EXACT CALCULATION OF THE EFFECT OF THREE-BODY AXILROD-TELLER INTERACTIONS ON VAPOUR-LIQUID PHASE COEXISTENCE

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ABSTRACT

The Gibbs ensemble algorithm is implemented to determine the vapour-liquid phase coexistence of a pure fluid interacting via a two-body Lennard-Jones + three-body Axilrod-Teller potential. The contribution of both two-body and three-body interactions are calculated exactly. The results are compared with both experiment and two-body only simulation data. The position of the vapour branch of the coexistence curve is almost unaffected by the inclusion of three-body interactions. In contrast, the liquid branch occurs at substantially lower densities compared with Lennard-Jones simulation data. However, the approach to the critical point is improved by including three-body interactions, and the estimated critical point is in good agreement with experiment.

INTRODUCTION

The phase equilibria exhibited by fluids is the direct consequence of intermolecular interactions. Historically, theories of liquids have almost invariably assumed that intermolecular interaction is limited to pairs of molecules. Consequently, calculations of phase coexistence (Sadus, 1992) typically ignore the contributions of three- or more-body interactions. The available evidence (Barker et al., 1971; Monson et al., 1983; Rittger, 1990a-c; Elrod and Saykally, 1994) suggests that the effect of three-body interactions may be important in some circumstances. However, the role of three-body interactions on phase equilibria is unclear. The few studies (Smit et al., 1992; Miyano, 1994) which have attempted to include three-body interactions have relied on various approximation procedures rather than rigorous calculation. Recently, simulations have been reported (Sadus and Prausnitz, 1996; Sadus, 1996) which estimate the contribution of three-body effects via periodic calculation of three-body interactions. Although these approximations can provide a valuable insight into the relative magnitude of three-body interactions, an exact calculation is required to determine their effect on phase coexistence.

In this work, the Gibbs ensemble (Panagiotopoulos et al., 1988) is used to calculate the vapour-liquid phase coexistence of a fluid interacting via a Lennard-Jones + Axilrod-Teller intermolecular potential. Unlike earlier work, the calculation of three-body interactions is exact. Both two- and three-body interactions contribute to the acceptance criterion of each and every attempted Monte Carlo move. Therefore, the coexistence properties of the fluid are the outcome of both the two- and three-body interactions. The results are compared with both experimental data and two-body only simulation data.
**THEORY**

**Intermolecular Potential**

The intermolecular potential \( u \) is the sum of contributions from two-body interactions \( u_{ij} \) and three-body dispersion interactions \( u_{ijk} \), i.e.,

\[
u = u_{ij} + u_{disp}^{\text{ijk}}
\]

The Lennard-Jones potential was used to calculate interactions between pairs of molecules separated by a distance \( r_{ij} \)

\[
u_{ij} = 4\varepsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right]
\]

where the \( \varepsilon \) and \( \sigma \) parameters are characteristic of the strength of intermolecular interaction and molecular size, respectively. For argon, \( \varepsilon/k = 119.8 \) K and \( \sigma = 0.341 \) nm.

The Axilrod-Teller term (Axilrod and Teller, 1943) accounts for the contribution of three-body dispersion interactions

\[
u_{disp}^{\text{ijk}} = \frac{\nu \left(1 + 3\cos\theta_i \cos\theta_j \cos\theta_k\right)}{r_{ij} r_{ik} r_{jk}^3}
\]

where \( \theta \) refers to the inside angles of a triangle (see Fig. 1) formed by three molecules \( i, j \) and \( k \), and \( \nu \) is the non-additive coefficient. This potential is negative for near-linear configurations and positive for acute triangular arrangements. Accurate values of the nonadditive coefficient are available (Leonard and Barker, 1975) for all the noble gases. For argon, \( \nu = 7.3382 \times 10^{-90} \) J cm

**Simulation Details**

The NVT-Gibbs ensemble (Panagiotopolous et al., 1988) was used to simulate the coexistence of liquid and vapour phases. A total of 50 molecules were partitioned between two boxes to simulate the vapour and liquid phases. The temperature of the entire system was held constant and surface effects were avoided by placing each box at the centre of a periodic array of identical boxes. Equilibrium was achieved by attempting molecular displacements (for internal

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Fig. 1. Triplet configuration of atoms \( i, j \) and \( k \) in Eq. (3).
equilibrium), volume fluctuations (for mechanical equilibrium) and particle interchanges between the boxes (for material equilibrium).

