

## Thermodynamics of inhomogeneous systems

John S. Rowlinson

Physical Chemistry Laboratory, South Parks Road, Oxford, OX1 3QZ, U.K.

**Abstract** - This lecture is an enquiry into the extent to which we can define uniquely local thermodynamic functions in an inhomogeneous system at equilibrium. It is argued that this can be done if the length scale of the inhomogeneity is macroscopic, but generally cannot be done if the scale is of the range of the intermolecular forces, as, for example, in systems with interfaces. In these cases the temperature and the chemical potential remain constant throughout the system and the local density is well-defined, but the pressure, and so other thermodynamic functions, are not. Recent proposals by Baus and Lovett to find a unique form of the pressure are analysed and are shown to lead to other, as yet unresolved, difficulties.

### INTRODUCTION

Thermodynamics is essentially a human science; it started with steam engines and went on to describe many physical and chemical systems whose size is of the order of a metre. Its laws are not truly a theory but a highly condensed and abstract summary of our experience of how such systems behave. We have, therefore, no right to expect them to apply to other quite different systems, whether extremely large or extremely small. They clearly are inapplicable to the solar system or to galaxies. Here gravity is the dominant force; there is no equilibrium, the energy is no longer proportional to the amount of material, and so there are no extensive functions. Clausius's famous remark that the energy of the universe is constant but its entropy is increasing to a maximum is derived from the behaviour of a closed adiabatic system of constant volume. The universe is neither closed in any classical sense, nor of constant volume. Clearly classical thermodynamics is not a useful branch of science in cosmology; we have extrapolated too far from its human-sized origins.

The problem of large systems is, however, not my concern here. I wish to examine the other limit; that is, how far can we use the concepts of classical thermodynamics in systems that are at equilibrium but are inhomogeneous and so, in some sense, small? We can easily generate paradoxes here, for if a system is finite, with say  $N$  atoms, then we can be sure that it does not conform exactly to all the conventional results of thermodynamics. Thus the phase rule does not apply exactly to a finite system of a pure liquid in equilibrium with its vapour, for there will be a small increase of pressure (of the order of  $N^{-1}$ ) during the process of condensation. We formally avoid this problem by taking what is called the *thermodynamic limit*, that is, we consider not the real finite system but the one that results when we take the limits  $N \rightarrow \infty$ ,  $V \rightarrow \infty$ , with  $(N/V) = \text{constant}$ . Clearly this hypothetical infinite system is one in which we tacitly agree to neglect the effects of the gravitational attraction between its parts that would dominate its behaviour as  $N$  becomes infinite. Our thermodynamic limit is therefore an abstraction, but nonetheless a justifiable one, and one that is useful in practice since our human size of  $N \sim 10^{23}$  is large enough for  $N^{-1}$  to be neglected but small enough to avoid gravitational complications.

### SCALES OF INHOMOGENEITY

The finite systems we handle in the laboratory are always inhomogeneous. We live in a gravitational field, and the walls of the containing vessel adsorb (or maybe repel) the molecules of our system. It is easy to see that a weak external gravitational field, as distinct from one generated between the constituent parts of the system, poses little restriction on the use of classical thermodynamics in a one-phase system. The characteristic length we associate with the thermal effect of a gravitational field is  $(kT/mg)$ , where  $m$  is the mass of a molecule and  $g$  the

gravitational field. At the surface of the earth this is 9.0 km, which is clearly large on a laboratory scale. Thus although there is a substantial difference of atmospheric pressure between Snowbird, Utah (altitude 2.4 km) and sea level, we can make thermodynamic measurements in both places. Formally we can say that the thermodynamic potentials, pressure and chemical potential, of the Earth's atmosphere, which we may assume to be nitrogen, are functions only of the local temperature and density. At a point  $\mathbf{r}$

$$p(\mathbf{r}) = p[T(\mathbf{r}), \rho(\mathbf{r})] \quad \text{and} \quad \mu(\mathbf{r}) = \mu[T(\mathbf{r}), \rho(\mathbf{r})] . \quad (1)$$

If there is more than one fluid phase then the effects of gravity are not so trivial. The configuration of a system of liquid and vapour in a closed vessel with no gravitational field can be either that of a free-floating spherical drop of liquid or that of all the walls being covered by the liquid phase, according to the relative strengths of the intermolecular forces within the liquid and between molecules of the liquid and those of the walls. Even a gravitational field that is weak compared to the strength of the intermolecular forces changes both configurations drastically, to produce the familiar system with liquid at the bottom of the vessel, vapour at the top, and an interface between them whose instantaneous departures from planarity – the thermal fluctuations that we call capillary waves – depend in a subtle way on the size of the system and the strength of the gravitational field (ref. 1). If  $g = 0$  then the amplitude of these waves increases as  $(\ln A)^{1/2}$ , where  $A$  is the area of the interface, and if  $A^{-1} = 0$ , then the amplitude increases as  $(-\ln g)^{1/2}$ . Thus we have weak divergence in an infinite system in zero field, but if either  $A^{-1}$  or  $g$  is non-zero (or both) then the amplitude of the capillary waves is finite, and, indeed, generally small on a laboratory scale. Although the amplitude of the capillary waves diverges as  $g$  becomes zero (if  $A^{-1} = 0$ ) the surface tension,  $\sigma$ , remains finite; the corresponding singular term in  $\sigma$  is proportional to  $(g \ln g)$  which goes slowly to zero as  $g$  becomes zero.

