure tensor[38] near a line of contact, on an analysis[39] in terms of the square-gradient approximation for ψ, and from statistical mechanical arguments.[40] So the line tension of soap solutions, where ξ is large, is probably an upper limit; for simple liquids $|\tau|$ is probably no more than $10^{-11}\,\mathrm{N}$.

There are, however, physical systems of interest of dimensions smaller than 1 μm, and for which line tension may have to be considered. Thus thin soap films (Newton's black films) are less than 10^{-8} m thick. The films that surround the drops in micro-emulsions, and lipid bilayers in biological membranes are also structures with a characteristic length of 10^{-8} m or less. Nucleation is a phenomenon in which surface properties are important on scale of length as small as 10^{-9} m.

The effect of curvature on line tension can be expressed by an equation[26] similar to Tolman's equation for surface tension, but the length ε that is the analogue of δ in (4.7) is again of the order of magnitude of 1 nm. Any change of τ with curvature is therefore probably undetectable.

6 Conclusions

Much more remains to be done. The field covered in this survey has been restricted to the simplest types of system, for I have scarcely touched on the problems of aerosols, foams, colloids, emulsions, cells, membranes *etc.*, and ignored the fact that many of their important properties arise from the presence of electrolytes. Dielectric problems on a micro-scale, and transport properties are discussed by Alder *et al.*[41] What I have attempted to do, however, is to describe the theoretical foundations on which the discussion of the properties of these systems must be

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[36] I am indebted to Dr. J. C. Wheeler for a discussion on this point.

[37] D. Platikanov, M. Nedyalkov, and A. Scheludko, *J. Colloid Interface Sci.*, 1980, **75**, 612; D. Platikanov, M. Nedyalkov, and V. Nasteva, *J. Colloid Interface Sci.*, 1980, **75**, 620.

[38] F. P. Buff and H. Saltsburg, *J. Chem. Phys.*, 1957, **26**, 23.

[39] J. Kerins and B. Widom, *J. Chem. Phys.*, 1982, **77**, 2061.

[40] P. Tarazona and G. Navascués, *J. Chem. Phys.*, 1981, **75**, 3114.

[41] B. J. Alder, W. E. Alley, and E. L. Pollack, *Ber. Bunsenges. Phys. Chem.*, 1981, **85**, 944.

based, and to describe recent progress in the building of theoretically sound, if so far simplified structures on those foundations. The aim, as Maxwell[42] said of classical thermodynamics, is to create 'a science with secure foundations, clear definitions, and distinct boundaries'.

I have laid particular stress on the three major scales of length:

$$\text{the gravitational length } kT/mg \sim 10^4\,\text{m}$$

$$\text{the capillary constant } a \sim 10^{-3}\,\text{m}$$

and the correlation length ξ, which, for good reasons, is also equal to the thickness of an interface, l, and generally equal also to the range of the intermolecular potential, d, to the separation of z_e and $z_s(\delta)$, and, finally, to the ratio $|\tau/\sigma|$. Thus

$$\xi \sim l \sim d \sim \delta \sim |\tau/\sigma| \sim 10^{-9}\,\text{m}$$

The physics of small systems depends on where, with respect to this triple hierarchy, the radius of curvature, or other measure of smallness, lies. Moreover, the shortest of these three distances, ξ *etc.*, is the smallest distance at which the methods of classical thermodynamics can be used. For systems or inhomogenitics smaller than ξ, thermodynamics and statistical mechanics lose their meaning.

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[42] J. C. Maxwell, quoted by J. W. Gibbs, 'Collected Works', Vol. 2, Longmans, New York, 1928, p. 262.