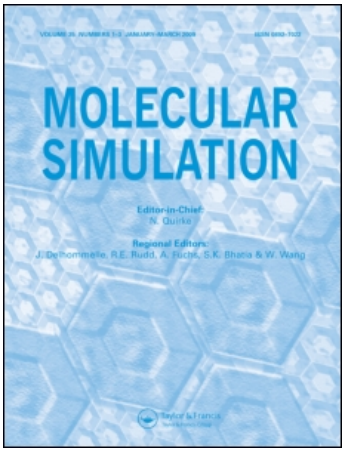

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Direct Determination of Fluid Phase Equilibria by Simulation in the Gibbs Ensemble: A Review

Athanassios Z. Panagiotopoulos[a]
[a] School of Chemical Engineering, Cornell University, Ithaca, NY

To cite this Article Panagiotopoulos, Athanassios Z.(1992) 'Direct Determination of Fluid Phase Equilibria by Simulation in the Gibbs Ensemble: A Review', Molecular Simulation, 9: 1, 1 — 23
To link to this Article: DOI: 10.1080/08927029208048258
URL: http://dx.doi.org/10.1080/08927029208048258

Molecular Simulation, 1992, Vol. 9, pp. 1–23
Reprints available directly from the publisher
Photocopying permitted by license only

DIRECT DETERMINATION OF FLUID PHASE EQUILIBRIA BY SIMULATION IN THE GIBBS ENSEMBLE: A REVIEW*

ATHANASSIOS Z. PANAGIOTOPOULOS

School of Chemical Engineering, Cornell University, Ithaca, NY 14853–5201

(*Received November 1991, accepted December 1991*)

This paper provides an extensive review of the literature on the Gibbs ensemble Monte Carlo method for direct determination of phase coexistence in fluids. The Gibbs ensemble technique is based on performing a simulation in two distinct regions in a way that ensures that the conditions of phase coexistence are satisfied in a statistical sense. Contrary to most other available techniques for this purpose, such as thermodynamic integration, grand canonical Monte Carlo or Widom test particle insertions, the Gibbs ensemble technique involves only a single simulation per coexistence point. A significant body of literature now exists on the method, its theoretical foundations, and proposed modifications for efficient determination of equilibria involving dense fluids and complex intermolecular potentials. Some practical aspects of Gibbs ensemble simulation are also discussed in this review. Applications of the technique to date range from studies of simple model potentials (for example Lennard–Jones, square-well or Yukawa fluids) to calculations of equilibria in mixtures with components described by realistic potentials. We conclude by discussing the limitations of the technique and potential future applications.

KEY WORDS: Simulation, fluid phase equilibria, Gibbs ensemble, Monte Carlo

1. INTRODUCTION

The prediction of thermodynamic and transport properties of fluids and their mixtures is one of the main goals of research in applied thermodynamics and statistical mechanics. Among the various properties of interest, knowledge of the phase behavior of a system is arguably the most desirable from the point of view of applications. Large sections of standard monographs on liquids [1] are devoted to phase equilibria. Until recently, practical methods for modeling phase equilibria in fluid mixtures with sufficient accuracy for engineering applications were based on combination of information on the intermolecular forces in a system with approximations required to obtain analytical expressions for the macroscopic thermodynamic properties [2]. Simulation-based techniques do not require any approximations other than initial assumptions about the intermolecular interactions. Results from such techniques can be used in two complementary ways, namely (a) to test statistical mechanical theories by providing essentially exact results for model systems and (b) to predict the phase behavior of real fluids at conditions for which experimental data are difficult or impossible to obtain. When used for predictions, molecular simulation techniques have the potential to provide significantly more reliable results than it is possible with

*Invited paper.

approximate theoretical methods, since they eliminate all uncertainties in connecting macroscopic properties to the microscopic characteristics of a system.

Computer simulation methods have been used in the study of liquids for almost half a century. Starting with the first papers on Monte Carlo [3] and molecular dynamics [4] these methods have significantly added to our knowledge of structure and thermodynamics of liquids. Until the early 1970's, information available from computer simulation studies of liquids was restricted to simple mechanical or structural properties, such as energy, pressure, enthalpy or pair correlation functions. Statistical properties (entropy and free energy) are generally much harder to obtain from simulations. Specialized techniques developed for the calculation of statistical properties include grand canonical Monte Carlo [5], the Widom test particle method [6, 7] and coupling parameter techniques [8]. An extensive review of free-energy calculation methods is given in reference [9]. The availability of these techniques has made it possible, at least in principle, to determine the phase behavior of model systems from molecular simulations. For this purpose, a series of simulations is performed for a number of state points in the vicinity of a phase transition, and the states that satisfy the thermodynamic conditions of phase coexistence (equality of pressure and chemical potentials of all components) are located numerically. For example, the Widom test particle technique has been used for the determination of phase diagrams for pure components [10, 11] and binary mixtures [12, 13]. The major disadvantages of this "indirect" method are that a large number of simulations is required for multicomponent systems, and that significant uncertainties present in numerical interpolations of the chemical potential hinder the accurate determination of phase boundaries. As a consequence, the method has found relatively limited applicability. Application of the indirect method is significantly easier for one-component systems at low temperatures, because the density of the liquid phase corresponds essentially to zero pressure and the only unknown quantity is the chemical potential of the close-to-ideal-gas vapor phase. A combination of constant-pressure simulations with chemical potential determination techniques is accurate and convenient [14] for this case. Another simulation method for determining phase separation boundaries in binary mixtures involves observing a "kink" in the radial distribution functions due to microscopic demixing [15, 16]. However, the technique gives only an approximate determination of the properties of the coexisting phases. A new promising method is density-scaling Monte Carlo [17], based on performing "umbrella sampling" covering a region of densities. The method computes the relative free energy as a function of density, which in turn can be used to locate phase transitions. The method has been used to locate the coexistence curve of the restricted primitive model for ionic solutions [18].

A direct technique for the determination of phase behavior from simulation is interfacial simulations. Applications of direct interfacial simulations have been reviewed by Rowlinson and Widom [19] and more recently by Gubbins [20]. Despite the apparent simplicity of the technique, there are several problems associated with setting up and equilibrating a system with two coexisting phases. In particular, simulations involving many particles and very long equilibration times are often required [21]. Even with large systems, a siginificant fraction of particles are close to the interface (p. 20 in [28]). When the density difference between the two coexisting phases is small, it is often not possible to set up a stable two-phase system. Finally, for fluids with low vapor pressures, for any reasonable system size, practically no particles can be found in the gas phase [22].

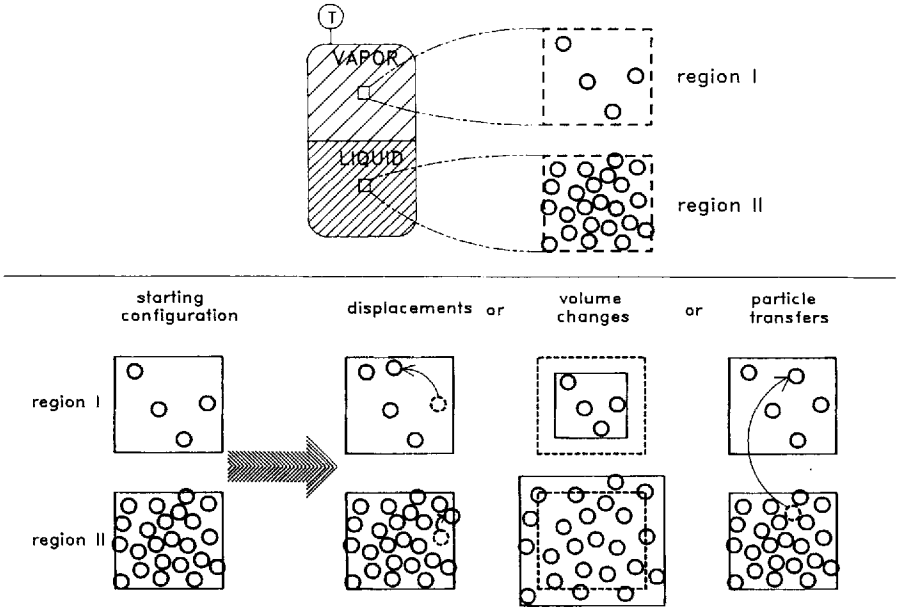

Figure 1 Schematic illustration of the Gibbs ensemble methodology.

A recent detailed review of molecular simulation techniques for the determination of phase equilibria was given by Gubbins [20]. In the present review, we focus on the Gibbs ensemble techqnique for determination of phase equilibria in fluids, updating and expanding significantly a brief review article that appeared in 1989 [23]. At present, the technique appears to be the best available method for determination of phase equilibria by simulation for the systems it can be applied to. The plan of this paper is as follows: In the next section, we review the principles of the Gibbs ensemble technique and its theoretical foundations. Several modifications of the technique to improve its efficiency are presented. Some practical aspects of simulations in the Gibbs ensemble are also discussed in the same section. Applications are described in section 3. Calculations for pure fluids are presented first, followed by applications to mixtures. We conclude by a discussion of the limitations of the methodology and potential future extensions.

