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PHASE EQUILIBRIA FOR FLUID MIXTURES FROM MONTE-CARLO SIMULATION

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ABSTRACT

The Gibbs-ensemble Monte-Carlo simulation method is extended for simulation of systems containing polyatomic molecules. This extension is used to predict phase-equilibria in systems containing pure and mixed lower alkanes. To describe interactions between different groups, we use *OPLS* potential energy functions. We also give results for the simulated vapor-liquid coexistence curve of water, using a *TIP4P* potential function.

I) INTRODUCTION

Over the last three decades, we have witnessed the birth and growth of molecular simulation. Computer experiments, as molecular simulations are often called, have become a standard way of testing theory because they give the theorist the possibility of comparing with exact "experimental" results for specific models (Gubbins, 1989, Kollman, 1987).

Molecular simulation for prediction of thermodynamic properties of fluids has also seen significant advances over the last decade, but has generally been restricted to the study of uniphase systems because conventional methods for the simulation of multiphase systems are cumbersome and time-consuming (Allen and Tildesley, 1987). Recently, however, Panagiotopoulos (1987, 1988) has devised a powerful technique for Monte-Carlo simulation of multiphase systems at equilibrium. The so-called Gibbs-ensemble simulation method provides coexistence properties without resorting to expensive iterative methods. With this new tool at hand, it is conceivable that in a few years, it will be possible to "measure" accurately, via computer simulation, phase-equilibrium properties that are difficult to probe experimentally, i.e. properties of coexisting phases at extreme conditions of pressure and temperature.

So far, only the coexistence properties of pure spherical Lennard-Jones (LJ) fluids, pure dipolar-sphere fluids, and binary mixtures of spherical LJ fluids (Panagiotopoulos et al., 1988) have been determined through simulation in the Gibbs ensemble. In this work, we have applied the Gibbs-ensemble method to the simulation of coexistence curves of small hydrocarbons whose molecules consist of several atomic sites and therefore have an orientation dependence. Since water-hydrocarbon mixtures play an important role in engineering, we have also simulated phase equilibria for pure water and we are currently attempting to simulate the water-methane system. To improve the simulation statistics for these systems, we propose a variant of the Gibbs-ensemble technique.

II) MONTE-CARLO SIMULATION IN THE GIBBS ENSEMBLE

a) GIBBS-ENSEMBLE SIMULATION OF PURE FLUIDS

Monte-Carlo simulations are usually carried out in the canonical (NVT) ensemble, the isobaric-isothermal (NPT) ensemble, or the grand-canonical (μVT) ensemble (Allen and Tildesley, 1988). The Gibbs ensemble is a combination of these three ensembles. Figure 1 illustrates the three kinds of moves that compose the Gibbs-ensemble simulation of a pure fluid. These are random particle displacements (Figure 1a), volume changes (Figure 1b), and particle transfer moves (Figure 1c). For the study of a two-phase system, the simulation "box" is divided into two distinct regions (see Figure 1), each representing one of the equilibrium phases. These two regions are not in contact through a physical interface but their respective evolutions through phase-space are not independent. While in a μVT simulation particles are inserted or deleted at random from a single box, in a Gibbs- ensemble simulation a particle is deleted from one region and simultaneously inserted into the coexisting region. Similarly, for pure fluids in the two-phase region, a volume increment in one of the regions is accompanied by a volume reduction of exactly the same amount in the coexisting region. For mixtures, volume moves in coexisting regions are independent of each other and the pressure of the system can be specified à priori.

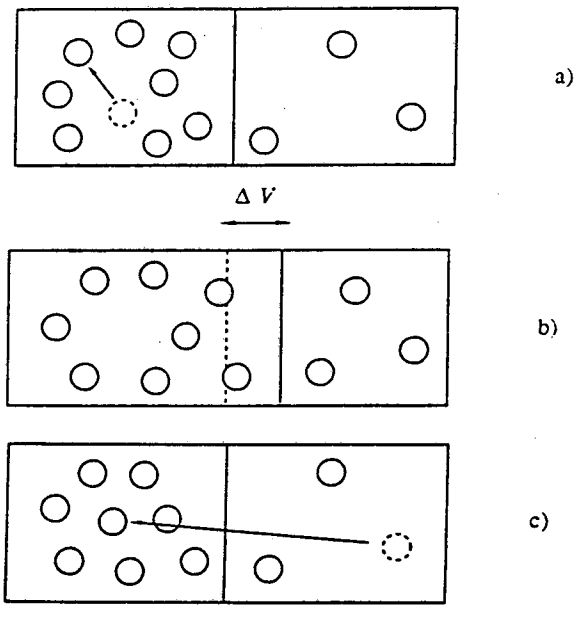


FIGURE 1
The basic steps of a Gibbs-ensemble Monte Carlo simulation. a) Random particle displacement in each region. b) Volume displacement. c) Particle exchange.

