

LIVERSIDGE LECTURE*

The Surface of a Liquid

By J. S. Rowlinson

PHYSICAL CHEMISTRY LABORATORY, SOUTH PARKS ROAD,
OXFORD, OX1 3QZ

1 Introduction

Until about ten years ago it was common to read in books and reviews that little was understood about the structure and properties of liquids, in contrast with our detailed understanding of gases and solids. The position has now changed dramatically; quantitatively acceptable theories of the structure and equilibrium properties of liquids have been developed and tested exhaustively.¹ There are still problems of relating structure to intermolecular forces in liquids composed of polar, flexible, or ionized molecules, and in understanding the dynamic properties, but we now understand well the relation between structure and intermolecular forces for liquids and liquid mixtures composed of simple molecules.

Our understanding of the molecular structure of the gas-liquid surface is, however, still at the primitive state of our understanding of bulk liquids fifteen years ago. There are several reasons for this. First, the diffraction and scattering experiments that have proved so powerful in determining the structure of bulk matter and of the gas-solid surface have been much less effective for probing the structure of the gas-liquid surface. Visible light is reflected from the surface and can reveal structure on a scale down to about 10^{-5} cm, but this is still in the continuum or hydrodynamic regime—nothing molecular can be seen on such a scale. The technique of ellipsometry can in principle extend this range to 10^{-6} cm, or even lower for the gas-solid surface,² but this is still a large distance when compared with the thickness of the surface layer separating a vapour from its liquid near its triple point, which is generally about 10^{-8} – 10^{-7} cm. Optical reflectance is useful only at higher temperatures, close to the critical point, where the thickness of the surface layer grows to 10^{-5} cm and beyond.³

Shorter wavelengths, X-rays or neutrons, have been little used, since it is difficult to distinguish between the scattering from the surface and that from the bulk. If, however, the refractive index of the liquid is less than unity then the rays

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¹ For recent reviews see J. P. Hansen and I. R. McDonald, 'Theory of Simple Liquids', Academic Press, London, 1976; J. A. Barker and D. Henderson, *Rev. Mod. Phys.*, 1976, **48**, 587.

² For the study of surface films by ellipsometry see *Symposia Faraday Soc.*, 1970, No. 4.

³ J. S. Huang and W. W. Webb, *Phys. Rev. Letters*, 1969, **23**, 160; E. S. Wu and W. W. Webb, *Phys. Rev. (A)*, 1973, **8**, 2065.

that are totally reflected are on the gas side of the surface not, as is usual, on the liquid side. Rice and Lu⁴ are exploiting this fact to study the total reflection of X-rays from a clean mercury surface. The refractive index is only a little less than unity ($n \approx 1 - 10^{-6}$) and so the angle for total reflection is close to the grazing angle. The experiment is difficult, but is a promising way of determining surface profiles when the refractive index permits.

The second difficulty in determining the molecular structure of the gas-liquid surface is that of developing a molecular theory—that is, a self-contained theory which allows us to deduce the structure from a knowledge of the intermolecular forces.⁵ The statistical mechanics of inhomogeneous systems is a difficult and, until recently, little studied branch of theory.

There are two ways of making progress when faced with such experimental and theoretical difficulties. As a substitute for experiment we can turn to computer simulation, and as a substitute for the statistical theory of realistic systems we can turn to the study of model systems that are theoretically tractable but physically less realistic than we would wish. This review describes some recent work along both these lines.

2 Computer Simulation of the Surface

There are two kinds of computer simulation, conventionally called Monte Carlo (MC) and molecular dynamic (MD) simulation,⁶ and in each we model a small portion of the system of interest by establishing within the computer store a set of co-ordinates to describe the positions of (usually) between 100 and 1000 molecules, and a specification of the intermolecular energy between each pair. In a MC simulation we specify the temperature, and then move the molecules in such a way that each configuration appears with a probability proportional to its Boltzmann factor, $\exp(-U_{\text{config}}/kT)$, where U_{config} is the sum of all the intermolecular energies. Averages over many such configurations give the equilibrium but not the dynamic properties of the system. In a MD simulation, one gives each molecule a randomly chosen velocity and then solves Newton's equations of motion to find out how the system evolves in time. After a system of fixed initial energy has come to equilibrium the average temperature is steady, but subject to statistical fluctuations, and equilibrium properties can be found from an average over time. Here dynamic properties can also be calculated since the successive states of the system are generated in their correct time sequence.

It is only recently that these techniques have been applied to the gas-liquid surface. The main difficulty is in devising constraints that maintain a plane surface fixed in 'laboratory' (*i.e.* computer) co-ordinates without distorting the molecular structure of the surface. In the real world a weak gravitational field, acting on a system large compared with the range of the intermolecular forces, gives this stability. This will not do for a system of 1000 molecules, since over a

⁴ S. A. Rice and B.-C. Lu, personal communication.

⁵ For a recent review of statistical theories of the gas-liquid surface see S. Toxvaerd, 'Statistical Mechanics', ed. K. Singer (Specialist Periodical Reports), The Chemical Society, London, 1975, Vol. 2, p. 256.