The characteristic length that governs the propagation of capillary waves is called the *capillary length*,  $l_c$ ;

$$l_c^2 = 2 \sigma / g (\rho_l - \rho_g) , \quad (2)$$

where  $\rho_l$  and  $\rho_g$  are the (mass) densities of the liquid and gaseous phases. For water at 0 °C at the surface of the Earth,  $l_c = 3.9$  mm, a length that is small compared with the characteristic gravitational length but large compared with the range of intermolecular forces. Since  $l_c$  is of human size, capillary phenomena are easily studied in the laboratory and so it is not surprising that, from the eighteenth century onwards, they were one of the first manifestations of the actions of intermolecular forces to receive serious quantitative study.

Thus the thermodynamics of inhomogeneous systems can be handled satisfactorily for bodies with the characteristic scales of length that we associate with gravitational fields, although some care is needed if there is more than one fluid phase. Matters are less simple if the inhomogeneities with which we are concerned are on the scale that we call the *correlation length*,  $\xi$ , which is about 1 nm in a simple liquid. This length is a measure of the range of density correlations in a fluid. Thus if we know that there is a molecule with its centre at  $\mathbf{r}_1$ , we can ask what is the probability of there being one in a small volume  $d\mathbf{r}_2$ , about a point  $\mathbf{r}_2$  which is distant from  $\mathbf{r}_1$  by  $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ . If  $r_{12} \gg \xi$  then this probability is  $\rho(\mathbf{r}_2)d\mathbf{r}_2$ , where  $\rho(\mathbf{r}_2)$  is the number density at  $\mathbf{r}_2$ . At small separations  $r_{12}$  the probability differs from this – it may be larger or smaller – and the separation at which these departures first become significant is a rough measure of  $\xi$ . It is not surprising that this length is of the same order of magnitude as the range of the intermolecular forces, except in those pathological states we know as critical points, where  $\xi$  diverges to infinity. Many of the natural inhomogeneities that we study in the laboratory have a characteristic length that is of the order of magnitude of  $\xi$ , since these inhomogeneities are themselves the result of the operation of the intermolecular forces. Examples are:

- (1) The thickness of interfaces, whether gas-solid, gas-liquid or liquid-solid, are of the order of  $\xi$ . That is, at distances from the interface large compared with  $\xi$  we are in the homogeneous bulk phases.
- (2) The ratio of surface energy per unit area to bulk energy per unit volume is a length of the order of  $\xi$ . For liquid argon at its normal boiling point the first is 36 mJ m<sup>-2</sup> and the second  $1.97 \times 10^8$  J m<sup>-3</sup>, a ratio of 0.2 nm.
- (3) When three interfaces meet in a line there is a small contribution to the free energy of the system above that accounted for by the bulk phases and by the areas and surface tensions of the interfaces. This contribution, per unit length, is called the *line tension*,  $\tau$ . For aqueous

solutions (the only ones for which there are satisfactory measurements) the ratio of  $\tau$  to  $\sigma$  is about  $2 \times 10^{-9}$  N to 70 mN m<sup>-1</sup>, or a length of 0.3 nm.

(4) The surface tension of a curved surface differs from that of a planar surface by a term of the order of  $(\delta/R)$ , where  $R$  is the radius of curvature of the surface and  $\delta$  is a small length (Tolman's length) which is hard to determine but which is of the order of 0.5 nm or less (see below).

(5) Cavities in molecularly ordered systems such as zeolites or clathrates generally have widths in the range 0.3 – 1.5 nm. Larger cavities would not be stable.

Thus we can make the generalisation that the natural inhomogeneities that arise from the operation of intermolecular forces have a scale of length that is of the order of magnitude of  $\xi$ . The question I want to address in this lecture is whether we can define and use consistently local thermodynamic functions in systems in which the density is changing substantially over distances of the order of  $\xi$ . I have already supposed, without argument, that we can define a local number density,  $\rho(\mathbf{r})$ , at a point  $\mathbf{r}$ , so must first justify this assumption and then ask if one can extend the argument to other densities such as an energy density,  $\phi(\mathbf{r})$ , or a free-energy density,  $a(\mathbf{r})$ , or to the classic trio of intensive thermodynamic functions, the pressure  $p(\mathbf{r})$ , the temperature  $T(\mathbf{r})$ , and the chemical potential  $\mu(\mathbf{r})$ .

