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PHASE EQUILIBRIA OF QUADRUPOLEAR FLUIDS BY SIMULATION IN THE GIBBS ENSEMBLE

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Vapour-liquid phase diagrams for pure fluids and mixtures of molecules with Lennard-Jones plus quadrupole-quadrupole interaction potentials were determined by Monte Carlo simulation in the Gibbs ensemble [1]. This is the first reported application of the method to molecular fluids. We have demonstrated that the Gibbs method works reliably for strongly interacting molecular fluids at liquid densities. Pure fluid calculations were performed for reduced quadrupole strengths, $Q^* = Q/(\epsilon\sigma^5)^{1/2}$ equal to 1 and $\sqrt{2}$, typical of molecules like C_2H_2 and C_2H_4 . It was found that the critical temperature of the quadrupolar fluid increased rapidly with increasing quadrupolar strength, in good agreement with previous computer simulation and theoretical results. A single mixture with components characterized by identical Lennard-Jones parameters and $Q_1^* = +1$, $Q_2^* = -1$ was studied at three temperatures. A negative azeotrope was observed at the lowest temperature studied, as seen experimentally in the CO_2/C_2H_2 mixture. The perturbation theory calculations are in good agreement with the simulation results for all properties except coexisting liquid densities. The results illustrate some of the strengths and limitations of perturbation theories based on the Padé approximant for the free energy of polar fluids.

KEY WORDS: Monte Carlo, Gibbs ensemble, phase equilibria, quadrupolar fluids, Lennard-Jones fluids.

1 INTRODUCTION

Computer simulation techniques have been used since their inception for the calculation of basic thermodynamic and structural properties of liquids. In recent years, a large effort has been directed towards improving computer simulation techniques for the estimation of free energies [2, 3], with a primary goal being the prediction of phase equilibria. A recently proposed technique, Monte Carlo simulation in the Gibbs ensemble [1] has significant advantages for this purpose over previously available techniques. 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 equilibria, equality of temperature, pressure and chemical

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potentials of all components in the two phases, are satisfied in a statistical sense. The method has been used to predict bulk vapour-liquid, liquid-liquid and osmotic equilibria for binary Lennard-Jones mixtures [4], but has not been previously applied to fluids with orientationally-dependent forces. The principal objective of this work is to demonstrate the applicability of the method for an important class of molecular fluids, quadrupolar mixtures.

Multipolar forces, resulting from the presence of asymmetric molecular charge distributions, play an important role in determining the structure and phase equilibrium behavior of fluids. A study of the effect of multipolar forces and anisotropic shape using thermodynamic perturbation theory [5] has demonstrated that most of the experimentally observed classes of phase equilibrium behavior can be obtained if such forces are present. Quadrupolar mixtures in particular have been the subject of several theoretical [6, 7, 8, 9] and computer simulation studies [10, 11, 12]. It is therefore important to compare theoretical methods with exact computer simulation results for the phase behavior of this class of mixtures.

In Section 2 of this work, we describe certain methodological aspects of Gibbs-ensemble simulations for quadrupolar mixtures. In Section 3, we present the results of the simulations performed and a comparison between thermodynamic perturbation theory and simulation results. We studied two pure Lennard-Jones quadrupolar (LJQ) fluids with $Q^* = +1$ and $Q^* = \sqrt{2}$ typical of molecules like C_2H_2 and C_2H_4 , where the reduced quadrupolar moment $Q^* = Q/(\epsilon\sigma^5)^{1/2}$. Phase diagrams for a symmetric binary LJQ mixture, with identical ϵ and σ parameters for the two components and $Q^* = +1$ and $Q^* = -1$, were studied at three reduced temperatures. Section 4 summarizes the conclusions from the present study. Technical details of the simulations performed are given in the Appendix.

2 METHODOLOGY

The aim of this part of the paper is to present an outline of the structure of the Gibbs-ensemble Monte Carlo simulation program which we used to study phase coexistence properties of quadrupolar fluids. A detailed description of initial conditions and other technical parameters of the simulations performed, as well as the form of the potential model used in this work is given in the Appendix.

We followed the Gibbs Monte Carlo methodology as described in [4] with some additional features appropriate for the simulation of molecular fluids. A simulation is performed in two boxes, with N^I molecules in a volume V^I in box I and N^{II} molecules in a volume V^{II} in box II. The simulation consists of three distinct Monte Carlo trial moves: molecular displacements and rotations within each box, volume changes and molecular transfers between the two boxes.

In the combined rotation-displacement move, a trial position and orientation were chosen for a molecule in one of the two boxes, as explained in the Appendix, and the change in energy between the new and old configurations calculated, ΔE . The move is accepted with a probability

$$\mathcal{P}_{\text{move}} = \min(1, \exp(-\beta\Delta E)) \quad (1)$$

where $\beta = 1/kT$. A cycle over all molecules in both boxes was performed before attempting trial volume changes or transfers.

