

## Statistical thermodynamics of small systems and interfaces

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**Abstract** - This review sets out the differences between the theory of small systems and of the infinite systems of conventional statistical thermodynamics. The best choice of thermodynamic potential is the grand potential,  $\Omega$ , which is a function of temperature,  $T$ , chemical potential,  $\mu$ , and a functional of the external potential,  $\psi(\underline{r})$ .

Various forms of the virial expansion of  $\Omega$  and of its partition function,  $\Xi = \exp(-\Omega/kT)$ , are examined and the virtues of the latter function are emphasised for systems such as fluids in zeolites.

The local distribution of molecules in small systems is expressed in terms of the intermolecular forces by means of integral equations based usually on the one-body functions. These functions lead to the calculation of the surface tension, but there are difficulties in the definition of this property for highly curved surfaces and for fluids in contact with walls. Consideration of such systems leads to a brief review of the theory of wetting and of similar phase changes.

### INTRODUCTION

The familiar equations of statistical thermodynamics apply only to systems of infinite size; that is, they are the equations we obtain by going to the *thermodynamic limit*,  $N \rightarrow \infty$ ,  $V \rightarrow \infty$ ,  $(N/V) = \text{constant}$ , where  $N$  is the number of molecules in a system of volume  $V$ . They apply also only to systems in which there is no external potential, such as gravity. Such systems are, on average, homogeneous even if they comprise more than one phase, since the phases occupy all possible positions if there is no external field to restrain them. These limitations are necessary if we are to obtain from the statistical equations the even more familiar results of classical thermodynamics, eg. the phase rule.

Small systems are ones to which these restrictions do not apply; they are of finite size, they have external potential fields (including those that constitute the boundaries of the system), they are inhomogeneous, they may have well-defined interfaces between phases of definite shape and size, and they do not obey the phase rule or many other of the rules of classical thermodynamics.

The statistical theory of such systems has developed rapidly in the last ten years, although the roots of the subject go back to the nineteenth century. In this review I describe the tools that have been developed for this field, and give, in outline, some of the recent results.

### CHOICE OF THERMODYNAMIC POTENTIAL

The statistical thermodynamics of infinite homogeneous systems can be handled in many different ensembles, all of which become equivalent in the thermodynamic limit. The choice between them is one of convenience only. In small and inhomogeneous systems that is no longer so; the different ensembles correspond to different choices of external constraints and give rise to different physical behaviour. The choice between the ensembles becomes therefore not merely a matter of convenience, but is dictated by the physical problems we wish to solve.

A one-component system with a planar interface between two phases, eg. liquid and gas, can be handled in either the canonical ensemble,  $F(N,V,T)$ , or in the grand canonical ensemble,  $\Omega(\mu,V,T)$ , where  $F$  is the Helmholtz free energy, and  $\Omega$  is the grand potential. The balance of convenience is generally with  $\Omega$ . The Gibbs free energy,  $G(N,p,T)$ , is less useful, indeed there is more than one way of defining it for such a system (ref. 1).

If we turn to inhomogeneous systems of less simple geometry then the choice of the grand potential becomes almost inevitable. A fluid in a narrow pore, or in the cage of a clathrate or zeolite structure, may contain few molecules, and is usually studied as an open system by equilibrating it with a homogeneous and effectively infinite reservoir of known  $p$ ,  $T$  and  $\mu$ . Two of these variables,  $T$  and  $\mu$ , are well-defined also inside the pore or cage, and are everywhere equal to their value in the reservoir. Formally we can write

$$T(\underline{r}) = T, \quad \mu(\underline{r}) = \mu, \quad (1)$$

where  $\underline{r}$  is a point inside the system of interest. It is important to note that there is no similar expression for  $p(\underline{r})$ , which is well-defined in the reservoir, but is an incompletely defined tensor inside an inhomogeneous system, and so also at any interface between two phases (ref. 2 - 4).

The volume of a small system may also be imperfectly defined, since the molecules are confined not by geometrical boundaries but by the force field of the intermolecular potentials of the atoms, ions or molecules that form the cage. We avoid, therefore, not only  $p$  but also its conjugate variable  $V$ , in writing the fundamental equation for a small change in  $\delta\Omega$ , caused by small changes  $\delta T$ ,  $\delta\mu$ , and  $\delta\psi(\underline{r})$ ;

$$\delta\Omega = -S \delta T - \bar{N} \delta\mu + \int d\underline{r} \rho(\underline{r}) \delta\psi(\underline{r}), \quad (2)$$

where  $S$ ,  $\bar{N}$ , and  $\rho(\underline{r})$  are the mean entropy, number of molecules, and local density, in a system defined by  $T$ ,  $\mu$ , and  $\psi(\underline{r})$ , where  $\psi(\underline{r})$  is the potential of the external field. Clearly

$$\bar{N} = \int d\underline{r} \rho(\underline{r}). \quad (3)$$

The grand potential of an infinite homogeneous system is  $-pV$ , and if there is an interface of area  $A$ , then it will contain an additional term  $+\sigma A$ , where  $\sigma$  is the surface tension. In a system of complex geometry the potential cannot be expressed in such geometric terms, but nevertheless all measurable properties such as energy, heat capacity, local density, etc. can be expressed in terms of it.