2 THE GIBBS ENSEMBLE METHODOLOGY

2.1 *Theoretical Foundations*

The Gibbs ensemble Monte Carlo simulation methodology was originally developed [24] as a response to the question: "is there a way to perform a molecular simulation so as to satisfy, in an average sense, phase equilibrium cirteria in a system?" A schematic of the technique is shown in Figure 1. Let us consider a macroscopic system with two phases coexisting at equilibrium. Gibbs ensemble simulations are performed in two microscopic regions within the bulk phases, away from the interface. In practical terms, this implies that each region is embedded within periodic boundary

conditions with replicas of itself. The thermodynamic requirements for phase coexistence are that each region should be in internal equilbrium, and that temperature, pressure and the chemical potentials of all components should be the same in the two regions. System temperature in Monte Carlo simulations is specified in advance. The remaining three conditions are respectively satisfied by performing three types of Monte Carlo "moves," displacements of particles within each region (to satisfy internal equilibrium), fluctuations in the volume of the two regions (to satisfy equality of pressures) and transfers of particles between regions (to satisfy equality of chemical potentials of all components).

The original development of the acceptance criteria for the Gibbs ensemble [24] was performed using arguments from fluctuation theory. A more complete development of the statistical mechanical definition of the ensemble was subsequently given by Panagiotopoulos *et al.* [25], Smit *et al.* [26] and Smit and Frenkel [27]. We reproduce here the main lines of reasoning of Smit *et al.* Let us consider a one component system at constant temperature T, total volume V, and total number of particles N. The system is divided into two regions, with volumes V_I and V_{II} ($= V - V_I$) and number of particles N_I and N_{II} ($= N - N_I$). The partition function for this system, Q_{NVT}, is

$$Q_{NVT} = \frac{1}{\Lambda^{3N} V N!} \sum_{N_I=0}^{N} \binom{N}{N_I} \int_0^V dV_I V_I^{N_I} V_{II}^{N_{II}} \int d\xi_I^{N_I} \exp\left[-\beta U_I(N_I)\right] \times \int d\xi_{II}^{N_{II}} \exp\left[-\beta U_{II}(N_{II})\right], \quad (1)$$

where Λ is the thermal de Brogile wavelength, $\beta = 1/k_B T$, ξ_I and ξ_{II} are the scaled coordinates of the particles in the two regions and $U(N_i)$ is the total intermolecular potential of interaction of N_i particles. In the original presentation of Equation (1) in reference [26], the factor V was not present in the prefactor of the right-hand-side, an omission which did not effect any of the results. Equation (1) represents an ensemble with probability density, $\mathcal{P}(N_I, V_I; N, V, T)$ proportional to

$$\mathcal{P}(N_I, V_I; N, V, T) \propto \exp\left(\ln \frac{N!}{N_I! N_{II}!} + N_I \ln V_I + N_{II} \ln V_{II} - \beta U_I(N_I) - \beta U_{II}(N_{II}) \right). \quad (2)$$

Smit *et al.* [26] used the partition function given by Equation (1) to prove that the Gibbs ensemble and the canonical ensemble are formally equivalent, by showing that the free energy densities are equal in the thermodynamic limit. They also used a free-energy minimization procedure to show that for a system with a first-order phase transition, the two regions in a Gibbs ensemble simulation will reach the correct equilbrium densities.

The acceptance criteria for the three types of moves can be immediately obtained from Equation (2). For a displacement step internal to one of the regions the probability of acceptance is the same as for conventional constant-NVT simulations:

$$\mathcal{P}_{\text{move}} = \min\left[1, \exp\left(-\beta \Delta U\right)\right], \quad (3)$$

where ΔU is the configurational energy change resulting from the displacement. For a volume change step during which the volume of region I is increased by ΔV with

a corresponding decrease of the volume of region II,

$$\mathcal{P}_{\text{volume}} = \min\left[1, \exp\left(-\beta\Delta U_{\text{I}} - \beta\Delta U_{\text{II}} + N_{\text{I}} \ln \frac{V_{\text{I}} + \Delta V}{V_{\text{I}}} + N_{\text{II}} \ln \frac{V_{\text{II}} - \Delta V}{V_{\text{II}}}\right)\right], \tag{4}$$

and for a particle transfer step from region II to region I:

$$\mathcal{P}_{\text{transfer}} = \min\left[1, \exp\left(-\beta\Delta U_{\text{I}} - \beta\Delta U_{\text{II}} - \ln \frac{(N_{\text{I}} + 1)V_{\text{II}}}{N_{\text{II}} V_{\text{I}}}\right)\right]. \tag{5}$$

Equation (5) can be readily generalized to multicomponent systems. The only difference is that the number of particles of species j in each of the two regions, $N_{\text{I},j}$ and $N_{\text{II},j}$ replace N_{I} and N_{II} respectively in Equation (5).

Equations (3–5) are valid for a simulation in which the total system is considered to be at constant number of molecules, temperature and volume. For pure component systems, this is the only possibility because the phase rule requires that only one intensive variable (in this case system temperature) can be independently specified when two phases coexist. The vapor pressure is obtained from the simulation. By contrast, for multicomponent systems pressure can be specified in advance, with the total system being considered at constant-NPT. The probability density for this case, $\mathcal{P}(N_{\text{I}}, V_{\text{I}}; N, P, T)$ is proportional to

$$\mathcal{P}(N_{\text{I}}, V_{\text{I}}; N, P, T) \propto \exp\left(\ln \frac{N!}{N_{\text{I}}!N_{\text{II}}!} + N_{\text{I}} \ln V_{\text{I}} + N_{\text{II}} \ln V_{\text{II}} - \beta U_{\text{I}}(N_{\text{I}}) - \beta U_{\text{II}}(N_{\text{II}}) - \beta P V_{\text{I}} - \beta P V_{\text{II}}\right). \tag{6}$$

and the only change necessary in the algorithm is that the volume changes in the two regions are now made independently. The acceptance criterion for a volume change step in which the volume of region I is changed by ΔV_{I} and the volume of region II by ΔV_{II} is then

$$\mathcal{P}_{\text{volume}} = \min\left[1, \exp\left(-\beta\Delta U_{\text{I}} - \beta\Delta U_{\text{II}} + N_{\text{I}} \ln \frac{V_{\text{I}} + \Delta V_{\text{I}}}{V_{\text{I}}} + N_{\text{II}} \ln \frac{V_{\text{II}} + \Delta V_{\text{II}}}{V_{\text{II}}} - P(\Delta V_{\text{I}} + \Delta V_{\text{II}})\right)\right]. \tag{7}$$

Simulations of phase equilibria in the Gibbs ensemble do not require prior knowledge or calculation of the chemical potentials of components in a system. However, it is a useful test of the convergence of simulations to ensure that the values of the chemical potentials in the liquid and gas phases are equal. During the particle transfer steps, the change in configurational energy of a region that would have resulted by addition of a particle is clearly related to the "test particle" energies, U^+, used in the Widom equation for calculation of chemical potentials in constant-NVT simulations:

$$\mu_i = -kT \ln \langle \exp(-\beta\Delta U^+) \rangle + kT \ln \rho_i, \tag{8}$$

where μ_i is the chemical potential of component i and ρ_i is the density of component i ($\rho_i = N_i/V$). Smit and Frenkel [27] have obtained a similar expression valid for

Gibbs ensemble simulations, written here for region I:

$$\mu_i = -kT \ln \left\langle \frac{V_I}{N_{I,i} + 1} \exp(-\beta \Delta U_I^+) \right\rangle, \tag{9}$$

where U_I^+ is the configurational energy change of region I during attempted transfers of particles of species i. The difference between the two expressions is that Equation (9) takes into account fluctuations in volume and number of particles in the regions of a Gibbs ensemble simulation. The calculated values of the chemical potentials from Equations (8) and (9) typically differ less than simulation uncertainty [27], except when very few particles are present in one of the two regions.

2.2 *Practical Considerations for Gibbs Ensemble Simulations*

Gibbs ensemble simulations are necessarily more complicated than constant-NVT ensemble calculations from the point of view of programming because of the requirement to perform three different types of steps. A Gibbs ensemble simulation program typically has the following parts:

2.1.1 *Initialization*

In this part of the program, the initial position of the particles in the two regions are assigned, and any values required later (such as matrices of distances and interaction energies between pairs of particles) are calculated based on the initial particle positions. The initial positions are normally obtained by placing particles on a regular lattice, or from a previous simulation at a similar temperature. The initial placement is not critical, since there is always a period of equilibration of the system which is not taken into account in the statistical averages. At conditions close to a freezing line, it might be advantageous to start from a disordered state of the system, since melting of an initial regular lattice may be slow. The relative amounts of the two phases should be chosen so that, after equilibrium, there is a reasonable number of particles in both regions. Of course, since the final densities are usually unknown before performing a simulation, some trial and error may be required to achieve this.

