Current Advances in Monte Carlo Methods

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In this review paper, we outline the principles of Monte Carlo simulation of fluid mixtures, with emphasis on methods for calculation of free energies and phase equilibria. We begin with a brief introduction to common intermolecular potential models. We discuss density-dependent potentials that can accurately represent properties over a wide range of densities. A number of Monte Carlo techniques are outlined in the main section of the paper. After an introduction to importance sampling, we discuss interfacial simulations, Widom test particle insertions and Grand Canonical Monte Carlo as well as the Gibbs ensemble method. Recent developments, including configurational-bias sampling, Gibbs-Duhem integration, thermodynamic-scaling Monte Carlo and finite-size scaling methods are the primary focus of the article. We close with a summary and a discussion of future prospects.

1. INTRODUCTION

This paper provides a brief introduction to Monte Carlo simulation methods applied to calculations of phase equilibria in fluids and mixtures. The need for accurate description of phase equilibria for multicomponent fluid mixtures encountered in chemical processes has been the main driving force for the development of chemical engineering thermodynamics over the past fifty years. As a result, high-quality experimental data and good modeling techniques are now available for many classes of mixtures. Nevertheless, mixtures such as aqueous or highly polar systems at elevated pressures, systems containing polymeric molecules, ionic solutions, associating fluids and solutions with amphiphilic molecules present significant difficulties. Even for systems for which current modeling techniques are adequate, the models are mostly phenomenological, relying on regression of experimental data for determination of their parameters. The models cannot be extrapolated with confidence to conditions outside the range of experimental measurements.

An attractive alternative to conventional engineering modeling techniques is large-scale molecular simulations starting from an assumed intermolecular potential model between the components of interest. Engineering models rely on assumptions about the intermolecular forces as well as theoretical approximations (such as mixing rules for equations of state) to render the statistical mechanics tractable. Because fewer approximations are made, molecular simulation methods can provide results applicable over wider ranges of process conditions and transferable from one set of conditions to another (e.g. predicting high pressure fluid-fluid equilibria from parameters determined from low-pressure vapor-liquid measurements). The possibility for calculating phase equilibria by simulation has existed from the early days of computer simulation, but has been until recently impractical for multicomponent systems due to the large number of simulations required and the significant uncertainties associated with the calculations. A number of recent developments have

greatly expanded the range of systems that can actually be studied by simulation and will be discussed in this paper.

There are two main classes of molecular simulation techniques, namely molecular dynamics and Monte Carlo methods. Molecular dynamics methods are based on solving the time-evolution equations for a system and can be used for the determination of transport properties and time correlation functions. Monte Carlo methods sample phase space directly and are primarily useful for equilibrium properties. The focus of the present paper is on Monte Carlo techniques. An excellent introductory textbook to molecular simulation methods for liquids is by Allen and Tildesley [1], but it unfortunately does not cover recent advances in the field. Recent review articles include proceedings of a workshop devoted to computer simulation [2,3]. Applications of molecular simulation to systems relevant for supercritical fluid extraction are reviewed in [4] - the present contribution is in many ways an updated (and significantly shorter) version of that article.

2. INTERMOLECULAR POTENTIAL MODELS

A recent review of intermolecular potentials for condensed phase simulations is available [5]. For most simulations of systems of interest to chemical engineers classical intermolecular potentials are employed. Many common intermolecular potential models contain terms of the Lennard-Jones type,

$$U_{ij}(r) = 4\varepsilon_{ij}\left[\left(\sigma_{ij}/r\right)^{12} - \left(\sigma_{ij}/r\right)^{6}\right] \tag{1}$$

where U_{ij} is the configurational energy of interaction between centers i and j located at a distance r, and ε_{ij} and σ_{ij} are characteristic energy and size parameters for the ij interactions. This potential, although not a good representation of the actual intermolecular forces for any particular substance [6], enjoys continued popularity for reasons of computational simplicity and because of availability of a large number of results for its properties.

In real fluids, three-body forces contribute significantly to the configurational energy of condensed phases [6] and have a significant impact on the phase behavior [7]. However, simulations using fully explicit three-body potentials are quite expensive computationally. It is common practice to utilize simplified, pair-wise additive potentials. Such potential models are fundamentally incapable of reproducing accurately both low-density (e.g. second virial coefficients) and dense-phase properties. A potentially promising path for overcoming this limitation while retaining the computational convenience of pair-wise additivity is the use of density-dependent potentials [8,9]. A simple mean-field treatment [10] of the Axilrod-Teller triple-dipole interactions suggests that a linear dependence of the potential well depth parameter is physically meaningful.

