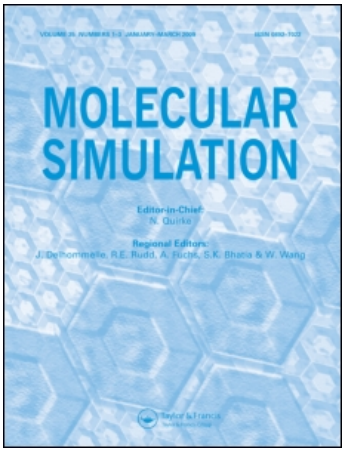

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The Role of Computer Simulation in Studying Fluid Phase Equilibria

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THE ROLE OF COMPUTER SIMULATION IN STUDYING FLUID PHASE EQUILIBRIA†

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Computer simulations provide a method for studying mixtures in which the intermolecular forces are precisely defined. They can be used to study specific systems, where laboratory experiments may be too costly, time consuming, or difficult, or to develop better theoretical equations of state. In this paper we first review some of the most promising methods for studying phase equilibria in fluid mixtures. These can be divided into direct methods, which simulate the two-phase system itself, and indirect methods in which the chemical potential of a homogeneous phase is determined. Examples of the use of each of these approaches given, including the determination of vapour-liquid equilibria for binary mixtures and of the properties of dilute solutions. This is followed by an application in which the objective is to develop a better equation of state for polar and associated fluids. Here, computer simulation is used to develop a more suitable reference term in the equation of state for such fluids.

KEY WORDS: Simulation, fluid phase equilibria, equations of state.

1 INTRODUCTION

An understanding of phase equilibria is of fundamental importance in such diverse areas as the chemical process and pharmaceutical industries, in geology, biology and the study of planetary atmospheres. In most cases the system of interest is a mixture, and the range of possible compositions, temperatures, and pressures is enormous. It is not feasible to experimentally determine the phase diagrams for all of the mixtures of practical interest. In a recent study of methods for determining phase equilibria in mixtures of concern to the chemical industry, it was estimated that laboratory experiments to measure the vapour-liquid part of the phase diagram for a simple binary mixture would typically cost about $20000 and take 60 man days by an experienced scientist [1]. By contrast, methods based on empirical or theoretical (e.g. perturbation theory) equations for the free energy require only $10–700 and a fraction of a day for the same task. Corresponding estimates for the cost and time for direct computer simulation of phase equilibria are difficult to make, since they depend so strongly on the complexity of the molecular model and the accuracy desired. For simple molecular models, at the level of Lennard-Jones or two-centre Lennard-Jones, for example, such calculations might cost a few thousand dollars and take a few hours of supercomputer time, using a direct technique such as the Gibbs ensemble method (see Sec. 2); simulations are therefore somewhat less expensive than laboratory experiments in money and time. For more complex molecules these figures could be much larger. These figures suggest that there are compelling practical, as well as theorectical, reasons for developing reliable theories and simulation techniques for the determination of phase equilibria.

†Invited paper.

Computer simulation can be expected to play an increasingly important role in developing better predictive methods for phase equilibria. There are two somewhat different approaches to the problem. In the first the phase diagram itself is calculated from a series of simulations for some model intermolecular potential that is chosen to represent the system of interest. Such calculations require special techniques, but can be broadly divided into direct methods, in which the properties of the coexisting phases are calculated directly, and indirect methods in which the free energy or chemical potentials are calculated, and then used to determine the phase equilibrium conditions. A second, alternative, approach is to use the simulations to build better theoretical equations for the thermodynamic properties, and then to use these equations to determine phase equilibria. Included in this approach is the use of computer simulation to study important reference substances that include essential features of the intermolecular interactions, such as the hard core repulsions between molecules, polarity, or molecular association. Less major effects of the interactions can then be included via perturbation terms, and computer simulations for more realistic potential models can again be used in developing the most appropriate form of these.

Methods for directly determining phase equilibria are discussed in Section 2, followed by a description of indirect methods based on determination of chemical potentials in Section 3. In Section 4 the role of simulation in building better theoretical equations for determining phase equilibria is discussed. While some of the methods can be used to study phase equilibria involving solid phases, this review will be limited to the study of fluid–fluid phase equilibria.

2 DIRECT SIMULATION METHODS

The most obvious method for studying phase equilibria is to carry out a simulation for a two-phase system in a box, the phases being separated by an interface. Such simulations have been extensively used to study the properties of the interfacial region, but can also be used in principle to obtain the properties of the coexisting

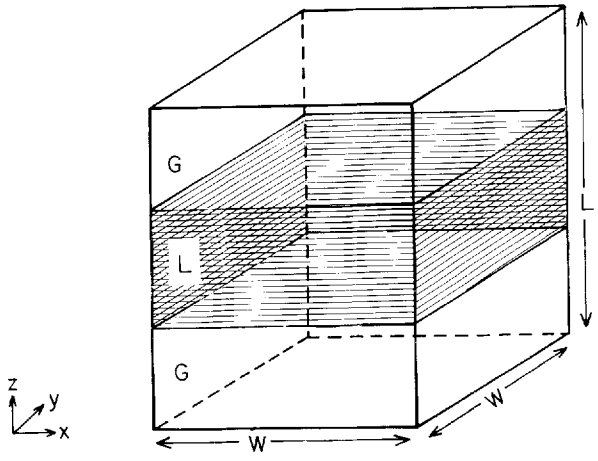

Figure 1 Direct simulation of a system of coexisting gas and liquid phases.

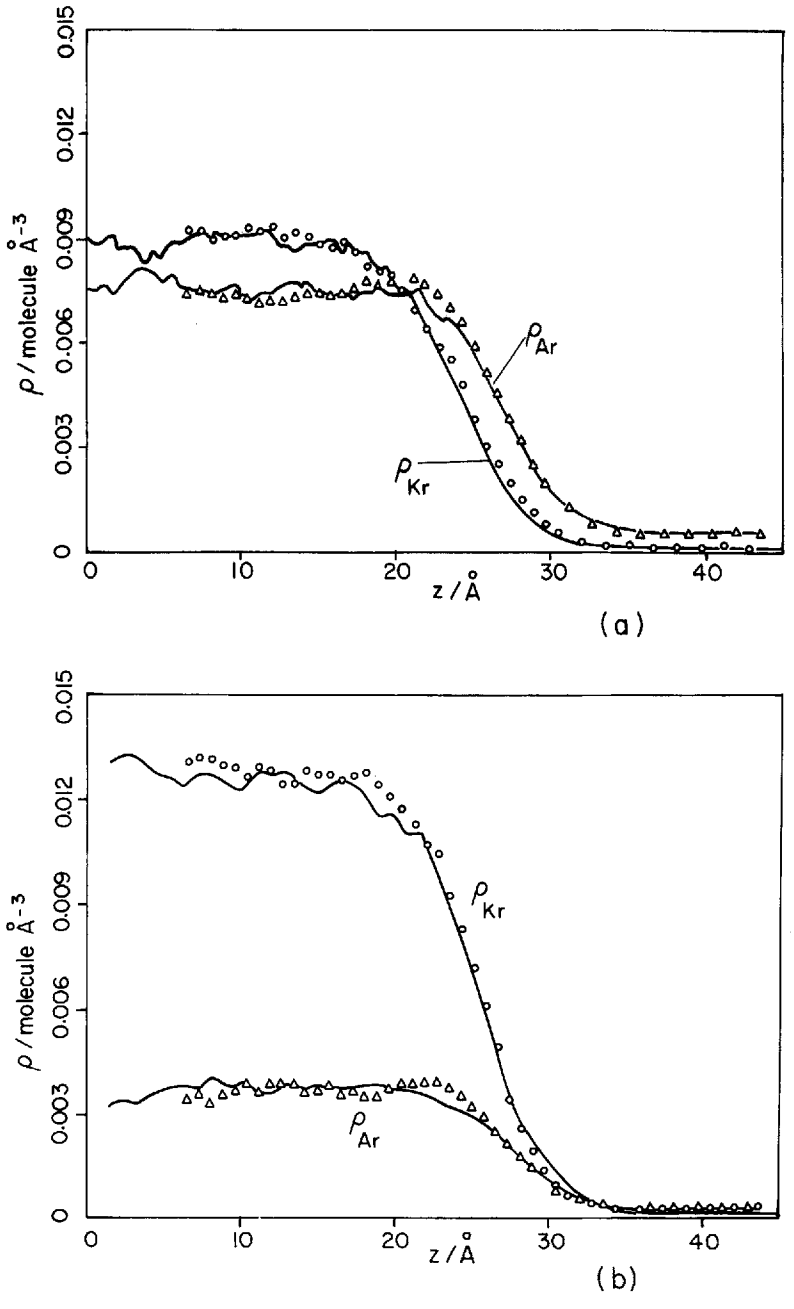

Figure 2 Density profiles from direct MD simulation of the vapour-liquid interface for a Lennard-Jones model of argon-krypton mixtures at $T = 115.77$ K: (a) $N_{Ar}/N = 0.5$, (b) $N_{Ar}/N = 0.25$. Solid lines are results for $N = 512$, points are for $N = 256$. In this simulation periodic boundary conditions were used in the x, y, and z directions.

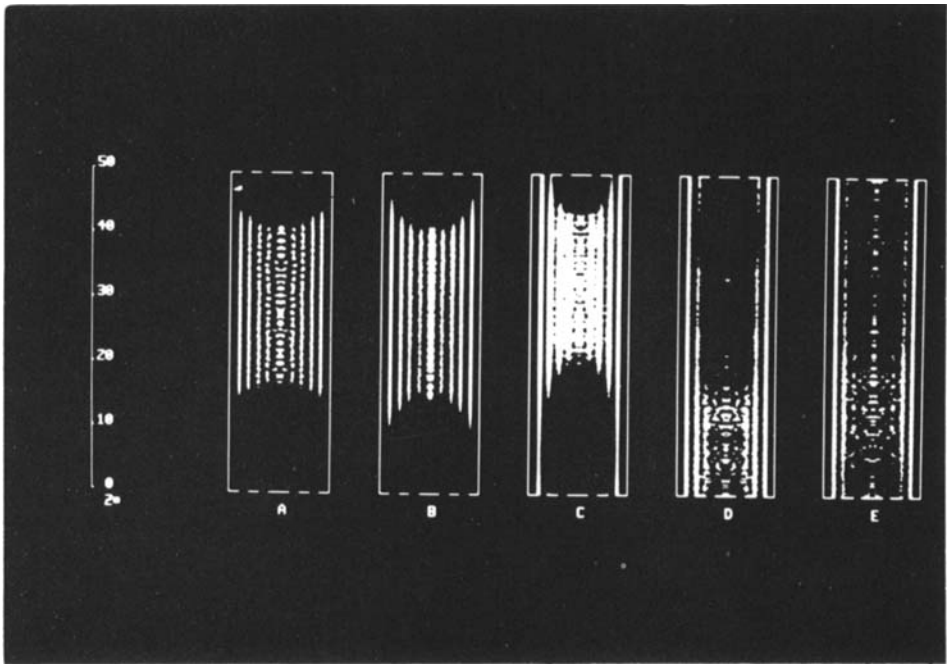

Figure 3 Vapour-liquid equilibria for a Lennard-Jones fluid in a cylindrical pore of radius R 5σ at reduced temperatures T^* of 0.5 (A), 0.7 (B), 0.85 (C), 1.0 (D), and 1.35 (E), from direct MD simulation. The light intensity is proportional to fluid density. (See reference [7].) (See colour plate I.)