A formal definition of  $\rho(\mathbf{r})$  would start by considering a small volume  $\delta V$ , which includes  $\mathbf{r}$ , and then observing our equilibrium system many times. On each observation we record the number,  $\delta N$ , of molecules with centres in  $\delta V$ . We repeat this process with different  $\delta V$ . The density  $\rho(\mathbf{r})$  is defined as the limit as  $\delta V \rightarrow 0$  of the ratio  $\langle \delta N \rangle / \delta V$ , where  $\langle \delta N \rangle$  is the average of  $\delta N$  over a sufficiently long series of observations. (We could instead make one observation of a large ensemble of identical systems.) Such a thought-experiment would be difficult to carry out in the laboratory, but is easy in a computer simulation, and is unobjectionable as a definition.

We can extend the argument to any property that depends only on the state of single molecules. Thus if we were to count both the number of molecules,  $\delta N$ , and their translational kinetic energies,  $\delta K$ , then we could define the local temperature,  $T(\mathbf{r})$ , by the equation

$$(3k/2) T(\mathbf{r}) = \text{Limit}_{\delta V \rightarrow 0} [\langle \delta K \rangle / \langle \delta N \rangle] . \quad (3)$$

This equation holds for any system at equilibrium for which quantal corrections to the translational motion are negligible, whatever the local density or its gradients. Moreover, as we shall see,  $T(\mathbf{r})$  so defined is, in fact, a constant,  $T$ , throughout the whole system.

Other thermodynamic properties cannot be defined by the states of single molecules but are determined, in part, by the strength and range of the intermolecular forces. The total energy of a system is the sum of the translational kinetic energies,  $3kT/2$ , any internal molecular energies (which we may ignore in this discussion) and the configuration energy that arises from the mutual interaction of the molecules and from the interaction with external force fields, including those exerted by the walls of the containing vessel. Even if we make the simplest possible assumption that the mutual interaction is a function only of the pair separations,  $r_{ij}$ , we cannot unambiguously ascribe the pair energy to a region of space of dimensions smaller than  $\xi$ . We could ascribe half of  $u(r_{ij})$  to  $r_i$  and half to  $r_j$ , but we could, equally plausibly, ascribe it all to  $\frac{1}{2}(r_i + r_j)$ . In a homogeneous fluid it would not matter which choice we made since all would lead to the same energy density  $\phi = \langle U \rangle / V$ , the average energy per unit volume. But if the point  $\mathbf{r}$  is at a position where  $\rho(\mathbf{r})$  is changing rapidly on the scale of  $\xi$  then each arbitrary division of  $u(r_{ij})$  leads to a different value of  $\phi(\mathbf{r})$ .

A similar argument can be applied to the force between the molecules since this is the derivative  $du(r_{ij})/dr_{ij}$ . Such an argument leads to the conclusion that the stress within an inhomogeneous fluid, or its negative, the pressure, is also ill-defined on a scale shorter than that of  $\xi$ . Moreover, since the force between a pair of molecules is a vector, while the energy is a scalar, we find that the pressure, however defined, is a more complicated quantity than an energy density. It is a symmetric tensor of nine components but if the surface has one of the usual kinds of symmetry (e.g. a plane, a sphere or a cylinder) then this can be reduced to a diagonal tensor with two independent components, e.g.  $p_{xx} = p_{yy}$  and  $p_{zz}$  for an interface in the  $x$ - $y$  plane. Figure 1 is a sketch that shows how the density  $\rho(z)$  and the normal (or  $zz$ ) and transverse (or  $xx$  and  $yy$ ) components of the pressure tensor change with  $z$  through a typical liquid-gas interface. The surface tension,  $\sigma$ , is the integral of the difference of these components, and the surface of tension,