More realistic potentials are commonly constructed by using multiple interaction centers, often of the Lennard-Jones type, to describe molecules that deviate significantly from spherical shape. For polar molecules, dipole, quadrupole and charge interaction terms can also be added. Potentials for multisegment molecules such as hydrocarbons often contain terms to describe internal molecular flexibility. Such terms could include bond bending or, less commonly, bond stretching energies, and torsional potentials that are periodic functions of the dihedral angle defined by four consecutive carbon atoms.

Long chain molecules are often described by lattice models, since simulations of the time and length scale required for describing collective phenomena in such systems taxes the capabilities of even the most powerful computers. Such models range from simple cubic lattice homopolymer models to complex bond-fluctuation models [11] that are significantly closer in level of detail to the more realistic continuous-space models.

No matter which intermolecular potential model is used, simulations must be performed on a *finite* system, although in most cases the properties we are interested in are those of a *macroscopic* collection of interacting molecules. To minimize surface or wall inhomogeneity effects on the computed properties of a system with only a few hundred particles, simulations are performed under periodic boundary conditions. The particles being followed are placed in a space-filling central cell, for example a cube in three dimensions. The simulated system consists of an infinite number of replicas of the central cell. Despite the artificial periodicity imposed by this scheme, properties calculated for systems away from critical points are then not greatly affected by system size, and can be considered representative of the properties of a bulk fluid.

For most potential models, it is relatively straight-forward to correct the results for the effects of intermolecular potential cutoff on the calculated thermodynamic properties. Corrections are normally performed assuming a uniform distribution of particles for distances greater that the ones contained within the central simulation cell. A special difficulty arises in this respect for potentials that contain polar and ionic terms, which decay with the third and first power of distance, respectively. For these systems, the most common method for long-range corrections is the Ewald summation method, in which all the potential contributions from the complete infinite periodic array of cells are summed with the aid of Fourier transformations. A tutorial introduction to Ewald sums for applications to molecular simulations of polar and ionic systems is given in [1].

3. MONTE CARLO SIMULATION TECHNIQUES

3.1. Importance Sampling Monte Carlo

The main molecular simulation method used for the calculation of free energies and phase equilibria is the Monte Carlo method, even though some of the techniques described later in this section have counterparts using molecular dynamics. In general, Monte Carlo methods in statistical mechanics are used to sample configuration space of a system with a specified Hamiltonian. In the canonical ensemble (constant temperature, volume and number of particles), states occur with probability density, ρ_m^{NVT},

$$\rho_m^{NVT} = \frac{\exp(-\beta U_m)}{\sum_{\text{all states}} \exp(-\beta U_m)} \tag{2}$$

where U_m is the configurational energy of a state and $\beta = 1/k_B T$, where k_B is Boltzmann's constant and T is the absolute temperature.

In order to sample configuration space with the correct probability density, the following scheme is used. An initial state is constructed, in principle arbitrarily, but preferably close to the set of states of interest. The state is then perturbed, commonly by moving a particle to a new position or

orientation, thus generating a new trial state. The *a priori* probability, α_{mn}, of generating trial state *n* from state *m* must satisfy the important condition of microscopic reversibility,

$$\alpha_{mn} = \alpha_{nm}, \tag{3}$$

in order to sample the correct limiting distribution (equation 2). In addition, the set of moves selected must be *ergodic*, covering the whole of configuration space for the systems of interest. Acceptance of the new state is then performed probabilistically (hence the name Monte Carlo), most commonly according to the Metropolis criterion [12],

$$\begin{aligned} \wp_{mn} &= \alpha_{mn} && \rho_n \geq \rho_m \quad m \neq n \\ \wp_{mn} &= \alpha_{mn}\, \rho_n / \rho_m && \rho_n < \rho_m \quad m \neq n \\ \wp_{mm} &= 1 - \sum_{m \neq n} \wp_{mn} \end{aligned} \tag{4}$$

where $\wp_{mn}$ is the acceptance probability of trial state *n* from state *m* [1].

A Monte Carlo simulation consists of a large number of "steps" performed according to the acceptance criterion of equation 4. How large a number is required depends on the complexity of the intermolecular potential studied and the desired accuracy of the results. For determining thermodynamic properties of a fluid interacting with a Lennard-Jones potential, simulations of approximately 10^4-10^5 Monte Carlo steps per particle are normally sufficient. Much longer simulation runs are required for systems with strong or long-range interactions, such as ionic, associating or long chain systems, or systems close to a critical point.

