

Exact Calculations of Fluid-Phase Equilibria by Monte Carlo Simulation in a New Statistical Ensemble¹

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A recently proposed method, Monte Carlo simulation in the Gibbs ensemble, allows the prediction of phase equilibria from knowledge of the intermolecular forces. A single computer experiment is required per coexistence point for a system with an arbitrary number of components. The new technique has significant advantages relative to free-energy methods that have been used for phase equilibrium calculations in the past. In this work, a variation of the Gibbs method appropriate for calculations in mixtures with large differences in molecular size is developed. The method is applied for the calculation of high-pressure phase equilibria in two mixtures of simple monatomic fluids, the systems argon-krypton and neon-xenon. Pairwise additive potential functions of the Lennard-Jones type are used to describe the intermolecular interactions. Agreement with experimental results is generally good over a wide range of temperatures and pressures, including the fluid-fluid immiscibility region for the neon-xenon system. Results from the Van der Waals one-fluid theory are compared with experimental data and computer simulation predictions. Agreement is excellent for the mixture with small differences in size (argon-krypton), but the theory fails to describe the coexistence curve for the highly asymmetric system neon-xenon.

KEY WORDS: computer simulation; intermolecular potential functions; Lennard-Jones; Monte Carlo; phase equilibria; vapor-liquid equilibria.

1. INTRODUCTION

Computer simulation techniques have been used since their inception for calculating basic thermodynamic and structural properties of liquids [1]. In recent years, efforts have been directed toward improving computer

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simulation techniques for the estimation of free energies [2], with a primary goal being the prediction of phase equilibria. Several successful predictions of the phase equilibrium properties of mixtures have been reported for atomic and molecular fluids [3, 4] using the Widom test particle method [5]. The computer time requirements for these calculations are high because of the need to perform a large number of simulations at different densities and compositions. The number of simulations needed increases rapidly with the number of components in a mixture.

The Gibbs-ensemble Monte Carlo simulation method [6] offers significant improvements relative to free-energy calculation methods. The method involves performing a simulation in two distinct, coupled regions with generally different densities and compositions, in a way that ensures that the criteria for phase equilibrium, equality of temperature, pressure, and chemical potentials of all components in the two phases, are satisfied in a statistical sense. The method has been used to predict vapor-liquid, liquid-liquid, and osmotic equilibria for binary Lennard-Jones mixtures [7], phase transitions for fluids in pores [8], and equilibria for quadrupolar fluids [9].

The central theme of this paper is the calculation of phase equilibria in real fluid mixtures using the Gibbs method. Specific objectives include (a) development of techniques that expand the range of validity of the Gibbs method to systems with large differences in component size, (b) testing of simple, pairwise additive intermolecular potential functions for their ability to represent phase equilibrium data of real fluid mixtures, and (c) comparisons of the simulation results with commonly used engineering and theoretical models. In Section 2, we give some background information on the Gibbs method and present a modification necessary for handling mixtures with large differences in molecular size. In Section 3, we describe the potentials used to model the intermolecular interactions in the systems studied. The results and comparison with experimental data and theoretical predictions from the Van der Waals one-fluid theory are presented in Section 4, and the conclusions from the present work are summarized in Section 5.

2. THE GIBBS METHOD

2.1. Basic Concept

The methodology for determination of phase equilibria in mixtures using the Gibbs method has been previously described in detail for pure fluids [6] and mixtures [7]. The method involves setting up a Monte Carlo simulation in a two-region system. The two regions are not in physi-

cal contact (therefore, no interfaces are present). Conventional spatially periodic boundary conditions are applied for each region separately. Three types of perturbations are performed: (a) random displacement steps in each region separately, to ensure equilibration within each region; (b) concerted changes in the volumes of the two regions that result in equality of the average pressure; and (c) random transfers of molecules from one to the other region of the simulation that result in equality of the chemical potential of all components present in the two regions.

The primary advantage of this method over previously available techniques based on the calculation of free energies is the ability to determine coexistence properties for a system with an arbitrary number of components from a single computer experiment.

