

Molecular simulation of fluid phase equilibria

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Abstract - Recent advances in direct and indirect methods of molecular simulation for studying fluid phase equilibria are reviewed. The emphasis is on phase equilibria for fluids of nonspherical molecules, including ionic fluids, aqueous mixtures, hydrocarbons and chain molecules.

INTRODUCTION

The use of Molecular Dynamics (MD) or Monte Carlo (MC) simulation methods to calculate the so-called "statistical" properties - free energy, chemical potential or entropy - is less straightforward than for the "mechanical" properties, such as internal energy or pressure. In essence, the difficulty is that conventional methods sample phase space where the Boltzmann factor $\exp(-U/kT)$ is large (here U is configurational energy), whereas for the statistical properties other regions of phase space make major contributions (ref. 1). Several ways around this problem exist, including special sampling techniques and integration over a range of thermodynamic states. For reviews see refs. 2,3,4,5, and references therein. More recently, methods for simulating fluid phase equilibria directly have been developed, and are fast and convenient where they can be applied.

Simulations of this sort find several applications: (a) for testing statistical mechanical theories, where identical models for the molecules (and any surfaces present) are used in both simulation and theory, so that the comparison tests only the statistical mechanical approximations in the theory; (b) comparisons with experiment, which give information about the suitability of the assumed intermolecular potential; (c) prediction of phase equilibria in cases where experimental measurements are difficult or impossible, e.g. because of extreme temperatures or pressures. The cost and reliability of such simulations are very strongly dependent on the complexity of the molecules involved, in contrast to laboratory experiments. For a simple fluid for which the spherical Lennard-Jones (LJ) potential is adequate, for example, it has recently been estimated (ref. 5) that a typical MC run (500 molecules, 5 million configurations) for a single state point costs about \$4.5 (CPU time only) and takes 5 hours on a Decstation 5000. However, the costs rise rapidly with molecular complexity, as roughly n^3 for small nonpolar molecules, where n is the number of potential sites in the molecule. Costs on a current supercomputer, such as the Cray YMP, would be substantially (about 20 times) higher, while costs for massively parallel machines currently lie between those for the workstations and supercomputers.

The principal limitation of these simulation methods at present is the reliability of the intermolecular potentials used. Computers are still too slow for reliable ab initio potentials to be used for any but the simplest molecules, and as a result most workers use semiempirical potentials, developed by using a combination of knowledge from theory (quantum mechanics, electrostatics) and experimental data. An example of such semiempirical potentials is the OPLS (optimized potentials for liquid simulations) model developed by Jorgensen and coworkers (e.g. ref. 6), in which the potential sites are taken to be the nuclei or CH_n groups and the interactions between these sites are described by isotropic potentials that include LJ and Coulomb terms. More sophisticated

site-site models (ref. 7), involving anisotropic site-site potentials and distributed multipoles, provide a more accurate description of the potential, at some additional cost in computing requirements.

In the remainder of this paper a brief survey is given of some developments in this area over the last five years. Both direct and indirect (via calculation of the chemical potential) methods for calculating phase equilibria are considered, with an emphasis on applications to fluids of complex or nonspherical molecules, such as ionic fluids, aqueous solutions, and chain molecules.