3.2. Simulations With an Explicit Interface

Conceptually, the easiest method for calculating phase equilibria by simulation is to set up a system at conditions for which more than one phase would be present in the thermodynamic limit. Applications of direct interfacial simulations, which can be performed by Monte Carlo or molecular dynamics, have been reviewed by Rowlinson and Widom [13] and more recently by Gubbins [14]. Despite the simplicity of the approach, there are difficulties associated with setting up and equilibrating a system with two coexisting phases. Simulations involving many particles and very long equilibration times are often required [15]. Even with large systems, a significant fraction of particles are close to the interface. When the density difference between the two coexisting phases is small, it is often impossible to set up a stable two-phase system. For fluids with low vapor pressures, for any reasonable system size, few particles can be found in the gas phase. Despite these limitations, two-phase simulations are often used when no other practical alternative can be found [16].

3.3. Widom Test Particle Insertions and Grand Canonical Monte Carlo

In classical thermodynamics, the chemical potential of a component is a quantity for which no simple mechanical interpretation can be given. The chemical potential is a "statistical" property and as such is harder to obtain from simulations than "mechanical" quantities such as the configurational energy or pressure. An elegant theorem proposed by Widom [17] provides a simple way of calculating chemical potentials in Monte Carlo or molecular dynamics simulations.

$$\beta\mu = -\ln\left\langle \exp\left(-\beta U_{test}\right)\right\rangle + \ln\rho \tag{5}$$

where μ is the chemical potential of a component in a system (to within a temperature-dependent constant that does not affect phase equilibrium calculations), U_{test} is the energy experienced by a "test" particle of that component placed in a random position in the simulation cell and ρ is now the molar density. Most attempted insertions of test particles result in overlap with existing particles in the fluid, with U_{test} large and positive. These insertions do not contribute significantly to the ensemble average in equation 5. For simple single-site intermolecular potentials, such as the Lennard-Jones potential, sampling using the Widom test particle method can be performed throughout the fluid state. Sampling fails for ordered solid phases.

The chemical potential of a system can also be obtained from Grand Canonical Monte Carlo (GCMC) simulations, which have a comparable range of applicability as Widom test particle insertions. In GCMC, a simulated system is considered at conditions of constant temperature T ($\beta = 1/k_B T$), volume V, and chemical potential μ. In addition to particle displacements, attempted creations and destructions of particles are performed and accepted with the following probabilities.

$$\wp(N \rightarrow N+1) = \min\left[1, \frac{V}{N+1}\exp\left(-\beta\Delta U + \beta\mu\right)\right]$$
$$\wp(N \rightarrow N-1) = \min\left[1, \frac{N}{V}\exp\left(-\beta\Delta U - \beta\mu\right)\right] \qquad (6)$$

where N is the instantaneous number of particles in the system. In GCMC simulations, therefore, the density of the system that corresponds to a given value of the chemical potential is obtained as an ensemble average over the simulation.

Determination of phase coexistence from Widom test particle insertions or GCMC is performed as follows. From a series of canonical simulations with Widom test particle insertions, or a series of GCMC simulations, one can obtain the dependence of the chemical potential on pressure for the gas and liquid. The coexistence condition is found at the point of intersection of the two branches. Away from the critical point, a small change in chemical potential for the liquid results in a large change in pressure, because the liquid is incompressible. For this case, the number of simulations required is quite small. These ideas have been applied in [18] and.[19] to obtain the coexistence properties of the pure Lennard-Jones fluid to high accuracy. Uncertainties of a fraction of a percent for the liquid density and approximately 1% for the gas density and vapor pressure were achieved. This method has been used recently to obtain optimized intermolecular potentials for carbon dioxide [20].

For binary and multicomponent systems, or for one-component systems close to a critical point, the method described suffers from the serious disadvantage that the number of simulations required to locate the point of phase coexistence rapidly increases. For these systems, the method of choice is the Gibbs ensemble Monte Carlo technique described in the following section.

3.4. The Gibbs Ensemble Method

The Gibbs ensemble method [21,22,23,24] is based on performing a simulation in a system with two regions, each representative of a small volume of a homogeneous phase. There are no explicit interfaces present in the system. Conditions of phase equilibrium between the two regions are satisfied by internal displacements of particles, changes of the volumes of the two regions to achieve equality of

pressures, and particle transfers between regions to ensure chemical potential equality. Volume change steps can be performed at constant total volume or constant pressure, corresponding respectively to the physical processes of an isothermal flash into a constant-volume container or to a specified pressure. Since its inception, the method has been used to obtain phase diagrams of pure fluids and mixtures. Recent reviews of the method and its applications are available [25,4,26]. The method in its original form is applicable without major difficulties for components that can be described with a small number of interaction centers, depending also on the strength of the interactions and the density. For components with more segments, or at high densities, the particle transfer step has a low probability of success and the statistical uncertainty of the results rapidly increases.