⁶ I. R. McDonald and K. Singer, *Quart. Rev.*, 1970, **24**, 238.

distance of about 10 molecular diameters the change in the earth's gravitational potential is only about 10^{-6} of the intermolecular energy, and so without effect. To use a much more powerful gravitational potential would risk distorting the delicate molecular structure of the surface. The problem can be overcome to a large degree by using a device that is, in any case, necessary on other grounds. We assume that the rectangular prism that contains the molecules is surrounded on each of its four vertical sides by an infinite set of replicas of itself. Each molecular x - and y -coordinate is thus repeated in each cell, but the molecules can pass freely through these vertical walls. In this way a molecule leaving the cell through, say, the right-hand wall is deemed to re-enter through the corresponding point on the left-hand wall; the fluid can be regarded as having an infinite extent in the x - and y -directions. Once a planar surface has been established, the repetition of the x - and y -coordinates ensure that it remains planar on the square grid formed where this plane cuts the vertical walls.

Most of our work has been carried out in a cell $5\sigma \times 5\sigma$ in the x - and y -dimensions and 25σ in vertical or z -direction, where σ is the molecular diameter (Figure 1). The liquid phase is anchored to the bottom half of the cell by placing

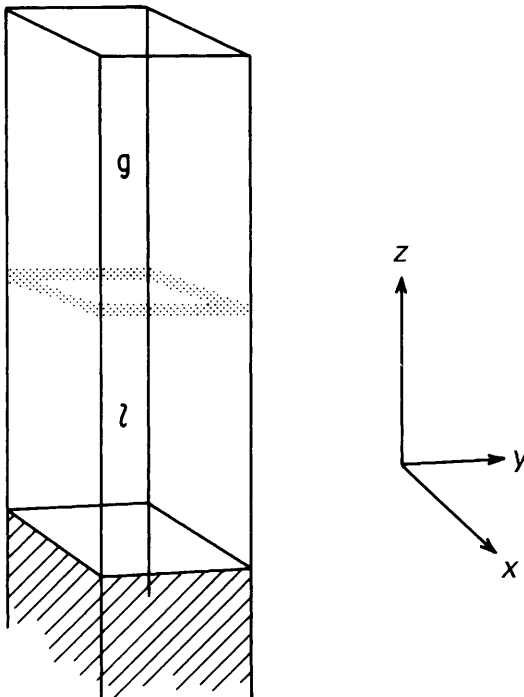


Figure 1 Sketch of the cell used for a computer simulation. The gas is in the upper half and the liquid is anchored to the lower half by the intermolecular forces emanating from a simulated homogeneous liquid phase below the bottom wall of the cell (shown shaded). The top and bottom walls are reflecting boundaries, but the molecules pass freely through the four vertical walls

beneath the bottom wall a crude representation of the bulk liquid which interacts with the molecules in the cell through an averaged intermolecular potential.⁷ The top and bottom walls are impenetrable to the molecules and this constraint induces a distortion of the local fluid densities near these boundaries, $z = 0$ and $z = 25\sigma$; that at the bottom is clearly visible in the graphs shown below, but is unimportant if we are interested only in the fluid near the gas-liquid surface at about $z = 13\sigma$.

Other workers⁸ have used similar constraints, but Barker and his colleagues⁹ rely solely on the repetition of the x - and y -co-ordinates to keep a two-sided semi-infinite slab of liquid near the centre of the cell, with two planar surfaces, and gas in the bottom and top thirds of the cell. This arrangement avoids the distortion of impenetrable boundaries but allows the slab of liquid to move as a whole in the z -direction.

Almost all work up to now⁷⁻¹¹ has used a Lennard-Jones intermolecular potential

$$u(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] \quad (1)$$

where $u(\sigma) = 0$, and $-\epsilon$ is value of u at its minimum. (The potential is sometimes put equal to zero beyond $r = 2.5\sigma$ or 3σ for computational convenience). This is, in fact, a simple effective potential for the liquid inert gases, but an assembly of Lennard-Jones molecules is properly regarded as a realistic model, rather than as the best representation of a real system. The properties of the bulk gas and liquid phases of this model fluid are now well established by computer simulation, and we show below how this technique can be used to study the properties of the gas-liquid surface

3 The Structure and Properties of the Liquid Surface

A. The Surface Profile.—The density of a vapour near its triple point is generally only 10^{-3} or less of that of the liquid in equilibrium with it. This great change is believed to take place over a distance comparable with the size of a molecule or with the effective range of its intermolecular potential. The difference in density decreases at high temperatures, vanishing at the critical point, and the thickness of the interface increases, becoming infinite at the critical point. The first question of interest is therefore, what is the function $\rho(z)$ which represents this change of density, $\rho = N\sigma^3/V$ with height, z . Figure 2 shows the computed surface profiles for three reduced temperatures $\tau = kT/\epsilon$ for a Lennard-Jones fluid, whose triple point is at $\tau = 0.68$ and whose critical point at $\tau = 1.34$. As the

⁷ G. A. Chapela, G. Saville, and J. S. Rowlinson, *Faraday Discuss. Chem. Soc.*, 1975, No. 59, p. 22.

⁸ A. C. L. Optiz, *Phys. Letters (A)*, 1974, **47**, 439; K. S. Liu, *J. Chem. Phys.*, 1974, **60**, 4226.

⁹ F. F. Abraham, D. E. Schreiber, and J. A. Barker, *J. Chem. Phys.*, 1975, **62**, 1958.