DIRECT METHOD: GIBBS ENSEMBLE MONTE CARLO

The Gibbs ensemble Monte Carlo (GEMC) method, first proposed by Panagiotopoulos in 1987 (ref. 8), involves setting up two coexisting phases that are in equilibrium with each other, but not in physical contact. The two phases (I and II) are contained in two simulation boxes of volumes V_I and V_{II} and containing N_I and N_{II} molecules, respectively. The system of two boxes is at a uniform temperature T , and the usual periodic boundaries are used with each box to minimize surface effects. The simulation involves three kinds of trial moves (ref. 8) designed to achieve (a) internal equilibrium in each box through the usual Monte Carlo molecular moves, (b) equality of pressures between the two phases (mechanical equilibrium) through volume changes to the two phases, and (c) equality of chemical potential between phases (chemical equilibrium) through exchange of molecules between the two boxes. The derivation of the Gibbs method is given in detail by Smit et al. (ref. 9), and the implementation of the method, programming considerations and applications have been recently reviewed (refs. 5,10). The most important advantage of the method is speed of computation, since the method is direct, and the molecules do not have to diffuse across a physical interface in order for the system to reach equilibrium. The method is particularly useful for mixture phase equilibria, where the indirect methods become very tedious. Its principal limitation arises from the molecule transfer step. In common with several of the indirect methods (discussed briefly below), the probability of successful insertion of a molecule when placed at random into a dense fluid or solid falls off very rapidly above a certain density (densities equal to or greater than that of a dense liquid), so that the method in its unmodified form fails for very dense systems. This problem becomes more acute when the molecules are highly nonspherical, e.g. H-bonded systems or chain molecules. This difficulty can be largely overcome by various biased sampling methods for liquids, but so far the method has not been successfully applied to solids or liquid crystals.

Some recent applications of the method to pure fluids and mixtures are summarized in Table 1. More complete listings are given elsewhere (refs. 5,10). Many of the recent applications have been to vapor-liquid equilibria in fluids of more complex molecules, such as electrolytes, water and aqueous mixtures, chain molecules, and so on. Two

TABLE 1.
Applications of the Gibbs Ensemble Monte Carlo Method

Pure Fluids	Mixtures
Lennard-Jones (LJ) fluid [8,11]	LJ mixtures: noble gases [12]
Square Well (SW) fluid [13]	supercritical behavior [14]
Ionic fluids ^a [15]	Polydisperse mixtures [16]
Square well tangent diatomics [17]	He/N ₂ mixtures [18]
Polar LJ fluid [19,20,21]	He/H ₂ mixtures [22,23]
Gay-Berne fluid [24,25]	Hydrocarbon mixtures [26,27]
Associating fluid, LJ+SW sites [28]	Associating fluid mixtures [28]
Water: TIP4P model [29,30,31]	Water/methanol mixtures [32]
SPC model [30,33]	Water/NaCl mixtures [32]
Chloroform, methanol (OPLS model) [30]	Water/methanol/NaCl mixtures [32]
Hydrocarbons [26,27]	Surfactant solutions [34]
Chain molecules [35,36]	Protein solutions [34]

^a Restricted primitive model of an ionic fluid, consisting of charged hard spheres of equal diameter and unit charge.

examples of applications to pure fluids are shown in Figs. 1 and 2. The results in Fig. 1 are for the restricted primitive model of a 1:1 electrolyte (charged hard spheres of equal diameter and unit charge). In such simulations special care is needed in the ion transfer step, and in the treatment of the long range forces by the Ewald sum method (ref. 15). The estimated critical point of $T_c^* = kT_c/\epsilon = 0.056$ and $\rho_c^* = \rho_c \sigma^3 = 0.04$ are slightly lower in temperature and gas density than an estimate by Valleau (ref. 37), a difference which seems to be due to the use of different methods for correcting for long range forces in the two calculations. Several earlier estimates of the coexistence curve are also shown in Fig. 1; these include early simulation results (—; ref. 38), a lower limit of the gas density due to Gillan (---; ref. 39), and approximate theories due to Stell et al. (-.-.-; ref. 40) and Friedman and Larsen (.....; ref. 41). The Gibbs ensemble results are believed to be more accurate than any of the earlier results. The critical constants for this ionic system are much smaller than those for non-ionic systems, a result of the very strong Coulomb forces. The Gibbs method has recently been applied to chain molecules (refs. 35,36), and some of these results are shown in Fig. 2. Conventional (random) sampling methods fail for such molecules, and it is necessary to bias the sampling in a way that 'looks' for available space (see section below).