As for all simulation methods, a limitation of the Gibbs ensemble technique is the inability to capture the growth of fluctuations on approach to a critical point, because of the use of finite systems. Finite-size effects can result in shifts in the apparent critical point and the coexistence curve in its vicinity. The nature and expected magnitude of finite-size effects in the Gibbs ensemble has been the subject of several recent studies [27,28,29,30]. Finite-size effects are particularly important for two-dimensional systems and for systems studied under fixed total volume conditions, while for three dimensional potentials such effects are usually small. With careful control of linear system size for the two regions, estimates of critical parameters with accuracy better than 1% in the critical temperature are possible [30].

Examples of applications of the method that have appeared in the past year include calculations of phase diagrams for diatomic Lennard-Jones molecules [31], dipolar and quadrupolar fluids [32,33], a realistic potential model for methanol [34] and methyl iodide [35]. Extensions of the technique to reactive and associating systems [36] as well as ionic systems [37] are available.

3.5. Dealing with sampling difficulties: Configurational-Bias Monte Carlo

For multisegment molecules (for example a unified-atom model of an *n*-alkane), particle insertion or transfer moves for the Grand Canonical and Gibbs ensembles become impractical because of steric overlaps. A major improvement in sampling efficiency for such systems results from introduction of configurational-bias methods as suggested by [38,39] and, independently, [40]. Configurational-bias sampling draws upon ideas originated by Rosenbluth and Rosenbluth [41] and relies on the "smart" insertion of one segment at a time of the molecule being transferred. A number of trial directions is selected at each growth step, and the choice of the direction along which to proceed is made based on the Boltzmann factor of the energies of interaction experienced by the growing segments. For computational efficiency [42] it is advisable to use an increasing number of trial directions as one proceeds along a chain, so that the computational effort that has been "invested" in early stages of a given attempted insertion not be wasted because only a limited number of growth directions is tested at later stages. The bias introduced by the preferential sampling along favorable directions is removed through incorporation of appropriate factors (termed “Rosenbluth weights”) in the acceptance criteria. Combination of configurational-bias sampling and the Gibbs ensemble has been used to predict the phase behavior of *n*-alkanes [43]. Modeling of adsorption of long-chain alkanes in zeolites has also been achieved by use of this powerful method [44,45].

3.6. Gibbs-Duhem Integration

While the Gibbs ensemble technique can be used to obtain the densities and compositions of two coexisting phases at one temperature from a single simulation, it relies on insertions of particles to equalize the chemical potentials, and therefore experiences difficulties for dense phases and long molecules. If a single point on the coexistence curve is known (e.g. from long Gibbs ensemble simulations), the remarkably simple and novel method of Kofke [46,47] enables the calculation of the complete phase diagram from a series of constant-pressure simulations that do not involve any transfers of particles. For one-component systems, the method is based on integrating the Clapeyron equation over temperature. Extensions of the method to multicomponent systems are presented in [48,49]. The method is applicable to calculations of phase diagrams involving solid phases [50,51], a task for which most of the other techniques described in this paper are not suitable.

3.7. Thermodynamic Scaling Monte Carlo

Umbrella-sampling methods were suggested relatively long ago [52,53] as a way to obtain free energies from simulations in which a broader range of states is sampled relative to conventional (Metropolis) importance sampling. The probability of states in the canonical ensemble is $\mathcal{P}_\nu \propto \exp(-\beta U_\nu)$ where $\mathcal{P}_\nu$ is the probability of microstate ν and U_ν is the (configurational) energy. In thermodynamic scaling Monte Carlo, states are sampled with a general probability function, $W(\boldsymbol{r}^N)$, which depends on temperature and density and is selected so as to ensure a uniform sampling over the range of states of interest. The canonical ensemble average of a general thermodynamic function, $X(\boldsymbol{r}^N)$ for a sample obtained with probability proportional to $W(\boldsymbol{r}^N)$ is then given by [54]

$$< X(\mathbf{r}^N) >_{NVT} = \frac{< X(\mathbf{r}^N) \exp(-\beta_i U(\mathbf{r}^N) / W(\mathbf{r}^N) >_W}{< \exp(-\beta_i U(\mathbf{r}^N) / W(\mathbf{r}^N) >_W} \tag{1}$$