¹⁰ M. Rao and D. Levesque, *J. Chem. Phys.*, 1976, **65**, 3233.

¹¹ M. H. Kalos, J. K. Percus, and M. Rao, *J. Stat. Phys.*, 1977, **17**, 111.

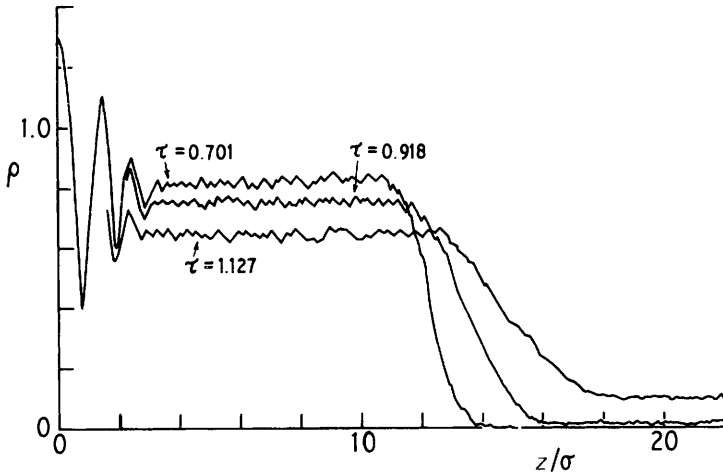


Figure 2 Three density profiles. The local density ρ is shown as a function of the height z for three reduced temperatures, $\tau = 0.701, 0.918,$ and 1.127 . The oscillations for $z < 4\sigma$ are artefacts induced by reflection of molecules at the bottom wall, $z = 0$

temperature rises the liquid density falls, the gas density rises, and the thickness increases. The last is conventionally defined by

$$d = (\rho_l - \rho_g)[|\rho'(z^*)|]^{-1} \quad (2)$$

where z^* is the height at which the profile is steepest and $|\rho'(z^*)|$ the absolute value of the slope at that point. The thickness calculated from these runs increases from 1.5σ just above the triple point ($\tau = 0.70$) to 2.2σ at $\tau = 0.92$ and 3.1σ at $\tau = 1.13$.

These results agree with our expectations, but when we turn to the effect of the size of the system, in the x - and y -directions, on the shape of the profile $\rho(z)$, then the position is not so happy. It is our hope that, as the area \mathcal{A} of the system increases indefinitely, such functions as $\rho(z)$ quickly settle down to a steady value that is independent of \mathcal{A} . Such limits undoubtedly exist for the properties of homogeneous fluids, although their existence is often difficult to prove, and the steady values of the functions are said to be those of the *thermodynamic limit*.

To study the existence of such a limit for $\rho(z)$ we used not only cells of $5\sigma \times 5\sigma$ in cross-section (containing 255 molecules, see Figures 1 and 2), but also $10\sigma \times 10\sigma$ (1020 molecules) and $20\sigma \times 20\sigma$ (4080 molecules). The computing runs¹² take much longer with these large samples and only sparse information could be obtained. The thickness (Figure 3) is, however, found to increase with \mathcal{A} at all temperatures. It may be approaching a finite limit, or it may be diverging weakly to infinity—the evidence is inconclusive—but at least no limit has been reached at an area of $400\sigma^2$. There are recent theoretical arguments which suggest

¹² G. A. Chapela, G. Saville, S. M. Thompson, and J. S. Rowlinson, *J.C.S. Faraday II*, 1977, **73**, 1133.

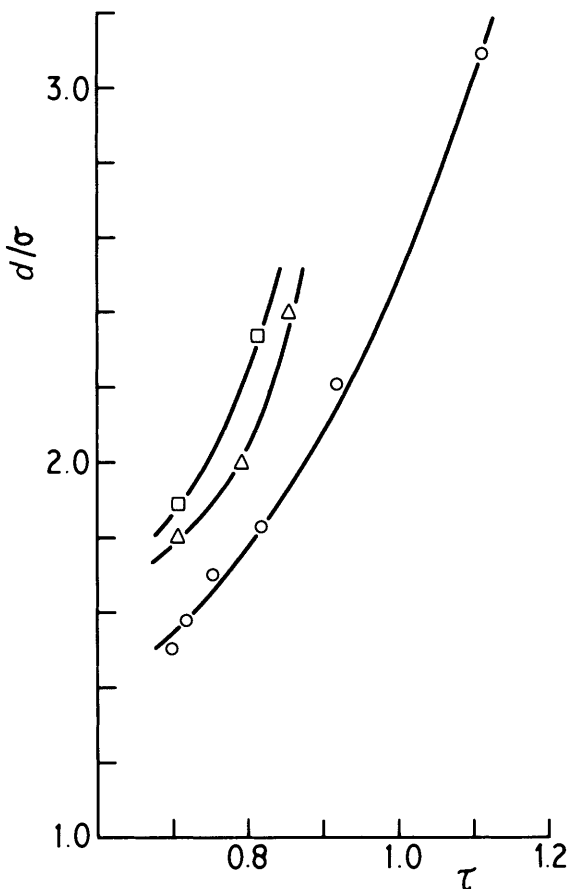


Figure 3 The thickness of the surface, as defined in equation (2), as a function of the reduced temperature τ , for three different surface areas: \circ , $A = 25\sigma^2$; \triangle , $A = 100\sigma^2$; \square , $A = 400\sigma^2$

that the correct result is a slow divergence.^{11,13} Even a weak gravitational field probably suppresses the divergence, which arises from the build-up of long but feeble capillary waves, so if we are to look for the divergence experimentally it will have to be on the surface of a large sphere of liquid in a space laboratory.