In [4] it was proposed that the volume change steps for simulation of mixtures can be performed in two distinct ways. In the first, the total system samples the constant- NVT ensemble, so that the coexistence pressure is not known in advance. In the second, each region samples the constant- NPT ensemble during the volume change steps. The constant- NPT method was found to have convergence advantages for the mixtures studied in [4]. However, the quadrupolar systems investigated in this work have very narrow coexistence envelopes in pressure-composition space. For a Gibbs simulation to be successful, the initial conditions must be in a two-phase region of a phase diagram. Because of this, it was not possible to perform constant- NPT simulations for the quadrupolar mixtures. All simulations were performed in the constant- NVT ensemble. In this ensemble, to attempt a trial volume rearrangement, a volume ΔV is added to the volume of one box, and subtracted from the volume of the other box, thus keeping the total volume ($V^I + V^{II}$) constant. The change in energy for this move is calculated by separately scaling the terms that depend on the 12th, 6th and 5th power of the intermolecular separation for the Lennard-Jones and quadrupole potentials in both boxes. If the resulting changes in energy in the two boxes are ΔE^I and ΔE^{II} , the move is accepted with a probability,

$$\mathcal{P}_{\text{vol}} = \min \left(1, \exp \left(-\beta \left[\Delta E^I + \Delta E^{II} - N^I kT \ln \frac{V^I + \Delta V}{V^I} - N^{II} kT \ln \frac{V^{II} - \Delta V}{V^{II}} \right] \right) \right) \quad (2)$$

In the molecular transfer move for the quadrupolar mixture, we first decided at random, but with equal probability, which of the two species is to be moved. Since the two components have equal size, this results in approximately the same percentage of successful transfers for the two species. We then decided at random with equal probability the direction of the transfer, either from box I to box II, or from box II to box I. A test molecule of the species chosen was then inserted into the receiving box. A random position and a random orientation were chosen for the molecule. The energy of the test particle, ΔE^I if the transfer originates in region II, was calculated and if it was less than a cutoff value (set equal to $100 kT$) a molecule of the same species was chosen at random from the box which was to provide the molecule for transfer. The real particle interaction-energy of this molecule was determined, δE^{II} , unless there were no molecules of this species in the box. In this situation the existing configuration was counted as the new one, and the next Monte Carlo trial move attempted. The transfer move was accepted or rejected with a probability,

$$\mathcal{P}_{\text{transfer}} = \min \left(1, \exp \left(-\beta \left[\Delta E^I + \Delta E^{II} + kT \ln \frac{V^{II}(N^I + 1)}{V^I N^{II}} \right] \right) \right) \quad (3)$$

A number of transfers were attempted starting from the same configuration of the fluid. The number was selected so as to result in at least a few thousand accepted transfers for any given run. Thus, a much larger number of attempted transfers were required for the runs at lower temperatures with higher coexisting liquid densities. The number of attempted transfers and the percentage of successful transfers for all simulations performed are given in the Appendix.

Following [4] we used the test particle interaction energies, E_t , calculated during the transfer steps and the Widom test particle expression,

$$\beta\mu_{i,r} = -\ln \langle \exp(-\beta E_i^r) \rangle \quad (4)$$

to obtain estimates for the residual chemical potential, $\mu_{i,r}$, of the components in the two phases. Equation 4 is exactly valid only in the canonical ensemble, and is only an approximation for the Gibbs ensemble.

3 RESULTS

3.1 Pure fluids

In Table 1 we present the results of the simulations of the pure quadrupolar fluids. The run numbers refer to Table 5 in the Appendix where we have set out a complete description of the initial conditions of all the simulations performed. All thermodynamic properties in the tables are given in reduced units. In the liquid and vapour phases we calculated the density $\varrho^* = \varrho\sigma^3$, the pressure, $P^* = P\sigma^3/\varepsilon$, the excess internal energy, $E^* = E/\varepsilon$, and the chemical potential, $\mu^* = \mu/\varepsilon = (\mu_r/\varepsilon + T^*\ln\varrho^*)$. The associated error reported with each result is the standard deviation of averages calculated over 100-cycle blocks during the production phase of the simulation. No error estimates are reported for the chemical potential because Equation (4) was applied in integrated form for the results of the full production phase of a simulation. From the results for the chemical potentials in Table 1, it would appear that significant uncertainties remain in the estimated values for the vapour densities and saturated pressures. However, this is a result of using the (inexact) Equation (4) to estimate the chemical potentials. The internal consistency and agreement with independent calculations indicate that the error estimates of the coexistence pressure and vapour densities (of the order of 5%) are realistic. Simulations performed at the same state conditions, but starting from different initial conditions or with a different number of attempted transfers per cycle converged to the same averages within the error limits.

Figure 1 shows the coexistence curves for the $Q^* = 1$ and $Q^* = \sqrt{2}$ quadrupolar fluids obtained in this work, and the coexistence curve for the pure Lennard-Jones fluid from the Gibbs ensemble simulations reported in [1]. Also shown on Figure 1 are the predicted coexistence curves from perturbation theory [6], using an argon [13] and Lennard-Jones equation of state [14] for the calculation of the properties of the reference fluid. The choice of the reference fluid equation of state is quite important. The argon equation of state does not give a perfect description of the properties of the pure Lennard-Jones fluid because the intermolecular potential of argon is different from the Lennard-Jones potential. The Lennard-Jones equation of state [14], although obtained from computer simulation results for this fluid, was not fitted to the coexistence properties of the Lennard-Jones fluid and gives a higher critical temperature than the one obtained from recent Gibbs ensemble simulations.

We have also plotted the umbrella-sampling Monte Carlo simulation results of Shing and Gubbins [11] for the coexistence curve of the $Q^* = \sqrt{2}$ quadrupolar fluid. As the magnitude of the quadrupole moment is increased from $Q^* = 0$ to 1 to $\sqrt{2}$ the reduced critical temperature, T_c^* , of the fluid increases. We have estimated the reduced critical density, ϱ_c^* , of the fluids using the law of rectilinear diameters and have found that ϱ_c^* is approximately constant with increasing quadrupole moment. The estimates for T_c^* and ϱ_c^* are given in Table 2. There is excellent agreement between our results and those of Shing and Gubbins for the $Q^* = \sqrt{2}$ fluid over the tem-

Table 1 Results for phase coexistence properties of pure quadrupolar fluids†.