where we have allowed each state to be at a different temperature for generality. The standard arithmetic-mean rule for averaging properties in canonical simulations performed with the Metropolis algorithm is recovered by setting $W(\boldsymbol{r}^N) = \exp(-\beta_i U_\nu)$. One of the major advantages of this sampling technique is that free energy differences between two states can be easily obtained [54] as

$$\beta_j A^{ex}(\rho_j, T_j) - \beta_i A^{ex}(\rho_i, T_i) = \ln \frac{< \exp(-\beta_i U(\mathbf{r}^N) / W(\mathbf{r}^N) >_W}{< \exp(-\beta_j U(\mathbf{r}^N) / W(\mathbf{r}^N) >_W} \tag{2}$$

where $A^{ex}(\rho_i, T_i)$ is the Helmholtz energy of state *i*. Because of severe limitations in computer resources for the early simulations, these were performed with small system sizes and few configurations. As a result, the statistical accuracy for the thermodynamic properties was quite limited and the techniques were not pursued with great vigor. An additional difficulty preventing wide-spread use of umbrella-sampling methods was the need for trial-and-error selection of the weighting functions. Recently, however, Valleau has proposed a number of important extensions and refinements of the techniques [55,56] and has demonstrated that they can be used to obtain data of high precision for systems that are difficult to sample by conventional methods, such as ionic systems [57]. One

important refinement is the development of ways to obtain the sampling functions $W(\mathbf{r}^N)$ without extensive trial and error calculations.

Thermodynamic scaling Monte Carlo allows sampling of a range of temperatures and densities in a single run, and is particularly suitable for the study of one-component systems in the vicinity of critical points. In our group, we have recently started to use thermodynamic scaling Monte Carlo to study ionic systems, and we find that it allows much higher accuracy for one-component systems than Gibbs ensemble simulations of comparable duration. Methodological developments are needed to extend thermodynamic scaling techniques to chain and multisegment molecules.

3.8. Finite-size Scaling Methods

Finite-size scaling methods were originally developed in the context of studies of critical phenomena of lattice spin models (such as the Ising model), and provide a way to obtain accurate estimates of critical parameters [58]. The methods are based on performing GCMC simulations over a range of system dimensions. Recently, the techniques have been extended to fluid models [59]. A combination of finite-size scaling technique with extended sampling methods have been recently used [60] to obtain the critical point of the three-dimensional Lennard-Jones potential cutoff at 2.5σ to an accuracy of 0.03 % in temperature and 0.1 % in density. Although the methods still require a fair amount of computer time, it is clear that they are likely to be the main source of high-quality data for critical properties, and they can even be applied to temperatures significantly below the critical point.

4. SUMMARY AND FUTURE OUTLOOK

There has been rapid progress in the field of molecular simulation of phase equilibria over the past decade. Before the mid-1980's, even the calculation of a phase diagram for a potential as simple as the Lennard-Jones potential was considered to be a major research project. The Gibbs ensemble technique for simple fluids greatly facilitated the calculation of phase diagrams for pure components and mixtures. The Gibbs-Duhem integration method allows rapid calculations of complete phase diagrams even for systems that include solid phases. Configurational-bias methods have greatly contributed towards a solution of the sampling problems encountered for complicated potentials and chain molecules. Applications of finite-size scaling methods are starting to appear for continuous-space systems that promise to allow accurate determinations of critical points.

Availability of increasingly accurate methodologies that can handle complicated potentials ensure that molecular simulation will play an increasing role in modeling phase equilibria. It is worth considering what changes this is likely to bring. Direct simulations can be used to refine theoretical approximations or to 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. Simulation will never replace experiment in providing primary data for process development and design. However, it can certainly play an important role in extending the range and "filling in the gaps" of experimental measurements. The recent calculation of Siepmann *et al.*[43] for the critical properties of long-chain alkanes is a case in point. With potentials fitted to experimental data for the lower alkanes, molecular simulation can be used to predict the

critical properties of higher alkanes that are experimentally inaccessible due to thermal decomposition. Another example is the calculation of the critical point for molten salts [37].

The main limitation of molecular simulation is, at present, the lack of intermolecular potentials that can adequately describe complex components. *A priori* quantum mechanical techniques are not yet in a position to give potentials accurate enough for calculations in dense phases. The most promising approach for the next few years will be using empirical potentials with parameters fitted to experimental phase equilibrium and thermodynamic data. A coordinated research effort to obtain a database of potential parameters will greatly enhance the practical usefulness of molecular simulation methods.

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