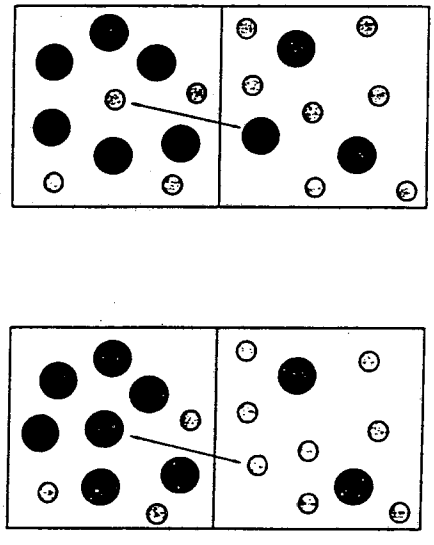


FIGURE 2
Identity-interchange move in a Gibbs-ensemble Monte-Carlo simulation. For simplicity, the particles shown in this figure are spherical. In practice, however, particles need not be spherical.

Gibbs-ensemble simulations are attractive for phase-equilibrium calculations because equilibrium between coexisting phases is established automatically, without requiring chemical-potential calculations. In a conventional μVT simulation, particle insertions are accepted with probability

$$P_{\mu VT} = \min\left(1\,,\,\exp\left(-\beta\left[U_N - U_{N+1}\right] + \ln\frac{zV}{N+1}\right)\right), \tag{1}$$

where $z = \exp(\beta\mu)/\Lambda^3$ is the activity, Λ is the de Broglie wavelength, μ is the chemical potential, and $\beta = 1/k_BT$. Here N is the number of particles, and U_N and U_{N+1} denote the potential energies of the system before and after

insertion, respectively. In a Gibbs ensemble, a move consisting of an insertion into region (′) is accompanied by simultaneous deletion from phase (″); therefore, the activity z is eliminated from the acceptance/rejection criteria; particle transfers are accepted with probability

$$P_{transfer} = \min\left(1\,,\,\exp\left[-\beta(\Delta U' + \Delta U'' + \frac{1}{\beta}\ln\frac{V''(N'+1)}{V'N''})\right]\right), \tag{2}$$

where $\Delta U'$ represents the change in potential energy of phase (′) as a result of the particle insertion, and $\Delta U''$ represents the change in potential energy of phase (″) as a result of the particle removal. V' and V'' are the volumes of phases (′) and (″), and N' and N'' are the numbers of particles in phases (′) and (″).

To apply Equation (1) in a μVT ensemble, an activity z must be specified. The activity of coexisting phases, however, is initially unknown because the molar orthobaric densities are unknown; calculation of coexistence curves therefore requires iteration which can be long and expensive. In contrast, prior knowledge of the chemical potential is not necessary for transfer of particles in a Gibbs ensemble [Equation (2)].

For a pure fluid, a volume increment ΔV in phase (′), and an equivalent volume reduction in phase (″), are accepted with probability

$$P_{volume} = \min \tag{3}$$

$$\left(1\,,\,\exp\left[-\beta(\Delta U' + \Delta U'' - \frac{N'}{\beta}\ln\frac{V'+\Delta V}{V'} - \frac{N''}{\beta}\ln\frac{V''-\Delta V}{V''})\right]\right).$$

Having specified the temperature, a two-phase, pure-fluid system has no additional degrees of freedom. Pressure, which is established internally during the course of a Gibbs-ensemble simulation, can be calculated via the virial (Allen and Tildesley, 1987). For low or moderate pressures, however, a virial equation of state truncated after the second term gives a much simpler and yet excellent approximation to the pressure.

b) GIBBS-ENSEMBLE SIMULATION OF MIXTURES

The Gibbs-ensemble simulation of mixtures is similar to that of pure fluids. The three basic steps of the simulation are also those shown in Figure 1. In mixtures, however, the pressure can be specified à priori. In that case, volume changes in coexisting regions are independent of each other, and volume moves are accepted with probability

$$P_{volume-m} = \min \tag{4}$$

$$\left(1\,,\,\exp\left[-\beta(\Delta U' + \Delta U'' - \frac{N'}{\beta}\ln\frac{V'+\Delta V'}{V'} - \frac{N''}{\beta}\ln\frac{V''-\Delta V''}{V''} + P(\Delta V' + \Delta V''))\right]\right),$$

where $\Delta V'$ and $\Delta V''$ denote, respectively, the volume changes in regions (′) and (″).

c) THE INFLATING-FLEA METHOD

Unfortunately, the Gibbs ensemble method suffers from most of the disadvantages that are found in μVT simulations, viz. the difficulty of successfully inserting particles in dense media. In fluids of LJ spheres, the insertion acceptance ratio ranges from about 0.1% at high densities, to about 10% at low densities . However, in fluids of non-spherical (orientation-dependent) particles, this ratio is dramatically reduced, thereby requiring a prohibitively long simulation. It is therefore necessary to devise strategies for increasing the percentage of

successful particle insertions.