The existence of such a divergence is therefore of little practical importance, but its theoretical significance is considerable. If we cannot go to the thermodynamic limit, without applying a gravitational field, then the development of a rigorous statistical mechanics of the gas-liquid surface is going to be much more difficult than might be expected. Indeed the status of $\rho(z)$ calculated for theoretical models (see *e.g.* Section 4) is called in question. This is not a problem that can be

¹¹ M. S. Wertheim, *J. Chem. Phys.*, 1976, **65**, 2377; J. D. Weeks, *ibid.*, 1977, **67**, 3106; H. T. Davis, *ibid.*, 1977, **67**, 3636.

pursued here except to remark that the calculated profiles may represent an average local profile at a fixed time, in which the long capillary fluctuations are ignored.

B. Temperature, Pressure, and Chemical Potential.—Once the profile $\rho(z)$ has been determined it is natural to ask about the behaviour in the surface of the temperature, pressure, and chemical potential, *i.e.* about the functions, $T(z)$, $p(z)$, and $\mu(z)$. These each have the same value in the two bulk phases, for this is a condition of equilibrium. How do they behave in the surface region where $\rho(z)$ is a rapidly changing function of z ? Before this question can be answered we need an operationally meaningful definition of the local values of these functions.

A local temperature can be defined in terms of a local density of kinetic energy. In a classical, but not in a quantal system, the kinetic energy of the monatomic molecules is strictly separable from all other energies and so its local density can be used to define a local temperature. Figure 4 shows that molecules in the

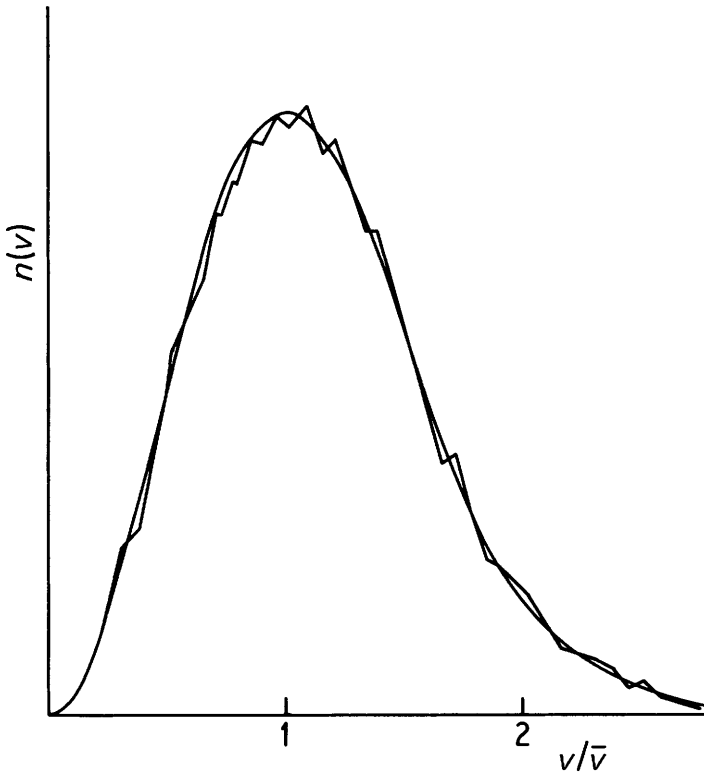


Figure 4 The distribution function of molecular speeds, $n(v)$, in arbitrary units, for molecules in the surface layer ($\tau = 0.708$). The segmented curve is the result of the computer simulation and the smooth curve is the Maxwell-Boltzmann function for this temperature

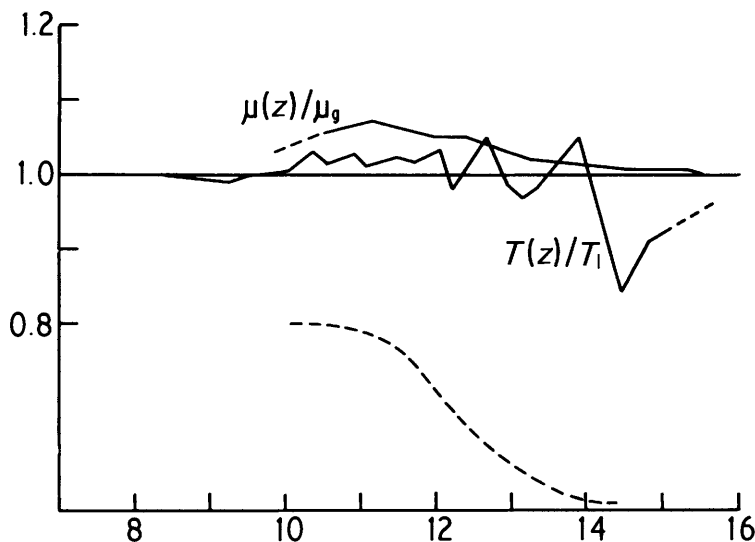


Figure 5 Temperature and chemical potential in the surface layer. The two functions plotted are the ratios $T(z)/T_1$ and $\mu(z)/\mu_g$ where $T(z)$ and $\mu(z)$ are the local values of the temperature and the configurational chemical potential. The statistics of the computation are such that T_1 and μ_g are relatively easy to estimate but T_g and μ_l are difficult. The dashed curve in the lower part of the diagram is a sketch of $\rho(z)$ from Figure 2, which serves to show the position of the gas-liquid surface

surface layer have a Maxwell-Boltzmann distribution of speeds, and Figure 5 shows that $T(z)$ is, within the statistical error, a constant independent of z .