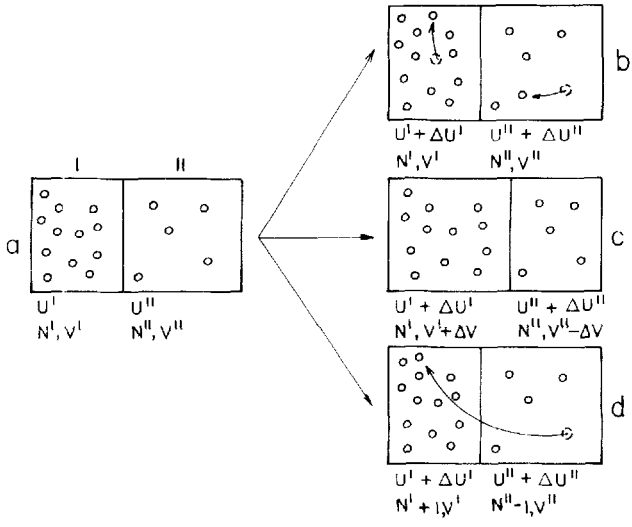

Figure 4 Steps involved in the Gibbs ensemble Monte Carlo method (from reference 9).

phases. Vapour-liquid interfacial studies up to 1981 have been reviewed by Rowlinson and Widom [2]. More recent studies of this type have included the vapour-liquid interfaces for square well [3] and Stockmayer [4] fluids. In the usual procedure, N molecules are placed in a rectangular prism dimensions $x = y = W$ and $z = L$ (see Figure 1), with the usual periodic boundaries in the x and y directions. The liquid is confined to the center of the cell, with vapour on either side of it. At each end of the cell in the z direction one may have a reflecting wall [3, 4], or alternatively use periodic boundary conditions [5, 6]. The use of a reflecting wall has no significant effect on the liquid surface at low temperatures, where the vapour density is very low, provided that L is sufficiently large. A simulation is started by placing a slab of previously equilibrated liquid in the centre of the cell, with a vacuum on either side. Provided the initial bulk liquid has a density close to the coexisting density, evaporation occurs to form a stable two-phase system. If the initial conditions are chosen so that the system as a whole has no resultant translational or rotational velocity, than this configuration is quite stable without the need for artifical external forces. Typically, the centre of mass of the system is observed to move less than $0.1\,\sigma$ in the course of a simulation. A typical result for the density profile $\varrho(z)$ by this method is shown in Figure 2. The density of the coexisting phases can be immediately obtained by averaging $\varrho(z)$ over the bulk phase regions of z.

A variant of this method has been used by Chapela *et al.* [3] to study the square well fluid. Instead of starting the equilibration from a slab of homogeneous liquid with a vacuum on either side, they confine a fluid that is initially homogeneous and has a density close to the critical value between parallel hard walls that are perpendicular to the z direction. A fast spinodal decomposition then condenses a slab of liquid at the center of the box. This technique has the advantage over the method described above that it is not necessary to have any prior knowledge of the coexisting liquid density, so that equilibration should be faster. Essentially the same method of spinodal decomposition has been successfully used to study capillary condensation of Lennard-Jones fluids and fluid mixtures in narrow cylindrical pores with Lennard-Jones fluid-wall forces [7]. Some typical results are shown in Figure 3.

The methods described above offer the attractive feature of being natural, in the sense that the simulated system approximates the experimental two-phase system. In addition, these methods can be applied to liquid phases of any density, in contrast to many of the methods described below. However, they also possess some significant disadvantages. The simulations are slow because of the need for relatively large systems and for long run times in order to equilibrate the interface that is present. The confinement of the fluid phases between parallel walls can influence both the density and pressure of the coexisting phases, so that one is simulating a confined fluid rather than coexisting bulk phases. These methods appear to be most appropriate to the study of the interfacial region and of fluid behaviour in pores at the moment, but may become more attractive for studying coexisting bulk phases as computer power increases.

A novel and quite different approach to the problem has been proposed recently by Panagiotopoulos [8, 9]. The method is a Monte Carlo one, and is called the Gibbs ensemble method. It involves setting up two homogeneous phases that are in thermodynamic equlibrium but not in physical contact. Since there is no interface between the two regions that present the two coexisting phases the equilibration times and run times are shorter than the methods described above. The Gibbs Monte Carlo method is illustrated in Figure 4. The two coexisting phases (I and II) are contained

in two simulation boxes of volumes V^{I} and V^{II}, containing N^{I} and N^{II} molecules, respectively; thus the fluids in the two boxes are of different density and composition. The simulation is usually started with densities in each of the boxes being chosen to lie within the spinodal region. Each box is at the centre of a periodic array of identical boxes to avoid surface effects, and the entire system of two boxes is at a uniform temperature T. The simulation involves three separate moves [9]:

(a) Molecule displacement. In each box molecules are moved according to the usual Metropolis method. Each box is treated independently, and since N, V, and T are fixed (canonical ensemble) in each case, the states must occur with probability proportional to $\exp(-\beta U)$, where U is the configurational energy for the fluid for the box in question. A trial move of a molecule chosen at random is accepted with probability given by $\min(1, \mathscr{P}^{I}_{move})$, where $\mathscr{P}^{I}_{move}$ is the ratio of the probabilities of the new and old states. Thus for box I

$$\begin{aligned} \mathscr{P}^{I}_{move} &= \exp(-\beta U^{I}_{new})/\exp(-\beta U^{I}_{old}) \\ &= \exp(-\beta \Delta U^{I}) \end{aligned} \tag{1}$$

where $\beta = 1/kT$ and ΔU^{I} is the energy change of the trial move. If a move is rejected the old state is recounted in the Markov chain of states.

(b) Volume rearrangement. In this step a random volume change ΔV^{I} is made to the volume of box I, and a corresponding change $-\Delta V^{I}$ to the volume of box II. Thus the total volume of the system of two boxes is conserved. By considering the two boxes (separately) as part of an isothermal-isobaric ensemble (variables $N^{I}PT$ and $N^{II}PT$, respectively) it is easy to show that the overall ratio of the probabilties for the combined moves is [9]:

$$\mathscr{P}_{vol} = \exp\left(-\beta\left[\Delta U^{I} + \Delta U^{II} - N^{I}kT\ln\frac{V^{I}+\Delta V}{V^{I}} - N^{II}kT\ln\frac{V^{II}-\Delta V}{V^{II}}\right]\right) \tag{2}$$

and the move is accepted with a probability given by the $\min(1, \mathscr{P}_{vol})$. Again if a trial is rejected the old state is recounted in the Markov chain. In deriving (2) the assumption is made that the Markov chains sampled by each region are not affected by the fact that the two volume changes are perfectly correlated. This is a good approximation away from the critical point and is expected to have an effect which is comparable to that of using periodic boundary conditions.

(c) Molecule interchange. In this last step a molecule is moved from box II to box I. Thus the total number of molecules, $N^{I} + N^{II}$, is conserved, and we can consider each box as part of a grand canonical ensemble (variables $\mu V^{I} T$ and $\mu V^{II} T$, respectively). A trial move consists of a molecule creation in box I and a molecule destruction in box II, with overall probability [9]:

$$\begin{aligned} \mathscr{P}_{int} &= \mathscr{P}^{I}_{int} \times \mathscr{P}^{II}_{int} \\ &= \exp\left(-\beta\left[\Delta U^{I} + \Delta U^{II} + kT\ln\frac{V^{II}(N^{I}+1)}{V^{I}N^{II}}\right]\right). \end{aligned} \tag{3}$$

A trial interchange is accepted with a probability given by the $\min(1, \mathscr{P}_{int})$, and rejected moves are recounted in the Markov chain. This step is similar to the particle addition and removal trials used in grand canonical Monte Carlo (see Sec. 3.2).

The above equations are written for atomic fluids. For molecular fluids move (a) involves an additional orientational displacement, and the molecule moved in (c) must be given a random orientation.

The Gibbs method has been applied to both pure and mixed fluids. In Figure 5 results for the pure Lennard-Jones fluid obtained by the Gibbs method are compared with previous results that had been obtained by thermodynamic integration [10] and by the grand canonical ensemble [11, 12] methods (see next section for a discussion of these methods). Good agreement among the results of these various methods is obtained except at temperatures approaching the critical value, where uncertainties are expected to be larger. An important advantage of this method is the ease with which it can be applied to mixtures [9]. The only change to the procedure described above is in the molecule interchange step, (c). The quantities N^{I} and N^{II} in equation (3) are now the number of molecules of the particular species being interchanged, and care must be taken to ensure that the condition of microscopic reversibility holds [9]. For mixtures the Gibbs method can be carried out with the total system in the isothermal-isobaric ensemble, so that the pressure can be specified in advance. This involves a modification to equation (2) for the volume change, since the total volume is no longer constant [9]. The constant pressure Gibbs method offers the advantage that there is no uncertainty in the coexistence pressure of the mixture; it gives rather smaller uncertainties for the compositions and somewhat larger uncertainties for the densities of the two phases than the constant volume method. Thus the constant

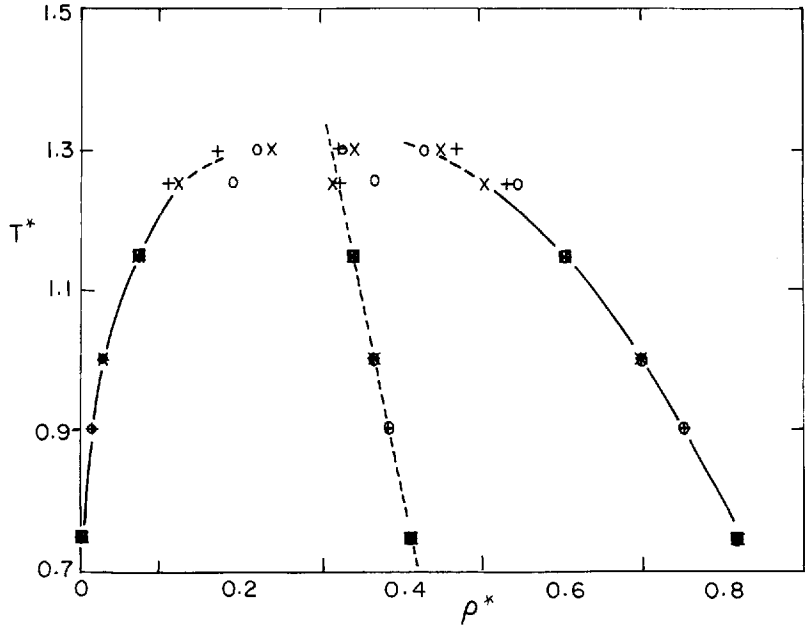

Figure 5 The liquid-vapour coexistence curve (——) and line of rectalinear diameters (– – –) for the pure Lennard-Jones fluid. Points represent results from simulations using: the Gibbs method, $N = 500$ (x) and $N = 300$ (+); the thermodynamic integration [11] method (□); and the grand canonical [12, 13] method (○). Here $T^* = kT/\varepsilon$, $\varrho^* = \varrho\sigma^3$. (From reference 9.)

pressure method is generally to be preferred for the study of mixtures. Some typical results from both the constant volume and constant pressure methods are shown in Figures 6 and 7 for Lennard-Jones mixtures. Results from the test particle method for calculating the chemical potential (see next section) are shown for comparison [13]. Agreement between these three methods is within the estimated uncertainties of the data.