The simulations were performed in cycles with each cycle typically consisting of 50 attempted displacements, a single volume fluctuation, and 150 interchange attempts. The maximum molecular displacement and volume changes were adjusted to obtain, where possible, a 50% acceptance rate for the attempted move. The number of attempted particle interchanges depends on the achievement of a satisfactory acceptance rate (5-10%). Ensemble averages were accumulated only after the system had reached equilibrium. The equilibration period was 10000 cycles and a further 10000 cycles were used to accumulate the averages. The calculations were truncated at intermolecular separations greater than half the box length, and appropriate long-range corrections (Allen and Tildesley, 1987) were used to obtain the full contribution of pair interactions to energy and pressure. The full (untruncated) three-body potential was calculated to avoid uncertainties that arise when calculating three-body long-range corrections from unknown pair-distribution functions. Alternative computational approaches for long-range corrections are available (Rittger, 1992).

The contributions of both two-body and three-body interactions to the configurational energy of the fluid were recalculated for each attempted move and the configurational properties were updated after each successful move. Therefore, changes to both two-body and three-body interactions contributed to the acceptance criterion and the predicted phase coexistence curve is the result of two-body and three-body forces. A typical run required 8 CPU hours on a Cray YMP-EL.

RESULTS AND DISCUSSION

The vapour-liquid coexistence data obtained from molecular simulation are summarised in Table 1. The normal convention was adopted for the reduced density ($\varrho^* = \varrho \sigma^3$), temperature ($T^* = kT/\varepsilon$), energy ($E^* = E/\varepsilon$), chemical potential ($\mu^* = \mu/\varepsilon$) and pressure ($P^* = P\sigma^3/\varepsilon$). The chemical potential was calculated using the formula proposed by Smit and Frenkel (1989).

<table>
<thead>
<tr>
<th>$T^*$</th>
<th>$\varrho^*$</th>
<th>$P^*$</th>
<th>$P^*_{LJ}$</th>
<th>$P^*_{AT}$</th>
<th>$E^*$</th>
<th>$E^*_{LJ}$</th>
<th>$E^*_{AT}$</th>
<th>$\mu^*$</th>
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<td>0.033(8)</td>
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<td>0.00016(8)</td>
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<td>0.016(4)</td>
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<table>
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†Values in parentheses indicate the uncertainty in the last digit.
Exact calculations of three-body interactions in fluids are rare because of the very large increase in computation required compared with two-body calculations. Typically, two-body Gibbs ensemble simulations are reported with between three to five hundred molecules. However, to feasibly conduct three-body calculations, we have limited the simulations to fifty molecules. The accuracy of the Gibbs ensemble is remarkably insensitive to the number of molecules and the main limitation of using such a small number of molecules is that it is difficult to obtain reliable data at high temperatures, particularly near the critical point, where there is a high probability of interchange between the phases.

The Axilrod-Teller potential only represents the contribution of instantaneous dipoles to three-body interactions. Other higher multipole terms can also contribute to three-body interactions but their effect is generally negligible (Rittger, 1990b; Elrod and Saykally, 1994). Consequently, the triple-dipole term as represented by the Axilrod-Teller potential, is likely to be a good representation of three-body dispersion interactions. Earlier work (Sadus, 1996; Sadus and Prausnitz, 1996) indicated that Axilrod-Teller interactions typically contribute 5% to the energy of the liquid phase whereas their contribution to the vapour phase is negligible. The data in Table 1 support this conclusion with Axilrod-Teller interactions contributing typically 4% to the overall energy of the fluid. A comparison of the contribution of Axilrod-Teller interaction to the energy of the liquid with the approximate calculations of Sadus and Prausnitz (1996) is illustrated in Fig. 2. The difference between the approximate results and the exact values is well within the statistical uncertainties in the simulations.