It is related to the molecular properties through the grand partition function  $\Xi$ ;

$$\Omega = -kT \ln \Xi, \quad (4)$$

$$\Xi = \sum_{N=0}^{\infty} \frac{\lambda^N}{N!} V_N, \quad (5)$$

where  $\lambda$  is the absolute activity, which is proportional to  $\exp(\mu/kT)$ , and  $V_N$  are generalised volumes that are integrals of the Boltzmann factors of the total intermolecular energy  $U(\underline{r}^N)$ , and the total external potential  $\Psi(\underline{r}^N)$ , where  $\underline{r}^N$  denotes the positions of the  $N$  molecules,  $\underline{r}_1, \dots, \underline{r}_N$ . If we restrict the integration to  $N-n$  of the molecules then we obtain the generalised volumes  $V_N(\underline{r}^n)$  that can be used to define the molecular distribution functions  $\rho(\underline{r}^n)$  that are proportional to the probability of simultaneously finding molecules at  $\underline{r}_1, \dots, \underline{r}_n$ .

$$V_N(\underline{r}^n) = \int d\underline{r}_{n+1} \dots d\underline{r}_N \exp[-(U(\underline{r}^N)/kT) - (\Psi(\underline{r}^N)/kT)], \quad (6)$$

$$V_N \equiv V_N(\underline{r}^0), \quad (7)$$

$$\rho(\underline{r}^n) = \Xi^{-1} \sum_{N=n}^{\infty} \frac{\lambda^N}{(N-n)!} V_N(\underline{r}^n). \quad (8)$$

These are the basic equations of the statistical thermodynamics of inhomogeneous systems. We now see how they can be turned into working equations for the calculation of physical properties.

## VIRIAL EXPANSIONS

In a homogeneous system it is customary to expand  $p = -\Omega/V$  either in powers of the activity  $\lambda$  or of the uniform density  $\rho$ . The coefficients of  $\lambda$  and  $\rho$  are expressible in a well-known graphical notation in which, for pair-wise additive potentials, the bonds of the graphs represent the Mayer function  $f_{ij} = \exp(-u_{ij}/kT) - 1$ , where  $u_{ij}$  is the pair intermolecular potential. The coefficients of the powers of  $\lambda$  are the set of *connected graphs*,  $b_\lambda$ , and the coefficients of the powers of  $\rho$  are the *irreducibly connected graphs*,  $\beta_\lambda$  (ref. 5).

In an inhomogeneous system  $\Omega$  has similarly expansions in powers of  $\lambda$  and of  $\bar{N}$ . The former is essentially of the same form as in a homogeneous system, but the latter is not. It can be written in two forms of which the first is the more elegant, and the second the more useful for calculations. The first (ref. 6 - 7) has powers of  $\rho(\underline{r}_i)$  inside the integrals instead of the powers of  $\rho$  outside, but is otherwise of the usual form. However the  $\rho(\underline{r}_i)$  are the, *a priori*, unknown local densities. The second (ref. 8) has local weightings of the known functions  $\exp(-\psi(\underline{r}_i)/kT)$  inside the integrals, but the irreducible set of graphical integrals has to be supplemented by a set of connected but reducible integrals and those integrals obtained by cutting these at their *nodes*, that is, at the points where several bonds meet at a point.

These results are a formal solution to the problem of obtaining a virial expansion. They can be put into specialised forms for particular problems, as was first done by Bellemans (ref. 9) for molecules near planar *ideal wall*, that is, a wall at which the potential rises from zero to positive infinite on crossing a plane, say  $z = z_0$ . His results were extended to more complicated walls by Sokołowski and Stecki (ref. 10 - 13).

It is natural in these cases to divide  $\Omega$  into a bulk part ( $= -pV$ ) and a remaining surface part  $\Omega(s)$ , and to equate the latter to  $\sigma A$ . There is no problem at a planar ideal wall, but for an arbitrary wall potential the surface tension so defined can be shown (ref. 14) not to be the same as that obtained from the two-body distribution functions by another statistical route (ref. 15). Thus there is, in general, no unique way of defining a surface contribution to  $\Omega$  unless we are dealing with a planar ideal wall.