In addition to its use for vapour-liquid equilibria, the Gibbs method has been applied to membrane equilibria [9] and to capillary condensation in narrow pores [14]. The method offers the advantage of speed, since without the need to deal with interfacial regions one can use relatively small numbers of molecules and short runs. With a system of a few hundred molecules one can calculate the densities and compositions of the two phases within a few percent in a short run; typically, for a binary mixture of 600 molecules with 500 interchange attempts per cycle the time required is 5 CPU minutes per 10^6 configurations on a CRAY XMP supercomputer. This appears to be an order of magnitude faster than the time required to make similar calculations by the test particle method [9]. The method is particularly attractive for studies of mixtures. Thus the time needed for binary mixture calculations is only about 50–100% higher than for pure components. The principal limitations of the method are likely to be: (a) difficulty in treating high density fluid phases (e.g. dense molecular liquids, liquid phases in liquid–liquid equilibria) or solids, due to the difficulty of molecular interchange, and (b) difficulty in treating equilibria between phases of similar density and composition, e.g. fluid phases near critical points or the nematic-isotropic transition. Difficulty (a) is the same one that occurs in the grand canonical Monte Carlo method; for pure Lennard-Jones fluids the problem becomes

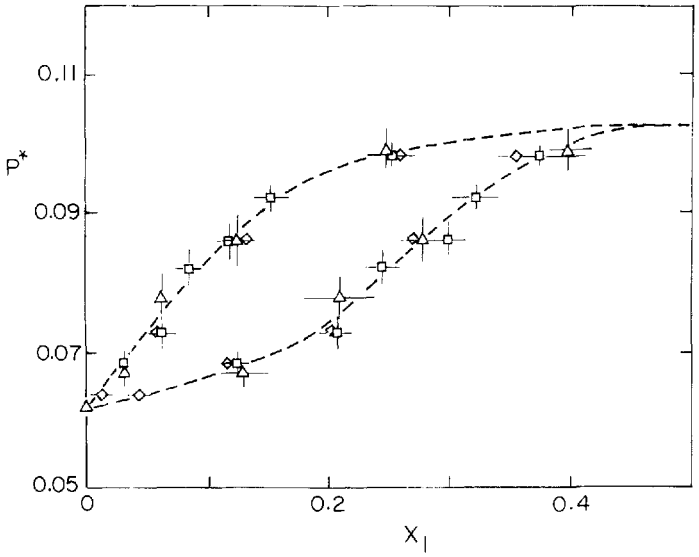

Figure 6 Vapour-liquid coexistence curve at $kT/\varepsilon_{11} = 1.15$ for a Lennard-Jones mixture with $\varepsilon_{22}/\varepsilon_{11} = 1$, $\varepsilon_{12}/\varepsilon_{11} = 0.75$, $\sigma_{22}/\sigma_{11} = \sigma_{12}/\sigma_{11} = 1$. Here □ = Gibbs method at constant volume; ◇ Gibbs method at constant pressure; △ test particle method, based on a series of NVT Monte Carlo simulations [13]. Vertical and horizontal lines through the points indicate the estimated uncertainties. Here $P^* = P\sigma_{11}^3/\varepsilon_{11}$. This mixture is symmetrical about $x_1 = 0.5$, since the only departure from ideality arises from the departure of $\varepsilon_{12}/\varepsilon_{11}$ from unity. (From Panagiotopoulos et al. [9].)

serious for reduced densities ($\varrho\sigma^3$) of 0.8 and above. Difficulty (b) arises because one must guess a starting density that is intermediate between the densities of the two coexisting phases. However, these difficulties are shared by most of the other methods.

3 INDIRECT SIMULATION METHODS: THE CHEMICAL POTENTIAL

In these methods the chemical potential (or free energy for pure substances) is calculated in the simulation for a series of state points; phase equilibria are then determined by finding points in the state space where two phases have the same chemical potential, pressure, and temperature. For most phase equilibria applications the calculations are therefore slower than the direct methods of the previous section. Unfortunately, the conventional Monte Carlo and molecular dynamics methods do not yield thermal properties such as the free energy or entropy, but only mechanical properties such as the energy or pressure. Thus the Metropolis sampling used in Monte Carlo simulations is designed to obtain the average configurational energy efficiently, but is not appropriate for the partition function or free energy [15]. Similar problems occur in molecular dynamics simulations. Hence, a variety of special techniques have been proposed to obtain such properties. Since these have been extensively reviewed [15, 16, 17, 18, 19, 20, 21, 22], only a rather brief account will be given here.

3.1 Test Particle Method

The residual chemical potential $\mu_{\alpha r}$ for a component α in a mixture can be simply related to the interaction of a "test particle" in the fluid with all N of the surrounding molecules [23, 24],

$$\mu_{\alpha r} = -kT \ln \langle \exp(-\beta U_{t\alpha}) \rangle_N \tag{4}$$

where $U_{t\alpha}$ is the intermolecular potential energy of interaction of an imaginary test molecule of species α with all the N (real) molecules in the system. The ensemble average in (4) can be thought of as being a Boltzmann-weighted average over the coordinates of all of the N real molecules, the test molecule being at some fixed coordinates. The test molecule is a fictitious or 'ghost' molecule that measures the interaction, without influencing the N real molecules in any way. Another form of (4) that is useful for computer simulation work is [25]

$$\mu_{\alpha r} = -kT \ln \int_{-\infty}^{\infty} f(U_{t\alpha}) \exp(-\beta U_{t\alpha}) \mathrm{d}U_{t\alpha} \tag{5}$$

where $f(U_{t\alpha}) + dU_{t\alpha}$ is the probability that $U_{t\alpha}$ lies in the range $U_{t\alpha}$ to $U_{t\alpha} + dU_{t\alpha}$.

An alternative but closely related expression can also be derived:

$$\mu_{\alpha r} = kT \ln \langle \exp(\beta U_{t\alpha}) \rangle_{N+1} \tag{6}$$

Here the test molecule is a *real* molecule, rather than a 'ghost'. The average is over all $N + 1$ molecules and the test molecule influences the structure and other properties of the fluid. Equation (6) can also be written in a form that is often useful in simulations [25]:

$$\mu_{\alpha r} = kT \ln \int_{-\infty}^{\infty} g(U_{t\alpha}) \exp(\beta U_{t\alpha}) dU_{t\alpha} \tag{7}$$

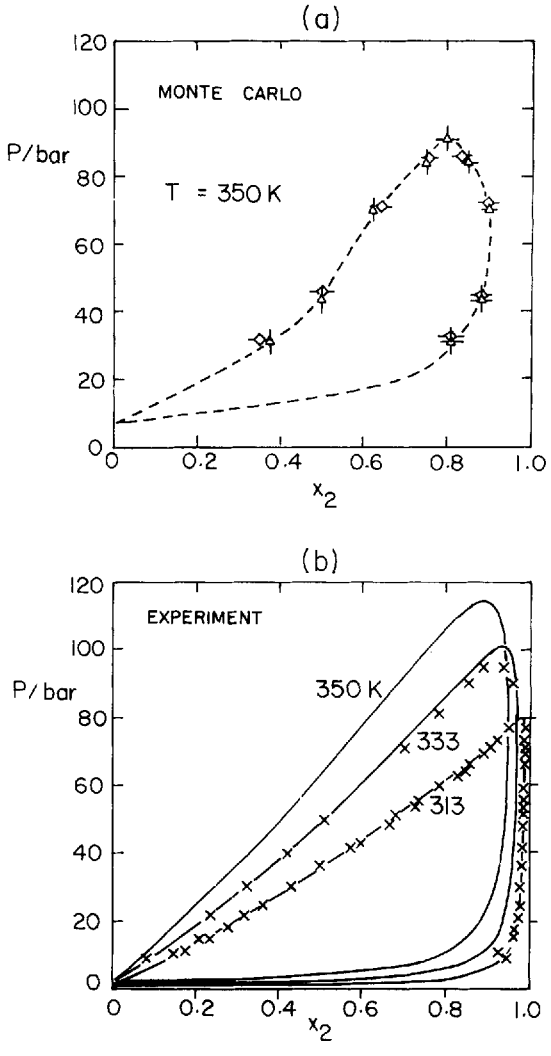

Figure 7 (a) Vapour-liquid coexistence curve at $kT/\varepsilon_{11} = 0.928$ for a Lennard-Jones mixture with $\varepsilon_{22}/\varepsilon_{11} = 0.597$, $\varepsilon_{12}/\varepsilon_{11} = 0.773$, $\sigma_{22}/\sigma_{11} = 0.768$, $\sigma_{12}/\sigma_{11} = 0.884$, from Monte Carlo simulation. Here □ = Gibbs method at constant volume; ◇ = Gibbs method at constant pressure; △ test particle method at constant volume. This mixture is a simple model of the acetone (1)-carbon dioxide (2) system; the temperature is above the critical value for carbon dioxide. (b) Experimental (x) and empirical equation of state (——) results for the mixture acetone-carbon dioxide. (From Panagiotopoulos et al. [9, 13].)

where $g(U_{1\alpha})\, dU_{1\alpha}$ is the probability that $U_{1\alpha}$ lies in the range $U_{1\alpha}$ to $U_{1\alpha} + dU_{1\alpha}$ when the test molecule is a real molecule and interacts with its neighbours. For a given $U_{1\alpha}$ the distribution functions f and g are simply related by [25]