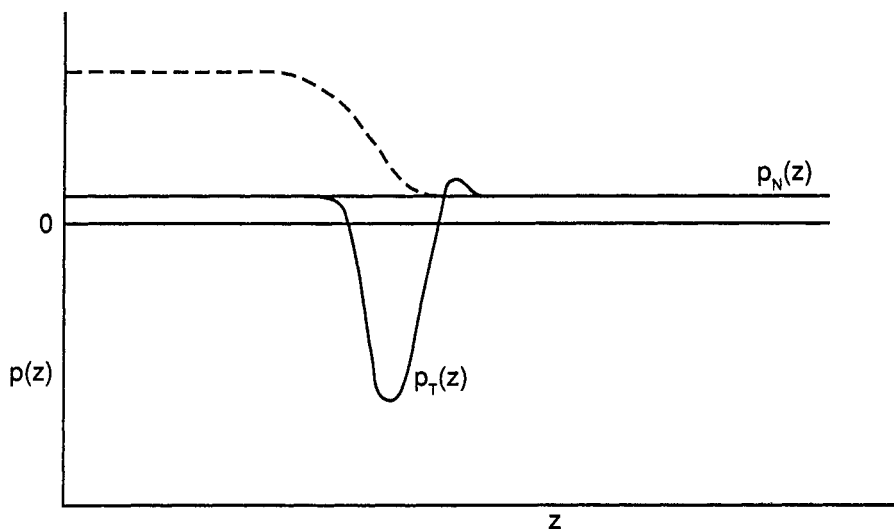


Fig. 1. The normal ( $N$ ) and one form of the tangential ( $T$ ) components of the pressure tensor as a function of height,  $z$ , through a planar liquid-gas interface. The dashed curve is the density,  $kT\rho(z)$ . The normal component,  $p_N(z)$ , is constant throughout but the tangential component,  $p_T(z)$ , is negative in the interface and not uniquely determined.

$z_s$ , which is the height at which the surface tension acts, is often expressed as the first moment of this difference

$$\sigma = \int_{-\infty}^{+\infty} dz [p_N(z) - p_T(z)] \quad \text{and} \quad \sigma z_s = \int_{-\infty}^{+\infty} dz z [p_N(z) - p_T(z)] . \quad (4)$$

The uncertainty in the definition of the tensor  $p$  is such that the first of these integrals is invariant to the choice of definition but the second is not, so that  $z_s$ , so defined, is uncertain by a distance of the order of  $\xi$  (ref. 1).

Although the argument for the lack of exact definition of the energy has generally been accepted, that for the pressure has sometimes been resisted. The reasons for this probably lie in the more complicated nature of the pressure and in the different status of energy density and pressure in conventional thermodynamics. We used to say at one time that pressure was an intensive property and energy extensive, so that the energy density was again an intensive property. We now accept that a more useful distinction is that made by Griffiths and Wheeler (ref. 2) between thermodynamic potentials and thermodynamic densities. The former comprise *inter alia* the classical trio of pressure, temperature and chemical potential. The latter comprise the number density, energy density, entropy density, mole fractions, etc. The important property of the potentials is that they are the same in all phases of a system at equilibrium. Formally we have, for the phases  $\alpha$  and  $\beta$ ,

$$\mu_i^\alpha = \mu_i^\beta, \quad T^\alpha = T^\beta \quad \text{and} \quad p^\alpha = p^\beta, \quad (5)$$

where  $i$  is here an index that numbers the independent components. There are naturally no such restrictions on the densities and so it is the presence of this additional constraint on the pressure imposed by eqn 5 and its extension to inhomogeneous systems (see below) that has made the idea of ambiguity in the location of pressure less acceptable to some scientists than that of ambiguity in the location of energy. [We may have, by chance, the same density in two phases. If that density is the mole fraction, we speak of *azeotropy*; if it is another density we have what may be called a generalised *azeotropy* (ref. 3).]

## EQUILIBRIUM IN INHOMOGENEOUS SYSTEMS

Before we generalise the macroscopic equations for phase equilibrium, eqn 5, to inhomogeneous systems it is instructive to look further at some microscopic descriptions. We have seen that these have suggested so far that we can give an exact definition of the local temperature,  $T(\mathbf{r})$ , but not of the local pressure. What of the local chemical potential,  $\mu(\mathbf{r})$ ? This is clearly not a one-body function of the same kind as  $T(\mathbf{r})$  since it is determined in part by the strength and range of the intermolecular potentials and so, at first sight, we might expect it to have the same uncertainty as  $p(\mathbf{r})$ . This is, however, not the case. Widom's potential distribution theorem (ref. 4) provides a recipe for its measurement and he later proved that  $\mu(\mathbf{r})$ , so defined, is, in fact, a constant throughout an inhomogeneous system at equilibrium in the same way as  $T(\mathbf{r})$  is constant (ref. 5). His recipe involves measuring the average value of  $\exp[-u_1(\mathbf{r})/kT]$ , where  $u_1(\mathbf{r})$  is the change of energy on the instantaneous insertion of an additional test molecule at point  $\mathbf{r}$ .

We have seen that two of the thermodynamic potentials,  $T$  and  $\mu$ , are well-defined, and, indeed, constant, throughout an inhomogeneous system, whilst the third, the pressure tensor, appears to be ill-defined at a molecular level. The macroscopic equations of equilibrium that correspond to eqn 5 in an inhomogeneous system are

$$\nabla \mu(\mathbf{r}) = 0, \quad \nabla T(\mathbf{r}) = 0 \quad \text{and} \quad \nabla \cdot \mathbf{p}(\mathbf{r}) + \rho(\mathbf{r}) \nabla v(\mathbf{r}) = 0 \quad (6)$$

where  $v(\mathbf{r})$  is the external potential at point  $\mathbf{r}$  which includes, for example, the gravitational field and the field of force generated by the walls of the containing vessel. All three of these equations have vectors on their left-hand sides, but they are of very different character since  $\mu$  and  $T$  are scalars and  $\mathbf{p}$  is a tensor. If the gradient of a scalar is everywhere zero then the scalar is a constant throughout the system. But, in a region in which  $v(\mathbf{r})$  is negligible, the fact that the vector formed by the gradient of the pressure tensor is zero does not imply that all the components of  $\mathbf{p}$  are constant. In the example shown in Fig. 1 we see that the normal component is a constant but the tangential component is not.