2.2.2 *Main program*

The three types of moves are performed. In order to satisfy microscopic reversibility, it is necessary to select at random, with *fixed* probabilities, which type of move will be performed. The relative ratio of the three types of moves is dictated by considerations of simulation efficiency. Since the aim of the three steps is to satisfy internal equilibration, pressure equality and chemical potential equality between the two coexisting phases, it makes sense to balance the relative frequency of the three types of moves so as to approach equilibrium at approximately the same rate. If, for example, an insufficient number of particle transfer steps is performed relative to the number of displacement steps, then a lot of computer time is wasted simulating two phases with densities and compositions that do not correspond to the equilibrium state of the system. A way to estimate the rate of approach to equilibrium of the various properties of the system is to obtain "control plots" of the instantaneous energy, pressure, density and number of particles in each of the two regions as a function of the number of configurations generated. Typically, the quantity that is the slowest to converge is the number of particles of each species present in each of the two regions. From our experience, a number of successful transfers of each component greater than several

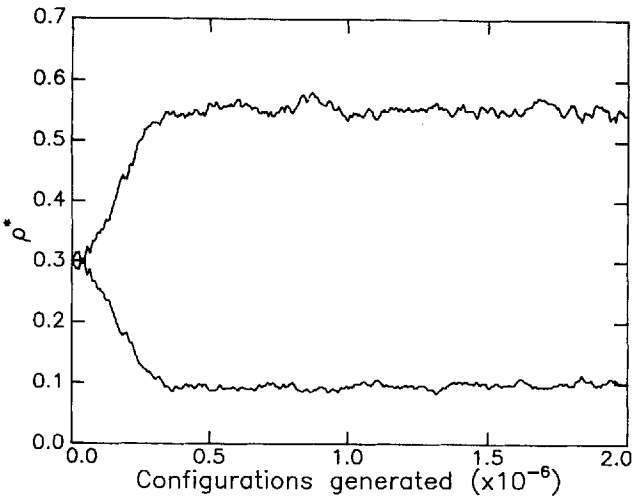

Figure 2 Reduced density ρ^*, versus the number of configurations generated for a system of 1800 Lennard-Jones particles at $T^* = 1.20$, initially in two regions of equal volume and density.

times the total number of particles of the component in the system is required for equilibration of particle numbers (and thus the chemical potentials). When the density of one or both of the coexisting phases is high, this requirement implies that a relatively large number of attempted transfers must be performed. For example, for such systems, typical ratios of attempted displacement : volume change : particle transfer steps are 100 : 1 : 1000.

2.2.3 *Analysis of results*

After the system has achieved equilibrium, as judged by the absence of sytematic drift of densities and compositions in the two phases, data are collected for the equilibrium properties. It is frequently helpful to perform at least a few simulations starting with the two phases at identical conditions in the interior of a postulated phase diagram, in order to verify that the system in indeed achieving spontaneous phase separation. Results from such a simulation for the pure Lennard-Jones fluid with $N = 1800$ total particles are shown in Figure 2. The appearance of a spontaneous phase split and absence of systematic drifts after the equilibrium period are apparent. Smit *et al.* [26] have observed that it is possible for a system to become "trapped" for extended periods of time at local minima of the free energy that do not correspond to the true phase separation. This becomes apparent in a plot of the results as V_1/V versus N_1/N. Also, at the vicinity of a critical point, it is possible that a spontaneous fluctuation would exchange the identity of the two phases. While the apparent long-term averages may indicate that the system is homogeneous, a plot of the probability densities would reveal that the system prefers to exist as two distinct phases.

As for all simulations, an important issue for Gibbs ensemble simulations is the size dependence of the results. In early work on phase coexistence properties of the Lennard-Jones fluid [24] and subsequent studies of this and other model potentials [28], no significant system size dependence of the phase coexistence properties and the location of the critical point was found for system sizes ranging from 64 to 512

particles. This observation was attributed in [28] to a fortunate cancellation or errors. By contrast, a study of finite-size effects using the two-dimensional lattice gas model [29] concluded that there are strong finite-size in Gibbs ensemble simulations close to the critical point, similar in magnitude to finite-size effects for grand canonical Monte Carlo simulations. However, preliminary results for the three-dimensional Lennard-Jones fluid using long simulations with large system sizes (up to 1800 particles) at the vicinity of the critical point [30] indicate that such effects are not present in Gibbs ensemble simulations for this system. This discrepancy remains to be resolved.

2.3 *Variations on the Gibbs Ensemble Theme*

Several modifications of the basic methodology have been proposed. The modifications can be classified in two general categories: (a) changes to apply the methodology to different equilibrium conditions (b) modifications to improve the efficiency of the technique.

An important area of potential application of Gibbs ensemble simulations is in the study of equilibria for confined fluids. The necessary methodological developments have been presented in [31]. For confined fluids, two primary types of equilibria can be described. The first is adsorption equilibrium between a bulk (free) fluid phase and the interior of an adsorbing material. Real adsorbents (such as activated carbon) have complex, often poorly characterized interior geometries. However, studies of adsorption are often performed for the idealized geometries of a slit or a cylindrical pore. The equilibrium constraints are that chemical potentials of all components in the bulk and in the interior of pore should be the same. There is no requirement for mechanical equilibrium. This implies that no volume change step is necessary for Gibbs simulations, only displacement and particle transfer steps. Gibbs ensemble simulations of adsorption are almost identical to grand canonical simulations, the only difference being that the total composition of the system is imposed, rather than the chemical potentials in the exterior of the pore. The second type of equilibria that are important for confined fluids are capillary condensation phenomena, which involve coexistence of two phases in the interior of a pore. Application of the Gibbs method for these systems requires internal, mechanical and chemical potential equality, just as for the case of bulk fluids. Mechanical equilibrium is achieved by changes in *length* (for the case of cylindrical geometry) or *area* (for the case of slits). An alternative technique for determining equilibria for confined fluids is direct simulation of a two-phase system [32], which is possible because the adsorbing walls act as a nucleation sites. Larger systems, and therefore longer simulations, are required for direct two-phase simulations, because of the presence of interfaces, but two-phase simulations have the advantage that they can provide information on the dynamics of the phase transition and the structure of the interfacial region.

A simple modification for the study of membrane equilibria in fluid mixtures has been proposed by Panagiotopoulos *et al.* [25]. The modification involves imposing the condition of chemical potential equality only for components that are membrane-permeable. A similar technique can be used for other systems for which some components are not found in one of the coexisting phases. Examples of such systems are equilibria involving sorption of small molecules in polymers and vapor–liquid equilibria in electrolyte solutions for which the concentration of electrolyte in the gas phase is negligible [33].

The main bottleneck in achieving convergence in Gibbs ensemble simulations

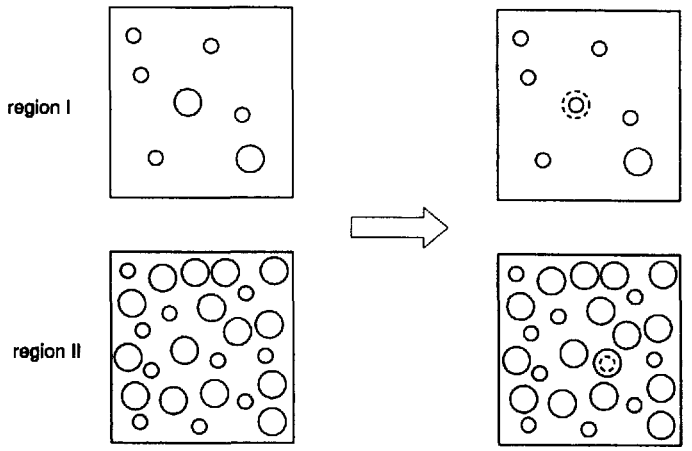

Figure 3 Schematic illustration of the particle identity change technique to speed-up particle transfers for asymmetric systems [34].

typically is chemically potential equilibration through particle transfers between phases. For dense fluid phases, especially for complex, orientation-dependent intermolecular potentials, configurations with "holes" in which an extra particle can be accommodated are highly improbable, and the converse step of removing a particle also involves a large cost energy. Because of these factors, the probability of successful particle transfers becomes prohibitively low. The same difficulties are present in chemical potential determination methods based on particle insertions, such as the Widom technique and grand canonical Monte Carlo. There have been several proposed modifications to the Gibbs methodology in order to improve its efficiency for dense fluids and complex potentials. The particle-identity exchange algorithm [34] is approriate for the study of mixtures of components that differ greatly in molecular size and has been inspired by the semi-grand canonical ensemble technique [35]. The technique is illustrated schematically in Figure 3. For systems in which a component is hard to transfer because of large size, equilibration of its chemical potential is achieved by identity exchanges between that component and particles of another component that is smaller and thus easier to transfer. In a similar vein, de Pablo and Prausnitz [36] have proposed the so-called "inflating-flea" method, in which a few small particles are intentionally introduced in a simulation to facilitate application of particle-identity change moves. The disadvantage of the "inflating flea" method is that the system simulated is no longer identical to the original system in the absence of added particles. Stapleton and Panagiotopoulos [37] have proposed a combination of the excluded volume map sampling technique [38] and the Gibbs ensemble, applicable to systems with very dense fluid phases. Cracknell *et al.* [39] have described a rotational insertion bias method applicable to dense phases of structured particles (e.g., water). The method biases the orientation, rather than the position, of the particle to be transferred.

A modification based on a thermodynamic model for the vapor phase is described in [40]. The technique eliminates the need to simulate the vapor phase, resulting in moderate savings of computer time for the systems studied in [40]. The disadvantage

of this method is that there is significant reduction in the accuracy of the results, especially at conditions for which the vapor phase deviates significantly from ideality. This idea is likely to be more useful for simulations involving two dense phases, for example solid-liquid equilibria [41]. In this case, utilizing an accurate equation of state

3 APPLICATIONS

The Gibbs ensemble method has been used to obtain phase diagrams for a variety of systems. As for other simulation techniques, the objectives of simulations in the Gibbs ensemble can be either to obtain accurate results for well-defined simple model fluids in order to test statistical mechanical theories, or to simulate the behavior of real systems using relatively complicated intermolecular potentials with parameters fitted to experimental data. In the following section, we describe studies of phase equilibria for pure fluids and mixtures performed in the recent years. Most studies of one-component systems have been performed to provide data for comparison with theories, while a significant fraction of the mixture studies aim at modeling real fluids.