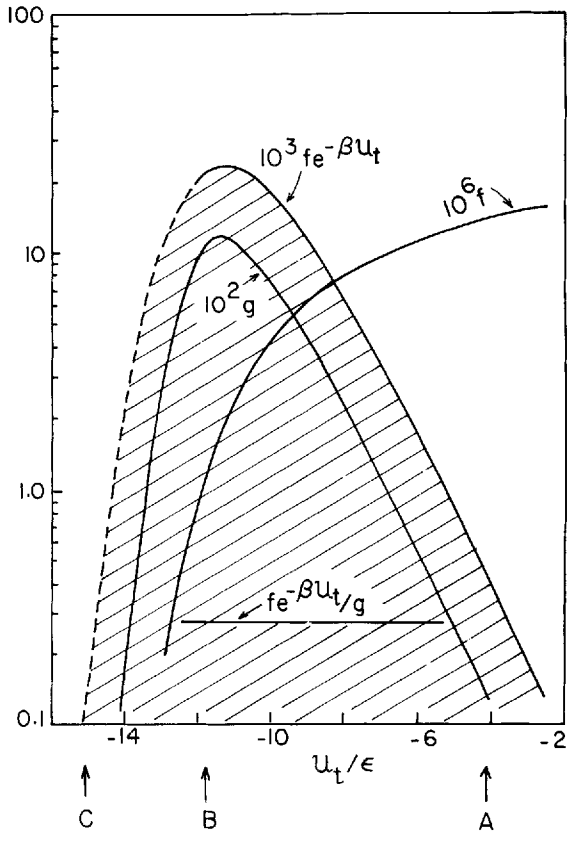

Figure 8 The distribution functions f and g, and the quantities f exp $(-\beta U_t)$ and f exp $(-\beta U_t)/g$ for a Lennard-Jones fluid at $kT/\varepsilon = 1.2$, $\varrho\sigma^3 = 0.85$ from MC simulation. The shaded area gives exp $(-\beta\mu_r)$ and hence the chemical potential (see eq. 5). The part of f exp $(-\beta U_t)$ that is shown as a solid curve (A to B) is obtained directly in the simulation, while the part shown as a dashed curve (B to C) can be obtained by the f–g sampling method. (From Shing and Gubbins [25].)

$$g(U_{t\alpha}) = \exp(\beta\mu_{\alpha r}) \exp(-\beta U_{t\alpha}) f(U_{t\alpha}) \tag{8}$$

Equations (4)–(8) are quite general; they do not rest on the assumption of pairwise additivity of the intermolecular forces, nor on any approximation concerning the molecules (spherical, rigid, etc.).

Equation (4) has been widely used to calculate chemical potentials in pure and mixed fluids, using both the Monte Carlo and molecular dynamics methods. It is usual to use an array of test molecules at fixed coordinates in the box, and average over all configurations of the N real molecules. Since the test molecules do not interact with the real ones, it is possible to calculate all of the usual properties (energy, pressure, structure, etc.) from the simulation, in addition to the chemical potential. Thus it is very simple to incorporate the chemical potential into a conventional simulation by the test particle method. In principle, (4) can be used to calculate $\mu_{\alpha r}$ at any density. In practice, the length of run needed to do this becomes prohibitive at higher density.

This is because attractive configurations make the dominant contribution to the average in (4), because of the $\exp(-\beta U_{i\alpha})$ term; however, these will be sampled less and less frequently as the density increases, or as the α-particle diameter increases in the case of mixtures. In such cases fluctuations in the density will occasionally create "holes" in the dense fluid, and such configurations make an unusually large contribution to the chemical potential. Such configurations are not well sampled by conventional methods (see however Sec. 3.3). The situation is illustrated in Figure 8. For pure Lennard-Jones fluids the test particle method seems to work satisfactorily up to $\varrho\sigma^3 \sim 0.65$, but above this density becomes difficult to use. The problems at high densities are generally more severe for nonspherical molecules.

Equations (6) and (7) are not directly useful in simulations, except possibly at high temperatures. The averages in these equations are dominated by repulsive configurations, where $\exp(\beta U_{i\alpha})$ is large. However, such configurations will be rare even at moderate densities, because the test particle is now a real molecule. However, as can be seen from (8), if there is a range of $U_{i\alpha}$ where both f and g can be calculated with reasonable accuracy, the chemical potential can be calculated (see Figure 8). Thus, (6) is often useful when combined with (4) even though (6) alone may not be useful. More sophisticated versions of this "f–g sampling" method have been discussed by Shing [25], and are found to give good results up to the triple point density for Lennard-Jones fluids. A convenient way [26] to present "f–g sampling" is based on a rearrangement of (8),

$$\ln \frac{f(U_{i\alpha})}{g(U_{i\alpha})} = \beta U_{i\alpha} - \beta\mu_{\alpha r} \tag{9}$$

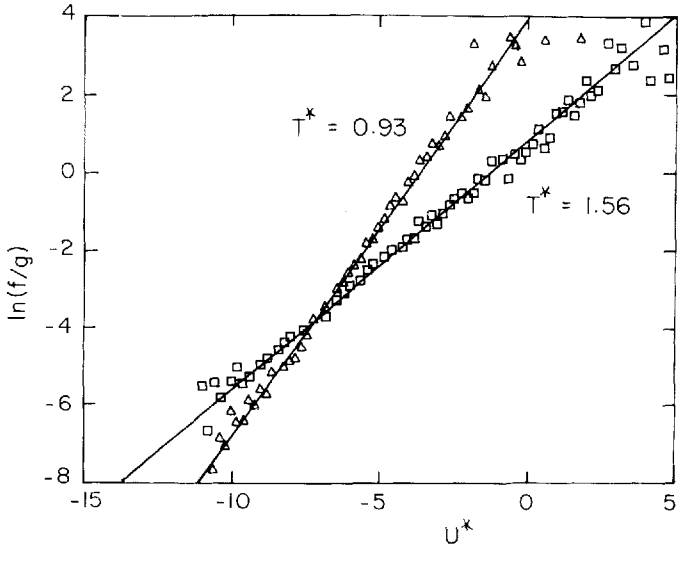

Figure 9 The function $\ln[f(U_i)/g(U_i)]$ vs. the test particle energy $U_i^* = U_i/\varepsilon$, for a pure Lennard-Jones fluid at $\varrho^* = \varrho\sigma^3 = 0.60$ and at two temperatures: $T^* = kT/\varepsilon = 0.93$ (triangles) and $T^* = 1.56$ (squares). The slope of the line is $\beta = 1/kT$ and the intercept is $\beta\mu_r$, as seen from equation (9). (From Panagiotopoulos et al. [13].)

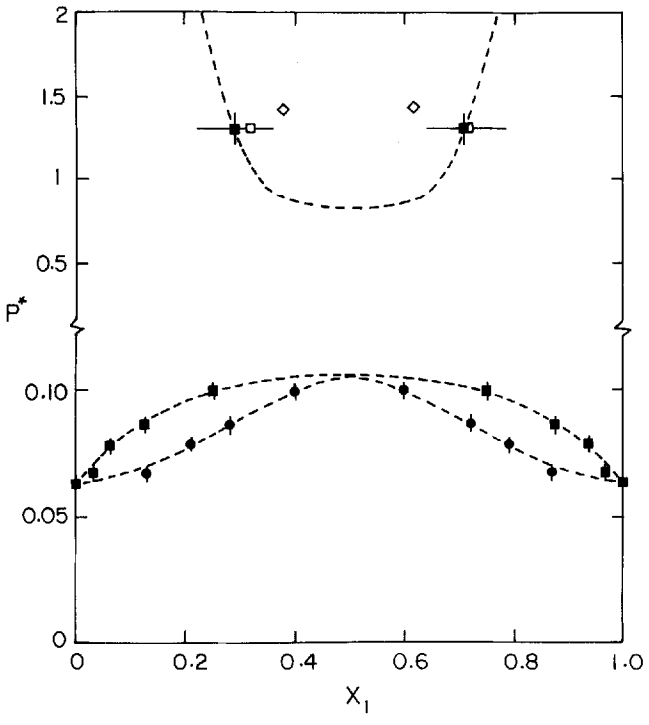

Figure 10 Vapour-liquid (lower curves) and liquid–liquid (top curve) equilibria for the mixture shown in Figure 6. Filled points are test particle results for the liquid (■) and gas (●) phases. Open points for liquid–liquid equilibria are from the constant volume (□) and constant pressure (◇) Gibbs method. The dashed lines are drawn through the points for clarity. (From Panagiotopoulos et al. [9, 13].)

A plot of $\ln [f(U_{t\alpha})/g(U_{t\alpha})]$ vs. $U_{t\alpha}$ then yields the chemical potential directly, and the scatter of the data about the straight line gives an estimate of the error in $\mu_{\alpha r}$. An example is shown in Figure 9.

The test particle method has been widely applied [for reviews see 15, 19–22]. Recent work has included several studies of fluid mixtures [13, 27, 28, 29, 30], as well as a study of pure trimer and hexamer ring compounds [31]. Some typical results for mixtures are shown in Figures 6 and 7. In addition to its use for vapour-liquid equilibria, the method has also been used to study liquid–liquid equilibria [9, 13]; these results are shown in Figure 10. The accuracy of these liquid–liquid calculations is much lower than for the vapour-liquid studies, because of the high density ($\varrho\sigma^3 \simeq 0.75$); this leads to poor sampling of phase space in the test particle method, and a small number of successful particle interchange steps in the Gibbs method, leading to large uncertainties and poor agreement between the two methods.

There are advantages to using the isothermal–isobaric ensemble in place of the canonical [28, 29]. This is because the NPT ensemble permits density fluctuations , whereas the NVT one does not; this is of particular importance when working at state conditions near the critical region, as in supercritical extraction. The N-dependence of the results is also less in the NPT ensemble than in the NVT one. The NPT ensemble enables us to fix the pressure in advance, an advantage in mixtures work.

In the NPT ensemble equation (4) is replaced by [29]

$$\mu_{ex} = -kT\ln[\langle V\exp(-\beta U_{12})\rangle/\langle V\rangle] \quad (9)$$

where $\langle V\rangle$ is the average volume. This method has been used to study the solubility of naphthalene in dense supercritical carbon dioxide [29]. Both the naphthalene and carbon dioxide were modeled as Lennard-Jones spheres with a central quadrupole, and no attempt was made to optimize the potentials. Typical results are shown in Figure 11. Although the simulations are not in quantitative agreement with experiment, they do show most of the qualitative trends correctly, e.g. the crossing of the isotherms near the critical pressure and the approximately linear dependence of ln y_1 on ϱ^* at moderate to high pressure. The temperature dependence of the calculated solubilities to high pressure. The temperature depedence of the calculated solubilities is too weak, but can be improved by adjusting the CO_2/naphthalene pair potential. In these calculations it was found that the test particle method failed at pressures much above $P^* \sim 0.5$; the test particles were not able to effectively sample the important regions of ocnfiguration space at these higher densities, and calculations were instead made by the Kirkwood method (see below).