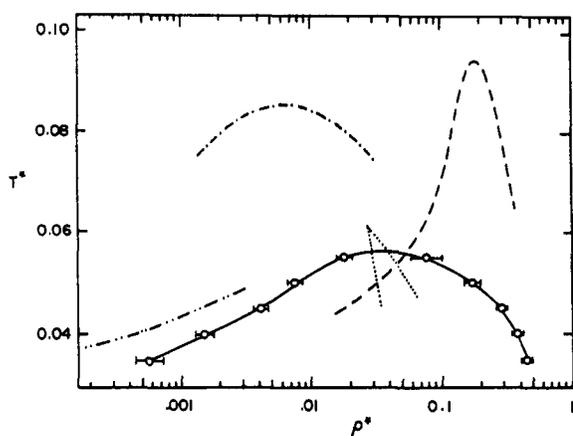


Fig. 1. Vapor-liquid equilibria for the restricted primitive model of an ionic fluid from Gibbs MC (solid line, circles) and earlier predictions (see text). From Panagiotopoulos (ref. 15).

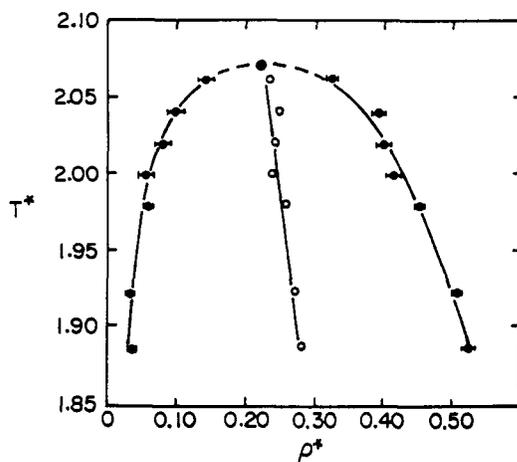


Fig. 2. Vapor-liquid coexistence curve for a fluid of chains of 8 LJ monomers, bond length σ , from Gibbs ensemble MC with configurational bias sampling. From Mooij et al. (ref. 35).

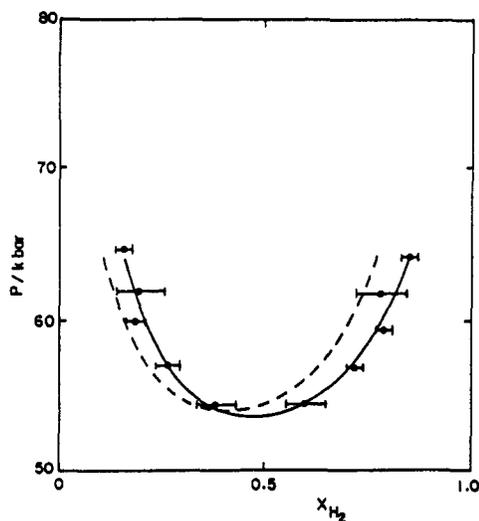


Fig. 3. Gas-gas equilibria for He/H₂ mixtures at 300 K from experiment (dashed line) and Gibbs MC with α -exp-6 potential (points and solid lines). From de Kuijper et al. (ref. 22).

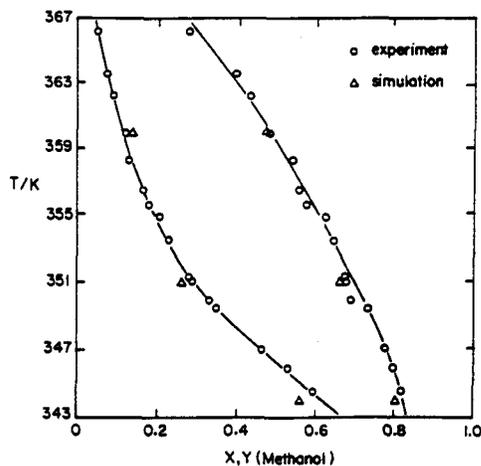


Fig. 4. Vapor-liquid equilibria for water/methanol mixtures at 1 atm from Gibbs MC (triangles) and from experiment (circles and line). From Strauch & Cummings (ref. 32).