2.2. Extension for Mixtures with Large Differences in Molecular Size

For pure fluids and simple mixtures, the Gibbs methodology as described in Refs. 6 and 7 works well even for densities close to the triple-point liquid densities. However, for mixtures with components that have large differences in molecular size, the method fails at high densities, because most attempts to transfer a molecule of the large species into a densely packed liquid are unsuccessful. The system neon-xenon that we attempt to model in this work is an example of a highly asymmetric mixture, with a volume ratio of the two components ($\sigma_{Xe}^3/\sigma_{Ne}^3 = 2.7$). For such systems, a modification of the Gibbs methodology can be implemented to increase significantly the range of liquid densities that can be covered.

Figure 1 gives a schematic representation of the modification to the Gibbs methodology for highly asymmetric mixtures. The modification affects only the particle transfer step. Let us designate the component with the smallest size in a binary mixture component 2. Component 1 has a

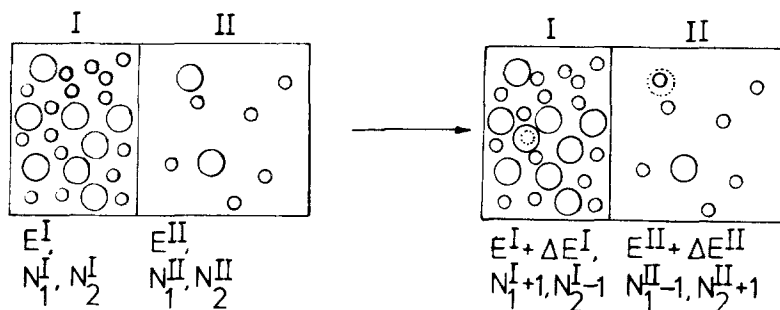


Fig. 1. Schematic illustration of the exchange step for highly asymmetric mixtures.

significantly larger size, and therefore it is difficult to obtain successful transfers of this component between regions. In the modified method, direct transfers between the two regions are attempted only for component 2. For component 1, the transfer step involves the following: in one of the two regions, a randomly selected particle of species 2 becomes a particle of species 1. At the same time, the inverse procedure is applied to the other region: a randomly selected particle of species 1 become a particle of species 2. The move is accepted with a probability:

$$P_{\text{exchange}} = \min \left(1, \exp \left\{ -\beta \left[\Delta E^I + \Delta E^{II} + kT \ln \frac{V^{II}(N_1^I + 1)}{V^I N_1^I} + kT \ln \frac{V^I(N_2^{II} + 1)}{V^{II} N_2^{II}} \right] \right\} \right) \quad (1)$$

The following conditions between the chemical potentials of the two components in the two regions are then satisfied in a statistical sense:

$$\begin{aligned} \mu_2^I &= \mu_2^{II} && \text{(from transfer step)} \\ \mu_2^I - \mu_1^I &= \mu_2^{II} - \mu_1^{II} && \text{(from exchange step)} \end{aligned} \quad (2)$$

which are sufficient to ensure the equality of chemical potentials of all components in the two phases. The method can be easily generalized for systems with more than two components.

The advantage of the proposed modification is that it is much more efficient to attempt to increase the size of an existing molecule than to attempt to place a molecule at a completely random position. In this respect the proposed modification is similar to the semi-grand ensemble Monte Carlo simulation technique [10]. Tests of the proposed modification for results obtained with the original Gibbs methodology [6] and the conventional Widom method [5] demonstrated that the new method gives results statistically indistinguishable from the old. For the mixture neon–xenon at high pressures ($P = 4000$ bar), the success ratio for the exchange attempts for xenon is two orders of magnitude higher than the corresponding ratio for the transfer attempts.

3. INTERMOLECULAR POTENTIALS

For modeling the intermolecular interactions in the systems of interest, we chose to use intermolecular potential of the Lennard–Jones (6, 12) type. We chose to use LJ potentials rather than more realistic intermolecular potentials for the rare gases determined from gas-phase and spectroscopic data [11] for the following reasons.