3.1 *Pure fluids*

3.1.1 *Lennard–Jones fluid*

The phase diagram for the pure Lennard–Jones fluid in three dimensions was determined from Gibbs ensemble simulations by Panagiotopoulos *et al.* [24, 25] and Smit [28]. The results are in general agreement with previous calculations using indirect techniques [42, 10, 11] except close to the critical point. The best estimate for the critical point of the pure Lennard–Jones fluid was obtained by Smit [28] as $T_c^* = 1.316 \pm 0.006$, $\rho_c^* = 0.304 \pm 0.006$. Smit [28] has also determined the phase behavior for the commonly used in molecular dynamics simulations truncated-and-shifted Lennard–Jones potential (with cutoff radius 2.5σ). The estimated critical temperature for this fluid is $T_c^* = 1.085 \pm 0.005$ and $\rho_c^* = 0.317 \pm 0.006$. Clearly, truncation of a potential has a strong effect on the observed phase equilibrium behavior. Phase diagrams for the pure LJ fluid confined in a cylindrical pore were determined by Panagiotopoulos [31]. It was observed that both critical temperature and critical density decrease as pore radius is decreased.

3.1.2 *Lennard–Jones fluid in two dimensions*

Two-dimensional systems are interesting for applications related to adsorption on solid or liquid interfaces. When compared to their three-dimensional analogs, the lower interfacial tensions for two-dimensional systems make it harder to obtain stable two-phase coexistence in Gibbs ensemble simulations, especially close to the critical point. There are three sets of results for the full Lennard–Jones potential, two of which are reproduced in Figure 4. The calculations of Singh *et al.* [43] give $T_c^* = 0.472$, $\rho_c^* = 0.33 \pm 0.02$, whereas those by Smit and Frenkel [44] and Nicolaides *et al.* [45] are in close agreement and give, respectively, $T_c^* = 0.515 \pm 0.002$ (0.522 ± 0.002) and $\rho_c^* = 0.355 \pm 0.003$ (0.366 ± 0.009). The difference seems to be due to the fact that the fitting procedure used to obtain estimates of the critical point heavily emphasizes points at the highest temperatures simulated. While the three sets of results are in good agreement for temperatures lower than $T^* = 0.46$, a single point with large uncertainty at $T^* = 0.47$ in the results of Singh *et al.* seems

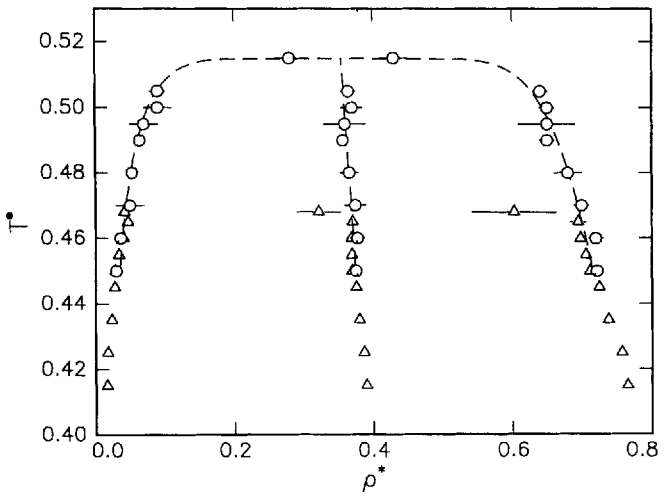

Figure 4 Reduced temperature, T^*, versus phase coexistence and rectilinear diameter densities, ρ^*, for the 2-dimensional Lennard–Jones fluid. (○) Smit and Frenkel [44]; (– – –) fitted lines to the coexistence and rectilinear densities of Smit and Frenkel [44]; (△) results of Singh *et al.* [43].

to be the cause of the low estimate of the critical temperature. It must, therefore, emphasized that in order to obtain good estimates of a critical point form Gibbs ensemble simulations, it is necessary to have results in its close vicinity.

3.1.3 *Square-well fluids*

Square-well fluids are of significant theoretical interest because they are the simplest systems with both attractive and replusive interactions. An extensive study of the phase behavior of square-well fluids of variable range was performed by Vega *et al.* [46]. The results for the shape of the coexistence curve for the relatively short-ranged fluids (range parameter $\lambda = 1.25, 1.375, 1.5$ and 1.75) can be described by a 1-term Wegner expansion with exponent β near the univeral value ($\beta = 0.325$). As Vega *et al.* point out, this is a somewhat surprising result since the calculations of phase coexistence in the Gibbs ensemble are necessarily performed with a finite system that prevents the true critical divergence of correlation length. A similar conclusion concerning the shape of the coexistence curve obtained from Gibbs ensemble simulation was reached by Pitzer [47]. An unexpected result in the study of Vega *et al.* was that for the fluid of longest range ($\lambda = 2$), the shape of the coexistence curve is best described by a near-classical exponent value ($\beta \approx 0.5$). Unfortunately, for the longer-ranged fluids, it was difficult to obtain results as close to the critical point as for the other fluids, and thus the difference in shape of the coexistence curves must be regarded as tentative. A study of a related potential, that of square-well tangent diatomics of range $\lambda = 1.5$ was performed by Yethiraj and Hall [48], who found that the most accurate theory in terms of phase equilibrium properties is a reference interaction site model (RISM) integral equation with a mean spherical approximation (MSA), while a second-order perturbation theory overestimates the critical temperature by 6–8%.

3.1.4 *Dipolar and quadrupolar fluids*

Polar fluids are important for many practical applications, and simple intermolecular potential models incorporating dipole-dipole interactions (Stockmayer fluids) or quadrupole-quadrupole interactions have been frequently studied by statistical mechanical techniques. Phase equilibria for Stockmayer fluids of dipolar strengths $(\mu^*)^2 = \mu^2/\varepsilon\sigma^3$ equal to 1.0 and 2.0 have been studied by Smit *et al.* [49]. Significant disagreements between Gibbs ensemble results and predictions of a perturbation theory of $O(\mu^4)$ were found. A Padé approximant of the perturbation series improves the results for the liquid density, but still overestimates the critical temperature. It is possible that part of the reason for the disagreement is the use of a reference term for the theory (Lennard–Jones potential) that does not accurately describe the pure fluid phase behavior. Better agreement is found between Gibbs ensemble calculations and perturbation theory for systems with quadrupole-quadrupole interactions [50, 51].

3.1.5 *Restricted primitive model*

Applications of the Gibbs ensemble methodology to the restricted primitive model (charged hard spheres of equal diameter) for ionic fluids have been described by Panagiotopoulos [52]. For the strongly interacting ionic fluids special consideration must be given to the method for chemical potential equilibration. The common technique for chemical potential calculations in ionic systems involves attempted insertions (transfers) of electrically neutral groups of ions. This is not practical at the low temperatures at which vapor-liquid equilibria for these systems are observed. One possible solution to this difficulty, namely transferring of individual ions, faces two potentially serious obstacles. The first is that the environments experienced by a single ion and a pair might not be identical. This is avoided in Gibbs ensemble simulation because of the fluctuation in number of ions in each region. The second obstacle to single-ion transfers is that the Ewald summation technique for handling long-range interactions requires that the total system be electrically neutral. The single-particle transfers can be made not to violate the total electroneutrality condition by assuming that each particle is embedded in a uniform neutralizing continuum of equal and opposite charge. The estimated critical point, at a reduced temperature $T_c^* = 0.056$ and density $\rho_c^* = 0.04$, is significantly different from previous theoretical estimates [53]. The recent calculations of Valleau [17] using the density-scaling Monte Carlo technique for the same system give $T_c^* = 0.07$, $\rho_c^* = 0.07$. The difference might be due to the use of different type of boundary conditions (Ewald sum in [52] versus minimum image in [17]).

3.1.6 *Yukawa fluids*

The Yukawa potential is of theoretical interest because it is a non-trivial model with attractive interactions analytically solvable within the mean spherical approximation, and has often been used to describe screened coulombic interactions. Rudisill and Cummings [54] performed studies of a hard core two-Yukawa model designed to approximate closely the Lennard–Jones potential, and found that the phase behavior of the Yukawa model is similar to that of the Lennard–Jones fluid. The authors were unable to use the Gibbs ensemble technique for calculating the properties of fluids with hard core Yukawa interactions:

$$U(r) = \begin{cases} \infty & r < \sigma \\ -\varepsilon \dfrac{\exp\left[-\lambda(r-\sigma)\right]}{r} & r > \sigma \end{cases} \tag{10}$$

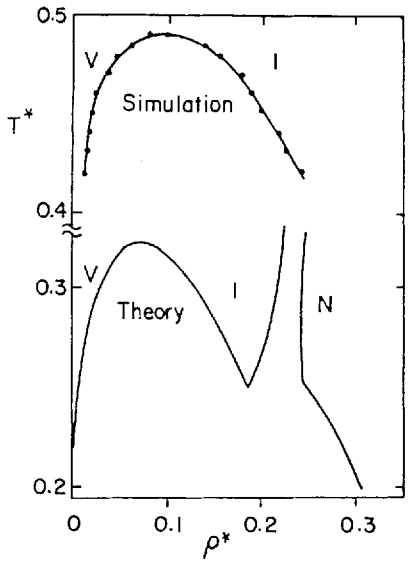

Figure 5 Liquid–vapour coexistence curves for the Gay–Berne fluid with $\kappa = 3$, $\kappa' = 5$, from the study of de Miguel *et al.* [57]. Upper curve represents Gibbs-ensemble simulation results and lower curve is the prediction of a density-functional theory approximation V = vapor phase : I = isotropic liquids; N = nematic liquid.

because the particles tend to "stick" together at $r = \sigma$ and thus the efficiency of volume changes is very small. This difficulty was resolved in the study of Smit and Frenkel [55] for the potential of Equation (10). Smit and Frenkel performed a large number of volume change steps, while keeping computational requirements modest by (a) continuously monitoring the minimum distance between any two particles in the box, thus immediately rejecting any volume change move that would have resulted in overlap, and (b) by developing an expansion of the energy of new configurations in powers of the fractional volume change.