Kofke and Glandt (1988) have proposed a semi-grand canonical ensemble in which particles are neither created nor destroyed; only the identity of different particles is interconverted. Indeed, the chances of successfully growing a particle in a place where a smaller particle was already present are better than those of inserting a full particle, at random, in the fluid. In the semi-grand ensemble, however, the chemical potential of one of the components in a mixture must be calculated.

Recently, Panagiotopoulos (1988) has applied similar ideas to the Gibbs-ensemble simulation of mixtures of spheres of different sizes; for a binary mixture of small spheres and big spheres (argon and krypton), particle transfers between coexisting phases are only attempted for the smaller of the two species. In addition to the transfer moves, however, interchange moves consisting of identity interconversion are also attempted. In an interchange move, a small particle in one phase exchanges identity with a large particle in the coexisting phase. Figure 2 illustrates an identity-interchange move. An identity interchange between a species-1 particle in phase (″) and a species-2 particle in phase (′) is accepted with probability

$$P_{interchange} = \min \tag{5}$$

$$\left(1 \, , \exp\left[-\beta(\Delta U' + \Delta U'' + \frac{1}{\beta}\ln\frac{V''(N'_1+1)}{V'N''_1} + \frac{1}{\beta}\ln\frac{V'(N''_2+1)}{V''N'_2})\right] \right),$$

where N'_i denotes the number of particles of species i in phase (′). This modification of the Gibbs-ensemble technique for mixtures increases its efficiency.

To increase the rate of successful insertions, we have found it useful to add to a pure fluid a small number of smaller particles whose chance of transfer between coexisting phases is larger than that for full-size particles. An originally pure fluid is thus considered to be a binary mixture where the mole fraction of "impurities" is negligible. In principle, the pressure of such a mixture can be specified à priori; volume moves are therefore accepted with a probability dictated by Equation (4). With such a procedure there is a danger of specifying a pressure where simultaneous phases do not coexist. However, a few short exploratory simulations are sufficient to determine whether one or two phases exist at a given pressure.

The smaller size of impurities facilitates their transfer between coexisting phases. Having attempted several transfer moves, several identity-interchange moves are performed. In effect, impurities play the role of "carriers" for full-size particles; they first find a "hole" in a dense fluid, and later they grow by means of an interchange. We propose the name "Inflating-Flea Method" for this modification of the original Gibbs-ensemble simulation algorithm. This name follows by analogy: a tiny flea can easily insert itself into the fur (or hair) of an animal. Once it has found a "comfortable" place, it can obtain nourishment and grow (inflate) to a larger size.

III) SIMULATION RESULTS FOR SPHERES

To test these ideas, we have performed a series of simulations of mixtures of LJ spheres. Appendix 1 gives details. In a system with a total of 500 particles, 5 of these, for example, have a smaller size. This represents an overall mole fraction of 10^{-2}. The potential-energy parameters for the small particles are chosen such that the numbers of successful transfers and interchanges are maximized. Table 1 shows typical results of simulations where the potential-energy parameters of the small particles are varied, while those of the full particles are kept constant. As these results indicate, smaller impurities can more easily be transfered between coexisting phases. However as the difference in size and energy between small and full particles becomes more

pronounced, it is more difficult to achieve an identity interchange.

Table 1 - Transfer and Interchange Acceptance Ratio for Different Impurity Size				
Monte Carlo Run	σ_s Å	ε_s/k_B K	% accepted transfers	% accepted interchanges
1	2.50	115.7	2.2	0.4
2	2.95	115.7	0.7	2.8
3	2.95	147.9	0.5	6.0
4	3.35	115.7	0.2	4.4

Subscript s denotes a small-particle or impurity parameter. The full-particle potential-energy parameters for these simulations are σ = 3.73 Å and ε/k_B = 147.9 K. For all runs, 500 particles are used; five of these are impurities. The density of the liquid is 26.4 mol/L and that of the vapor is 0.12 mol/L. The temperature is 111.5 K.

Table 2 compares pure-fluid simulation results to impure-fluid simulation results at different temperatures. The potential-energy parameters for the large particles are those for methane. Within the accuracy of our simulations, the equilibrium densities obtained by both methods, with and without impurities, are indistinguishable. However, simulations with impurities are more efficient, particularly at high liquid densities. Consider, for example, the results of runs 7 and 8 shown in Table 2. On average, out of a thousand identity-interchange attempts, about 28 are successful. In contrast, out of a thousand transfer attempts (without impurities) only one is successful. Granted, identity-interchange must be accompanied by tranfer of impurities; but the number of transfer attempts necessary to maintain enough impurities in each phase is small when compared to that of exchange attempts. The efficiency of the method can be further increased by employing more impurity particles. However, the larger the number of impurities, the more noticeable is their effect on the properties of a (nearly) pure system.