A local pressure can be defined, although not entirely without ambiguity,¹⁴ in terms of the local strength of the intermolecular forces. It is not a constant scalar quantity, independent of z , although this is the expected behaviour of its component normal to the surface; $p_N(z) = p_g = p_l \equiv p$. The transverse component of the pressure tensor $p_T(z)$ is not a constant, but reduces to p in the homogeneous bulk phases. It is the integrated difference between these two components that is measured by the surface tension

$$\gamma = \int_{-\infty}^{+\infty} dz [p - p_T(z)] \quad (3)$$

[The value of the integral is independent of any local ambiguity in defining $p_T(z)$]. For a computer calculation this equation is more conveniently re-written in a form, due to Kirkwood and Buff,¹⁵ to which we turn in the next Section.

The constancy of the chemical potential is a more subtle question. Gibbs¹⁶ asserted that $\mu(z)$ was a constant, equal to μ_g and μ_l , but did not define exactly what he meant by $\mu(z)$. The question has been debated many times since in classical thermodynamic terms,¹⁷ but it is one which can be resolved only in

¹⁴ A. Harasima, *Adv. Chem. Phys.*, 1958, **1**, 203.

¹⁵ J. G. Kirkwood and F. P. Buff, *J. Chem. Phys.*, 1949, **17**, 338.

¹⁶ J. W. Gibbs, 'Collected Works', Longmans, New York, 1928, Vol. 1, p. 219.

¹⁷ J. C. Eriksson, *Adv. Chem. Phys.*, 1964, **6**, 145.

terms of statistical mechanics. This was not done until 1963 when there was derived¹⁸ what is now usually called the *potential distribution theorem*. This allows us, by means of a thought-experiment, to measure chemical potential at a point by repeatedly adding an additional or test molecule at that point, observing the change in the Boltzmann factor, and then withdrawing the test molecule. The experiment is one more easily made on the computer than in the laboratory, but even there it is statistically difficult to get a good result. Figure 5 shows that $\mu(z)$ is, approximately, independent of z ; to be more precise our sampling technique shows a small mis-match between μ_g and μ_l , and that $\mu(z)$ in the surface layer is, at least, not behaving in some quite unforeseen way. We return to this point in the discussion of a model system in Section 4.

C. The Calculation of Surface Tension.—The mechanical definition of surface tension, equation (3), can be transformed into one relating the tension to a lack of balance of the intermolecular forces in the surface layer,

$$\gamma = \mathcal{A}^{-1} \left\langle \sum_{ij} \frac{r_{ij}^2 - 3z_{ij}^2}{r_{ij}} \frac{du(r_{ij})}{dr_{ij}} \right\rangle \quad (4)$$

where the sum is taken over all molecular pairs, i and j , and where this pair is separated by r_{ij} of which the vertical component is z_{ij} . The angle brackets denote an average over a system at equilibrium. By symmetry, $\langle r_{ij}^2 - 3z_{ij}^2 \rangle$ vanishes in a homogeneous fluid so that the whole of the effective contribution to the sum in equation (4) comes from the surface layer.

Figure 6 shows the results obtained by our and other computer simulations, and the line is the result of a perturbation theory developed by Toxvaerd.⁵ This calculation assumes a particular functional form of $\rho(z)$ and so is not an *a priori* calculation, but it is seen to be an accurate one. The possible conclusion is that the surface tension, although experimentally important, is not very sensitive to the precise form of $\rho(z)$ or to the molecular arrangements that give rise to it.

The surface tension vanishes at the critical point, but computer simulation cannot be used when the thickness of the surface becomes as large as the x - or y -dimensions of the cell.

D. Molecular Diffusion in the Surface Layer.—The properties of the surface layer discussed so far have all been equilibrium properties. Molecular dynamic simulation can also tell us of the dynamic or transport properties of a system, and the simplest of these is diffusion. In the laboratory we can measure a coefficient of self-diffusion if we can label a molecule isotopically in a way that has no effect on any relevant physical property. In a computer we can achieve the same end either directly, by keeping a record of each molecule's identity and position, or indirectly by studying the persistence of molecular velocities; the latter is technically the easier.

¹⁸ B. Widom, *J. Chem. Phys.*, 1963, **39**, 2808; J. L. Jackson and L. S. Klein, *Phys. Fluids*, 1964, **7**, 228.