In a second application of equation (9) Shing and Chung [30] have studied partial molal properties (μ_1, $\bar{V}_1$, $\bar{U}_1$, and $\bar{S}_1$) for Lennard-Jones mixtures in which the solute (1) is at infinite dilution in the solvent (2). In such mixtures these properties are a function of the parameter ratios $\varepsilon_{12}/\varepsilon_{22}$ and σ_{12}/σ_{22}, as well as the density and temperature. At low and moderate densities the test particle method worked well; at high densities and/or large solutes this method failed, and the Kirkwood method was used.

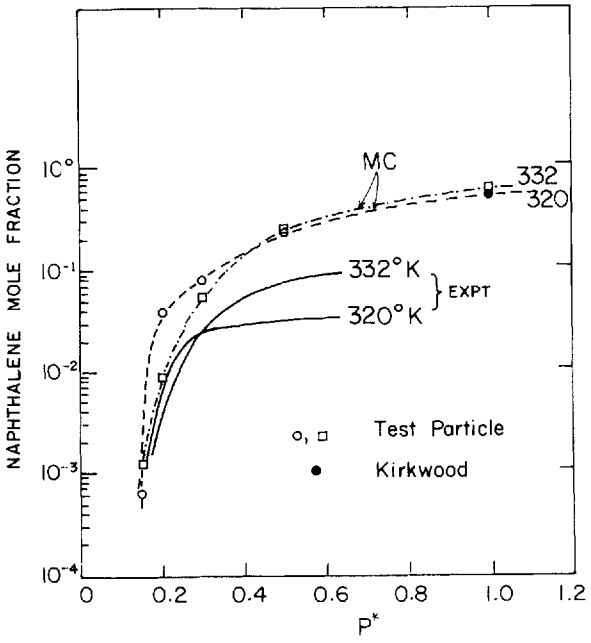

Figure 11 The solubility of naphthalene (1), y_1, in supercritical carbon dioxide (2) at various pressures ($P^* = P\sigma_{22}^3/\varepsilon_{22}$) from experiment (solid lines) and simulation (points and dashed lines). Here, open points (○ = 320K, □ = 332K) are from the test-particle method. The filled point ■ is from the Kirkwood method. (From Chung and Shing [29].)

Some typical results are shown in Figure 12. For such infinitely dilute solutions, evaluation of the chemical potential in a simulation immediately yields the Henry constant, K_1 [25, 27].

$$\lim_{x_1 \to 0} \mu_{ex}/kT = \ln(K_1/\varrho KT) \tag{10}$$

where

$$K_1 = \lim_{x_1 \to 0} f_1/x_1 \tag{11}$$

and f_1 is the fugacity of 1. If the solute is a gas or solid at the temperature in interest, it is often possible to calculate f_1 independently [32], so that (10) and (11) can be used to calculate the solute solubility from the simulation result for the chemical potential.

The test particle method offers several advantages over many of the methods described below. It can be incorporated in conventional MC or MD programs with minimal effort, and does not involve any "unnatural" sampling procedures (cf. Sec. 3.3), so that the usual thermodynamic and structural properties can be calculated in addition to the chemical potential. It can also be applied to inhomogeneous fluid systems [7, 33, 36]. Its principal limitation is its failure at high density and for large solutes.

3.2 Grand Canonical and Semigrand Ensembles

In the grand canonical ensemble μ, V, and T are fixed; the density fluctuates during the simulation, and the mean density is found as an ensemble average at the end of the run. The grand canonical MC method involves two steps. In the first, the molecules are displaced in the usual way. The second step involves adding or removing molecules according to the rules of the grand ensemble weighting function. A variety of schemes have been proposed for carrying out grand canonical Monte Carlo simulations, and are described in detail by Allen and Tildesley [15]. The method works best at higher temperatures and low to moderate densities. The addition of molecules is then allowed with sufficient frequency for adequate sampling of the density fluctuations. It is particularly well suited to studies near phase transitions or close to critical regions, and to studies of adsorption [34] and chemical reactions [35]. It has been found to provide a convenient route to the study of phase transitions near surfaces [7, 34, 36, 37]. The principal limitation of the method is its failure at high densities (much above $\varrho\sigma^3 = 0.6$ for Lennard-Jones fluids); this is due to the difficulty of adding molecules to the system, because of the high probability of overlap. Removal of a molecule also fails in the majority of cases because of the loss of attractive interactions as the liquid structure relaxes. As in the test particle method, the problem is more severe for angle-dependent potentials or for large solute molecules. The results are very sensitive to any errors in the random number generator used [38], a problem that is easily avoided as long as one is aware of it. We note that step (c) in the Gibbs method (Section 2) is closely related to the grand ensemble method; in the former, molecular exchange is between two systems of finite volume, whereas in the latter molecules are exchanged between a finite volume and an infinite reservoir.

The advantage of the grand ensemble method is that μ, and hence the Gibbs free energy, are specified in advance; the Helmholtz free energy is readily obtained from

$$A = \langle N \rangle \mu - \langle P \rangle V \tag{12}$$

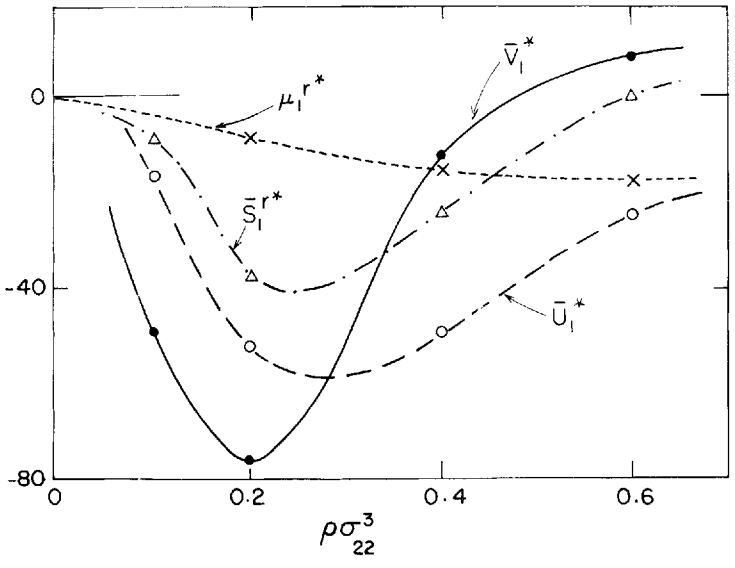

Figure 12 Partial molal properties at infinite dilution of the solute 1 for Lennard-Jones mixtures at a temperature $kT/\varepsilon_{22} = 1.5$, for a large ($\sigma_{12}^3 = 3.5\sigma_{22}^3$) and strongly interacting ($\varepsilon_{12} = 15\varepsilon_{22}$) solute. The values shown are made dimensionless using the solvent parameters: $\bar{V}_1^* = \bar{V}_1/\sigma_{22}^3$, $\mu_1^{r*} = \mu_1^r/\varepsilon_{22}$, $\bar{\mu}_1^* = \bar{\mu}_1/\varepsilon_{22}$, $\bar{S}_1^{r*} = \bar{S}_1^r/k$, where superscript r indicates the residual value. Values shown are obtained from the test particle method. (From Shing and Chung [30].)

where $\langle \ldots \rangle$ indicates a grand ensemble average. It has been used recently [39] to study the extraction of naphthalene using supercritical carbon dioxide and carbon dioxide-water mixtures as the solvent. Since the solvent is near the critical region the grand ensemble method is particularly appropriate. The molecules were modelled as Lennard-Jones spheres with the addition of point multipoles (dipoles for water, quadrupoles for naphthalene and carbon dioxide). For $n > \sim 100$ there was little system size dependence. These calculations show that water is a particularly effective cosolvent for this extraction. Some typical results are shown in Table 1. The addition of only 2 water molecules (about 2% water) causes the solubility of naphthalene to be increased by about 26 times. This dramatic increase in fluid density and solubility

Table 1 Effect of water addition on the solubility of naphthalene (1) in compressed carbon dioxide (2) at 340 K from grand canonical MC simulations[a]. From Nouacer and Shing [39].

B_1	-5.0	-5.0	-5.0
B_2	3.1	3.1	3.1
N_{H_2O}	0	1	2
$\rho\sigma^3$	0.15 ± 0.01	0.16 ± 0.01	0.36 ± 0.25
$\langle N_1 \rangle$	0.17 ± 0.03	0.23 ± 0.04	10.6 ± 8.4
$\langle N_2 \rangle$	44.7 ± 3.2	46.4 ± 3.5	92.8 ± 30.5
$y_1 = N_1/N$	0.0038	0.0049	0.10

[a] Here $B_1 = \mu_1^r/kT + \ln N_1$.

occurs because of clustering of the naphthalene molecules about the highly polar water molecules, as is readily seen from the water-naphthalene pair correlation function [39]. Since the CO_2 is already close to the critical region, the increase in the cohesive energy due to the water molecules leads to a significant increase in the fluid density. For a solute molecule as large as naphthalene the grand canonical method is found to fail for densities much above the critical value of carbon dioxide.