The expansions of  $\Omega$  are the natural generalisations of the expansions of  $p$  in homogeneous systems. There may, however, be great advantages (ref. 16) in expanding not  $\Omega$  itself but  $\Xi = \exp(-\Omega/kT)$ . The coefficients of the expansion in powers of  $\lambda$  are now the generalised volumes  $V_N$  (see eqn 6), and for a small system, such as a cage in a zeolite, this series terminates when the cage is full, since higher  $V_N$  are zero. The corresponding coefficients of the expansion of  $\Omega$ , the connected graphs  $b_\lambda$ , continue indefinitely but with alternating sign. Thus we can, in these small systems, sum a virial expansion to infinity to yield the ratio of two finite polynomials. This is a potentially powerful result which has yet to be fully exploited. So far it has led to some new formal results in graph theory, from a comparison of the expansions of  $\Omega$  and  $\exp(-\Omega/kT)$  (ref. 16 - 17), and has allowed us to obtain a complete and exact set of results for the distribution of hard rods on a line of finite length, that is in a one-dimensional cage (ref. 18). It should have further applications to fluids adsorbed into zeolites, particularly if it can be modified to allow the use of repeating boundary conditions to a model set of linked cages.

## INTEGRAL EQUATIONS FOR THE MOLECULAR DISTRIBUTION FUNCTIONS

In order to calculate the physical properties we need to know where the molecules are; that is, we need to know at least the first two members of eqn 8,  $\rho(\underline{r}_1)$  and  $\rho(\underline{r}_1, \underline{r}_2)$ . The direct route to these functions, via  $V_N(\underline{r}_1)$  and  $V_N(\underline{r}_1, \underline{r}_2)$  is usually too difficult to follow except for the special case discussed in the last section. A variety of relations between distribution functions of different kinds can be generated by operating on both sides of eqn 8, and by similar methods. These relations are collectively known as the *integral equations*, and their solution, with varying degrees of approximation, is one of the main avenues of progress in this field.

Thus if we take the gradient of  $\rho(\underline{r}_1)$  we obtain the first Yvon-Born-Green equation, (ref. 19) which, if  $U(\underline{r}^N)$  is composed only of pair potentials, takes the form

$$-kT \nabla_1 \rho(\underline{r}_1) = \rho(\underline{r}_1) \nabla_1 \psi(\underline{r}_1) + \int d\underline{r}_2 \rho(\underline{r}_1, \underline{r}_2) \nabla_1 u(r_{12}). \quad (9)$$

To solve this equation we need first an expression for  $\rho(\underline{r}_1, \underline{r}_2)$ , and this we could get in principle by taking the gradient of the second member of eqn 8, and so obtaining  $\nabla_1 \rho(\underline{r}_1, \underline{r}_2)$  as an integral over  $\rho(\underline{r}_1, \underline{r}_2, \underline{r}_3)$ . Historically this second member of the hierarchy was studied intensively before the first, since it is the first non-trivial equation in a homogeneous system. For an inhomogeneous system, however, the first, eqn 9, is non-trivial,

and, in practice, the only one that has been studied in detail.

Clearly this set of equations is an infinite regress and, for interfacial systems, we break the chain in the simplest way possible by inserting into eqn 9 an approximation for  $\rho(\underline{r}_1, \underline{r}_2)$  that expresses it in terms of known functions, eg  $\rho(\underline{r}_1, \underline{r}_2)$  for a homogeneous system. In this way Toxvaerd (ref. 20), Fischer and Methfessel (ref. 21), and Nieminen and Ashcroft (ref. 22) have been able to obtain profiles for the density across a planar gas-liquid interface that are in reasonable agreement with those obtained by computer simulation (ref. 4, 23, 24).

The first Yvon-Born-Green equation is essentially the condition of mechanical equilibrium which can be expressed more concisely in terms of the gradient of the pressure tensor,

$$\underline{\nabla} \cdot \underline{p}(\underline{r}) + \rho(\underline{r}) \underline{\nabla} \psi(\underline{r}) = 0 \quad (10)$$

Thus although  $\underline{p}$  itself is not precisely defined in an inhomogeneous system its gradient is (ref. 2 - 4). The condition of mechanical equilibrium is, in turn, equivalent to the condition of constancy of the chemical potential throughout the system (eqn 1); this was shown recently by Henderson (ref. 25) who then related both conditions to a further useful result, the *potential distribution theorem*.