Table 2 - Comparison Between Pure-Fluid and Impure-Fluid Simulations						
Monte Carlo Run	σ_s Å	ε_s/k_B K	ρ_l (mol/L)	ρ_v (mol/L)	% accepted transfers	% accepted interchanges
5 (T=172.0K)	2.95	115.7	19.0 ± 0.2	2.46 ± 0.03	8.6	17.2
6	-	-	18.7 ± 0.2	2.60 ± 0.02	3.3	-
7 (T=111.5K)	2.95	115.7	26.4 ± 0.1	0.117 ± 0.002	0.7	2.8
8	-	-	26.2 ± 0.1	0.116 ± 0.001	0.07	-

While an impure-fluid simulation might prove to be valuable for the simulation of fluids containing polyatomic molecules with complicated structures, we must bear in mind the disadvantages of the inflating-flea method as discussed here: specifying the pressure of the system can result in a uniphase system, and it also gives rise to larger density fluctuations than those found in a pure-fluid simulation. Further, to maintain a small mole fraction of impurities, the simulated system must be relatively large.

IV) SIMULATION OF SMALL ALKANES

In practice, chemical engineers seldom deal with spherical molecules. With the exception of noble gases, most molecules are a collection of atoms connected in a fixed manner. A convenient way for treating polyatomic molecules is to assign interaction sites to different parts of a molecule. These sites can (but need not) correspond to the atomic nuclei in the molecule. A methane molecule, for example, can be considered to be a sphere with a single site located at the sphere's center, or a five-site particle with each site located at the nuclei of the hydrogen and carbon atoms. Alkane molecules appear to be represented adequately by assigning sites only to the carbon atoms (Jorgensen et al., 1984).

Site-interaction potential parameters, determined by regression of a few single-phase properties (liquid density and heat of vaporization at the normal-boiling point, and spectroscopic measurements) have been determined for a variety of groups (Jorgensen et al., 1983, 1984). These authors have called their intermolecular potential functions "Optimized Intermolecular Potential Functions for Liquid Simulations" (*OPLS*). These functions are of the Lennard-Jones type (see Appendix 1); they contain two parameters per site in addition to the molecule's geometrical information (e.g. bond lengths and bond angles). For these functions, only the hydrogen atoms located on heteroatoms are considered explicitly; each CH_n group is considered to be a single site centered on the carbon atom. *OPLS* potential parameters (see Appendix 1) are assumed to be transferable from one molecule to the other; in effect, such a procedure is a group-contribution method at an atomic level. Table 3 shows some of these parameters.

Table 3 - Optimized Lennard-Jones Parameters for Hydrocarbons (from Jorgensen et al.)

group	example	σ (Å)	ε/k_B (K)
CH_4	methane	3.730	147.9
CH_3 (C_1)	ethane	3.775	104.6
CH_3 (C_2)	n-butane	3.905	88.1
CH_3 (C_3)	isobutane	3.910	80.5
CH_2 (sp^3)	n-butane	3.905	59.4
CH_2 (sp^2)	1-butene	3.850	70.4
CH (sp^3)	isobutane	3.850	40.3
CH (sp^2)	2-butene	3.800	57.9
CH (*arom*)	benzene	3.750	55.3

C_n signifies that the atom adjacent to the group's carbon atom has n nonhydrogen attachments. For a more extensive list of parameters see Jorgensen et al.(1984).

For pure fluids, *OPLS* parameters can be used to calculate thermodynamic properties for conditions where experimental data are scarce. Jorgensen (1981) has performed molecular simulations of butane up to pressures of 15000 *atm*, and found good agreement with experiment for the molar density.

Table 4 shows the calculated orthobaric densities and the heat of vaporization for methane, ethane, and propane at their corresponding normal boiling points. Our results for the liquid density and for the heat of vaporization are consistent with those of Jorgensen et al.(1984). As discussed earlier, an important quantity in

Gibbs-ensemble simulations is the acceptance ratio for particle transfers between coexisting phases. Table 4 shows this ratio for pure methane, ethane and propane.

Table 4 - Transfer Acceptance Ratio and Calculated Thermodynamic Properties for Lower Alkanes

molecule	T (*K*)	ρ_l *mol/L*	ρ_v *mol/L*	ΔH_v *kcal/mol*	% accepted transfers
methane	111.5	26.2 ± 0.1	0.116 ± 0.001	1.95 ± 0.01	0.07
ethane	184.5	18.4 ± 0.1	0.089 ± 0.001	3.47 ± 0.02	0.01
propane	231.1	12.4 ± 0.1	0.056 ± 0.001	4.10 ± 0.01	0.03

Figures 3, 4 and 5 show coexistence curves for lower alkanes. In general (except near a critical point), the calculated liquid densities are within one or two percent of the corresponding experimental values. Vapor densities, however, are predicted with less accuracy. These deviations are not totally unexpected, as the potential-energy parameters of Table 3 have only been adjusted to fit liquid density and heat of vaporization at the normal boiling point. As the critical point is approached (but in a region where Gibbs-ensemble simulations are still feasible), disagreement between simulation and experiment becomes more pronounced. Jorgensen et al.(1984) have pointed out that the optimum Lennard-Jones parameters should be temperature dependent, to reach quantitative agreement with experiment over a wide range of temperature. Recently, Gupta (1988) has performed molecular-dynamic simulations for phase-equilibrium calculations in systems of ethane-like molecules; our results are consistent with those of Gupta, who concludes that deviations from experiment (as the critical region is approached) may result from not including three-body interactions in the potential energy. Benmekki and Mansoori (1988) have also discussed the effect of three-body interactions on the shape of calculated coexistence diagrams.