3.1.7 *Gay–Berne fluids*

The Gay–Berne potential is a generalization of the Lennard–Jones potential to include anisotropic interactions. In has two shape parameters, the elongation $\kappa = \sigma_{\parallel}/\sigma_0$, and the well-depth ratio, $\kappa' = \varepsilon_{\parallel}/\varepsilon_{\perp}$. For $\kappa = \kappa' = 1$, the Gay–Berne potential reduces to the Lennard–Jones potential. The model with $\kappa = 3$ and $\kappa' = 5$ exhibits a nematic phase [56]. De Miguel *et al.* calculated equilibrium between a vapor and an isotropic liquid phase for the same model [57]. It is interesting to note that a local density functional theory for this model underestimates the critical temperature of the system by more than 30%, as shown in Figure 5. Further studies by the same group [58] have investigated the effect of molecular elongation on the shape of the coexistence curve, and demonstrated that a two-parameter corresponding states principle does not apply to this potential when the elongation ratio κ is varied.

3.1.8 *Water*

Because of its technological importance, water has been the subject of a large number of simulation studies. Until recently, however, no studies had been performed of the

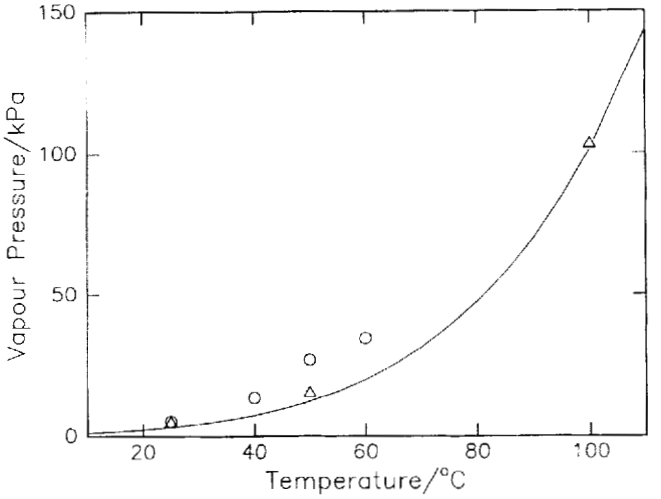

Figure 6 Simulated and experimental vapour pressure versus temperature for water from the study of Cracknell *et al.* [39]. (○) TIPS2 water; (△) TIP4P water (——) experimental data.

phase behavior of realistic intermolecular models for water. The first Gibbs ensemble simulation study of such a model was by de Pablo and Prausnitz [36] who used the TIP4P model of Jorgensen *et al.* [59] and covered the range of approx. 100°C to the critical point. The same model, as well as the older TIPS2 model [60], has been studied at lower temperatures by Cracknell *et al.* [39], using the rotational insertion bias method. Results from the latter study are shown in Figures 6 and 7. In these two studies, spherical truncation of the potential at distances beyond half the box length

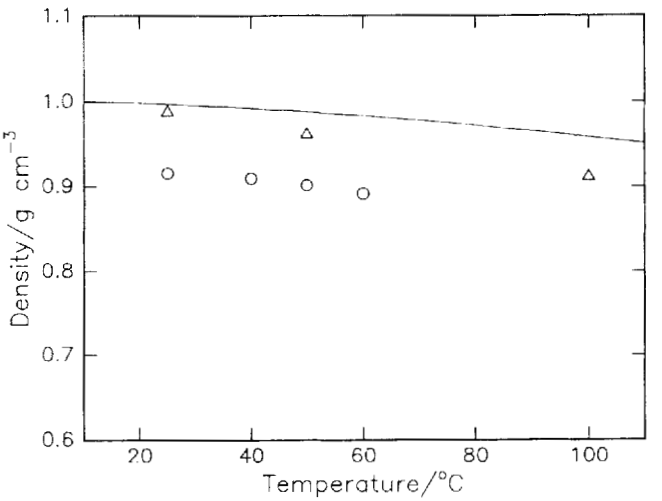

Figure 7 Simulated and experimental liquid density versus temperature for water from the study of Cracknell *et al.* [39]. (○) TIPS2 water; (△) TIP4P water; (—) experimental data.

was performed. Some dependence of the results on system size is expected for polar and ionic systems when spherical truncation is used, because of the fluctuation in density and number of molecules in each of the two phases. The Ewald summation technique which is less sensitive to system size was used by Pablo *et al.* [61] to study the SPC model for water [62]. The SPC model reproduces the dielectric constant of water more closely than other model potentials [63], but its phase behavior was found in [61] to deviate significantly from experiment, expecially at higher temperatures.

3.2 *Mixtures*

3.2.1 *Lennard–Jones mixtures*

The first applications of the Gibbs ensemble technique to mixtures [25] were for three Lennard–Jones systems previously studied by indirect techniques [13], performed primarily in order to establish the validity of the new technique. Studies of phase equilibria for mixtures of noble gases modeled as Lennard–Jones particles are discussed in [34]. Good agreement between experimental data and simulation results was obtained for the system Ar/Kr without any fitted parameters. For the more asymmetric system Ne/Xe, it was necessary to adjust one mixture parameter to obtain agreement with experimental data. Studies of the effect of interaction parameters on the behaviour of mixtures in the supercritical region, including ternary systems, have appeared in [64]. Reference [65] presents a systematic study of a binary system with pure components corresponding to Ar and Kr and unlike–pair interaction parameter that were varied to induce liquid–liquid immiscibility. Studies of Lennard–Jones mixtures to test a statistical mechanical equation of state are presented in [66]. Harismiadis *et al.* [67] performed a systematic investigation of the phase behavior of mixtures of Lennard–Jones particles in which the unlike-pair interactions are described as conventional Lorentz–Berthelot combining rules. The range of parameters covered was energy ratios of up to two, and volume ratios up to eight. This range significantly exceeds that of previous calculations of excess thermodynamic properties for similar mixtures [1]. Comparisons of the results with a simple theoretical model (the van der Waals one-fluid theory of solutions) revealed surprisingly good agreement. Typical results are shown in Figure 8, corresponding to a mixture with $\sigma_2/\sigma_1 = 1.5$. The conclusion from this study was that simple solution theories have a much wider range of applicability in terms of their ability to predict phase equilibria than previously believed.

3.2.2 *Hard sphere and soft disk mixtures*

A study of mixture of symmetric non-additive hard spheres (with $\sigma_1 = \sigma_2$, $\sigma_{12} = 1.2\sigma_1$) was performed by Amar [68]. For such a mixture, there is no requirement for performing volume change steps, since the densities of the coexisting phases must be equal by symmetry. One could also completely avoid the direct particle transfer steps, utilizing instead particle identity changes [34], since the composition of the coexisting phases must also be symmetric. In reference [68], conventional direct particle transfers were performed. The results were in good agreement with perturbation theory predictions, except close to the critical point. In a study of the related system of non-additive soft disks by Mountain and Harvey [69], particle-identity changes were utilized for the symmetric cases. Analysis of the results for the symmetric systems at the vicinity of the critical point indicates that the Gibbs ensemble results obey Ising-like behavior. As for the non-additive hard sphere mixtures, perturbation theory

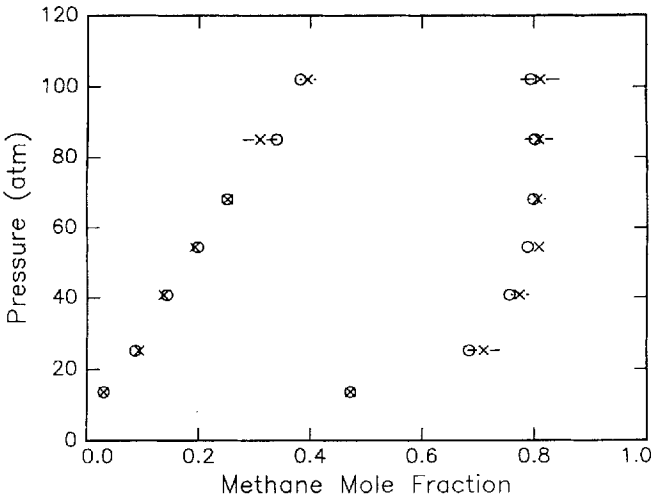

Figure 10 Simulated and experimental pressure-composition curve for a methane-*n*-pentane mixture at $T = 104.4°C$ from the study of de Pablo *et al.* [74]. (×) simulation results; (○) experimental data.

polydispersities typical of solutions of spherical micelles close to the critical micelle concentration. For wider distribution of sizes and for systems with energy polydispersity, the phase envelope was observed to shift significantly relative to the monodisperse fluid.

3.2.5 *Hydrocarbon mixtures*

Gibbs ensemble simulations of realistic models for hydrocarbon mixtures were first performed by de Pablo and Prausnitz [36], who used the "Optimized Intermolecular Potential Functions for Liquid Simulations" (OPLS) site-site potentials of Jorgensen *et al.* [73]. The arithmetic-mean combining rules for the energy parameters suggested for use with OPLS in [73] were found to give significantly worse results than the more commonly used geometric-mean combining rules. Further studies by de Pablo *et al.* [74] have shown that excellent agreement with experimental data for these mixtures can be obtained over a wide range of temperatures, at the cost of introducing some density dependence for the energy potential parameter. Results for pressure-composition and pressure-density envelopes of the binary mixture methane-*n*-pentane are shown in Figures 10 and 11. It is clear from these studies that it is possible to use the Gibbs ensemble technique for modeling real mixtures to a sufficient precision for engineering applications, provided that the intermolecular parameters are fitted to experimental data. Most engineering (macroscopic) models for phase equilibria also rely on fitting parameters to experimental data, and are significantly "cheaper" to apply. However, the potential advantage of molecular simulation is that the parameters that are obtained are likely to be applicable over a much wider range of conditions, since no approximations are made after the effective intermolecular interactions have been determined. This proposition, however, remain to be proved for a wide range of systems.