This differentiation of pressure from its two fellow potentials is reflected in other related properties. The three conserved quantities at elastic molecular collisions are mass, energy and momentum. The first two are scalars and the third is a vector, or an axial vector if the momentum is angular, but rotational motion of molecules is ignored in this lecture. If the conditions of equilibrium, eqn 6, are violated the rates of transport of mass, energy and momentum are governed by the transport coefficients of diffusion, thermal conductivity and viscosity. As is well-known, the third is again more complicated than the first two, having, in general, shear and bulk components. These parallel properties are set out in Table 1.

TABLE 1. The three conserved quantities and the properties related to each.

Conserved quantity	Vector character	Transport property	Condition of equilibrium
mass	scalar	diffusion	$\nabla \mu = 0 \Rightarrow \mu = \text{constant}$
energy	scalar	thermal conductivity	$\nabla T = 0 \Rightarrow T = \text{constant}$
momentum	vector	viscosity	$\nabla \cdot \mathbf{p} = 0 \not\Rightarrow \mathbf{p} = \text{constant}$

We consider next whether the presumed uncertainties in the definitions of the local densities or of the local pressure have any observable consequences. No problems arise with the energy density or, by extension, with other thermodynamic densities that may be presumed to behave similarly, such as the local densities of enthalpy, entropy, and the free energies, since they also depend on the strength of the intermolecular potential. I know of no method of measuring such energies with a precision sufficient to differentiate between any of the possible definitions we might use. With the pressure the position is not so clear. The range of definitions is restrained by the condition of mechanical equilibrium, eqn 6, and by the symmetry of the system. Nevertheless there is still a

large, and generally infinite number of possibilities, as has been shown by Schofield and Henderson (ref. 6). The two most widely used definitions of the transverse component,  $p_T(z)$ , at a planar interface are those associated with the names of Irving and Kirkwood (ref. 7) who distributed the force evenly along the line joining a pair of interacting molecules, and Harasima (ref. 8) who placed it on a trajectory of two straight lines joining the molecules, one parallel and one perpendicular to the interface. The first is, perhaps, the more natural; the latter leads to a simpler expression. Both give the same surface tension (as they must, since it is a measurable property) but they differ in their prediction of the height of the surface of tension,  $z_s$ . Computer simulation of the liquid-gas surface shows that the surface associated with Irving and Kirkwood's definition lies about half a molecular diameter (say  $0.2 \xi$ ) further into the liquid than that associated with Harasima's definition (ref. 9). It is, however, hard to think of a method by which this difference could be detected directly, even in principle. The one problem where it might matter is in the change of surface tension with (spherical) curvature. The distance  $\delta = z_e - z_s$ , where  $z_e$  is Gibbs's equimolar surface and where  $z$  is increasing in the direction from liquid to gas, is known as Tolman's length (ref. 10). It governs the change of surface tension with the radius of a drop,  $R$ , according to the equation,

$$\sigma_R = \sigma_\infty \left( 1 - \frac{2\delta}{R} \right). \quad (7)$$

There are exact expressions for  $\sigma_R$  and  $\sigma_\infty$  in terms of the direct correlation function in the interface (ref. 11), and so, in principle, it should be possible to determine  $\delta$ . In practice, statistical mechanics is not sufficiently well-developed for this programme to be carried out, except in the case of a particular model in which the discrimination between the different definitions of  $z_s$  disappears (ref. 12).

#### RECENT DEVELOPMENTS

The position I have set out above is, I believe, an accurate representation of the consensus of opinion that has been hammered out over the last fifteen years or so. This consensus has recently been challenged in an important series of papers by Baus and Lovett whose view I shall try to describe correctly in this last part of the lecture, but with which I do not always agree.