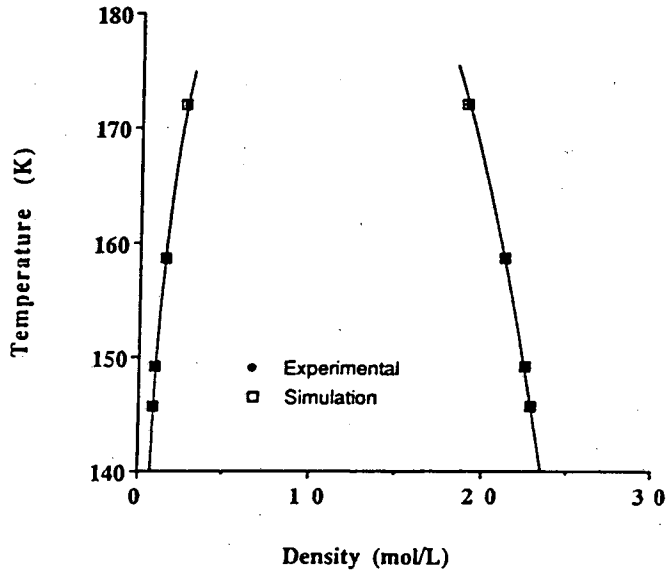


FIGURE 3
Coexistence curve for methane. The black circles show experimental data. The open squares are results from Gibbs-ensemble simulations, using potential-energy parameters given in Table 3.

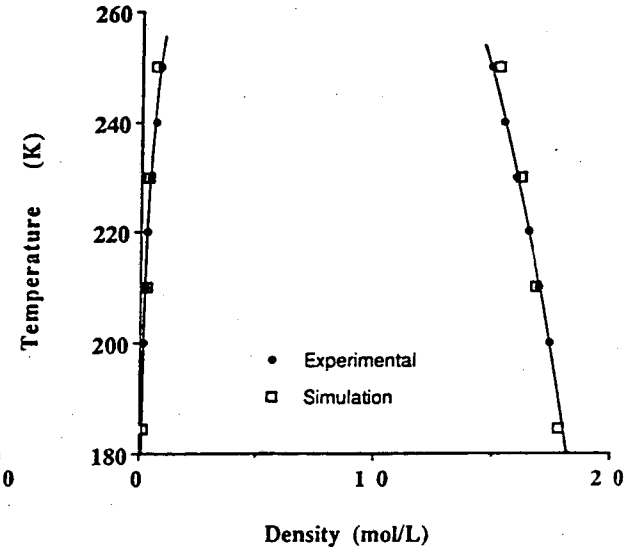


FIGURE 4
Coexistence curve for ethane. The black circles show experimental data. The open squares are results from Gibbs-ensemble simulations, using potential-energy parameters given in Table 3.

Figure 6 shows the results of simulations for mixtures of methane and ethane. Taking into account that potential-energy parameters were obtained from only two single pieces of experimental information, agreement between simulation and experiment is surprisingly good. Two types of combining rules were used for these calculations. The triangles respresent simulations with geometric-mean combining rules for both size and energy parameters. These are the combining rules proposed by Jorgensen and co-workers (1984) to be used in conjunction with *OPLS* parameters. The squares represent simulations with a geometric-mean combining rule for the energy parameter but with an arithmetic-mean combining rule for the size parameter. Our simulations indicate that the latter choice gives better agreement with experiment. Unfortunately, *OLPS* parameters reported by Jorgensen have been obtained in conjunction with geometric-mean combining rules.

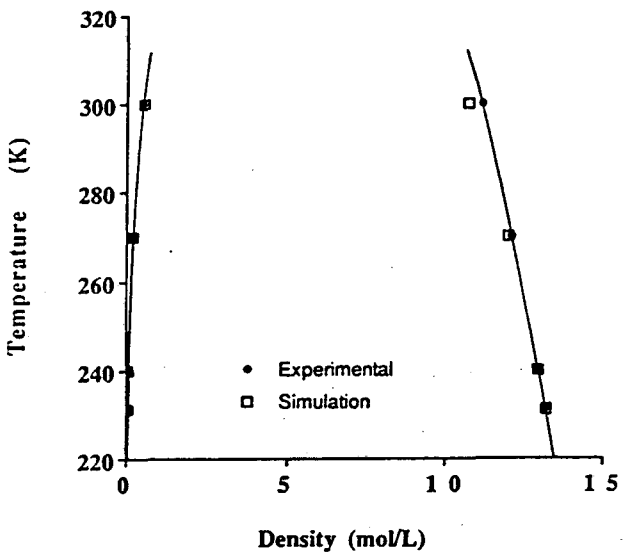


FIGURE 5
Coexistence curve for propane. The black circles show experimental data. The open squares are results from Gibbs-ensemble simulations, using potential-energy parameters given in Table 3.