This theorem has had a complicated history. In its simplest form, as put forward by Widom in 1963 (ref. 26), it related the density  $\rho$  and the activity  $\lambda$  (normalised to reduce to  $\rho$  as  $\rho$  goes to zero) in a homogeneous system,

$$\rho/\lambda = \langle \exp(-u_1/kT) \rangle, \quad (11)$$

where  $u_1$  is the change in energy inserting an extra test particle into a typical equilibrium configuration. The average was taken in the canonical ensemble. He showed similarly that  $\rho(r_{12})$  is related similarly to the change in energy on inserting two test particles separated by a distance  $r_{12}$ . The scope of the theorem was greatly increased when he showed that the results were equally valid for  $\rho(\underline{r}_1)$  and  $\rho(\underline{r}_1, \underline{r}_2)$  in an inhomogeneous system, such as an interface (ref. 27 - 29). Later the scope of the theorem was increased further by extending both the one-body (ref. 15) and multibody (ref. 30) forms to the grand canonical ensemble. There is also an inverse form of the theorem that yields the ratio  $\lambda/\rho$ , but this has proved less useful in practice (ref. 31, 32).

The ratio  $\rho(\underline{r})/\lambda$  plays an important role in the theory of inhomogeneous systems since it defines the lowest member of another set of functions, the *direct correlation functions*  $c(\underline{r}_1)$ ,  $c(\underline{r}_1, \underline{r}_2)$ , ---,  $c(\underline{r}^n)$ , etc. The second of these was the first to be studied in detail, since it is the lowest non-trivial function in a homogeneous system, but again it is the first that is the prime object of calculation in an inhomogeneous system since it is directly related to  $\rho(\underline{r}_1)$ .

$$c(\underline{r}_1) = \psi(\underline{r}_1)/kT + \ln[\rho(\underline{r}_1)/\lambda]. \quad (12)$$

If we make a small change in density at a nearby point,  $\delta\rho(\underline{r}_2)$ , then the change in  $c(\underline{r}_1)$  is the second direct correlation function; that is, in the language of functional differentiation,

$$\delta c(\underline{r}_1)/\delta\rho(\underline{r}_2) = c(\underline{r}_1, \underline{r}_2). \quad (13)$$

The hierarchy can be continued;  $c(\underline{r}_1, \underline{r}_2, \underline{r}_3)$  is the functional derivative of  $c(\underline{r}_1, \underline{r}_2)$  with respect to  $\rho(\underline{r}_3)$ . The second function is related to the usual density distribution function,  $\rho(\underline{r}_1, \underline{r}_2)$ , by the *Ornstein-Zernike equation* which, for an inhomogeneous system takes the form

$$\begin{aligned} \rho(\underline{r}_1, \underline{r}_2)/\rho(\underline{r}_1)\rho(\underline{r}_2) &= 1 + c(\underline{r}_1, \underline{r}_2) \\ &+ \int d\underline{r}_3 c(\underline{r}_1, \underline{r}_3)\rho(\underline{r}_3) [\rho(\underline{r}_2, \underline{r}_3)/\rho(\underline{r}_2)\rho(\underline{r}_3) - 1]. \end{aligned} \quad (14)$$

Functional differentiation of  $\rho(\underline{r}_1)$  with respect to the external field  $\psi(\underline{r}_2)$  yields further relations between the one- and two-body functions. These are first and second *Yvon equations*.

$$\rho(\underline{r}_1, \underline{r}_2) - \rho(\underline{r}_1)\rho(\underline{r}_2) = -\rho(\underline{r}_1)\delta(\underline{r}_1 - \underline{r}_2) - kT \frac{\delta\rho(\underline{r}_1)}{\delta\psi(\underline{r}_2)}, \quad (15)$$

$$\rho(\underline{r}_1)\rho(\underline{r}_2)c(\underline{r}_1, \underline{r}_2) = \rho(\underline{r}_1)\delta(\underline{r}_1 - \underline{r}_2) + \frac{1}{kT} \frac{\delta\psi(\underline{r}_1)}{\delta\rho(\underline{r}_2)}, \quad (16)$$

where  $\delta(\underline{r}_1 - \underline{r}_2)$  is Dirac's delta function.

The direct correlation functions also have virial expansions. In homogeneous systems the re-summing of some of the graphs in the density expansion of the pair function,  $c(r_{12})$ , is one route to the well-known integral equations that carry the names *Percus-Yevick* (PY) and *hyper-netted chain* (HNC). In inhomogeneous systems we again start with the first member of the series  $c(\underline{r}_1)$  and are led to the expansion of Massignon (ref. 6) and Arinshtein (ref. 33) in which the graphs in the density expansion are the singly-rooted irreducible graphs with the field points over which we take the integrations weighted with the local densities  $\rho(\underline{r}_2)$ ,  $\rho(\underline{r}_3)$ , etc. This result has come to prominence recently as the basis of approximate methods of studying the melting of a solid, which is a special case of an inhomogeneous system in which the inhomogeneity has the periodicity of a lattice. This field is beyond the scope of this review, but it is one that is developing rapidly (ref. 34 - 39). Only tentative explorations have yet been made of the possibility of using this expansion for inhomogeneous fluid systems (ref. 16).