In their first papers (ref. 13,14) Baus and Lovett set out to establish a unique form for the pressure tensor by adding a second condition on its form that supplements the condition of equilibrium (eqn 5). They argue, as follows. Consider a small deformation of the system so that each point  $\mathbf{r}$  is moved to  $\mathbf{r} + \mathbf{s}(\mathbf{r})$ , where the vector  $\mathbf{s}(\mathbf{r})$  is everywhere a small displacement. The change of density that is caused by this deformation is

$$\delta\rho(\mathbf{r}) = -\nabla \cdot [\rho(\mathbf{r}) \mathbf{s}(\mathbf{r})], \quad (8)$$

and the corresponding strain tensor,  $\mathbf{S}(\mathbf{r})$  is the symmetrical form of the gradient of  $\mathbf{s}(\mathbf{r})$ ,

$$\mathbf{S}(\mathbf{r}) = \frac{1}{2} [\nabla \mathbf{s}(\mathbf{r}) + (\nabla \mathbf{s}(\mathbf{r}))^\dagger], \quad (9)$$

where the dagger denotes the transpose of the tensor. The six components of the strain tensor do not overdetermine the three of the vector displacement since they have to satisfy an additional 'condition of compatibility', as was first shown by St. Venant in 1864 (ref. 15). This condition is

$$\nabla \times [\nabla \times \mathbf{S}(\mathbf{r})]^\dagger = 0. \quad (10)$$

The change of free energy that results from this strain is

$$\delta A = - \int d\mathbf{r} \rho(\mathbf{r}) [\nabla v(\mathbf{r}) \cdot \mathbf{s}(\mathbf{r})] \quad (11)$$

$$= - \int d\mathbf{r} \mathbf{p}(\mathbf{r}) : \mathbf{S}(\mathbf{r}), \quad (12)$$

where the integration is over the whole system, including the boundary walls.

Baus and Lovett impose St. Venant's condition not only on the strain tensor but also on the stress tensor, and so ensure that the stress (or its negative, the pressure tensor) is everywhere uniquely determined. It becomes, however, a non-local property ; that is, its value at a point  $\mathbf{r}$  is determined not only by the state of the fluid at  $\mathbf{r}$ , and within a correlation length's distance of this point, but by the state of the whole system. There seems to be no compelling reason to apply St. Venant's condition of compatibility to the stress (or pressure). It is, I believe, a hypothesis of which Baus and Lovett are exploring the consequences.

At a planar interface, St. Venant's condition requires that  $d^2 p_T(z)/dz^2$  is zero and, since  $p_T(-\infty) = p^l = p^g = p_T(+\infty)$ , this seems to imply that  $p_T$  is everywhere a constant, and so that the surface tension is also zero (see eqn 4). Baus and Lovett note, however, that the non-local character of their pressure tensor leads to a contribution to the free energy from eqn 12 that arises from the strain where the interface meets the boundary walls of the system, and that this change of free energy is just that obtained in the usual (Kirkwood-Buff) calculation of the surface tension from the strength of the intermolecular forces. This leads also to the same result for the position of  $z_s$ , the surface of tension, as that found from the form of the pressure tensor of Irving and Kirkwood. Baus and Lovett's pressure tensor, although it may be physically unattractive, does not lead to unacceptable conclusions for a system of planar symmetry.

If, however, we have a spherical drop of liquid at the centre of a spherical vessel then the interface never touches the walls. The drop can be maintained there by a weak external potential that acts only on the liquid near the centre of the drop and which can legitimately be ignored in determining the state of the system. The condition of mechanical equilibrium, eqn 6, becomes, for a spherical system,

$$\frac{d}{dr} p_N(r) + \frac{2}{r} [p_N(r) - p_T(r)] = 0 , \tag{13}$$

and St. Venant's condition would require also that (ref. 16)

$$\frac{2}{r} F(r) \mathbf{1} + \left[ \frac{1}{r^2} \frac{d}{dr} F(r) - \frac{1}{r^3} F(r) \right] \mathbf{I} = 0 , \tag{14}$$

where  $\mathbf{1}$  is the unit tensor and  $\mathbf{I}$  is a moment of inertia tensor,

$$\mathbf{I} = r^2 \mathbf{1} - \mathbf{r} \mathbf{r} , \tag{15}$$

and

$$F(r) = \frac{d}{dr} p_T(r) - \frac{1}{r} [p_N(r) - p_T(r)] . \tag{16}$$

The conditions expressed by eqn 13 and eqn 14-16 require that

$$\frac{d}{dr} [p_N(r) + 2p_T(r)] = 0 . \tag{17}$$

We know, however, that at the centre of the drop of liquid the normal and tangential components are both equal to the scalar pressure  $p^l$ , and outside the drop they are both equal to  $p^g$ . For a drop of radius  $R$  we have (Laplace's equation),

$$p^l - p^g = 2\sigma/R , \tag{18}$$

so that the imposition of St. Venant's condition seems again to lead to a vanishing of the surface tension without, in this case, a contribution from the intersection of the interface with the boundary walls. They have acknowledged that the spherical problem needs further study (ref. 17). Baus and Lovett's form of the pressure tensor is an unambiguous but non-local function. It is not easy to form a physical picture of it and it has yet to be shown to be applicable to systems more complicated than those with a planar interface. It is, moreover, essentially a mechanical solution to the problem and does not directly resolve the question of how to define uniquely local thermodynamic functions. In their latest paper (ref. 18) they address this point and claim that they can construct a scalar function that has all the thermodynamic properties required. This