Run	T^*	$(Q^*)^2$	q_L^*	P_L^*	$-E_L^*$	$-\mu_L^*$	q_V^*	P_V^*	$-E_V^*$	$-\mu_V^*$
1	1.168	1.0	0.820 (08)	-0.01 (04)	8.11 (09)	4.79	0.0160 (011)	0.0169 (011)	0.25 (02)	5.10
2	1.168	1.0	0.815 (08)	0.03 (03)	8.07 (10)	4.97	0.0126 (013)	0.0158 (013)	0.19 (02)	5.19
3	1.168	1.0	0.816 (10)	-0.01 (04)	8.06 (12)	4.99	0.0148 (007)	0.0157 (007)	0.23 (01)	5.14
4	1.335	1.0	0.731 (09)	0.05 (02)	6.95 (10)	4.67	0.0453 (040)	0.0479 (036)	0.76 (05)	4.70
5	1.335	1.0	0.724 (12)	0.03 (03)	6.84 (13)	4.78	0.0402 (016)	0.0440 (013)	0.52 (02)	4.78
6	1.502	1.0	0.613 (10)	0.12 (02)	5.64 (11)	4.37	0.1153 (144)	0.1065 (066)	1.30 (17)	4.40
7	1.502	1.0	0.615 (18)	0.12 (02)	5.65 (17)	4.42	0.1217 (039)	0.1108 (039)	1.39 (04)	4.37
8	1.502	1.0	0.610 (17)	0.11 (04)	5.62 (15)	4.38	0.1071 (072)	0.1046 (039)	1.22 (07)	4.45
9	1.502	1.0	0.612 (14)	0.12 (04)	5.62 (13)	4.44	0.1083 (031)	0.1030 (040)	1.25 (04)	4.44
10	1.530	1.0	0.593 (17)	0.13 (04)	5.44 (13)	4.55	0.1569 (055)	0.1259 (073)	1.71 (06)	4.35
11	1.550	1.0	0.576 (22)	0.14 (03)	5.24 (20)	4.48	0.1464 (062)	0.1304 (077)	1.61 (09)	4.34
12	1.580	1.0	0.424 (66)	0.14 (02)	3.99 (53)	4.67	0.1535 (298)	0.1357 (107)	1.62 (31)	4.43
13	1.800	2.0	0.845 (10)	0.04 (08)	12.18 (20)	7.25	0.0275 (012)	0.0424 (021)	0.68 (04)	7.01
14	1.900	2.0	0.804 (12)	0.09 (07)	11.38 (20)	6.16	0.0518 (038)	0.0754 (052)	1.18 (12)	6.51
15	2.000	2.0	0.715 (14)	0.08 (03)	9.98 (20)	6.35	0.0577 (025)	0.0903 (043)	1.20 (06)	6.67
16	2.000	2.0	0.740 (14)	0.09 (05)	10.34 (20)	6.20	0.0601 (014)	0.0909 (018)	1.25 (05)	6.57
17	2.100	2.0	0.675 (22)	0.15 (05)	9.27 (32)	5.82	0.1005 (040)	0.1445 (044)	1.86 (08)	6.27
18	2.200	2.0	0.414 (81)	0.20 (02)	6.02 (95)	5.86	0.1606 (198)	0.1977 (109)	2.74 (35)	6.01
19†	2.200	2.0	0.445	0.21	6.35	5.99	0.1828	0.2014	3.17	5.94

† No error estimates are available for this simulation.

‡ All thermodynamic quantities are given in reduced units. The numbers in parentheses indicate the uncertainty in units of the last decimal digit: 0.820 (08) means 0.820 ± 0.008 .