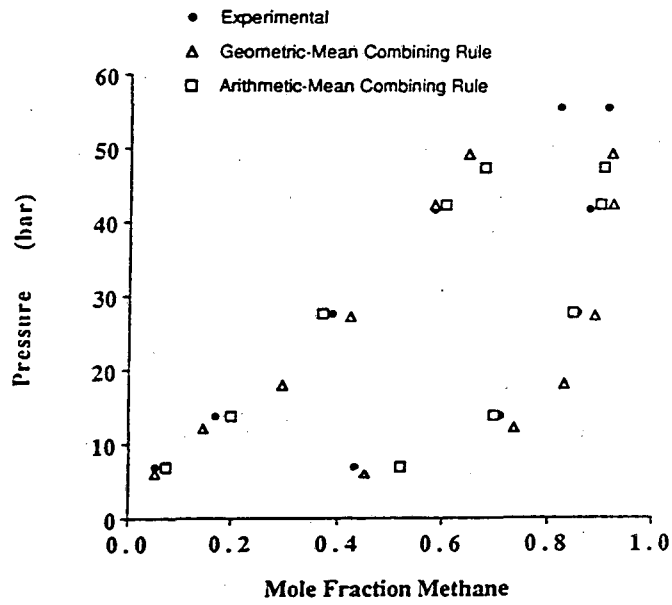


FIGURE 6
Isothermal coexistence curve for methane/ethane mixtures at T=213.7 K. The solid circles show experimental data. The open triangles are from Gibbs-ensemble simulations, using potential-energy parameters given in Table 3 and using geometric combining rules for size and energy parameters. The open squares are from Gibbs-ensemble simulations with the same parameters, but using an arithmetic-mean combining rule for the size parameter.

We must bear in mind that *OPLS* parameters have been determined only from pure-component properties; not from mixture properties. In mixtures of methane and propane (Figure 7), to reach quantitative agreement with experiment, we need a cross-interaction energy parameter, given by

$$\varepsilon_{ij} = (\varepsilon_i \, \varepsilon_j)^{1/2} (1 - k_{ij}) \quad , \tag{6}$$

where k_{ij} is a binary constant, and ε_i is the energy parameter for interaction of two sites of type i. For the particular model of propane used here, we find that agreement with experiment is good for $k_{ij} = 0.12$.

For the simulations shown in Figures 6 and 7, we have chosen conditions of pressure and temperature such that both branches of the coexistence curve are "far" from the ordinate axis. The significance of "far" depends on the size of the system. If one of the equilibrium phases is very dilute in one of the components (on the order of 10^{-4} mole fraction), very long simulations are required to reduce the uncertainty in the calculated properties.

V) SIMULATION OF WATER

Over the past decade a number of water models have been proposed. Levesque et al.(1987) give a brief account of the status quo of water simulation. One of our objectives is to study phase equilibria for water-hydrocarbon mixtures. Of those models that are simple enough for simulations of reasonable length, only the *TIP4P* model (Jorgensen et al., 1983) has been used in conjunction with *OPLS* parameters to study the hydrophobic effect (Jorgensen et al., 1985). In this work we only use a *TIP4P* model, even though recent findings indicate that other models are better for reproducing, for example, the dielectric properties of water (Strauch and Cummings, 1989).

A *TIP4P* water molecule consists of a sphere with four sites (Figure 8). One of these sites is located at the oxygen atom; it interacts only with other oxygen sites through a van der Waals (LJ) potential. The other three sites correspond to electrostatic charges distributed as shown in Figure 8. These charges interact only with those in other molecules through a Coulomb potential. The two positive charges are located at the hydrogen atoms, while the negative charge is moved off the oxygen and towards the hydrogens at a point M on the bisector of the *HOH* angle.

In their study of water intermolecular potentials, Jorgensen and co-workers (1983) compared the experimental and the simulated liquid density only at 25 C and 1 atm and at the normal boiling point; for these conditions, agreement with experiment is excellent.

Table 5 - Transfer Acceptance Ratio and Calculated Thermodynamic Properties for *TIP4P*-Water

T (K)	ρ_l mol/L	ρ_v mol/L	$E_{i(l)}$ $kcal/mol$	% accepted transfers
373.15	51.5 ± 0.4	0.045 ± 0.001	-8.93 ± 0.04	0.12

$E_{i(l)}$ denotes the internal energy of the liquid phase.

Table 5 shows results for *TIP4P*-water at 100°C. Figure 9 shows the experimental and simulated coexistence curve for *TIP4P*-water; this model yields liquid orthobaric densities that are only one or two percent lower than experiment. Vapor densities, however, are predicted less accurately. Unfortunately, as the temperature rises to about 500 K, agreement with experiment deteriorates rapidly.