function,  $p(\mathbf{r})$ , satisfies the condition of mechanical equilibrium, which now takes the simpler form,

$$\nabla p(\mathbf{r}) + \rho(\mathbf{r}) \nabla v(\mathbf{r}) = 0, \quad (19)$$

and also serves as the negative of the density of Gibbs's grand potential,  $\Omega$ ;

$$\Omega = - \int d\mathbf{r} p(\mathbf{r}). \quad (20)$$

In a homogeneous system  $\Omega$  is  $-pV$  so eqn 20 requires that  $p(\mathbf{r})$  reduces to the conventional scalar pressure within each homogeneous phase of the system. Lovett and Baus's claim extends only to systems for which  $\nabla v(\mathbf{r}) \times \nabla \rho(\mathbf{r})$  vanishes everywhere, which is true for all cases with planar, spherical or cylindrical symmetry. It would not be true for more complicated systems, such as a fluid adsorbed into the pores of a zeolite.

If Lovett and Baus's claim is accepted then they have solved the problem of defining uniquely the local thermodynamic functions since we could construct a Helmholtz free-energy density,  $a(\mathbf{r})$ ,

$$a(\mathbf{r}) = \mu \rho(\mathbf{r}) - p(\mathbf{r}). \quad (21)$$

From this we can obtain an energy density by using the Gibbs-Helmholtz equation, an entropy density by subtracting energy from free energy, etc.

The claim may, however, not be sustainable since there is one model system for which we can calculate the function  $p(\mathbf{r})$  that satisfies eqn 19 and its integral does not give the grand potential when inserted into eqn 20. This model (ref. 19) is somewhat artificial but this lack of realism is no bar to using it as a test-case. It comprises molecules between which there is a repulsive intermolecular potential such that, at a fixed temperature,  $T_0$ , the Boltzmann factor of the potential has a Gaussian form;

$$\exp[-u(r_{12})/kT_0] = 1 - \exp(-r_{12}^2/l^2). \quad (22)$$

A set of such molecules is confined to a parabolic potential well,

$$v(r) = r^2/L^2, \quad (23)$$

where  $r$  is the distance from the origin of the coordinate system. For this assembly we can calculate the local density  $\rho(r)$  and the virial coefficients (ref. 19). Preliminary calculations show that the function  $p(r)$  that satisfies eqn 19 does not satisfy eqn 20; the discrepancy appears first at the level of the second virial coefficient. Until this counter-example is explained satisfactorily I believe that we should not accept that the existence of a unique thermodynamic scalar pressure,  $p(\mathbf{r})$ , has been established.

A second system in which we can make explicit calculations is an assembly of molecules in a spherical cavity of dimensionality,  $d$ . A scalar pressure within such a cavity satisfies eqn (19) which can be integrated to give

$$\begin{aligned} p(r) &= \int_r^\infty ds \rho(s) (dv(s)/ds) \\ &= -kT \int_r^\infty ds [\rho(s) \exp(v(s)/kT)] (d/ds) [\exp(-v(s)/kT)]. \end{aligned} \quad (24)$$

If, as Lovett and Baus claim, this pressure is also the density of the grand potential,  $\Omega$ , then we can obtain their grand potential by integration over the cavity;

$$\Omega_{LB} = - \int_0^\infty dV_d p(r), \quad (25)$$



where  $V_d$  is the volume of a  $d$ -dimensional sphere of radius  $r$ ;  $dV_d = 4\pi r^2 dr$ , if  $d = 3$ . If we substitute  $p(r)$  from eqn (24) and integrate by parts, we have

$$\Omega_{LB} = \int_0^{\infty} dr V_d \left[ \rho(r) e^{u(r)/kT} \right] \frac{d}{dr} \left[ e^{-u(r)/kT} \right] . \quad (26)$$

If the cavity has hard walls and if its radius is  $R$ , this gives

$$\begin{aligned} \Omega_{LB}/kT &= - \int_0^{\infty} dr V_d \left[ \rho(r) e^{u(r)/kT} \right] \delta(r-R) \\ &= - V_d \rho_w(R) , \end{aligned} \quad (27)$$

where  $\rho_w(R)$  is the density at the wall, since we know that  $\rho(r) e^{u(r)/kT}$  is continuous at the wall even although both factors are discontinuous there. Now

$$kT \rho_w(R) = - (\partial \Omega / \partial V_d)_{T, \mu} . \quad (28)$$

This equation has been derived explicitly for  $d = 1$  (ref. 20) and for  $d = 3$  (ref. 10), and certainly holds for all other dimensions. So

$$\Omega_{LB} = V_d (\partial \Omega / \partial V_d)_{T, \mu} . \quad (29)$$

If  $\Omega_{LB}$  is to be identified with  $\Omega$  then this differential equation has the solution