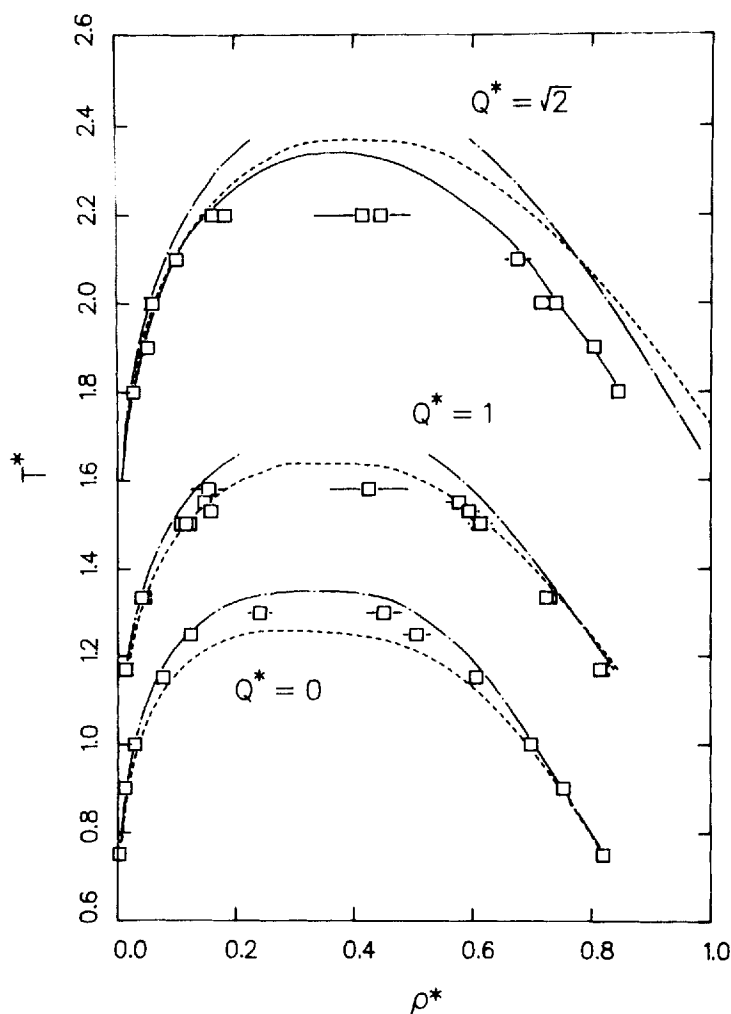


Figure 1 Vapor-liquid coexistence curve for three Lennard-Jones quadrupolar pure fluids. (\square) Gibbs ensemble simulation results from this work ($Q^* = 1$ and $\sqrt{2}$) and [1] ($Q^* = 0$), where $Q^* = Q/(\epsilon\sigma^5)^{1/2}$. (—) umbrella-sampling Monte Carlo results from [11]. (---) and (-.-.-) thermodynamic perturbation theory results using, respectively, the argon [13] and Lennard-Jones [14] equations of state for the reference fluid properties.

perature range $T^* = 1.8$ to $T^* = 2.1$. Their simulations were performed for two different system sizes, 108 and 32 molecules. In their paper the critical temperature estimated from the results of the 108-molecule simulations is significantly lower than that from the 32-molecule simulations. Following this trend, our estimate for T_c^* (using 500 molecules) is lower than their estimate with 108 molecules. As discussed in the Appendix, system size has a negligible effect on the Gibbs simulations reported here, and therefore the critical parameters given in Table 2 should be close to the infinite-system size limit.

Table 2 Critical densities and temperatures of the LJQ fluids.

Q^*	ρ_c^*	T_c^*	Source
0.0	0.31 ± 0.02	1.33 ± 0.02	[1]
1.0	0.34 ± 0.02	1.60 ± 0.03	This work
$\sqrt{2.0}$	0.34 ± 0.02	2.24 ± 0.04	This work

Thermodynamic perturbation theory using either reference fluid equation of state predicts liquid densities which are greater than the simulation results for the quadrupolar fluids, although both predict the coexistence properties of the pure Lennard-Jones fluid away from the critical point in good agreement with simulation results. The Lennard-Jones equation of state predicts a critical temperature for the pure Lennard-Jones fluid which is too high, and used in conjunction with the perturbation theory also predicts critical temperatures for the quadrupolar fluids which are significantly higher than our simulation estimates.

In Figure 2, the coexistence pressure is plotted versus inverse temperature. The simulation results lie close to the approximately straight lines predicted by the perturbation theory. Shing and Gubbins [11] used an umbrella sampling method to obtain the free energy over a range of temperatures, and therefore could not calculate the coexisting pressures. These pressures are calculated directly in the Gibbs simulation technique used here.

3.2 Mixtures

In Table 3 we present the simulation results for the phase coexistence properties of the $Q_1^* = +1$, $Q_2^* = -1$ quadrupolar fluid mixture at three reduced temperatures, $T^* = 1.168, 1.335$ and 1.502 (140, 160 and 180 K if the potential parameters for Ar, $\epsilon/k = 119.8$, $\sigma = 3.405$ Å are used for reference, as in [6]). The potential parameters ϵ and σ for the Lennard-Jones part of the potential were identical for the two components. At each temperature we performed simulations at three different mole fractions. Since the mixture is symmetric, only concentrations less than 0.5 need to be considered. The values of $\rho^* = \rho\sigma^3$, $P^* = P\sigma^3/\epsilon$ and $E^* = E/\epsilon$ are again reported for both phases, and also the chemical potential $\mu^* = (\mu_i/\epsilon + T^* \ln \rho^*)$ of the two components in each phase. The conditions for phase equilibrium are satisfied to good accuracy for the two higher temperatures.

For the three runs at the lowest temperature, $T^* = 1.168$, the difference between the chemical potentials of the two components in the two phases, as calculated by Widom's test particle method, differ on the average by 0.62, with the liquid-phase chemical potentials having systematically higher values. Previous calculations of the chemical potential in dense quadrupolar fluids [12] have resulted in uncertainties of similar magnitudes for the calculated chemical potentials when Widom's method is used. However, we believe that the results for the compositions and vapour-phase densities reported here are significantly more accurate than this difference would imply. This is based on the following observations: (a) control plots of the density, energy, pressure and number of molecules of each species in the two regions converge to stable values, independent of the initial conditions for all simulations reported here; (b) simulation results for the compositions of the coexisting phases at different overall mixture compositions are mutually consistent and in good agreement with pertur-