The Percus-Yevick integral equation has been used for systems in contact with a planar wall in two forms, the first of which might be described as a 'trick' solution and the second as the true PY equation. We recall first that for a homogeneous system the PY approximation is a relation for  $c(r_{12})$  in terms of  $\rho(r_{12})$ , namely

$$c(r_{12}) = [1 - \exp(u(r_{12})/kT)] \rho(r_{12})/\rho^2. \quad (17)$$

The combination of this result with the Ornstein-Zernike equation yields an integral equation for  $\rho(r_{12})$ .

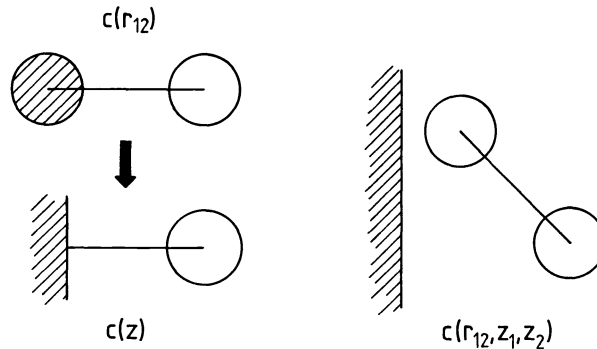


Fig. 1. Symbolic representation of the solutions of the Percus-Yevick equations. On the left we have the 'trick' solution, in which the pair correlation function of a system of unlike molecules is transformed into the singlet function in the presence of a plane wall. On the right we have the true PY solution.

This equation is readily generalised to a mixture of molecules of two different species, represented symbolically in Fig. 1, and then we can transform the equation by taking the limit as one species goes to infinite dilution but the size of the last remaining molecule becomes infinite. We have then one molecule (the circle) interacting with a planar wall (shaded). This may be called the trick PY solution; it is applicable to a fluid in contact with a planar wall. Nevertheless for that problem it is an acceptable solution to the determination of  $\rho(z)$ , where  $z$  is the distance from the wall, at least when the molecules are hard spheres or molecules for which the structure of the fluid is dominated by the repulsive forces (ref. 40).

A more exact theory follows from the generalisation of eqn 17 to an inhomogeneous system,

$$c(\underline{r}_1, \underline{r}_2) = [1 - \exp(u(r_{12})/kT)] \rho(\underline{r}_1, \underline{r}_2)/\rho(\underline{r}_1)\rho(\underline{r}_2), \quad (18)$$

and substituting this into the inhomogeneous Ornstein-Zernike equation, eqn 14. This generates an approximation for  $c(\underline{r}_1, \underline{r}_2)$ , or, in a planar system, as in Fig. 1, for a function

of three variables,  $c(r_{12}, z_1, z_2)$ . Unfortunately the solution of eqn 14 plus eqn 18, which is already a three-body problem (two molecules and the wall), cannot be undertaken without knowing first  $\rho(\underline{r})$ , or, in the planar case,  $\rho(z)$ . Fortunately there is a pair of equations, which follow from the two Yvon equations, that solve this difficulty. They are (ref. 41, 42),

$$\begin{aligned} \nabla_1 \ln \rho(\underline{r}_1) + \nabla_1(\psi(\underline{r}_1)/kT) \\ = - \int d\underline{r}_2 [\rho(\underline{r}_1, \underline{r}_2)/\rho(\underline{r}_1) - \rho(\underline{r}_2)] \nabla_2(\psi(\underline{r}_2)/kT) \end{aligned} \quad (19)$$

$$= \int d\underline{r}_2 c(\underline{r}_1, \underline{r}_2) \nabla_2 \rho(\underline{r}_2) . \quad (20)$$

The second of these equations relates  $c(\underline{r}_1, \underline{r}_2)$  to the gradients of the density at  $\underline{r}_1$  and  $\underline{r}_2$ , and, in principle, completes the solution of the true PY approximation for an inhomogeneous system. In practice the solution would be difficult to obtain except for the simplest geometry, and even there the problem is not trivial. It has been solved recently by Plischke and D. Henderson for the simplest cases, namely hard spheres (ref. 43) and Lennard-Jones molecules (ref. 44) near a planar ideal wall. Their results for hard spheres agree well with the results from the computer simulations of this system by Snook and D. Henderson (ref. 45) and by J.R. Henderson and van Swol (ref. 46), for both  $\rho(z)$  and for  $\rho(r_{12}, z_1, z_2)$ . The results for the HNC approximation are less good (ref. 43), as might be expected for a system with repulsive forces only.

## SURFACE TENSION

The integral equations of the last section give us, formally in principle, and to some degree in practice, a method of calculating the one- and two-body distribution functions for inhomogeneous systems. It is now a relatively simple matter to obtain the surface tension in terms of these functions.