We are currently attempting to simulate vapor-liquid equilibria for the water/methane system at high pressures.

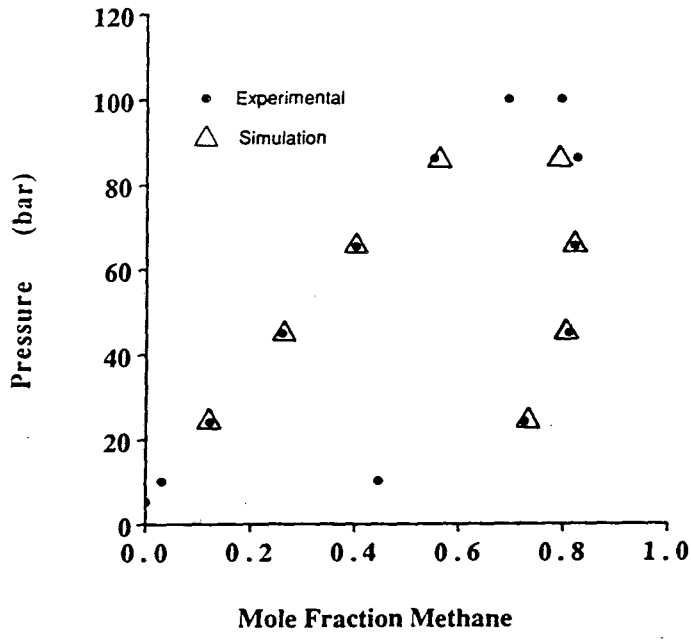
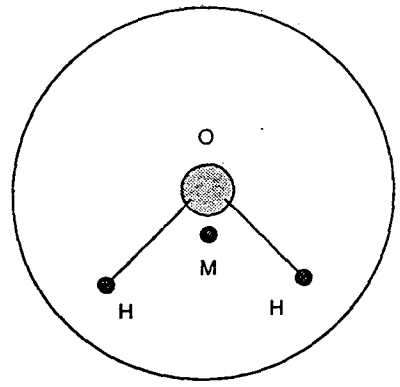


FIGURE 7
Isothermal coexistence curve for methane/propane mixtures at T = 277.13 K. The solid circles show experimental data, and the open triangles are from Gibbs-ensemble simulation using potential-energy parameters given in Table 3.



TIP4P Water Molecule

Charge on M = −1.04 *e*

Charge on H = 0.52 *e*

Angle *HOH* = 104.52 *deg*

Distance *OH* = 0.9572 Å

Distance *OM* = 0.1500 Å

FIGURE 8
TIP4P model for water. The molecule has one van der Waals interaction site, located at the oxygen atom. In addition, the molecule has electrostatic charges: two positive charges are located on the hydrogen atoms (H), and one negative charge is located at position M on the bisector of the *HOH* angle.

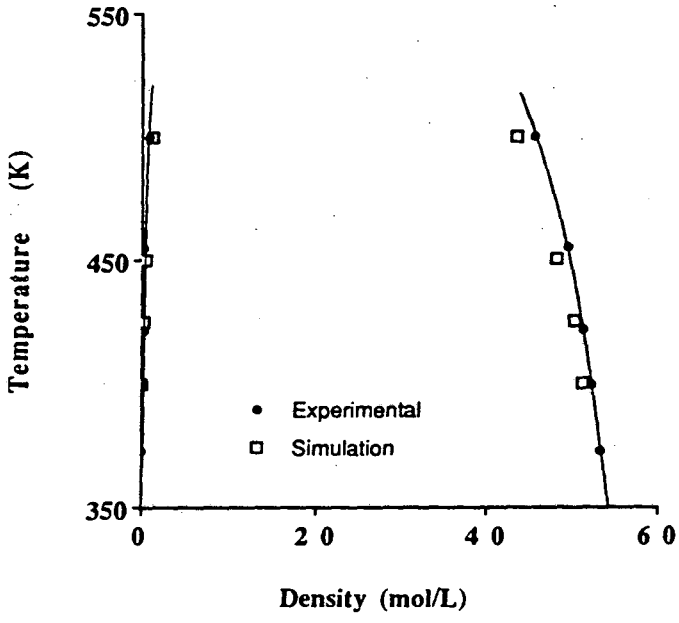


FIGURE 9
Coexistence curve for water. The black circles show experimental data. The open squares are from Gibbs-ensemble simulations using a *TIP4P* potential function for water.

VI) CONCLUSIONS

Our results for lower-alkane pure fluids and for their mixtures agree quantitatively with experiment. The pure-component parameters used to predict coexistence diagrams were obtained using only the liquid density and the enthalpy of vaporization at the normal boiling point. Molecular simulations are free of the approximations made to arrive at analytical equations of state. The predicting and extrapolating power of molecular simulation is therefore one of its main advantages over conventional, analytical methods. The *OPLS* parameters used in this work should be regarded as group-contribution parameters at the atomistic level. Our results indicate that for simple mixtures, these parameters can be used to study systems and conditions for which experimental data are scarce, provided that binary interaction parameters are introduced. We are currently in the process of evaluating these parameters for alkanes.