- (a) Real fluids do not obey the assumption of pairwise additivity of potentials. At least three-body (and possibly higher-order) terms are required for an accurate description of the thermodynamics properties of rare gas liquids. The pair potentials determined from gas-phase properties are known to give a worse representation of the liquid state properties than effective pairwise additive potentials of the LJ type [11]. The best modern pair potentials, augmented with the Axilrod–Teller three-body interactions and quantum corrections, give results for the liquid structure that are equally close to the experimental results as the pairwise additive effective potentials [12]. One objective of this study is to determine whether pairwise additive potentials can be obtained that give a good representation of the phase equilibrium properties over a wide range of temperatures and pressures. There are significant computational advantages in utilizing effective two-body, rather than three-body potentials, despite the inevitable loss of accuracy in the prediction of some properties.
- (b) One of the goals of this study is to provide data for well-defined model systems that can be used for the testing and development of theories for equations of state and mixing rules. There is a corresponding requirement that the model systems need to be simple. The LJ potentials satisfy this requirement, and a large amount of simulation results exists that can be used for development of theoretical models [13, 14].

The potential parameters for the pure fluids were selected to optimize the representation of the phase equilibrium properties and are, thus, slightly different from those determined from gas-phase values available in standard compilations [15]. The potential parameters used in this work are shown in Table I.

Table I. Potential Parameters

Component pair	ϵ_{ij}/k (K)	$\epsilon_{ij}/(\epsilon_{ii}\epsilon_{jj})^{1/2}$	σ_{ij} (Å)	$2\sigma_{ij}/(\sigma_{ii} + \sigma_{jj})$
Argon–argon	117.5		3.390	
Argon–krypton	135.4	0.984	3.505	1.002
Krypton–krypton	161.0		3.607	
Neon–neon	34.3		2.81	
Neon–xenon	60.7	0.688	3.47	1.033
Xenon–xenon	227.		3.91	

To obtain the mixture combination parameters, a common choice is the Lorenz–Berthelot rules,

$$\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2} \quad (3)$$

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad (4)$$

For the system argon–krypton, with relatively small differences in size and interaction energy parameters between the two components, these rules provide a reasonably good description of the phase equilibrium properties of the mixture. In this study we used parameters determined from a slightly more complicated set of combining rules [16],

$$\varepsilon_{ij}\sigma_{ij}^6 = 2 \frac{\varepsilon_{ii}\sigma_{ii}^6\varepsilon_{jj}\sigma_{jj}^6\alpha_i\alpha_j}{\varepsilon_{ii}\sigma_{ii}^6\alpha_j^2 + \varepsilon_{jj}\sigma_{jj}^6\alpha_i^2} \quad (5)$$

$$\varepsilon_{ij}\sigma_{ij}^{12} = \left[\frac{(\varepsilon_{ii}\sigma_{ii}^{12})^{1/13} + (\varepsilon_{jj}\sigma_{jj}^{12})^{1/13}}{2} \right]^{13} \quad (6)$$

where α_i is the polarizability of species i . The polarizabilities for the components studied obtained from [17].

For the highly asymmetric neon–xenon system, neither set of combining rules gave a satisfactory representation of the properties of the mixture. Instead, we used the experimentally determined value for the energy cross interaction parameter for this system, from measurements of the cross second virial coefficient [18]. For the parameter $\sigma_{\text{Ne-Xe}}$, there is considerable uncertainty in the experimentally determined value. Preliminary calculations indicated that the calculated phase diagram at high pressures is significantly influenced by small changes in $\sigma_{\text{Ne-Xe}}$. To obtain an estimate for this parameter, we adjusted its value starting from the value given by Eqs. (5) and (6), so as to obtain reasonable agreement for the calculated compositions at a single point ($T=223$ K, $P=900$ bar). There has been a previous study by simulation of the neon–xenon system [19]. The parameters used here are similar, but not identical, to the parameters obtained in Ref. 19 by fitting pure-component and mixture parameters to volumetric and phase equilibrium data at high pressures.