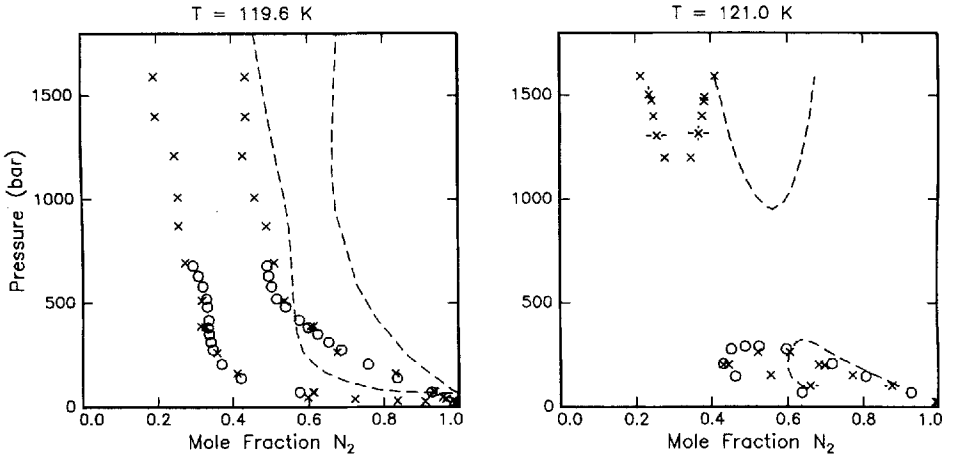

Figure 9 Phase diagrams for the binary system He/N_2 modeled by Lennard–Jones and quadrupole–quadrupole interaction potentials [37]. (×) Gibbs ensemble Monte Carlo results (○) experimental data; (— —) perturbation theory.

provides a good description of the simulation results, except close to the critical point. Mountain and Harvey [69] point out that molecular dynamics studies of the same systems give only a qualitative estimate of the location of the phase coexistence curve.

3.3.3 *High pressure phase equilibria*

Simulations of phase coexistence for mixtures using potentials approximating real fluids have been performed primarily in order to study fluid–fluid demixing at high pressures. Studies of noble-gas mixtures [34] have already been discussed in the section on Lennard–Jones mixtures. A study of high pressure phase equilibria in the system He/N_2, using Lennard–Jones and quadrupole-quadrupole interactions was performed using the excluded volume map sampling technique in the Gibbs ensemble [37]. The results, partly reproduced here in Figure 9, show excellent agreement between experiment and simulation. De Kuijper *et al.* [70] have studied mixtures with components interacting with the α – exp – 6 potential with potential parameters corresponding to the He/H_2 binary system. Good agreement was found between experiment and simulation, and it was established that the purely replusive α – exp – 6 potential also shows fluid-fluid demixing. In a subsequent study by the same group [71], the results were extended to higher temperatures, up to 2000 K, corresponding to pressures for demixing of up to 750 kbar. The study is an example of one of the possible uses of simulation, namely, extending experimental data into regions of the phase diagram for which obtaining experimental data may be difficult or impossible.

3.2.4 *Polydisperse fluids*

Stapleton *et al.* [72] have described applications of the Gibbs ensemble to polydisperse fluids. Such fluids are appropriate for the description of physical systems such as micellar solutions, the "particles" of which can have variable size or interaction energies, depending on their environment. In the study of Stapleton *et al.*, the effect of size polydispersity on the observed phase behavior was found to be small for

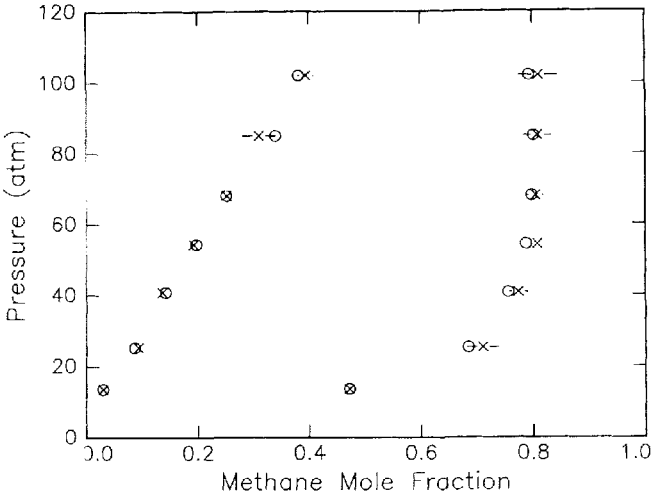

Figure 10 Simulated and experimental pressure-composition curve for a methane-*n*-pentane mixture at $T = 104.4°C$ from the study of de Pablo *et al.* [74]. (×) simulation results; (○) experimental data.

polydispersities typical of solutions of spherical micelles close to the critical micelle concentration. For wider distribution of sizes and for systems with energy polydispersity, the phase envelope was observed to shift significantly relative to the monodisperse fluid.

3.2.5 *Hydrocarbon mixtures*

Gibbs ensemble simulations of realistic models for hydrocarbon mixtures were first performed by de Pablo and Prausnitz [36], who used the "Optimized Intermolecular Potential Functions for Liquid Simulations" (OPLS) site-site potentials of Jorgensen *et al.* [73]. The arithmetic-mean combining rules for the energy parameters suggested for use with OPLS in [73] were found to give significantly worse results than the more commonly used geometric-mean combining rules. Further studies by de Pablo *et al.* [74] have shown that excellent agreement with experimental data for these mixtures can be obtained over a wide range of temperatures, at the cost of introducing some density dependence for the energy potential parameter. Results for pressure-composition and pressure-density envelopes of the binary mixture methane-*n*-pentane are shown in Figures 10 and 11. It is clear from these studies that it is possible to use the Gibbs ensemble technique for modeling real mixtures to a sufficient precision for engineering applications, provided that the intermolecular parameters are fitted to experimental data. Most engineering (macroscopic) models for phase equilibria also rely on fitting parameters to experimental data, and are significantly "cheaper" to apply. However, the potential advantage of molecular simulation is that the parameters that are obtained are likely to be applicable over a much wider range of conditions, since no approximations are made after the effective intermolecular interactions have been determined. This proposition, however, remain to be proved for a wide range of systems.

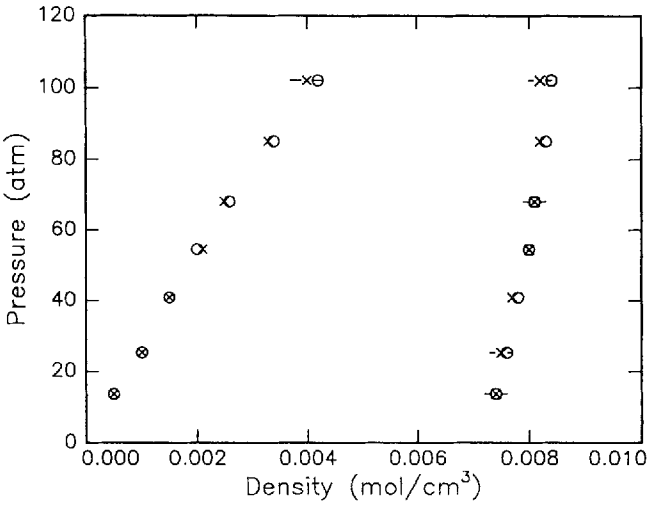

Figure 11 Simulated and experimental pressure-density curve for a methane-*n*-pentane mixture at $T = 104.4°C$ from the study of de Pablo *et al.* [74]. (×) simulation results; (○) experimental data.

4 LIMITATIONS OF THE GIBBS ENSEMBLE TECHNIQUE

The primary limitation of the Gibbs methodology is that for highly non-spherical, multisegment, or strongly interacting molecules, the particle transfer step has a very low probability of acceptance. This difficulty is common to simulation methods for the determination of chemical potentials. Although the principle of the technique is valid for equilibria involving solids or liquid crystalline phases, practical application of the technique seems problematic. For such systems, thermodynamic integration remains the technique of choice for determining phase coexistence properties [75, 76].

The techniques mentioned in section 2.3 can be used to improve the efficiency of the Gibbs method for systems with dense liquid phases. Among the proposed modifications, particle identity changes for asymmetric mixtures seem to be both efficient and easy to implement. The rotational bias method is likely to be useful for simulations involving water or other fluids with highly directional interactions. The practical upper limit of molecular size that can be handled with the Gibbs ensemble technique with its modifications seems at present to be the level of relatively small hydrocarbons, containing up to five or six carbon atoms.