A *TIP4P* water model yields a coexistence curve in agreement with experiment. However, our preliminary results suggest that this model is not accurate enough to predict, quantitatively, phase equilibrium in difficult systems, such as water-hydrocarbon mixtures. For these cases, the revised central-force model of Stillinger and Rahman (1978) [see, for example, Swope and Andersen (1984)] or the *SPC* model [see, for example, Strauch and Cummings (1989)] might be more suitable.

Molecular simulations can be used as "experiments", that yield computer-generated data only when "real" experimental information is not available. The use of molecular simulation on a routine basis, as needed for process design, is still out of the question. Further, at present, phase-equilibrium studies of highly dilute regions are hindered by the limited speed of currently available computers.

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APPENDIX 1

For all alkane simulations, we used *OPLS* intermolecular potential functions (Optimized Potentials for Liquid Simulations) with parameters reported in the literature (Jorgensen et al., 1984). For the interaction between two multi-site molecules a and b, these functions take the form

$$v_{ab} = \sum_{i}^{on\ a} \sum_{j}^{on\ b} \left(\frac{A_{ij}}{r^{12}_{ij}} - \frac{C_{ij}}{r^{6}_{ij}} + \frac{q_i q_j}{r_{ij}} \right) , \qquad \text{A1}$$

where v_{ab} is the interaction energy between molecules a and b. The first summation is over the interaction sites on molecule a, and the second summation is over the interaction sites on molecule b. Here r_{ij} denotes the distance between sites i and j. For parameters A_{ij} and C_{ij}, somewhat arbitrary combining rules are used, i.e., $A_{ij} = (A_{ii}A_{jj})^{1/2}$ and $C_{ij} = (C_{ii}C_{jj})^{1/2}$. Parameters A_{ii} and C_{ii} are related to the common Lennard-Jones parameters through $A_{ii} = 4\varepsilon_i\sigma_i^{12}$ and $C_{ii} = 4\varepsilon_i\sigma_i^{6}$. For mixtures, an arithmetic mean for the cross-interaction size parameter (σ_{ij}) is generally preferable over a geometric mean. In our work, however, we have kept Jorgensen's original combining rules. Parameters q_i represent a charge assigned to site i. While for hydrocarbons q_i is generally zero, a water molecule has several charges (see Figure 8). The total potential energy of the system is calculated by summing interactions between all pairs of molecules:

$$U = \sum_{b>a} v_{ab} . \qquad \text{A2}$$

All simulations were performed with Metropolis sampling and periodic boundary conditions. For each phase, a cutoff distance r_c for molecular interactions was set equal to half the side of the phase box. The cutoff is based roughly on the center-of-mass separations. During the course of simulations, a correction was made to account for all interactions neglected beyond the cutoff. For mixtures, these corrections are calculated for each phase from

$$U_{corr}' = 2\pi N'\rho' \sum_{lk} x_l x_k \int_{r_c}^{\infty} g_{lk}(r) v_{lk}(r) r^2 \, dr , \qquad \text{A3}$$

where l and k denote components of the mixture, and x_l and x_k denote their respective mole fractions. To evaluate the integral in Equation A3, it is assumed that beyond the cutoff, all g_{lk} are equal to unity. When using

Equation A3, it is important to recognize that interactions between molecules are calculated from a sum of interactions between all sites of the molecules.

Following Jorgensen et al. (1983), for the particular case of water simulation a spherical cutoff distance of 7.5 Å was applied. Since *TIP4P* parameters were originally adjusted without including cutoff corrections, no corrections have been implemented in our simulations of pure water.

In addition to three Cartesian coordinates (xyz), multisite molecules are described by a set of angles. The orientations of ethane molecules can be represented with only two angles; those of propane molecules require three (Euler) angles, and those of butane require a dihedral angle in addition to three Euler angles. Details on the geometrical construction of hydrocarbon model molecules are given elsewhere (Jorgensen et al., 1984, Allen and Tildesley, 1987); here it suffices to say that the length of a carbon-carbon (CC) bond in hydrocarbons is 1.53 Å. The angle between the two CC bonds of propane is 124° .

Simulations were performed in cycles, each comprising sequential NVT moves of all molecules in the system; several transfer moves were followed by a few hundred exchange attempts, and finally a volume move. The specific number of transfer and exchange moves was varied depending on the system. Most simulations required a period of equilibration of 500000 moves, followed by another 500000 moves for averaging. For water, however, 10^6 moves were used for equilibration and for averaging. To study the effect of a system's size, most simulations were performed first with 300 and then with 500 particles. All simulations were done on an IBM 3090 computer. The time required by a particular simulation depends on the number of particles as well as on the number of sites on the particles. For simple spheres, a simulation takes about 20 minutes, while for water molecules it takes more than an hour.

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