In addition to the values of the potential parameters, Table I presents the ratios of the cross interaction parameters for the systems studied to the values resulting from the Lorenz–Berthelot rules. For the argon–krypton system, these ratios are very close to unity, while for neon–xenon the cross interaction parameters deviate significantly from the values predicted from the Lorenz–Berthelot rules.

4. RESULTS AND DISCUSSION

A number of simulations for the two mixtures studied were performed. The simulation results included densities, compositions, and chemical potentials of all components for the coexisting phases. The results for the phase diagrams are compared with experimental results in Figs. 2–4.

The calculated phase diagrams as a function of temperature for the system argon–krypton are shown in Fig. 2. The agreement between the Monte Carlo simulations and the experimental results [20] is excellent for all temperatures. Small deviations occur for the near-critical region for the highest temperature studied ($T=193.15$ K). Also shown in Fig. 2 are results from the Van der Waals one-fluid theory. For the theoretical calculations, an accurate equation of state for argon [21] was used to determine the reference-fluid properties. Agreement between theoretical and experimental results is also excellent, a result of the fact that the argon–krypton mixture is very close to ideal.

Figure 3 presents the phase diagram for the neon–xenon mixture at pressures below 1000 bar as obtained from Gibbs-ensemble simulations

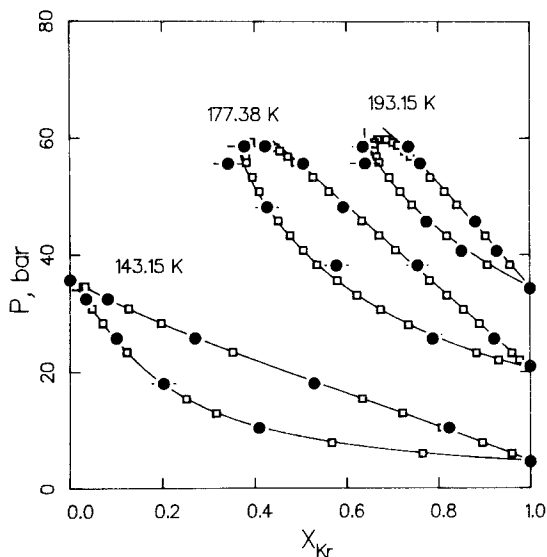


Fig. 2. Pressure–composition diagram for the system argon–krypton. (\square) Experimental data [20]; (\bullet) Gibbs-ensemble Monte Carlo simulations from this work. The horizontal lines through the simulation points represent the estimated uncertainty in the composition. (—) Theoretical predictions from the Van der Waals one-fluid theory, using the potential parameters in Table I and an equation of state of argon [21] as a reference.

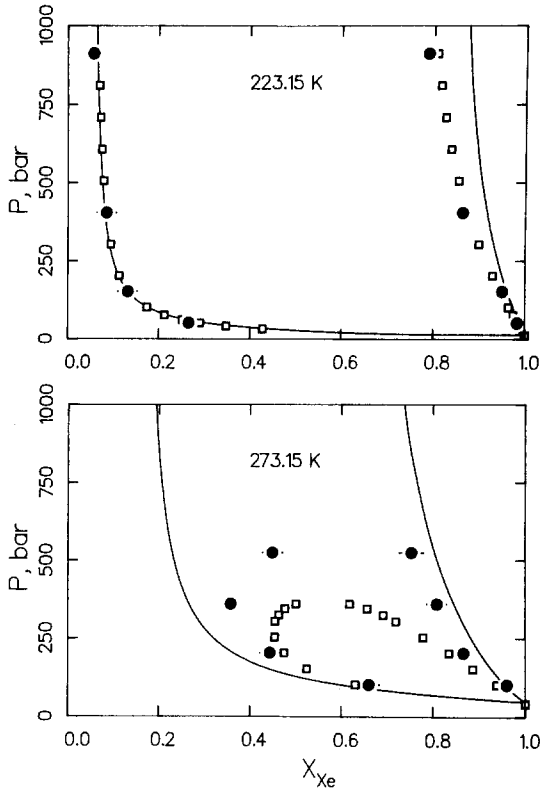


Fig. 3. Pressure-composition diagram for the system neon-xenon. Upper diagram, $T=223.15$ K; lower diagram, $T=273.15$ K. Symbols are as in Fig. 2. Experimental data are from Ref. 18.