In a homogeneous system there are two routes to the pressure, via the virial theorem and via the compressibility equation of the grand ensemble. There are similarly two routes to the surface tension of an interface, via the pressure tensor and via the direct correlation function.

We distinguish first two kinds of system for which the surface tension is well defined. First, we have a free interface, such as that between liquid and gas, or between two liquid phases. Such an interface can be fixed in space by an external field, eg. the gravity  $g$ , but we can let that field become arbitrarily weak, and calculate the tension in the limit of its becoming zero; in that sense it is a free surface. The thickness of such an interface, or, more generally, the function  $\rho(z)$ , may not be well-defined as  $g$  goes to zero, but the tension  $\sigma$  has a well-defined limit. Secondly, we have an interface against a wall in which we choose to consider the wall as a non-zero external potential rather than a phase whose molecular structure we try to calculate. The tension of such a tied system is also well-defined if the external potential has simple geometric properties.

The simplest free interface is the planar surface between a liquid and its vapour in a weak gravitational field. Here the tension can be expressed in either 'virial' or 'compressibility' form (ref. 19),

$$\sigma = \int_{-\infty}^{\infty} dz [p_N(z) - p_T(z)] \quad (21)$$

$$= \frac{1}{4} kT \int_{-\infty}^{\infty} dz_1 \rho'(z_1) \int d\underline{r}_2 \rho'(z_2) (r_{12}^2 - z_1^2) c(r_{12}, z_1, z_2) , \quad (22)$$

where  $p_N$  and  $p_T$  are the components of the pressure tensor normal and transverse to the interface. The pressure tensor can itself be expressed in more than one way in terms of the virial of the intermolecular forces,  $r_{12} u'(r_{12})$ , and the two-body distribution function  $\rho(r_{12}, z_1, z_2)$ . Although the pressure tensor is therefore not well-defined in the interface, the integral in eqn 21 is invariant to all choices that satisfy the condition of mechanical equilibrium. The equivalence of eqn 21 and 22 is not obvious, but has been proved by Schofield (ref. 47). Calculations based on eqn 21 and 22 agree well with computer simulations, and, given the uncertainties of our knowledge of intermolecular forces, with the surface tension of real simple liquids (ref. 23).

A curved free surface is more difficult. The scalar pressure  $p^\alpha$  and  $p^\beta$  are not equal in two homogeneous phases separated by a curved surface, but if we have a system at equilibrium  $p^\alpha$  and  $p^\beta$  must be everywhere constant within the bulk phases  $\alpha$  and  $\beta$ . Hence it is unprofitable to try to calculate the tension of surfaces of arbitrary curvature, although there have been attempts to do so (ref. 48 - 50); we are restricted to surfaces of constant total curvature. These surfaces form the class called unduloids, but the only cases of practical importance are the limiting ones of the sphere and the cylinder. In the former the two principal radii of curvature are equal ( $R_1 = R_2 = R$ ), in the latter one is infinite ( $R_1 = R, R_2 = \infty$ ). A thermodynamic argument due to Tolman (ref. 51) tells us that the tension of these surfaces differs from that of a plane surface:

$$\sigma(R) = \sigma(\infty)[1 - \delta(R_1^{-1} + R_2^{-1})] , \quad (23)$$

$$\delta = R_e - R_s , \quad (24)$$

and  $R_e$  and  $R_s$  are, respectively, the radii of Gibbs's equimolar surface, and the surface of tension defined by Laplace's equation.