$$\Omega = V_d f_1(T, \mu) = - p_w(T, \mu) V_d , \quad (30)$$

where  $f_1$ , the constant of integration, can be identified with the negative of the pressure in an infinite system at the same  $T$  and  $\mu$ , if  $\Omega$  is to behave correctly in the thermodynamic limit. But we know that  $\Omega$  has the form

$$\Omega = - p_w V_d + R^{-1} V_d f_2(T, \mu) , \quad (31)$$

where  $f_2$  is a function that contains all the information about the surface contributions to  $\Omega$ . If  $d = 3$ ,  $f_2$  is three times the surface tension at the wall. If  $d = 1$ , then  $V_d = 2R$ , and the second term in eqn (31) is a constant,  $2 f_2(T, \mu)$ , which is known explicitly for hard-rod molecules (ref. 20). Lovett and Baus (ref. 18) claim only to determine  $\Omega$  to within a constant but we see here that this constant contains all the interesting part of  $\Omega$  in an inhomogeneous system.

## CONCLUSION

We have seen that inhomogeneities of macroscopic scale length are benign; they do not prevent us defining local thermodynamic functions that are unique functions of other well-defined local variables. But if the scale of length of the inhomogeneity is of the order of the correlation length then we can define uniquely only a local number density and the two potentials, temperature and chemical potential, that are uniform throughout the system. There have been several attempts to define a wider class of local functions. Rayleigh and van der Waals both proposed that local functions be expressed in terms not only of  $\rho(r)$ , but of its gradient  $|\nabla \rho(r)|^2$ , but they knew that they were generating an approximation, not an exact definition (ref. 21,22). More recently, Baus and Lovett have attempted to define the pressure uniquely. If their results are accepted then unique definitions of other thermodynamic functions follow at once. There are, however, strong arguments to show that their results do not hold in general, but that they may be maintainable for systems with planar symmetry, although even in those cases they may not be easy to interpret physically.

## Acknowledgement

I thank Dr. Ronald Lovett for early copies of his papers and for much helpful correspondence.

## REFERENCES

1. J.S. Rowlinson and B. Widom, *Molecular Theory of Capillarity*, chap. 4, Oxford University Press, Oxford (1982).
2. R.B. Griffiths and J.C. Wheeler, *Phys. Rev. A* **2**, 1047-1064 (1970).
3. Ref. 1, Appendix 1.
4. B. Widom, *J. Chem. Phys.* **39**, 2808-2812 (1963).
5. B. Widom, *J. Statist. Phys.* **19**, 563-574 (1978).
6. P. Schofield and J.R. Henderson, *Proc. Roy. Soc. London A* **379**, 231-246 (1982).
7. J.H. Irving and J.G. Kirkwood, *J. Chem. Phys.* **18**, 817-829 (1950).
8. A. Harasima, *Adv. Chem. Phys.* **1**, 203-237 (1958).
9. J.P.R.B. Walton, D.J. Tildesley and J.S. Rowlinson, *Molec. Phys.* **48**, 1357-1368 (1983).
10. J.R. Henderson, in *Fluid Interfacial Phenomena*, ed. C.A. Croxton, chap. 12, Wiley, Chichester (1986).
11. S.J. Hemingway, J.R. Henderson and J.S. Rowlinson, *Faraday Symp. Chem. Soc.* **16**, 33-43 (1981).
12. S.J. Hemingway, J.S. Rowlinson and J.P.R.B. Walton, *J. Chem. Soc. Faraday Trans. 2* **79**, 1689-1698 (1983).
13. M. Baus and R. Lovett, *Phys. Rev. Lett.* **65**, 1781-1783 (1990).
14. M. Baus and R. Lovett, *Phys. Rev. A* **44**, 1211-1218 (1991).
15. [C.L.M.H.] Navier, *Resumé des Leçons données à l'École des Ponts et Chaussées sur l'Application de la Mécanique à l'Établissement des Constructions et des Machines*. Troisième édition avec des Notes et des Appendices par [A.J.C.] Barré de Saint-Venant, App. 3, § 32, p. 597, Dunod, Paris (1864).
16. J.S. Rowlinson, *Phys. Rev. Lett.* **67**, 406 (1991).
17. M. Baus and R. Lovett, *Phys. Rev. Lett.* **67**, 407 (1991).
18. R. Lovett and M. Baus, *Physica A* **181**, 309-328 (1992).
19. J.S. Rowlinson, *Proc. Roy. Soc. London A* **402**, 67-82 (1985).
20. A. Robledo and J.S. Rowlinson, *Molec. Phys.* **58**, 711 (1986).
21. Lord Rayleigh, *Philos. Mag.* **33**, 209-220 (1892).
22. J.D. van der Waals, *Zeit. Phys. Chem.* **13**, 657-725 (1893) ; English translation, *J. Stat. Phys.* **20**, 197-244 (1979).