and experiment [18]. The high-pressure points at $T=223.15$ K were used in fitting the cross interaction parameter σ_{Ar-Kr} , and therefore the agreement for the calculated compositions at that point is forced. However, there is also excellent agreement between Monte Carlo simulation and experimental results for the other points on the same isotherm. For the 273 K isotherm, there is only qualitative agreement between experiment and simulation. This is not entirely unexpected, as the potential model used is not an exact representation of the intermolecular forces of the system in question. Moreover, the temperature range around 273 K is a region where the coexistence pressure for the system is changing very rapidly with temperature [18]. Small differences between actual and model intermolecular potentials would be magnified in that region.

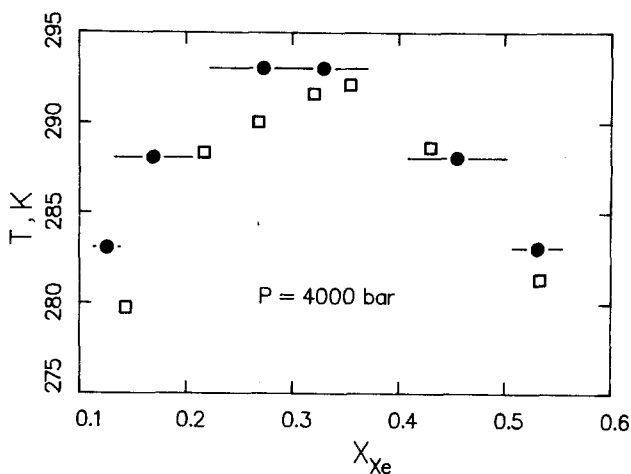


Fig. 4. Fluid-fluid immiscibility curve for the system xenon-neon at $P = 4000$ bar. Symbols are as in Fig. 2. Experimental data are from Ref. 24.

The Van der Waals one-fluid theory based on the equation of state for argon and using the same potential parameters as the Monte Carlo results fails to represent even approximately the phase diagram for the system. This disagreement is to be expected, given that previous studies [22, 23] have convincingly demonstrated the failure of the Van der Waals one-fluid theory for mixtures of molecules with large differences in size. It would be interesting to compare the results from the current simulation with modern perturbation theories [17] that are known to perform better for mixtures of molecules with large size differences. One possible difficulty for the application of perturbation theory to the neon-xenon mixture is that, in addition to large size differences, there are also significant deviations from the additivity (Lorenz) combining rule for the size parameter, and therefore the common additive-diameter hard-sphere reference system may not be adequately close to the system under study.

The results from the simulations for the phase diagram of the neon-xenon system at a much higher pressure ($P = 4000$ bar) are presented in Fig. 4. Experimental data are from Ref. 24. A surprisingly good agreement is found between simulation and experimental results. This is a significant finding: it appears that even with approximate pairwise additive potential models, very good agreement can be obtained for phase equilibrium results at very high pressures.

5. CONCLUSIONS

In this work, a new technique is developed that significantly extends the range of validity of the Gibbs technique in the case of a mixture with components differing greatly in size. Phase equilibria for two simple mixtures, Ar/Kr and Ne/Xe, are modeled using intermolecular potential functions of the LJ type. The first mixture is close to ideal and has a type I phase diagram. The second mixture has a type III phase diagram, with a fluid–fluid immiscibility region. For both mixtures, a description of the experimental results using pairwise additive LJ potentials is possible.

Available semiempirical and theoretical techniques for modeling the excess free energy for simple mixtures are adequate for mixtures with small differences in size but fail when the components of a mixture are significantly different. Data from the current study for mixtures with precisely defined intermolecular forces can be used for testing new mixing and combining rules.

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