Systems with polymeric molecules cannot at the present be simulated with the Gibbs ensemble technique. Until recently, the only practical technique for determining free energies and phase coexistence properties for truly macromolecular systems were thermodynamic integration and direct interfacial simulations. Some recent developments are likely to impact the field of free-energy and phase equilibrium calculations in macromolecular systems. Siepmann [77], Frenkel *et al.* [78] and de Pablo *et al.* [79] have developed a method to compute the chemical potential of chain molecules based on the Rosenbluth and Rosenbluth [80] segment-by-segment insertion algorithm. The technique has been tested to moderately long polymers (up to 30 segments at reduced densities $\rho^* = 0.60$). A complementary technique proposed by Kumar *et al.* [81] extends the validity of the Widom test particle method to polymers of arbitrary length

by computing the incremental chemical potential on extension of a polymeric molecule by a single monomeric unit. It is expected that a combination of these techniques with the Gibbs ensemble will result in an efficient algorithm for the determination of equilibria in polymeric systems.

5 CONCLUSIONS

The Gibbs ensemble technique is applicable to the determination of fluid-phase equilibria for pure components and mixtures with moderately complex intermolecular interactions. For these systems, the technique is more accurate and convenient than either indirect techniques involving computation of the chemical potential, or direct interfacial simulations. For more complex intermolecular potentials, and especially for systems involving solid or liquid crystalline phases, the technique fails because of inadequate sampling of the relevant regions of phase space. The Gibbs ensemble technique has been applied to the determination of phase equilibria for a number of systems, ranging in complexity from simple reference potentials to realistic molecular models for water and hydrocarbons. Recent developments in simulation methodologies for obtaining chemical potentials for polymeric systems suggest that future applications will also cover these systems.

The emerging ability to obtain phase diagrams for mixtures of molecules with arbitrary intermolecular interactions is likely to result in significant changes in the way thermodynamic modeling of phase equilibria is performed. Direct simulations can be used to refine theoretical approximations or fit molecular-based parameters to experimental data. While the latter approach is necessarily empirical in nature, it is preferable to fitting of macroscopic model parameters, because the resulting molecular-based models are likely to be applicable outside the range of experimental conditions from which they were derived.

Acknowledgements

It is a pleasure to thank K. Binder, A. de Kuijper, J. de Pablo, D. Frenkel, J.M. Prausnitz, L.F. Rull and B. Smit for providing preprints of papers prior to publication. Helpful discussions and valuable comments about the manuscript by K. Gubbins, J. Prausnitz, B. Smit, C. Tsonopoulos and Z. Tan are also acknowledged. Financial support for this work was provided by the U.S. Department of Energy and the National Science Foundation.

References

[1] J.S. Rowlinson and F.L. Swinton, *Liquids and Liquid Mixtures*, 3rd edition, Butterworth Scientific, London (1982).
[2] J.M. Prausnitz, R.N. Lichtenthaler and E.G. de Azevedo, *Molecular Thermodynamics of Fluid Phase Equilibria*, 2nd ed., Prentice-Hall, Englewood Cliffs, NJ (1986).
[3] M. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller, and E. Teller, "Equation of state calculations by fast computing machines", *J. Chem. Phys.*, **21**, 1087–1092 (1953).
[4] B.J. Alder and T.E. Wainwright, "Studies in molecular dynamics. I. General method", *J. Chem. Phys.*, **31**, 459–466 (1959).
[5] G.E. Norman and V.S. Filinov, "Investigations of phase transitions by a Monte-Carlo method", *High Temp.*, **7**, 216–222 (1969).
[6] B. Widom, "Some topics in the theory of fluids", *J. Chem. Phys.*, **39**, 2802–2812 (1963).

[7] K.S. Shing and K.E. Gubbins, "The chemical potential in non-ideal liquid mixtures. Computer simulation and theory", *Mol. Phys.*, **49,** 1121–1138 (1983).
[8] G.C.A.M. Mooij, S.W. de Leeuw, C.P. Williams and B. Smit, "Free-energy computations for mixtures of Stockmayer and polarizable Lennard–Jones fluids", *Mol. Phys.*, **71,** 909–911 (1990).
[9] D. Frenkel, "Free energy computations and first order phase transitions", in *Molecular Dynamics Simulations of Statistical Mechanical Systems*, (G. Ciccotti and W.G. Hoover, eds.), Proceedings of the 97th International 'Enrico Fermi' School of Physics (1985).
[10] D.J. Adams, "Calculating the low temperature vapour line by Monte Carlo", *Mol. Phys.*, **32,** 647–657 (1976).
[11] D.J. Adams, "Calculating the high-temperature vapour line by Monte Carlo", *Mol. Phys.*, **37,** 211–221 (1979).
[12] D. Fincham, N. Quirke and D.J. Tidesley, "Computer simulation of molecular liquid mixtures. I. A diatomic Lennard–Jones model mixture for CO_2/C_2H_6", *J. Chem. Phys.*, **84,** 4535–4546 (1986).
[13] A.Z. Panagiotopoulos, U.W. Suter and R.C. Reid, "Phase diagrams of non-ideal fluid mixtures from Monte-Carlo simulation", *Ind. Eng. Chem. Fundam.*, **25,** 525–535 (1986).
[14] D. Möller and J. Fischer, "Vapor liquid equilibrium of a pure fluid from test particle method in combination with NpT molecular dynamics simulations", *Mol. Phys.*, **69,** 463–473 (1990).
[15] M. Schoen and C. Hoheisel, "Static and dynamic cross correlation in thermodynamically stable and unstable mixtures. I. A molecular dynamics study using Lennard–Jones (12-6) pair potential functions with identical σ parameters", *Mol. Phys.*, **53,** 1367–1380 (1984).
[16] M. Schoen and C. Hoheisel, "Static and dynamic cross correlation in thermodynamically stable and unstable mixtures. II. Molecular dynamics on Lennard–Jones systems consiting of particles of unequal size", *Mol. Phys.* **57,** 65–79 (1986).
[17] J.P. Valleau, "Density-scaling: A new Monte Carlo technique in statistical mechanics", *J. Computational Phys.*, **96,** 193–216 (1991).
[18] J. Valleau, "The coulombic phase transition: Density-scaling Monte Carlo" *J. Chem. Phys.*, **95,** 584–589 (1991).
[19] J.S. Rowlinson and B. Widom, *Molecular Theory of Capillarity*, Ch. 6, Clarendon Press, Oxford (1982).
[20] K.E. Gubbins, "The role of computer simulation in studying phase equilibria", *Mol. Simulation*, **2,** 223–252 (1989).
[21] C.D. Holcomb, P. Clancy, S.M. Thompson and J.A. Zollweg, "A critical study of the subtleties of simulations of the Lennard–Jones Liquid-Vapor interface for pure fluids and binary mixtures", paper presented at the 11th Symposium on Thermophysical Properties, Boulder, CO, June 23–27 (1991).
[22] W.G. Madden "Monte Carlo studies of the melt-vacuum interface of a lattice polymer", *J. Chem. Phys.*, **87,** 1405–1422 (1987).
[23] A.Z. Panagiotopoulos and M.R. Stapleton, "The Gibbs method for molecular-based computer
[24] A.Z. Panagiotopoulos, "Direct determination of phase coexistence properties of fluids by Monte Carlo simulation in a new ensemble", *Mol. Phys.*, **61,** 813–826 (1987).
[25] A.Z. Panagiotopoulos, N. Quirke, M. Stapleton and D.J. Tildesley, "Phase equilibria by simulation in the Gibbs ensemble: alternative derivation, generalization and application to mixture and membrane equilibria", *Mol. Phys.*, **63,** 527–545 (1988).
[26] B. Smit, Ph. de Smedt and D. Frenkel, "Computer simultions in the Gibbs ensemble", *Mol. Phys.*, **68,** 931–950 (1989).
[27] B. Smit and D. Frenkel, "Calculation of chemical potential in the Gibbs ensemble", *Mol. Phys.*, **68,** 951–958 (1989).
[28] B. Smit, "Simulation of phase coexistence: from atoms to sufactants", PhD dissertation, Univ. of Utrecht, The Netherlands (1990).
[29] K.K. Mon and K. Binder, "Finite size effects for the simulation of phase coexistence in the Gibbs ensemble near the critical point", preprint (1991).
[30] A.Z. Panagiotopoulos and B. Smit, unpublished data (1991).
[31] A.Z. Panagiotopoulos, "Adsorption and capillary condensation of fluids in cylindrical pores by Monte Carlo simulation in the Gibbs ensemble", *Mol. Phys.*, **62,** 701–719 (1987).
[32] G.S. Heffelfinger, F. van Swol and K.E. Gubbins, "Liquid-vapor coexistence in a cylindrical pore", *Mol. Phys.*, **61,** 1381–90 (1987).
[33] H.J. Straugh and P.T. Cummings, "Gibbs ensemble simulation of vapor-liquid equilibrium in water/NaCl and water/methanol mixtures", paper number 171b, American Institute of Chemical Engineers National Meeting, Los Angeles, CA, Nov 17–22, (1991).