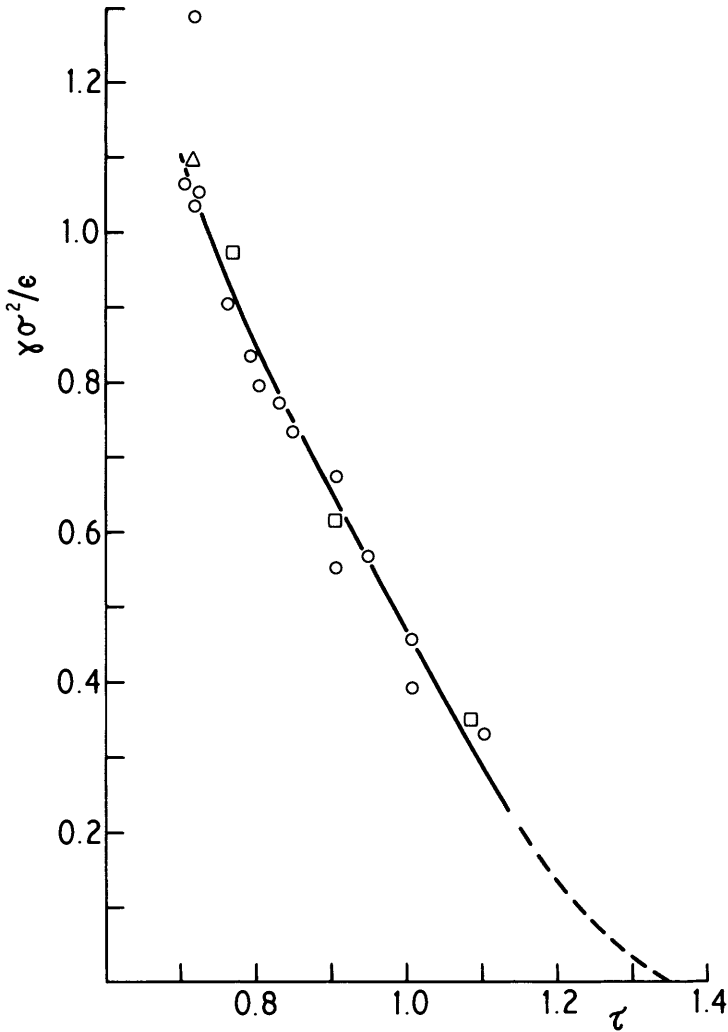


Figure 6 The reduced surface tension, $\gamma\sigma^2/\epsilon$, as a function of reduced temperature τ . ○, ref. 12; △, ref. 9; □, ref. 8. The surface tension vanishes at the critical temperature, $\tau^c = 1.34$, but computer simulation cannot be used near this temperature

Let $\mathbf{v}(0)$ be the velocity of a molecule at a time, taken to be zero, and $\mathbf{v}(t)$ its velocity at time t later. The average value of the scalar product of these two velocities $\langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle$ is a measure of the persistence of velocities, for this function of time starts at $\langle [\mathbf{v}(0)]^2 \rangle = 3kT/m$, and goes to zero as t becomes infinite. At very long times the average square of the speed of a molecule will still be of the order of $3kT/m$, but the direction of its velocity will be quite

uncorrelated with that at $t = 0$; hence the average value of the scalar product is zero. Einstein showed that the coefficient of diffusion is determined by an integral over all time of this velocity auto-correlation function,¹⁹ which we denote $\psi(t)$:

$$\psi(t) \equiv \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle / \langle v(0)^2 \rangle \quad (5)$$

$$D = \frac{3kT}{m} \int_0^\infty \psi(t) dt \quad (6)$$

In a dense homogeneous fluid the correlation function falls from $\psi(0) = 1$ to zero at a time of about 10^{-13} s, and is small and negative for longer times, becoming indistinguishable from zero after about 10^{-2} s. The negative region arises from the probable reversal of the direction of motion of a molecule in a liquid after it has moved for a distance comparable with the mean molecular spacing. This result is confirmed in our computer simulations²⁰ for those molecules which start at $t = 0$ in the middle of the liquid zone, *i.e.* at a height of around $z = 7\sigma$. If, however, we take the average in (5) only over those molecules which start in the surface layer, $12.4\sigma < z < 12.6\sigma$, then we obtain different preliminary results. It is instructive to analyse separately the motions in the z -direction and in the x - and y -directions. Neither $\psi_z(t)$ nor $\psi_x(t) = \psi_y(t)$ has a negative region, and the latter has a particularly pronounced long positive tail. The area under the curve for ψ_x or ψ_y is greater than that under ψ_z . We deduce that molecular motion parallel to the surface shows a greater persistence of velocity than that normal to the surface and so also it must have a greater coefficient of diffusion. Molecules moving along the surface seem almost to 'skate' without experiencing the hindrances of those molecules moving in or out of the liquid.

E. Adsorption.—In a mixture of two components, a and b, the surface structure can be defined by means of the two functions $\rho_a(z)$ and $\rho_b(z)$. These will generally be different functions since we know¹⁶ that the component of lower surface tension is present in excess in the surface layer. A measure of this excess is provided by the quantity Γ where

$$\Gamma = x_a^{-1}\Gamma_b - x_b^{-1}\Gamma_a \quad (7)$$

and Γ_a and Γ_b are the numbers of molecules of each component per unit area of the surface phase.²¹ Gibbs showed by thermodynamic arguments that Γ is proportional to the rate of isothermal change of surface tension with composition of the liquid phase.¹⁶ If the liquid mixture is ideal, then

$$(\partial\gamma/\partial x_b)_T = -\Gamma(kT/x_a^{-1}x_b^{-1}) \quad (8)$$

It is difficult to test this equation since Γ is not easily measured. The classic method of McBain was to use a microtome to slice off the surface layer, and

¹⁹ J. S. Rowlinson and M. Evans, *Ann. Reports (A)*, 1975, **72**, 5.