The *semigrand* ensemble [40, 41] combines features of the canonical and grand canonical ensembles, and has many of their advantages and disadvantages. In this ensemble the independent variables are T, V, N, and the chemical potential differences $\mu_i - \mu_o$. Thus these variables are fixed in the simulation, while U, P, the mole fractions x_i, and μ_o are calculated during the course of the simulation. The method has been successfully applied to the study of polydisperse fluid mixtures [41], i.e. mixtures of very many chemically similar species which are approximated as a fluid with a continuum of species. The infinity of components are characterized by a set of (usually one or two) identity variables, I, e.g. boiling temperature and liquid density, which are distributed among the mixture species according to a distribution function p(I). In this application the chemical potential differences $\mu_i - \mu_o$ are replaced by the difference function $\mu_i(I) - \mu_o(I)$, which must be specified at the beginning of the simulation. The probability distribution function p(I), which replaces the set of compositions x_i, is calculated in the simulation. Thus, although the number of molecules stays constant, their chemical identities are constantly changing. This method is particularly useful for the study of phase equilibria in polydisperse mixtures. The reference fluid chemical potential, μ_o, must still be calculated, but once it is known the infinity of other chemical potentials are immediately known. For a given T and distribution $\mu(I) - \mu_o(I)$ one needs only to equate the values of the pressure and μ_o in both phases, a much simpler task than matching the whole distribution $\mu(I)$. The reference chemical potential $\mu_o(I)$ can be obtained using the test particle method (suitably modified for this ensemble) or from a thermodynamic integration method [41]. Kofke and Glandt [41] have used this method to study a polydisperse mixture composed of Lennard-Jones molecules with continuously variable σ and ε values; the unlike pair parameters obey the Lorentz-Berthelot combining rules. The σ and ε values are taken to be completely correlated, with $\varepsilon_{ii}/\varepsilon_o = \sigma_{ii}/\sigma_o$, where ε_o and σ_o are values for some reference component I_o. A single identity variable I can therefore be used, and a Gaussian distribution of activities is assumed,

$$\mu(I) - \mu(I_o) = -kT(I - I_o)^2/2v \tag{13}$$

This distribution has a peak at $I = I_o$, and its width is determined by v. When $v = 0$ the pure fluid I_o is recovered (monodisperse fluid limit); increasing v leads to increasingly polydisperse mixtures. In each Monte Carlo step a molecule selected at random is moved randomly in each coordinate direction, and simulataneously its diameter σ (and energy parameter ε) are increased or decreased randomly. The CPU time for such a simulation of 512 molecules was found to be about 3 minutes per 100 000 configurations for a vectorized program on a Cyber 205. Some typical composition distributions determined by this method are shown in Figure 13. For values of v/σ_o^2 greater than about 0.1 the results become quite strongly dependent on the total number of molecules, N, probably because of the presence of large molecules within the wider distributions. Such N dependence could probably be reduced by truncating the activity distribution given by (13).

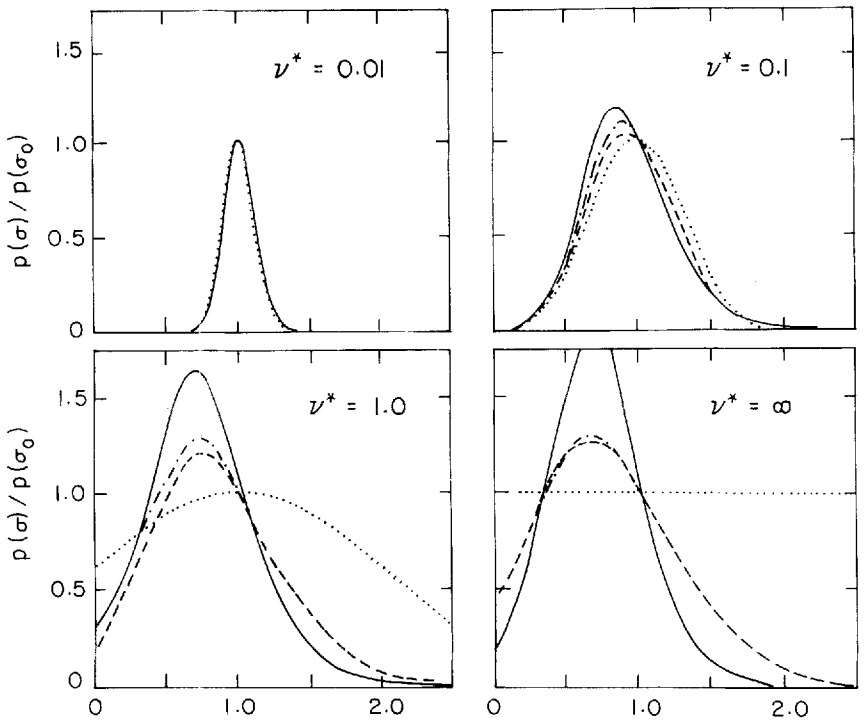

Figure 13 Reduced composition distributions $p(\sigma)/p(\sigma_0)$ for four values of the polydispersivity, $\nu^* = \nu/\sigma_0^3$. All calculations are for a state condition $kT/\varepsilon_0 = 1.0$ and $\varrho\sigma_0^3 = 0.819$. Three system sizes are shown: 216 molecules (– – –), 343 (–·–·–·–), and 512 (——). The dotted lines are the imposed Gaussian activity distributions, $\exp\{\beta[\mu(\sigma) - \mu(\sigma_0)]\}$. (From Kofke and Glandt [41]).

The semigrand ensemble would seem to be suitable for discrete mixtures, particularly if many components are present, and for reacting mixtures, in addition to polydisperse ones.

3.3 Modified Sampling Methods

The Gibbs, test particle, grand canonical, and semigrand methods all experience problems at high densities because of the difficulty of inserting or exchanging molecules. This difficulty also occurs in mixtures when the particle to be inserted or exchanged is large. As a result there have been efforts to develop modified sampling methods that increase the likelihood of successful particle insertion; in effect, one weights the sampling towards configurations in which a density fluctuation produces a 'hole', so that a particle can be inserted easily. This weighting must be introduced in such a way that its effects can be removed when taking averages over the course of the simulation. Several variants of this approach have been proposed, and these have been extensively reviewed [15–22]. Here we give only a brief account.

In the umbrella sampling method [16, 42, 43] a weight w is assigned to each value of the configurational energy U, with the weighting function chosen to sample regions

of U that are important in determining the free energy or chemical potential. To illustrate the method we consider its use to determine the chemical potential [44], in which case the weight w is applied to the test particle configurational energy U_t. Configurations are chosen with probability $w(U_t)\exp(-\beta U)$ instead of $\exp(-\beta U)$, where U is the energy of the N real molecules in the system. The required ensemble average (cf. eq. (4)) can now be expressed.

$$\langle \exp(-\beta U_{t\alpha})\rangle = \langle \exp(-\beta U_{t\alpha})/w\rangle_w / \langle 1/w\rangle_w \qquad (14)$$

where $\langle \ldots \rangle_w$ denotes an ensemble average over the weighted chain of configurations, and the subscript N on the average on the left side of (14) has been omitted for clarity. An alternate form of (14) is

$$\langle \exp(-\beta U_{t\alpha})\rangle = \langle 1/w\rangle_w^{-1} \int_{-\infty}^{+\infty} f_w(U_{t\alpha}) \exp(-\beta U_{t\alpha}) w(U_{t\alpha})^{-1}\, dU_{t\alpha} \qquad (15)$$

where $f_w(U_{t\alpha})dU_{t\alpha}$ is the probability that $U_{t\alpha}$ lies in the range $U_{t\alpha}$ to $U_{t\alpha} + dU_{t\alpha}$ in the weighted system. The weighting function w must be chosen so as to give a distribution f_w that is relatively flat (or 'umbrella-shaped') in the region A to C of Figure 8. In practice this is achieved by first carrying our a short run to estimate $f(U_{t\alpha})$ of eq. (5), and then making w proportional to f^{-1}. In cases where the region A to C is large (e.g. very high density, large solute molecules) the statistical errors in f in this region may be very large, so that it is not possible to estimate suitable weighting functions over the necessary range. In such cases several stages of umbrella sampling may be needed to cover A to C.

This method works for pure Lennard-Jones fluids up to the highest liquid densities; two stages of umbrella sampling are needed for the highest densities and low temperatures. It has also been used to study Lennard-Jones mixtures [45], including cases where one of the molecular species is large [25], and pure quadrupolar Lennard-Jones fluids [46]. Although it works well at higher densities, the method has several disadvantages. There is no clear cut way to determine a suitable weighting function; usually this must be obtained by trial and error, particularly if several stages are needed. It requires more program modification than the test particle method, and properties other than the chemical potential or free energy difference (energy, pressure, correlation functions, etc.) cannot usually be obtained with sufficient accuracy, so that a separate simulation is necessary to obtain these. This last drawback can be overcome at intermediate densities (up to $\varrho\sigma^3 \approx 0.75$ for Lennard-Jones fluids) by using a technique known as restricted umbrella sampling [25] in which the weighting function acts only on the test particle, and so does not influence the structure of the fluid; the test particle is now a "smart ghost" (the solvent molecules are unaware of the test particle, but the test particle seeks out the "holes"). Basically this same technique has been used to study the vapour-liquid coexistence line for a two-centre Lennard-Jones model of chlorine [47].

Several alternative procedures have been proposed. Mon and Griffiths [48] have suggested a method which involves gradually turning on the interaction of the test particle with the surrounding molecules. This is done by introducing a weakened interaction $U_{t\alpha}(\lambda)$ such that when $\lambda = 0$ we have $U_{t\alpha}(0) = 0$ and when $\lambda = 1\ U_{t\alpha}(1) = U_{t\alpha}$. The chemical potential is obtained by carrying out a series of simulations for λ in the range 0 to 1, and integrating over λ. This gradual insertion of the test particle is less traumatic for the system, and enables results to be obtained at higher densities. The only application seems to have been to the study of a two dimensional fluid [48]. Several methods have been proposed [49–51] for relating the

free energies between two fluids at different temperatures or with different potentials, by making use of the overlap of the distributions involved.

For simulations in the grand canonical ensemble, Mezei [52, 53] has modified the usual sampling procedure by increasing the number of insertion attempts in the region of a cavity in the fluid. In his cavity-biased Monte Carlo method a network of uniformly distributed test points is generated in the fluid, and the fraction of these points in a cavity of a suitable size is found. Insertion of new molecules in the region of these cavities is attempted, rather than at random points. The fraction of test points in the chosen cavities allows the proper normalization of the ensemble averages. The number of successful molecular insertions or deletions is usually increased by a factor of about 10 by this method, and it is possible to obtain satisfactory results up to the triple point density for Lennard-Jones fluids. The CPU time is typically increased by a factor of 2–3 over that for conventional grand canonical calculations. Even with cavity-biased sampling, very few insertion/deletion attempts were successful for water, and the calculated thermodynamic properties were in poor agreement with values from thermodynamic integration methods [53]. An alternative procedure for locating the cavities has been proposed [54, 55] which is based on a search for the protruding vertices of the Dirichlet-Voronoi polyhedra defined by the mass centres of the molecules in the fluid. The method does not seem to have been extensively tested yet, but appears to work for Lennard-Jones liquids up to the triple point.