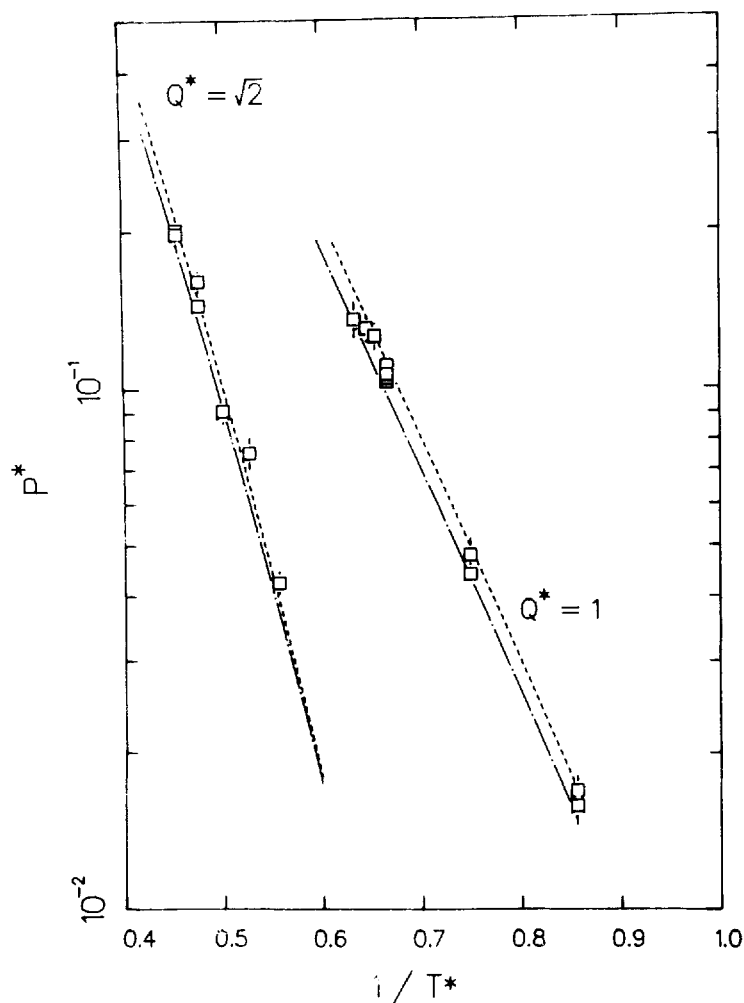


Figure 2 Reduced vapour pressure, $P^* = P\sigma^3/\epsilon$, versus the inverse of the reduced temperature, $1/T^*$, where $T^* = kT/\epsilon$, for pure quadrupolar fluids. Symbols are the same as for Figure 1.

bation theory calculations. Since both the Gibbs-ensemble simulations and Widom's test particle method calculations rely on insertions of particles at random positions, an interesting question is why the Gibbs simulations appear to converge faster than the calculation of the chemical potentials using Widom's method. A possibility is that the Gibbs technique uses both test- and real-particle interaction energies, in a similar way to the combined f - g sampling method [15]. Indeed, a recalculation of the results for the chemical potentials at the lower temperature using the f - g sampling technique resulted in an average deviation of only 0.29 between liquid- and gas-phase chemical potentials, as shown in Table 4, supporting our contention that the Gibbs simulation results are at equilibrium. We also performed two simulations in the constant- NVT

Table 3 Results for phase coexistence properties of $Q^*_l = +1$ $Q^*_l = -1$ quadrupolar fluid mixture †.

Run	T^*	$X_{l,L}$	ρ_L^*	P_L^*	$-E_L^*$	$-\mu_{L,L}^*$	$X_{l,V}$	ρ_V^*	P_V^*	$-E_V^*$	$-\mu_{l,V}^*$	$-\mu_{L,V}^*$
20	1.168	0.116 (5)	0.828 (08)	0.00 (4)	8.41 (09)	7.56	0.074 (09)	0.0153 (07)	0.0157 (08)	0.24 (02)	8.25	5.22
21	1.168	0.214 (4)	0.834 (06)	0.02 (5)	8.61 (08)	8.18	0.158 (15)	0.0131 (07)	0.0141 (08)	0.21 (01)	7.51	5.47
22	1.168	0.500 (8)	0.838 (05)	0.01 (4)	8.82 (07)	5.43	0.499 (26)	0.0126 (06)	0.0135 (06)	0.22 (01)	6.11	6.09
23	1.335	0.112 (4)	0.735 (15)	0.05 (5)	7.17 (17)	8.04	0.080 (07)	0.0379 (12)	0.0419 (14)	0.51 (03)	8.28	4.93
24	1.335	0.216 (6)	0.745 (09)	0.04 (3)	7.35 (10)	6.97	0.163 (12)	0.0390 (31)	0.0426 (29)	0.53 (05)	7.28	5.05
25	1.335	0.499 (6)	0.748 (08)	0.05 (3)	7.53 (09)	5.65	0.502 (21)	0.0312 (24)	0.0355 (25)	0.45 (04)	5.95	5.96
26	1.335	0.502 (7)	0.746 (04)	0.02 (3)	7.52 (18)	5.60	0.495 (20)	0.0341 (34)	0.0382 (29)	0.49 (04)	5.86	5.81
27	1.502	0.103 (3)	0.619 (08)	0.10 (3)	5.80 (07)	7.87	0.094 (07)	0.0932 (98)	0.0960 (70)	1.09 (11)	8.17	4.67
28	1.502	0.205 (5)	0.618 (19)	0.10 (2)	5.89 (16)	6.89	0.187 (12)	0.0964 (64)	0.0974 (56)	1.13 (07)	7.09	4.84
29	1.502	0.503 (8)	0.642 (17)	0.12 (2)	6.20 (15)	5.49	0.493 (23)	0.0940 (73)	0.0945 (48)	1.14 (10)	5.61	5.56

† See footnote to Table 1 for the notation used for the errors.

Table 4 Chemical potentials calculated using the *f-g* sampling technique.