$$p^\alpha - p^\beta = 2\sigma/R_s \quad (\text{sphere}) \quad (25)$$

$$= \sigma/R_s . \quad (\text{cylinder}) \quad (26)$$

The derivation of eqn 23 makes it clear that it holds only in the limit  $R^{-1} \rightarrow 0$ , so that  $\delta$  is the limit  $z_e - z_s$ , where  $z_e$  and  $z_s$  are the planar limits of  $R_e$  and  $R_s$ . Since  $\delta$  is of the order of the thickness of the surface, it is expected to be only of the order of the size of a molecule, say  $2 - 5 \text{ \AA}$ . It has, therefore, been difficult to test experimentally the correctness of Tolman's result. Fisher and Israelachvili found a change of  $\sigma$  with  $R$ , with  $\delta > 0$ , for cyclohexane (ref. 52), but could detect no change with water (ref. 53). It is rather easier to test the equation by the computer simulation of spherical drops, and confirmation of its correctness of the form has been obtained for systems with truncated Lennard-Jones potentials (ref. 54, 55). Moreover there is one model, the penetrable-sphere model, for which  $\delta$  can be obtained explicitly in mean-field approximation, and exactly at  $T = 0$  (ref. 56, 57). Explicitly for this model (ref. 58), and more generally by a Landau theory (ref. 59), it is possible to show that Tolman's equation has the correct form near the critical point, and to calculate the critical exponent of  $\delta$  which shows a weak ( $\sim -0.06$ ) divergence at the critical point, although Phillips and Mohanty (ref. 60) have suggested the exponent may be larger, namely a divergence as the correlation length ( $\sim -0.63$ ). There seems, nevertheless, little reason to doubt the correctness of Tolman's equation for spherical systems, i.e. drops and bubbles. For cylinders the thermodynamic argument is equally clear, but statistical mechanical arguments (ref. 61) show that the expansion here breaks down at order  $R^{-1}$ , not at  $R^{-2}$ ; that is, the Tolman expansion is not valid and only the planar surface tension has any meaning. This disagreement is a warning that classical thermodynamic arguments cannot be applied indiscriminately to bodies whose relevant dimensions (here the length,  $\delta$ ) are the molecular size.

The extension of the 'virial' and 'compressibility' equations to spherical surfaces yields

$$\sigma(R) = \int_0^\infty dr (R_s/r) [p_N(r) - p_T(r)] \quad (27)$$

$$= \frac{1}{4} kT \int_0^\infty dr_1 \rho'(r_1) \int d\underline{r}_2 \rho'(r_2) [r_2^2 - (\underline{e}_1 \cdot \underline{r}_2)^2] c(\underline{r}_1, \underline{r}_2) , \quad (28)$$

where  $\underline{e}_1$  is the unit vector in the direction of  $\underline{r}_1$ . The first gives us  $(\sigma/R_s)$  but not  $\sigma$  or  $R_s$  separately (cf. eqn 25). There is a similar equation for  $R_s$  (ref. 62), namely

$$\sigma(R) = \int_0^\infty dr (r/R_s)^2 [p_N(r) - p_T(r)] , \quad (29)$$

but unfortunately we do not know that eqn 27 and eqn 29 are consistent beyond the planar limit, that is, beyond  $R^0$ . Eqn 28 is the extension of eqn 22 to a spherical system (ref. 56) and is correct to  $R^{-1}$  as was shown above, since it was the equation for  $\sigma(R)$  used in the tests of Tolman's equation.

Henderson (ref. 15) extended these results to give the tension of a fluid at a planar or spherical wall. Little work has yet been done with these equations, except in one dimension (ref. 15, 18) but the results are, as stated above, at variance with the expressions for surface tension at walls obtained by virial expansions by Sokołowski and Stecki (ref. 10-13).

### PHASE TRANSITIONS IN INTERFACES

Interfacial systems exhibit changes of phase in the same way as bulk systems; that is, a change of a thermodynamic field,  $T$  or  $\mu$ , can bring about a qualitative macroscopic change in the structure of an interface. Such a change can be sudden, i.e. of first order, or continuous, i.e. of higher order, just as for bulk systems. The best known of these changes is the *wetting* transition which can occur at the surface of a solid (Fig. 2) or at the surface between two liquid phases (Fig. 3).

A liquid is said to wet a solid if it spreads over it in a continuous film. The surface tensions between the solid ( $\alpha$ ), the liquid ( $\beta$ ), and the vapour ( $\gamma$ ) satisfy Antonow's rule (ref. 63),

$$\sigma_{\alpha\gamma} = \sigma_{\alpha\beta} + \sigma_{\beta\gamma} . \quad (30)$$

A liquid does not wet a solid (or is sometimes said to wet it partially) if it does not spread smoothly, but meets the solid at an angle  $\theta$ . The tensions are then related by Young's equation

$$\sigma_{\alpha\gamma} = \sigma_{\alpha\beta} + \sigma_{\beta\gamma} \cos\theta . \quad (0 < \theta < \pi) \quad (31)$$

The local density,  $\rho(z)$ , as a function of the distance  $z$  across the  $\alpha$ - $\gamma$  surface, changes from a profile that denotes essentially infinite adsorption, to one of finite adsorption, as the angle  $\theta$  reaches the limit of 0.