²⁰ S. M. Thompson, G. Saville, and J. S. Rowlinson, unpublished results.

²¹ A. W. Adamson, 'Physical Chemistry of Surfaces', 3rd Edn., Wiley, New York, 1976, Section II, p. 6.

then to analyse it.²¹ More accurate is the use of β -active tracers whose emission has so short a range that the activity of the surface layer can be measured without too much contamination from the bulk liquid.²¹ Computer simulation allows a third method of test with the added bonus of telling us not only how much is adsorbed, but exactly where it is adsorbed; that is, we can study $\rho_a(z)$ and $\rho_b(z)$, and not merely integrals of these functions.

The system chosen for simulation¹² is one of two Lennard-Jones molecules with ϵ parameters chosen to represent rather crudely either argon (substance a) or krypton (substance b). The results (Figure 7) show that the lighter component

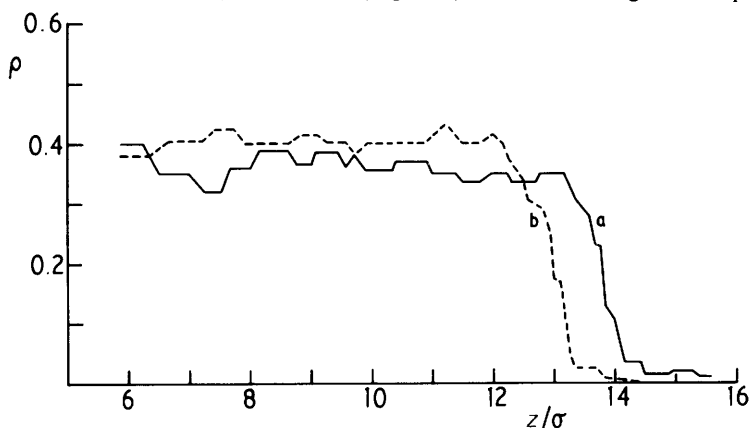


Figure 7 The surface profile for a binary mixture. The full curve, a, is the component of lower surface tension ('argon') and the dashed curve, b, that of higher surface tension ('krypton')

is adsorbed at the surface, and that the form of this adsorption is a monatomic layer of almost pure a; that is the profile $\rho_a(z)$ extends into the gas phase by about one more diameter σ than the profile $\rho_b(z)$. Figure 8 shows that the integrated amount of this excess is consistent, within the rather large errors, with the excess calculated from Gibbs's equation (8). The agreement is about as good as can be obtained by the microtome method, but rather less than the best β -isotope experiments, which are, however, restricted to surface-active materials.

4 The Penetrable Sphere Model

There is a long tradition in physics of devising models to represent phase transitions which are constructed in such a way that the theoretical difficulties are less than they would be for a real system. The classic case is the Ising model of ferromagnetism, and its vast literature is a measure of its value in studying the statistical mechanics of phase transitions.

The penetrable sphere model²² is particularly suitable for studying the gas-liquid transition, and the structure of the surface phase, since it is one in which

²² B. Widom and J. S. Rowlinson, *J. Chem. Phys.*, 1970, **52**, 1670.

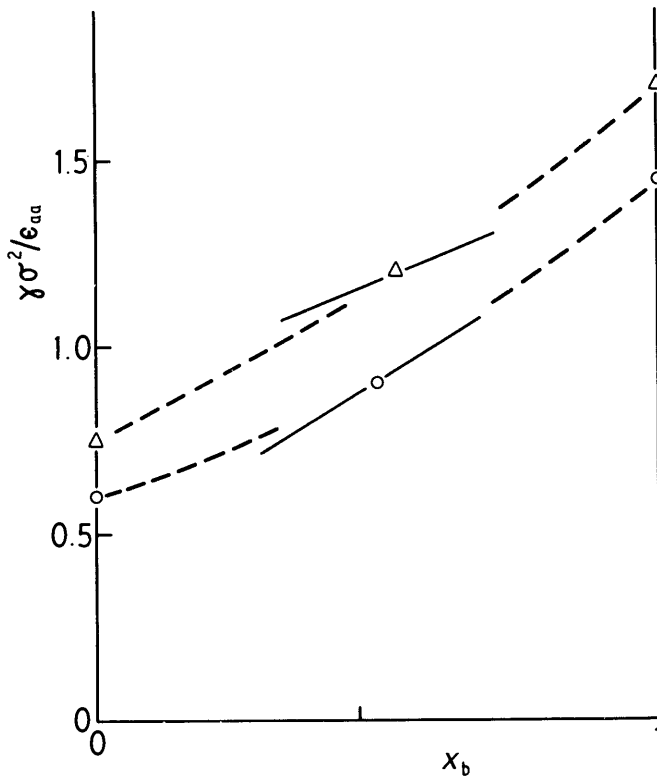


Figure 8 Reduced surface tension as a function of composition in a binary mixture. The circles are for a reduced temperature of $\tau_{aa} = 0.701$, and for a computer simulation by the Monte Carlo method. The triangles are for a reduced temperature of $\tau_{aa} = 0.713$, and for a Molecular Dynamic simulation. The straight lines are the slopes calculated from the adsorption by means of the Gibbs equation