<i>Run</i>	T^*	$-\mu_{1,L}^*$	$-\mu_{2,L}^*$	$-\mu_{1,V}^*$	$-\mu_{2,V}^*$
20	1.168	7.87	5.25	8.19	5.27
21	1.168	6.97	5.24	7.45	5.53
22	1.168	5.75	5.89	6.15	6.14

ensemble at the coexisting densities predicted by the Gibbs simulation 21. The Widom test particle expression, Equation (4), is exact in these simulations. However, we still observe an average deviation between liquid- and gas-phase chemical potentials of 0.36. The results of these simulations are given in the Appendix. It should be emphasized that the chemical potentials are not used in the course of the simulation. The evolution of the simulations according to the transition probability Equations (1–3) are exact for the Gibbs ensemble, and the chemical potentials are only calculated to check for possible large deviations from equilibrium.

In Figure 3 pressure versus mole fraction curves are shown for the quadrupolar mixture at three reduced temperatures. We have again included the results from perturbation theory for comparison. We observe a weak negative azeotrope for these mixtures of two quadrupolar fluids of opposite sign at $T = 140$ K, as observed experimentally in the $\text{CO}_2/\text{C}_2\text{H}_2$ mixture. The errors in the pressures at the other temperatures make it difficult to be certain of the form of the P-x projection. The agreement between the Gibbs simulations and the Lennard-Jones equation of state is close to our error estimates for all three temperatures. As the temperature is increased the results from the argon equation of state overestimate the pressures to a larger degree. It should be emphasized that the calculations using the constant- NVT Gibbs method are possible despite the very narrow pressure-composition phase envelope for this mixture, because in density-composition space the two-phase region is sufficiently extensive to permit initiation of the Gibbs simulation within that region. The uncertainties in the coexistence pressures (calculated from the gas phase) are a few percent of the total pressure, and thus allow the observation of a weak negative azeotrope.

Figure 4 shows the liquid densities of the mixtures as a function of mole fraction. The perturbation theory again fails in its prediction of the coexisting liquid densities. Both the Lennard-Jones and argon equation of state versions of the perturbation expansion produce densities which are significantly higher than the Gibbs simulation results. This is consistent with the trends observed for the pure quadrupolar fluids.

4 CONCLUSIONS

We have demonstrated that the Gibbs method can be applied for the calculation of phase equilibria for fluids that interact with strong orientationally-dependent forces. The simulations are successful even when coexisting liquid densities are as high as $\rho^* = 0.83$. Concentrations and densities for the coexisting phases are predicted with accuracies higher than those possible when the Widom test-particle method is used for the determination of the chemical potentials. Comparisons between the Gibbs-ensemble simulation results for pure quadrupolar fluids and corresponding results using extensive umbrella-sampling calculations for the determination of free energies illu-

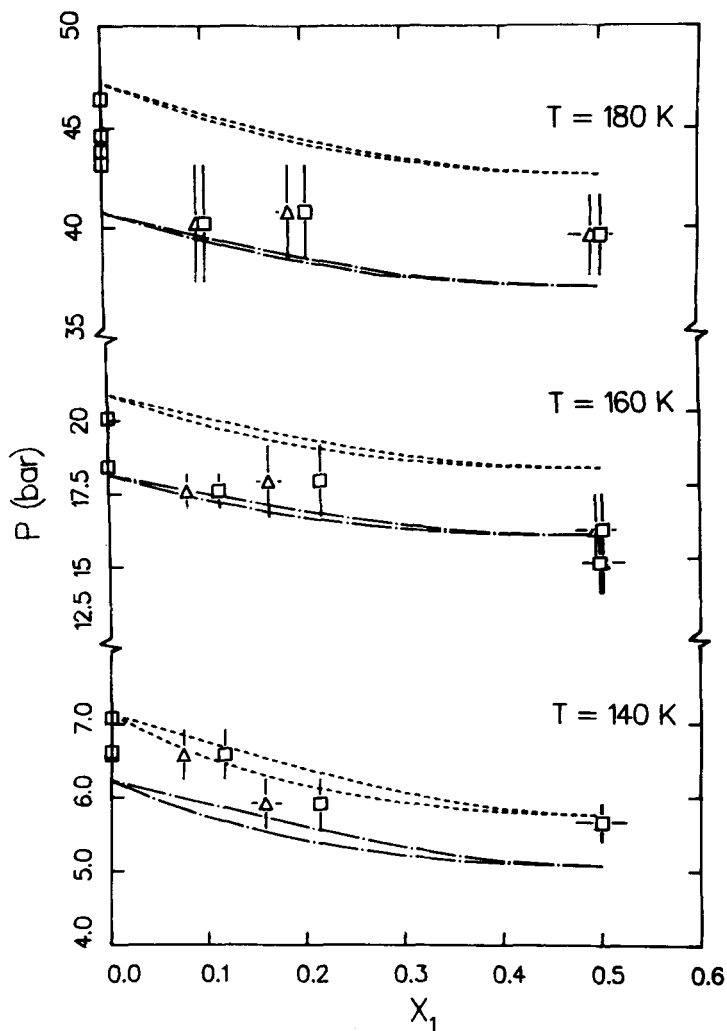


Figure 3 Pressure, P , versus mole fraction of component 1, X_1 , for the LJQ mixture with $Q_1^* = +1$, $Q_2^* = -1$ at three temperatures, where $Q^* = Q/(\epsilon\sigma^3)^{1/2}$. The potential parameters for Ar, $\epsilon/k = 119.8\text{ K}$ and $\sigma = 3.405\text{ \AA}$ are used to obtain values for T and P from the calculated reduced values. (Δ) Gibbs ensemble simulation results for the vapour phase, (\square) Gibbs ensemble simulation results for the liquid phase, (----) and (-.-.-) thermodynamic perturbation theory results using, respectively, the argon [13] and Lennard-Jones [14] equations of state for the reference fluid properties.

strate some of the advantages of the Gibbs technique: far fewer simulations are required and the thermodynamic properties for the coexisting phases are obtained in the course of a single simulation.