For mixtures the Gibbs method can be carried out in the isothermal-isobaric ensemble, so that the pressure can be specified at the start of the run. This is usually an advantage since there is then no uncertainty in the pressure, although there will be fluctuations in the density. The method has been applied to high pressure fluid phase equilibria, and an example is shown in Fig. 3 for hydrogen-helium mixtures (ref. 22). Further calculations for this system have been made to 2500 K and 700 kbar (ref. 23). Agreement is good, and these studies provide an example of the use of these methods to extrapolate existing data into regions that are difficult to reach experimentally. A second application to a more complex mixture, water with methanol, is shown in Fig. 4. Here the SPC model was used for water, and OPLS for methanol with potential parameters taken from the literature and used without adjustment. The compositions of the two phases agree with experimental data within a few percent.

INDIRECT METHODS

Indirect methods involve calculating the free energy or chemical potentials for a range of state conditions, from which the phase transition conditions can be determined. Such methods involve more computational effort than the Gibbs method, in general, but are useful because: (a) one often wants to know the values of the chemical potentials, e.g. in studying surface phase transitions or conformational changes (the Gibbs method does not yield the chemical potential unless special steps are taken in coding), and (b) the Gibbs method (and some of the indirect methods) fail for high densities because of the molecule insertion step. This is particularly the case for liquid crystals and solids.

Indirect methods include the test particle method, Grand Canonical Monte Carlo (GCMC), modified sampling methods, and thermodynamic integration over states. These methods have been reviewed elsewhere (refs. 2-5). The test particle and GCMC methods each involve attempts to insert a molecule into the fluid, and so suffer from the same difficulty as the Gibbs ensemble MC method at high densities. The modified sampling methods attempt to overcome this problem by modifying the MC sampling procedure, so that the probability of successful insertion attempts is greatly increased. These methods try to find the 'holes' in the fluid and put the molecule there.

For the most difficult systems, e.g. liquid crystals and solids, one must use thermodynamic integration. This involves carrying out a series of simulations for a range of thermodynamic temperatures, densities or intermolecular potentials, and using standard thermodynamic or statistical mechanical equations to obtain the chemical potential. An example in which several of these techniques must be used to obtain a

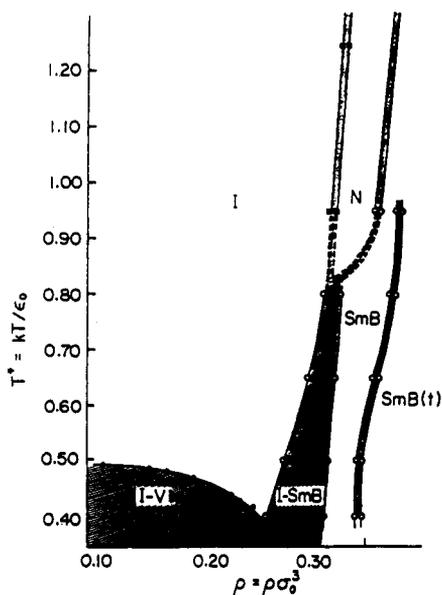


Fig. 5. Phase diagram for the Gay-Berne fluid with $\kappa=3$, $\kappa'=5$: I=isotropic liquid, V=vapor, N=nematic, SmB=smectic B, SmB(t)=smectic B tilt phase. From de Miguel et al. (ref. 42).