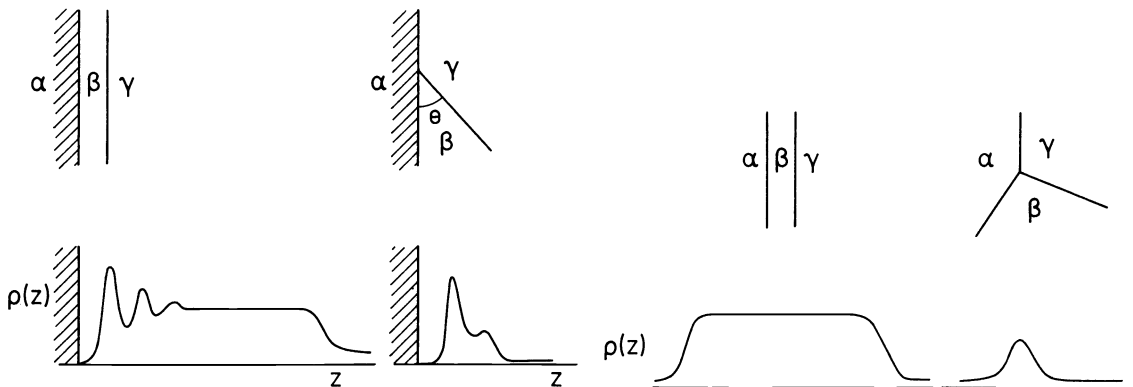


Fig. 2. The transition from wetting to partial wetting for a liquid ( $\beta$ ) at a solid ( $\alpha$ ) - vapour ( $\gamma$ ) interface. The lower part of the diagram shows the density of the fluid phases on crossing the  $\alpha$ - $\gamma$  surface.

Fig. 3. The transition from wetting to partial wetting for a second liquid phase ( $\beta$ ) at a liquid ( $\alpha$ ) - vapour ( $\gamma$ ) interface. The lower part of the diagram shows the density profile for a component found mainly in phase  $\beta$ , on crossing the  $\alpha$ - $\gamma$  surface.

In a mixture of two or more components, the liquid ( $\alpha$ ) - vapour ( $\gamma$ ) surface is said to be wetted by a second liquid phase ( $\beta$ ) if this spreads uniformly, or not to be wetted if it forms discrete drops with non-zero contact angles. The density profile,  $\rho(z)$ , of a component found predominantly in phase  $\beta$  again grows from a finite to an infinite adsorption as the wetting becomes complete. The most striking difference between  $\rho(z)$  for the solid-liquid-gas and liquid-liquid-gas interfaces is the presence in the former of strong peaks and troughs induced by the rigid wall of the solid.

The theoretical methods already described can give a detailed molecular description of an interface and so should be able to describe also these changes of phase. In practice they go into too much detail, and it becomes difficult to apply them to these situations without drastic approximations. A less detailed theoretical description has therefore been developed which foregoes much of the detail in order to develop more clearly the broad features of the change of phase. The treatment is based on *free-energy functionals*, which are generalisations of thermodynamic potentials, such as  $F$  or  $\Omega$ , to functionals of arbitrary density distribution,  $\rho(\underline{r})$ , which are not the equilibrium distribution for the prevailing values of the fields  $T$  and  $\mu_i$ . Thus if we divide the intermolecular potential into a short-ranged part and a long-ranged part, we can construct a Helmholtz free energy functional,  $F[\rho]$ , as follows (ref. 64),

$$F[\rho] = \int d\underline{r} f_r(\rho(\underline{r})) + \frac{1}{2} \int d\underline{r}_1 d\underline{r}_2 \rho(\underline{r}_1) \rho(\underline{r}_2) u_a(\underline{r}_{12}) , \quad (32)$$



and a grand potential functional,  $\Omega[\rho]$ ,

$$\Omega[\rho] = F[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) (\psi(\mathbf{r}) - \mu). \quad (33)$$

In these equations  $f_r(\rho(\mathbf{r}))$  is the Helmholtz free energy density of a homogeneous system of density  $\rho(\mathbf{r})$  and with only the repulsive part of the intermolecular potential. This function is well-defined since such a system has only one fluid phase. The energy  $u_a(r_{12})$  is the attractive part of the intermolecular potential. It is now readily seen (ref. 65) that  $\Omega[\rho]$  is a minimum, and equal to its equilibrium value  $\Omega$ , if  $\rho(\mathbf{r})$  is everywhere equal to the equilibrium distribution. The equations are therefore solved by choosing the distribution  $\rho(\mathbf{r})$  that minimises  $\Omega[\rho]$ . This, and related functionals, have been widely used, by, among others, Sullivan (ref. 66-67), by Evans, Tarazona, Telo da Gama and their colleagues (ref. 68-72), and by Gubbins and his colleagues (ref. 73), for studying wetting transitions at planar surfaces and in pores of different shapes. The results are promising but are restricted by two limitations. The first arises from a limitation of the first integral in eqn 32, namely that the form of  $f_r$  smooths out the layered structure shown for  $\rho(z)$  in Fig. 2. The second arises from the fact that the second integral is of essentially a mean-field form, and so is subject to all the restrictions of that approximation in its suppression of fluctuations, and in its improper treatment of critical points. Improvements to both integrals are in progress, and a full review of the rapidly growing field has recently been written by Sullivan and Telo da Gama (ref. 74).

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