Comparison of the simulation results with thermodynamic perturbation theory calculations using a Padé approximant for the free energy illustrate some of the

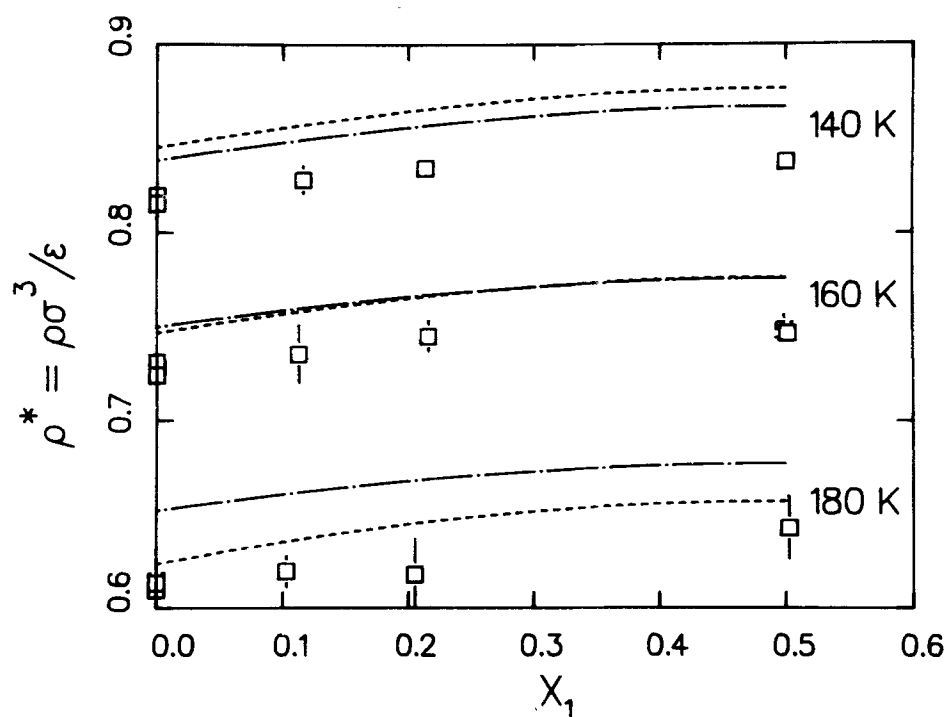


Figure 4 Reduced coexisting liquid density, $\rho^* = \rho\sigma^3/\epsilon$, versus mole fraction of component 1, X_1 , for the LJQ mixture with $Q_1^* = +1$, $Q_2^* = -1$ at three temperatures, where $Q^* = Q/(\epsilon\sigma^5)^{1/2}$. The potential parameter for Ar, $\epsilon/k = 119.8$ K was used to obtain T from the reduced temperature. Symbols are as in Figure 1.

strengths and limitations of existing theoretical techniques and reference fluid equations of state. For the particular form of perturbation theory used, the pressures and compositions of the coexisting phases are predicted accurately, but coexisting liquid densities are not. The deviations between theory and simulation increase as the quadrupole strength increases.

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APPENIX

1 Potential Model

The potential model used in this work consisted of the Lennard-Jones 12-6 potential and an embedded central quadrupole-quadrupole interaction given by [16],

$$E_{ij} = \frac{3Q_i Q_j}{4R_{ij}^5} [1 - 5c_i^2 - 5c_j^2 - 15c_i^2 c_j^2 + 2(c_{ij} - 5c_i c_j)^2] \quad (5)$$

Q_i is the quadrupole moment on the i^{th} molecule, R_{ij} is the distance between molecules i and j and,

$$c_i = \hat{e}_i \cdot \hat{R}_{ij},$$

$$c_j = \hat{e}_j \cdot \hat{R}_{ij},$$

$$c_{ij} = \hat{e}_i \cdot \hat{e}_j.$$

\hat{R}_{ij} is a unit vector pointing from molecule j to molecule i and \hat{e}_i and \hat{e}_j are unit vectors along the molecular axes.

2 Technical details of the simulations

The initial densities of the two regions were chosen from the results of a series of trial simulations which we performed to determine the approximate form of the vapour-liquid coexistence curves under investigation. The initial positions of the molecules in a particular region were chosen at random on a face centered cubic (FCC) lattice. The quadrupole vector \hat{e} of the first molecule was set at $(1/\sqrt{3}, 1/\sqrt{3}, 1/\sqrt{3})$ and then given a random rotation about a randomly chosen axis, using procedures described in [17]. The initial vector of a molecule i was chosen by performing the same procedure on the $(i-1)^{\text{th}}$ vector. In this way the initial configuration for a simulation consisted of a specified number of molecules placed on an FCC lattice with random orientations.

A spherical cutoff equal to half the box length was applied in both regions. Long range corrections to the energy and pressure were taken into account by integrating the potential and the virial respectively from the cutoff to infinity, setting $g(r) = 1.0$. The minimum cutoff distance used in this work was $R_c \sim 3.5\sigma$. The range of the correlations due to the orientations of the molecules is of the same order as the range of positional correlations in the fluid [7]. The integral over all orientations and positions from R_c to infinity for the quadrupolar interaction is therefore zero.