[34] A.Z. Panagiotopoulos, "Exact calculations of fluid-phase equilibria by Monte Carlo simulation in a new statistical ensemble", *Int. J. Thermophys.*, **10,** 447–457 (1989).
[35] D.A. Kofke and E.D. Glandt, "Monte Carlo simulation of multicomponent equilibria in a semigrand canonical ensemble", *Mol. Phys.*, **64,** 1106–1131 (1988).
[36] J.J. de Pablo and J.M. Prausnitz, "Phase equilibria for fluid mixtures from Monte Carlo simulation", *Fluid Phase Equil.*, **53,** 177–189 (1989).
[37] M.R. Stapleton and A.Z. Panagiotopoulos, "Application of excluded volume map sampling to phase equilibrium calculations in the Gibbs ensemble", *J. Chem. Phys.*, **92,** 1285–93 (1990).
[38] G.L. Deitrick, L.E. Scriven and H.T. Davis, "Efficient molecular simulation of chemical potentials", *J. Chem. Phys.*, **90,** 2370–2385 (1989).
[39] R.F. Cracknell, D. Nicholson, N.G. Parsonage and H. Evans, "Rotational insertion bias: a novel method for simulating dense phases of structured particles, with particular application to water", *Mol. Phys.*, **71,** 931–943 (1990).
[40] D.M. Tsangaris and P.D. McMahon, "A modified Gibbs ensemble method for calculating phase equilibria", *Mol. Simulation*, **7,** 97–103 (1991).
[41] D.A. Kofke and M. Mehta, "Gibbs ensemble simulation with an equation of state", paper number 169b, Americal Institute of Chemical Engineers meeting, Los Angeles CA, November 17–22, (1991).
[42] J.P. Hansen and L. Verlet, "Phase transitions of the Lennard-Jones system", *Phys. Rev.*, **184,** 151–161 (1969).
[43] R.R. Singh, K.S. Pitzer, J.J. de Pablo and J.M. Prausnitz, "Monte Carlo simulation of phase equilibria for the two-dimensional Lennard-Jones fluid in the Gibbs ensemble", *J. Chem. Phys.*, **92,** 5463–5466 (1990).
[44] B. Smit and D. Frenkel, "Vapor-liquid equilibria of the two-dimensional Lennard-Jones fluid(s)", *J. Chem. Phys.*, **94,** 5663–5668 (1991).
[45] D. Nicolaides, M.P. Allen and D.J. Tidesley, unpublished data (1991).
[46] L. Vega, E. de Miguel, L.F. Rull, G. Jackson and I.A. McLure, "Phase equilibria and critical behavior of square-well fluids of variable width by Gibbs ensemble Monte Carlo simulation", *J. Chem. Phys.*, in press (1991).
[47] K. Pitzer, "Some interesting properties of vapor-liquid or liquid-liquid coexistence curves for ionic and non-ionic fluids", *Thermochimical Acta*, **139,** 25–32 (1989).
[48] A. Yethiraj and C.K. Hall, "Square-well diatomics: bulk equation of state, density profiles near walls, virial coefficients and coexistence properties", *Mol. Phys.*, **72,** 619–641 (1991).
[49] B. Smit, C.P. Williams, E.M. Hendriks and S.W. de Leeuw, "Vapour-liquid equilibria for Stockmayer fluids", *Mol. Phys.*, **68,** 765–769 (1989).
[50] M.R. Stapleton, D.J. Tildesley, N. Quirke and A.Z. Panagiotopoulos, "Phase equilibria of quadrupolar fluids by simulation in the Gibbs ensemble", *Mol. Simulation*, **2,** 147–162 (1989).
[51] B. Smit and C.P. Williams, "Vapour-liquid equilibria for quadrupolar Lennard-Jones fluids", *J. Phys.: Condens. Matter*, **2,** 4281–4288 (1990).
[52] A.Z. Panagiotopoulos, "Molecular simulation of fluid-phase equilibria: Simple, polymeric and ionic fluids", *Fluid Phase Equil.*, submitted for publication (1991).
[53] G. Stell, K.C. Wu and B. Larsen, "Critical point in a fluid of charged hard spheres", *Phys. Rev. Lett.*, **37,** 1369–1372 (1976).
[54] E.N. Rudisill and P.T. Cummins, "Gibbs ensemble simulation of phase equilibrium in the hard core two-Yukawa fluid for the Lennard-Jones fluid", *Mol. Phys.*, **68,** 629–635 (1989).
[55] B. Smit and D. Frenkel, "Vapor-liquid equilibria of the hard core Yukawa fluid", *Mol. Phys.*, **74,** 35–39 (1991).
[56] E. de Miquel, L.F. Rull, M.K. Chalam and K.E. Gubbins, "Location of the isotropic-nematic transition in the Gay–Berne model", *Mol. Phys.*, **72,** 593–605 (1991).
[57] E. de Miguel, L.F. Rull, M.K. Chalam and K.E. Gubbins, "Liquid–vapour coexistence of the Gay–Berne fluid by Gibbs-ensemble simulation", *Mol. Phys.*, **71,** 1223–1231 (1990).
[58] E. De Miguel, L.F. Rull and K.E. Gubbins, "Effect of molecular elongation on liquid–vapor properties: computer simulation and virial approximation", *Physica A*, **177,** 174–181 (1991).
[59] W.L. Jorgensen, J. Chandrachekhar, J.D. Madura, R.W. Impey and M.L. Klein, "Comparison of simple potential functions for simulating liquid water", *J. Chem. Phys.*, **79,** 926–935 (1983).
[60] W.L. Jorgensen, "Revised TIPS for simulations of liquid water and aqueous solutions", *J. Chem. Phys.*, 77, 4156–4163 (1982).
[61] J.J. de Pablo, J.M. Prausnitz, H.J. Strauch and P.T. Cummings, "Molecular simultion of water along the liquid–vapor coexistence curve from 25°C to the critical point", *J. Chem. Phys.*, **93,** 7355-7359 (1990).

[62] H.J.C. Berendsen, J.M.P. Postma, W.F. von Gustersen and J. Hermans, "Interaction models for water in relation to protein hydration", in *Intermolecular Forces*, (edited by B. Pullman), *Jerusalem Symp. Quantum Chem. Biochem*, **14,** 331–342 (1981).
[63] H.J. Strauch and P.T. Cummings, "Computer Simulation of the Dielectric Properties of Water", *Mol. Simulation*, **2,** 89–104 (1989).
[64] A.Z. Panagiotopoulos, "Gibbs-ensemble Monte Carlo simulations of phase equilibria in supercritical fluid systems", *ACS Symposium Ser.*, "Supercritical Fluid Science and Technology", edited by (K.P. Johnston and J. Penninger) **406,** 39–51 (1989).
[65] M.E. van Leeuwen, C.J. Peters, J. de Swaan Arons and A.Z. Panagiotopoulos, "Investigation of the transition to liquid–liquid immiscibility for Lennard–Jones (12, 6) systems using Gibbs-ensemble molecular simulations", *Fluid Phase Equilibria*, **66,** 41–55 (1991).
[66] M.E. van Leeuwen, C.J. Peters, J. de Swaan Arons and A.Z. Panagiotopoulos, "Evaluation of a statistical-mechanical virial equation of state using Gibbs-ensemble molecular simulation", *Fluid Phase Equilibria*, **66,** 57–75 (1991).
[67] V.I. Harismiadis, K.K. Koutras, D.P. Tassios and A.Z. Panagiotopoulos, "How good is conformal solutions theory for phase equilibrium predictions?", *Fluid Phase Equil.*, **65,** 1–18 (1991).
[68] J.G. Amar, "Application of the Gibbs ensemble to the study of fluid–fluid phase equilibrium in a binary mixture of symmetric non-additive hard spheres", *Mol. Phys.*, **67,** 739–745 (1989).
[69] R.D. Mountain and A.H. Harvey, "Computer simulation of fluid–fluid phase coexistence in mixtures of nonadditive soft disks", *J. Chem. Phys.*, **94,** 2238–2243 (1991).
[70] A. de Kuijper, B. Smit, J.A. Schouten and J.P.J. Michels, "Fluid–fluid phase separation in a repulsive α-exp-6 mixture: a comparison with the full α-exp-6 mixture by means of computer simulations", *Europhysics Lett.*, **13,** 679–682 (1990).
[71] J.A. Schouten, A. de Kuijper and J.P.J. Michels, "The critical line of He–H_2 up to 2500 Kelvin and the influence of attraction on fluid–fluid separation", *Phys. Rev. B: Condens. Matter*, **44,** 6630–6634 (1991).
[72] M.R. Stapleton, D.J. Tidesley and N. Quirke, "Phase equilibria in polydisperse fluids" *J. Chem. Phys.*, **92,** 4456–4467 (1990).
[73] W.L. Jorgensen, J.D. Madura and C.J. Swenson, "Optimized Intermolecular Potential Functions for Liquid Hydrocarbons", *J. Am. Chem. Soc.*, **106,** 6638–6646 (1984).
[74] J.J. de Pablo, M. Bonnin and J.M. Prausnitz, "Vapor–liquid equilibria for polyatomic fluids form site–site computer simulations: pure hydrocarbons and binary mixtures containing methane", *Fluid Phase Equil.*, in press (1992).
[75] R. Eppenga and D. Frenkel, "Monte Carlo study of the isotropic and nematic phases of infinitely thin hard platelets", *Mol. Phys.*, **52,** 1303–1334 (1984).
[76] E.J. Meijer and D. Frenkel, "Melting line of Yukawa system by computer simulation", *J. Chem. Phys.*, **94,** 2269–2271 (1991).
[77] J.I. Siepmann, "A method for the direct calculation of chemical potentials for dense chain systems", *Mol. Phys.*, **70,** 1145–1158 (1990).
[78] D. Frenkel, G.C.A.M. Mooij and B. Smit, "Novel scheme to study structural and thermal properties of continuously deformable molecules", preprint (1991).
[79] J.J. Pablo, M. Laso and U.W. Suter, "Estimation of the chemical potential of chain molecules by simulation", preprint (1991).
[80] M.N. Rosenbluth and A.W. Rosenbluth, "Monte Carlo calculations of the average extension of molecular chains", *J. Chem. Phys.*, **23,** 356–359 (1955).
[81] S.K. Kumar, I. Szleifer and A.Z. Panagiotopoulos, "Determination of chemical potentials in polymeric systems from Monte Carlo simulations", *Phys. Rev. Lett.*, **66,** 2935–2938 (1991).