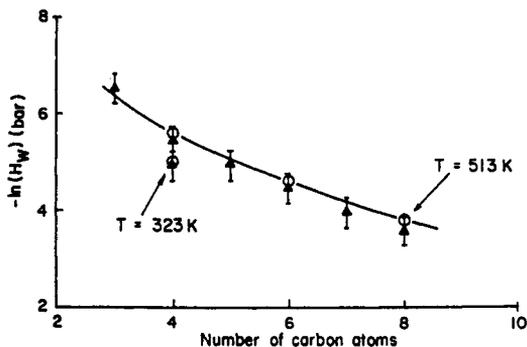


Fig. 6. Weight fraction Henry constants for alkanes dissolved in polyethylene: O, experiment; Δ , configurational bias MC. From de Pablo et al. (ref. 44).

phase diagram is shown in Fig. 5 (ref. 42). The intermolecular potential model used, the Gay-Berne, provides a simplified description of a prolate shaped molecule in which κ is the length:breadth ratio (3 in this case) for the molecule. The model includes anisotropic dispersion and repulsion forces, and at this elongation leads to a number of liquid crystal phases, as well as the usual isotropic liquid and gas phases. In the results shown in Fig. 5 the vapor-liquid region was determined by the Gibbs ensemble MC method, the isotropic liquid-nematic transitions were determined by thermodynamic integration, and the remaining transitions were determined approximately from order parameters (orientational correlation parameter P_2 , tilt angle ϕ and heat capacity C_v).

An advance of particular interest has been the extension of some of these methods to chain molecules. Two approaches have been put forward. The first, which we call the chain increment method, has been proposed by Kumar et al. (ref. 43). It is based on a test particle equation that gives an exact expression for the incremental chemical potential for adding a monomer unit to a chain molecule. It is found that this increment becomes essentially constant for chains longer than about 10-20 mers. By determining this limiting value, and obtaining the chemical potential for a relatively short chain, it is possible to calculate the chemical potential for long chains. The method has been applied recently (ref. 44) to obtain the phase diagram for a polymer melt of chains of length up to 100 mers. The merit of the chain increment method is that it can be applied to arbitrarily long chains. However, it is limited to homopolymers at present.

The second method for chain molecules is called the configurational bias MC method. It involves the insertion of a short chain into the fluid, followed by the addition of other segments to the end of the chain until a chain of the desired length has been grown. The method has been developed by two research groups independently (refs. 45,46,47), and involves choosing the configuration of the chain by a suitable weighting process, using another modified test particle equation. The method has several advantages: the full chemical potential is obtained in a single simulation, and it works for heteropolymers. Moreover, it can be used in Gibbs simulations to obtain phase equilibria directly. An example is shown in Fig. 2. However, this method is limited to rather short chains, up to about 20-30 mers. It has been used to study alkanes in polyethylene and in supercritical solvents (ref. 45). Some of these results are shown in Fig. 6.

CONCLUSION

Fast calculations of fluid phase equilibria have been made possible by the development of the Gibbs ensemble MC method, and this is now being extensively applied to a wide variety of systems for both bulk fluids and surface phase transitions. It is particularly advantageous for mixtures. For simple fluids it can be used to predict phase equilibria, and to extrapolate existing data to conditions that are inaccessible to laboratory experiments (e.g. Figs. 1,3). For more complex phase behavior, such as liquid crystals and polymers, techniques are now becoming available that involve indirect methods (Figs. 5,6). Current research is likely to focus on applying and extending these methods to difficult systems such as ionic fluids, associating and reacting liquids, liquid crystals, polymers and surfactants. A persistent problem in such work remains the determination of sufficiently accurate intermolecular potentials for prediction of phase equilibria in real systems. The use of reliable ab initio potentials is still some way off, because of the unfavorable scaling of CPU time with number of electrons. Advances in parallel architectures and algorithms will help here, but significant progress will require increases in speed of several orders of magnitude.

Acknowledgements It is a pleasure to thank G.C.A.M. Mooij, A.Z. Panagiotopoulos and B. Smit for helpful discussions, and D. Frenkel, M. Mezei, A.Z. Panagiotopoulos and U.W. Suter for sending papers prior to publication. I am grateful to the Gas Research Institute and the National Science Foundation for support of this work.

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