The simulations were performed in cycles. A cycle is defined as a single trial rotation-displacement move for each of the N molecules, followed by one attempted volume change and N_{TRANS} attempted transfers of a molecule from one region to the other. In the rotation-displacement move a trial position and orientation were chosen for a molecule. The trial position was sampled randomly from a uniform distribution. A parameter in the program controlled the maximum displacement of a molecule. The trial orientation was chosen by the same method used to set up the initial orientations. Another parameter limited the maximum random rotation about the chosen axis. From the results of our trial simulations was found that if we attempted to accept 50% of the rotation-displacement moves in the liquid phase, by varying both the maximum displacement and maximum rotation parameters simultaneously, the rotation part of the move dominated and the maximum displacement fell to small values. Convergence of the simulations was slow. To solve this problem without

Table 5 Technical details of simulations performed.

Run	Initial conditions						N_{EQ}	N_{PROD}	N_{TRANS}	% Acceptance
	$N_{1,L}$	$N_{2,L}$	$N_{1,V}$	$N_{2,V}$	ϱ_L^*	ϱ_V^*				
1	175	175	75	75	0.850	0.030	2000	1100	1000	0.15
2	70	280	30	120	0.820	0.020	2000	3000	1000	0.17
3	175	175	75	75	0.820	0.020	2000	3000	1000	0.17
4	175	175	75	75	0.750	0.060	2000	2000	500	0.80
5	70	280	30	120	0.730	0.040	1000	3000	400	0.86
6	175	175	75	75	0.610	0.110	1000	3000	150	2.8
7	350	350	150	150	0.610	0.110	1000	3000	150	2.6
8	70	280	30	120	0.610	0.110	1000	3000	150	3.0
9	175	175	75	75	0.940	0.050	2000	2000	300	2.9
10	175	175	75	75	0.550	0.150	2000	2000	30	3.0
11	175	175	75	75	0.600	0.100	2000	2000	30	3.7
12	150	150	100	100	0.570	0.150	2000	2000	30	9.9
13	175	175	75	75	0.850	0.030	2000	1000	1000	0.43
14	175	175	75	75	0.740	0.060	2000	2000	150	0.51
15	175	175	75	75	1.050	0.040	2000	2000	150	1.5
16	175	175	75	75	1.050	0.040	2000	2000	150	1.1
17	175	175	75	75	0.670	0.090	2000	2000	150	2.2
18	150	150	100	100	0.580	0.012	2000	2000	50	9.9
19	150	150	100	100	0.580	0.012	2000	2000	50	7.6
20	35	315	15	135	0.960	0.010	2000	2000	1000	0.14
21	70	280	30	120	0.820	0.020	2000	3000	1000	0.13
22	175	175	75	75	0.820	0.020	2000	3000	1000	0.13
23	35	315	15	135	0.850	0.030	2000	2000	500	0.77
24	70	280	30	120	0.730	0.040	1000	3000	400	0.63
25	175	175	75	75	0.730	0.040	1000	3000	400	0.67
26	175	175	75	75	0.730	0.040	2000	2000	500	0.63
27	35	315	15	135	0.550	0.100	2000	3000	100	2.6
28	70	280	30	120	0.610	0.110	1000	3000	150	2.8
29	175	175	75	75	0.610	0.110	1000	3000	150	2.3

separating the displacement and rotation of the molecules into two trial moves, we fixed the maximum rotation parameter in both regions at a typical liquid density value of 0.7 radians and varied the maximum displacement separately in the two regions to accept 30% of the trial moves. The value of the maximum displacement in the liquid region therefore increased and we observed much faster convergence of the simulations. The maximum displacement was updated every 10 cycles during the equilibration period to achieve the desired 30% acceptance and then fixed for the production phase of the simulation. A similar parameter determined the maximum change in the volume during the single attempted volume fluctuation. This parameter was also updated every 10 cycles during the equilibration phase of the simulation to accept 50% of volume fluctuation moves. In the transfer move a completely random orientation was generated using a rejection technique [17]. The position and orientation of the test particle are completely independent of the real particle's position and orientation for each attempted transfer.

In Table 5 we present the technical details of the simulations. For each run the initial numbers of each species in the two boxes, the initial densities and the number of equilibration and production cycles are shown. The number of attempted transfers per cycle, N_{TRANS} , is also given in the table together with the percentage of the total

number of attempted interchanges that were successful during the production phase of the simulation. The proportion of successful transfers is a sensitive function of liquid density.

Most of the simulations reported here were performed on a Cray XMP/48 computer. For 500 molecules and 150 attempted interchanges per cycle, a simulation of 2000 equilibration and 2000 production cycles (run 17) required 1000 CPU seconds. Two simulations, run numbers 16 and 18 were performed on an IBM 3090-600 which was approximately three times slower than the Cray XMP/48 for the program used in this work.

3 Validation and number dependence

The energy and pressure calculations were initially checked by reproducing previous simulation results for LJQ fluids [10]. We also performed two canonical simulations at $T^* = 1.168$ for the quadrupolar mixture at the values for the coexisting densities and mole fractions obtained from run 21. The values of the energies, pressures and chemical potentials calculated in these runs were in good agreement with the Gibbs-ensemble results: $q_L^* = 0.834$, $X_{1,L} = 0.214$, $E_L^* = -8.59$, $P_L^* = 0.01$, $\mu_{1,L}^* = -7.69$, $\mu_{2,L}^* = -5.01$ and $q_V^* = 0.0131$, $X_{1,V} = 0.158$, $E_V^* = -0.21$, $P_V^* = 0.0141$, $\mu_{1,V}^* = -7.42$, $\mu_{2,V}^* = -5.46$. One simulation was performed with twice the number of molecules, $N = 1000$, to check for system size effects. As shown in Table 1, the results of runs 6 and 7 which were performed with different numbers of molecules at the same conditions, agree within the error limits quoted.

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