3.4 Thermodynamic Integration

Standard thermodynamic identities relate the free energy or chemical potential to properties such as internal energy E or pressure P that are easily measurable in simulations, so that the former properties can be obtained by integration along a suitable thermodynamic path. Examples of such relations for the Helmholtz energy are

$$A(\varrho_1, T) = A(\varrho_0, T) + N \int_{\varrho_0}^{\varrho_1} \frac{P}{\varrho^2} d\varrho \tag{16}$$

and

$$\frac{A(\varrho, T_1)}{T_1} = \frac{A(\varrho, T_0)}{T_0} + \int_{T_0}^{T_1} E \, d\left(\frac{1}{T}\right) \tag{17}$$

In equation (16) it is usual to take $\varrho_0 = 0$, i.e. the ideal gas, and integrate along the isotherm to the density of interest, ϱ_1. If ϱ_1 is a liquid state there are problems in the two phase region. One way around this difficulty is to integrate along a supercritical isotherm, and then to use (17) to follow an isochore to the desired subcritical temperature. An alternate method is to divide the simulation cell into small volumes, and constrain the fluctuations in the density in each of these volumes, thus artificially preventing phase separation in the two phase region and enforcing homogeneity [10]. In order to use equation (17) the free energy must be known at some reference temperature T_0. For fluids with hard core potentials, e.g. square well or hard sphere with added dipole or quadrupole, $T_0 = \infty$ is used, corresponding to the hard core fluid. For crystalline solids (17) is often used with $T_0 = 0$.

The integration variable is not restricted to thermodynamic variables. It is often convenient to consider the configurational energy to be a function of some variable λ, in which case one can write

$$A(\lambda_1) = A(\lambda_0) + \int_{\lambda_0}^{\lambda_1} \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_\lambda d\lambda \tag{18}$$

For example, in the case of a dopolar hard sphere fluid, one can write for the pair potential $u(12; \lambda) = u_{HS} + \lambda u_{\mu\mu}$, where $u_{\mu\mu}$ is the dipole potential. In this case a series of simulations at various λ values in the range 0 to 1 can be used with equation (18) to calculate the difference in free energy between the dipolar fluid and the hard sphere fluid at the same temperature and density.

Among the recent applications of equations (16) and (17) have been studies of hard dumbells [56], Lennard-Jones [47, 57 and references therein], and Gaussian overlap [58] fluids, while (18) has been applied to hard spheres with added dipoles [59] and dipole plus quadrupole [60], Stockmayer fluids [59], two-centre Lennard-Jones diatomics with point quadrupoles [61], and water [22, 62, 63]. A more complete review of applications of the thermodynamic integration method has been given by Frenkel [21].

For interfacial properties it is often convenient to work in the grand canonical ensemble [2], in which case the appropriate free energy is the grand potential Ω; for a homogeneous system $\Omega = -PV$, but for an inhomogeneous system Ω also contains surface terms. Convenient expressions for the evaluation of Ω by thermodynamic integration are [2, 34, 64]

$$\Omega(\mu) = \Omega(\mu_0) - \int_{\mu_0}^{\mu} N(\mu')\, d\mu' \tag{19}$$

and

$$\Omega(T)/T = \Omega(T_0)/T_0 + \int_{T_0}^{T} (U - N\mu)\, d(1/T) \tag{20}$$

In (19) the integration path is at constant temperature, volume and surface area, while in (20) it is at constant chemical potential, volume and surface area. These expressions are convenient for use in grand canonical ensemble simulations, and have been used to study phase transitions in narrow capillary pores [64].

An equation similar to equation (18) was derived for the chemical potential by Kirkwood [65], and has been used recently for simulation studies of mixtures. Molecule 1, which is of species α, is coupled to the remaining N-1 molecules by a coupling parameter λ, so that the total configurational energy is $\lambda U_\alpha(x_1; x^{N-1}) + U_{N-1}(x^{N-1})$, where U_α is the energy of interaction of the fully coupled $\alpha 1$ molecule with all the remaining $N - 1$ molecules in the system and λ lies between 0 ($\alpha 1$ completely uncoupled from the system) and 1 ($\alpha 1$ fully coupled); x_i represents the coordinates needed to specify the location and orientation of molecule i. The residual chemical potential can be shown to be given by

$$\mu_{\alpha r} = \int_0^1 d\lambda \langle U_\alpha(x_1; x^{N-1}) \rangle_\lambda \tag{21}$$

where $\langle \ldots \rangle_\lambda$ means an average over the system with partial coupling of the $\alpha 1$ molecule. Equation (21) is the Kirkwood equation, and provides a means of calculating the chemical potential by carrying out a series of simulations for values of λ in the range 0 to 1. It has been used to study two-dimensional fluids [48], the solubility of naphthalene in supercritical carbon dioxide [29] (see Figure 11), a wide range of binary Lennard-Jones mixtures, including infinitely dilute mixtures [30] and mixtures of finite concentration with a wide range of intermolecular parameter ratios [66, 67,

68, 69], and the solubility of gases in aqueous solutions [70]. Haile and collaborators [66–69] have applied the method to the calculation of excess properties, activity coefficients, and Henry constants using NPT molecular dynamics. An example of their results is shown in Figure 14. A total of 48 simulations, with N = 256 and runs of 100000 time steps, were carried out in order to determine the excess properties for 14 mixtures. The accuracy of the excess Gibbs energies shown in Figure 14 is believed to be of the order 2% for cases where $|g^E/kT| > 0.005$.

Mezei and Beveridge [22] and also Cross [88] have proposed the use of nonlinear thermodynamic integration methods to calculate free energy differences. Such methods involve the use of modified and more general forms of equations (18) and (21), and may offer a more efficient numerical scheme.

Thermodynamic integration has several advantages for determining free energies or chemical potentials. It requires little or no change to conventional Monte Carlo or molecular dynamics programs, the quantities needed are statistically well-behaved, and the method preserves the natural molecular trajectories, so that all the usual properties (e.g. correlation functions) can be obtained in the same simulation. The most important advantage is that the method works well at high densities, and is frequently used to study phase transitions in solids [21]. The disadvantage is the time needed to determine a phase transition point, since a series of simulations must be carried out to find the free energy or chemical potential at a single state condition.

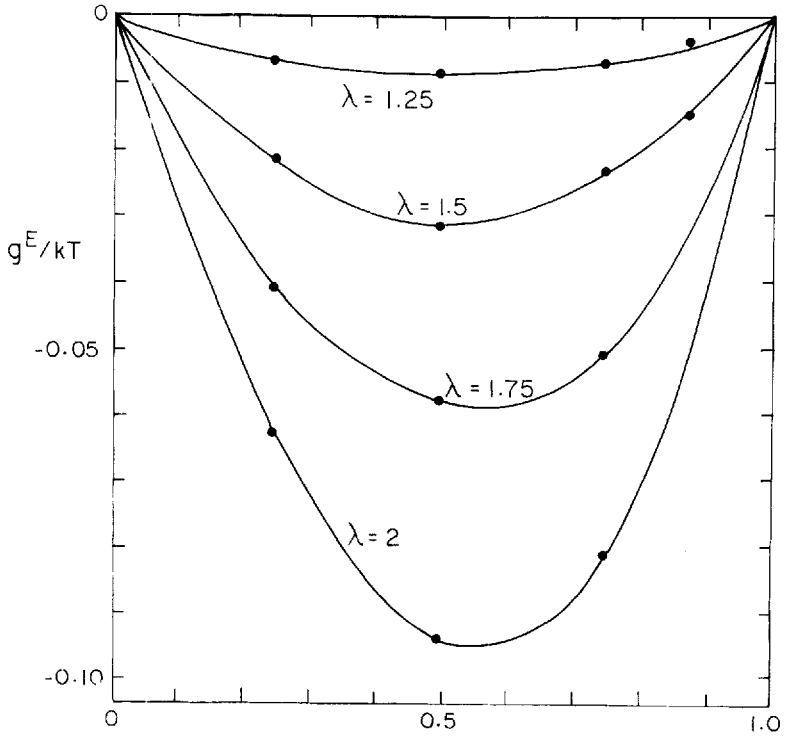

Figure 14 Excess Gibbs free energies of binary mixtures of WCA-repulsive soft spheres from MD simulations using the Kirkwood equation, at the state condition $kT/\varepsilon = 1$, $P\sigma_{AA}^3/\varepsilon = 0.5$. Here $\varepsilon_{AA} = \varepsilon_{BB} = \varepsilon_{AB} \equiv \varepsilon$, and $\lambda = \sigma_{BB}/\sigma_{AA}$. (From Haile [66].)

4 APPROXIMATE EQUATIONS OF STATE

The methods described in the previous sections are rigorous in that no approximations (beyond the usual statistical errors associated with sampling or run times) are made to the statistical mechanics. In principle we should obtain exact phase equilibrium results for a precisely defined intermolecular potential. For some applied work on complex systems this may not be the most practical approach at the present time, however. The engineer who must design separation units often has to know the properties of coexisting phases for multicomponent mixtures for hundreds of state points to high accuracy (typically 1 or 2% in the pressure and compositions), so that the CPU time becomes enormous for current machines. Moreover, for complex fluids (e.g. polar or hydrogen-bonded liquids, electrolyte/nonelectrolyte mixtures, polymers) the intermolecular potentials are not usually known with sufficient accuracy. In such cases a less rigorous approach is often useful, in which approximations are made in the statistical mechanics to obtain tractable equations of state. Several levels of approximation are usually possible. One may use the usual theories, e.g. perturbation theory, density functional theory, lattice models, and so on, as a starting point. Most of the equations of state that are commonly used by engineers are of the form

$$Z = \frac{PV}{RT} = Z_{ref} + Z_{pert} \tag{22}$$

Computer simulation plays an important role in the development of improved equations of this sort, and has been of great use in tests of convergence and in testing various approximations to the reference and perturbation terms (for reviews see, for example [20, 71, 72, 73, 74, 75]).

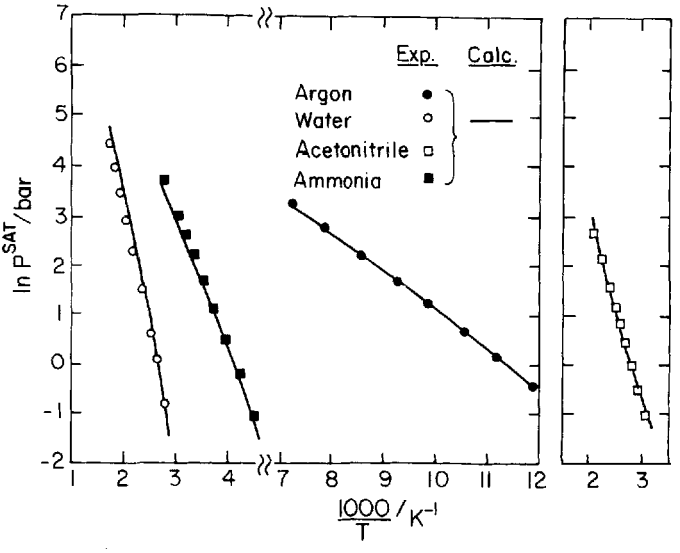

Figure 15 Calculated and observed vapour pressures for argon and several polar fluids from an equation of state of the form (22) with a reference fluid of dipolar hard spheres and a perturbation term of the form of equation (24). (From Bryan and Prausnitz [76].)