the molecules can move freely through space without restriction to lattice sites or cells (as in the Ising model). It is described by specifying the energy of interaction of a set of N molecules. Around each molecule draw a sphere of volume v_0 , and allow the molecules to occupy any set of positions $\mathbf{r}_1 \dots \mathbf{r}_N$ in a volume V . Let $W(\mathbf{r}_1 \dots \mathbf{r}_N)$ be the total volume covered by the N freely interpenetrating spheres (Figure 9) and let the energy of this configuration of the molecules be $U(\mathbf{r}_1 \dots \mathbf{r}_N)$ where

$$U(\mathbf{r}_1 \dots \mathbf{r}_N) = [W(\mathbf{r}_1 \dots \mathbf{r}_N) - Nv_0](\epsilon/v_0) \quad (9)$$

where ϵ is a characteristic energy. Clearly if no spheres overlap $W = Nv_0$, and U is zero. As the molecules become more closely packed overlapping will occur and $W < Nv_0$, so that $U < 0$. Hence the intermolecular energy is either zero or negative; that is, it is an 'attractive' intermolecular potential. At sufficiently low values of kT/ϵ such a system can be shown to form two phases, a gas and a

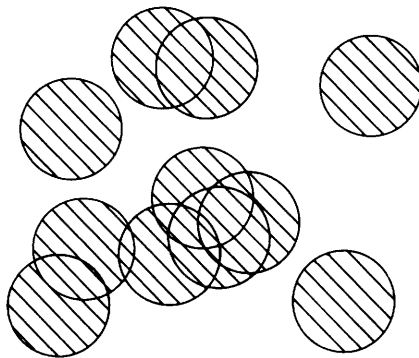


Figure 9 A typical cluster of $N = 11$ molecules in the penetrable sphere model. The shaded volume (area in this two-dimensional sketch) is that denoted $W(\mathbf{r}_1 \dots \mathbf{r}_N)$ in equation (9), and the energy $U(\mathbf{r}_1 \dots \mathbf{r}_N)$ is proportional to the difference between this volume and that of the eleven separate spheres, Nv_0

liquid. The critical temperature is not known exactly but is of the order of $kT_c \approx \epsilon$.

The intermolecular potential is quite unrealistic, but it has the two virtues of leading to a realistic phase transition, and, because of a hidden symmetry analogous to the spin-up–spin-down symmetry of the Ising model, of leading to tractable equations for $\rho(z)$ in the gas–liquid surface. In the simplest case this function is found to be a hyperbolic tangent.²³

The successful calculation of $\rho(z)$ allows us to use the model as a test-bed on which to try out ideas which seem to be plausible but which cannot be tested rigorously for more realistic systems. These have included:

(i) An explicit demonstration that the local chemical potential $\mu(z)$, as defined by means of the potential distribution theorem of Section 3B, is indeed a constant,²³ equal to μ_g and μ_l and independent of z .

(ii) A demonstration that the concept of a local Helmholtz free-energy density, a concept which has played an important role in theories of surface tension since the time of van der Waals, is useful near the critical temperature, but leads to inconsistencies at lower temperatures.^{23,24}

(iii) A demonstration that three apparently quite different theoretical routes to the calculation of the surface tension [one of which is equation (4) above] do, in fact, all lead to the same result.²⁵ This conclusion is well worth having since there had been some doubt of their equivalence,⁵ and although a proof for a model is not a proof in general, it goes a long way to setting such doubt at rest.

²³ C. A. Leng, J. S. Rowlinson, and S. M. Thompson, *Proc. Roy. Soc.*, 1976, **A352**, 1.

²⁴ J. M. Harrington and J. S. Rowlinson, unpublished results.

²⁵ C. A. Leng, J. S. Rowlinson, and S. M. Thompson, *Proc. Roy. Soc.*, 1978, **A358**, 267.

A mixture of penetrable sphere molecules is also a tractable model²⁶ and preliminary results²⁷ indicate that it will provide a possible theoretical test of Gibbs's adsorption equation at a molecular level.

Such results are an indication of the value of model systems in supplementing the few explicit theoretical results for realistic systems, and for testing the validity of theoretical ideas.

5 Conclusion

This review has not been a balanced review of recent work on the gas-liquid surface, but has had the aim of showing how two particular techniques can be used to increase our understanding of a surface at a molecular level. The first of these is computer simulation, which is justified when (and perhaps only when) the equivalent laboratory experiments are too difficult to carry out. The second is the use of a simple model system to answer questions on the statistical mechanics of a surface that are too difficult to be answered for more realistic representations of an actual surface. There is clearly much more work to be done along both lines.

This research could not have been carried out without the collaboration of those named in the references, and in particular without the computing skill of my former colleague Dr. Graham Saville of Imperial College. To these I owe my thanks.

²⁶ N. Desrosiers, M. I. Guerrero, J. S. Rowlinson, and D. Stubbley, *J.C.S. Faraday II*, 1977, 73, 1632.

²⁷ C. A. Leng, P. Turq, and J. S. Rowlinson, unpublished results.