Traditionally, the reference term Z_{ref} is taken to be that for a fluid of hard spheres while the perturbation term is either the first order perturbation term or some mean field approximation to it, the simplest being the original van der Waals form,

$$Z_{pert} = -a/RTv \tag{23}$$

where a is the van der Waals attraction constant. Such equations work quite well for mixtures of simple nonpolar fluids, particularly when the Carnahan-Starling equation is used for Z_{ref} and the molecular parameters are fitted to experimental thermodynamic data. For more complex fluids such equations fail. This is not surprising, since such molecular features as nonspherical shape, polarity, or off-centre attractive sites (hydrogen-bonding, complexing, etc.) all have a large effect on the fluid structure, and these effects are not included in a hard sphere reference. Much effort has been expended on attempts to improve the perturbation term, while maintaining the hard sphere reference. Such efforts generally obscure the real problem by adding more adjustable parameters in Z_{pert}.

Recently, there have been several attempts to introduce more realistic reference fluids in order to better treat fluids of more complex molecules. These have included reference fluids of nonspherical hard core molecules [71, 73–75], hard spheres with

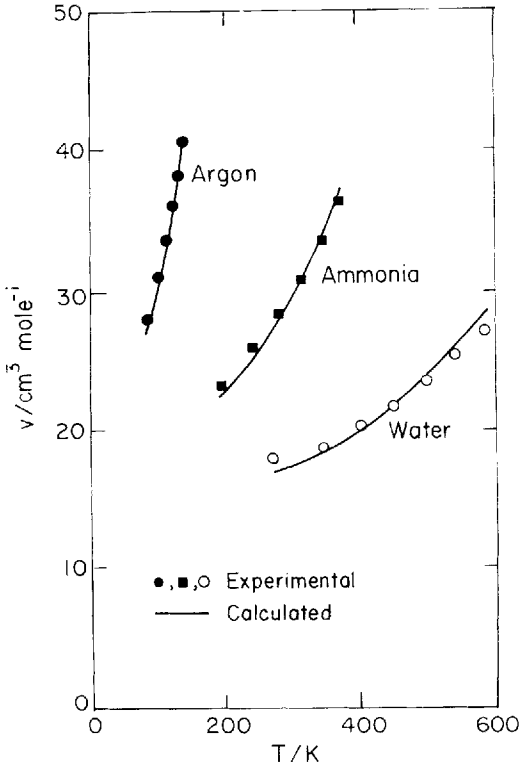

Figure 16 Calculated and observed saturated liquid molar volumes. (from Bryan and Prausnitz (76]).

central point dipoles [76], and hard spheres or chains of hard spheres with off-centre attractive sites [75, 77, 78]. The properties of the reference fluids are obtained from computer simulation results, or from theoretical equations that are known to match the simulation results closely.

These new equations have not been thoroughly tested yet but the inclusion of attractive sites or polarity in the reference fluid seems to offer the probability of substantial improvements for polar and associating fluids. Some results for an equation of the form (22) with a dipolar hard sphere reference fluid are shown in Figures 15 and 16. In this case equation (23) is replaced by [79]

$$Z_{\text{pert}} = -a/RT(v + 0.2b) \tag{24}$$

and a is allowed to vary with temperature, with a temperature-dependence chosen to fit the vapour pressure data of argon. The value of a at the critical temperature, together with $b = 2\pi\sigma^3/3$, are calculated from critical constant data for the fluid of interest. For polar fluids the use of the dipolar hard sphere reference gives distinctly better results than the hard sphere reference.

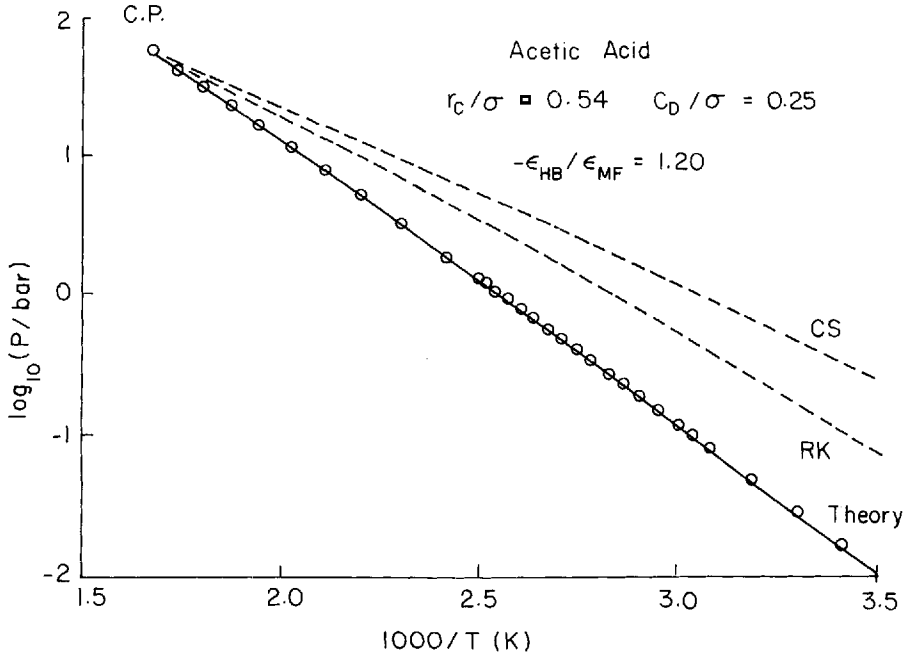

Figure 17 Calculated and observed vapour pressures for acetic acid. The calculations labelled Theory are based on an equation of state of the form of (22) with the reference system a fluid of hard spheres with a single square well attractive site placed off-centre (by a distance C_D) to mimic the associating interaction, and the perturbation term approximated by (23). Here r_c is the cutoff distance for the square well interaction, ε_{HB} is the strength of the square well ('hydrogen bond') interaction, and ε_{MF} is the strength of the mean field interaction, which is related through a constant to a of equation (23). The curve labelled CS is eqn. (22) with the reference term being for a hard sphere fluid and given by the Carnahan-Starling equation. The curve labelled RK is from the Redlich-Kwong equation, and is also based on a hard sphere reference fluid. (From Chapman et al. [78].)

For fluids with molecular assication, the renormalization theory of Wertheim [80, 81, 82, 83, 84] is in good agreement with simulation data for hard spheres with off-centre sites having strong, short-ranged attractive forces [75, 77, 78]. If the sites are suitably chosen they can mimic hydrogen-bonding or other associating intermolecular forces, and the theory can be used to provide Z_{ref} in an equation of the form (22) for such fluids. An example of a calculation of this sort is shown in Figures 17 and 18 for the properties of acetic acid.

5 CONCLUSIONS

Of the methods, for determining phase equilibria using simulation, the Gibbs method is likely to prove the fastest for moderate densities, particularly for mixtures, since it avoids the calculation of chemical potentials. The main drawback of this method is the poor convergence at high densities; the region of applicability is expected to be the same as that of the grand canonical ensemble method. Among the indirect methods the test particle and thermodynamic integration methods are the easiest to program. The test particle method has the advantage that it gives the chemical potential directly, without the need for making a series of simulations. This method fails rather abruptly above some moderate density limit, although this limit can be extended to about the triple point density of Lennard-Jones fluids by sampling using both real and ghost test particles ('f–g sampling'). By contrast, the thermodynamic integration

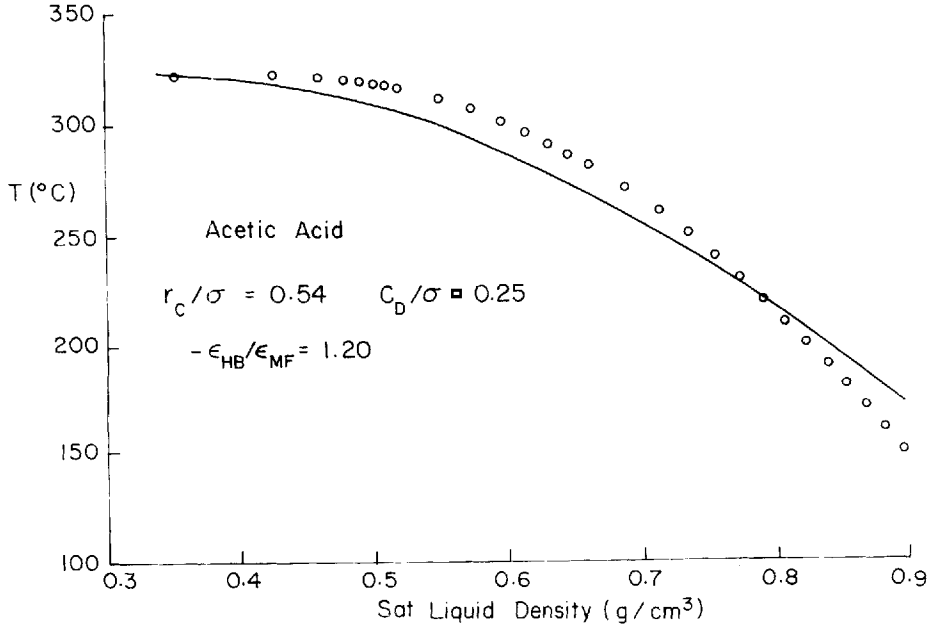

Figure 18 Calculated (line) and observed (points) saturated liquid densities for acetic acid. Calculations are from the theory described in the previous figure caption. (From Chapman et al [78]).

method can be used at any density, although it requires a series of simulations to obtain a free energy or chemical potential at a single state point. At the moment this seems to be the best method for phase equilibria at high densities, where the Gibbs method fails. The modified sampling methods can be used to extend the density range in which the test particle and grand canonical methods can be used, though it is doubtful whether these are significantly more efficient than thermodynamic integration. They may prove to be more useful if applied to the Gibbs method. There is a need for careful comparisons to be made between these various methods to determine their relative speeds and range of usefulness, using a set of prototype systems.

For the near term at least, computer simulation will continue to play an important role in the development of new theoretical and semitheoretical equations of state (e.g. of the form of (22)). This approach should prove particularly useful for more complex fluids, where simulation can provide data for new reference fluids.

The determination of free energies or chemical potentials from computer simulations has many applications besides phase equilibria (see, e.g. [22]), including conformational stability of large molecules, solvation potentials, and the effect of solvents on reaction rates. One area of recent interest has been the study of the stability of various conformations of biomolecules, where thermodynamic integration has been used to calculate the free energy for enzyme-inhibitor complexes [85, 86, 87]. Good agreement is obtained between the simulation results and experiment.

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