Fig. 2. Comparison of the contribution of Axilrod-Teller interaction to energy of the liquid phase reported here (○) with the approximate calculations of Sadus and Prausnitz (1996) (●). The approximate contribution of 3-body repulsion reported by Sadus and Prausnitz (1996) is also illustrated (■).
What effect does the relatively small contribution from three-body interactions have on vapour-liquid phase coexistence? Figure 3 compares the experimental (Vargaftik, 1975) vapour-liquid phase coexistence envelope of argon with simulations using the Lennard-Jones + Axilrod-Teller potential and the Lennard-Jones potential. The vapour branch of the coexistence curve is generally unaffected by three-body interactions. In contrast, the coexisting liquid phase of the Lennard-Jones + Axilrod-Teller fluid occurs at considerably lower densities than the liquid phase of the Lennard-Jones fluid. Overall, three-body interactions reduce the range of vapour-liquid coexistence.

![Graph](image)

Fig. 3. Comparison of the experimental (•) vapour-liquid coexistence of argon with simulations using the Lennard-Jones (□) and Lennard-Jones + Axilrod-Teller (O) intermolecular potentials. The solid lines indicate the fit obtained from Eqs (4) and (5).

Gibbs ensemble simulations cannot be used to determine directly the critical point. However, the critical temperature (\(T^*_c\)) can be estimated by fitting the data to the following power law.

\[
\rho_i^* - \rho_v^* = C \left| 1 - \frac{T^*_v}{T^*_c} \right|^{0.32}
\]

If the critical temperature is known, the critical density can be estimated from the law of rectilinear diameters.
\[
\frac{\rho^*_v + \rho^*_g}{2} = A(T^* - T^*_c) + B
\] (5)

Fitting the data in Table 1 to the above equations, we find that \(T^*_c = 1.253\) and \(\rho^*_c = 0.290\) for the Lennard-Jones + Axilrod-Teller potential which compare favourably with the experimental values of \(T^*_c = 1.259\) and \(\rho^*_c = 0.32\) for argon. In contrast, analysis of simulation data for the vapour-liquid coexistence of a Lennard-Jones fluid yields \(T^*_c = 1.317\) and \(\rho^*_c = 0.328\).

The comparison in Fig. 3 indicates that the addition of Axilrod-Teller three-body interactions can potentially improve the prediction of vapour-liquid equilibria in the vicinity of the critical point. However, this improvement is at the expense of reduced accuracy for the subcritical liquid phase branch of the coexistence curve. It appears that the Lennard-Jones + Axilrod-Teller potential does not accurately describe intermolecular interaction in the liquid phase. In contrast, the Lennard-Jones potential alone provides an adequate description of vapour-liquid coexistence at low to moderately high temperatures. There is only a small difference in the pressure predicted using the Lennard-Jones + Axilrod-Teller potential compared with results obtained for the Lennard-Jones potential (Fig. 4).

Fig. 4 Comparison of the pressure predicted using the Lennard-Jones (□) and Lennard-Jones + Axilrod-Teller (⊙) intermolecular potentials.
The Axilrod-Teller potential only accounts for attractive dispersion interaction. In reality, repulsive interaction from three-body overlap are also possible. Rittger (1990b) suggested that repulsive overlap could potentially explain inaccuracies in the analysis of some thermodynamic data for xenon. Sherwood et al. (1966) developed a model for electrostatic repulsion experienced by atomic triplets. Sadus and Prausnitz (1996) reported that the contribution to the configurational energy of three-body attraction is substantially offset by contributions from three-body repulsion, as represented by the electrostatic distortion model. The contribution of repulsive interaction, to the configurational energy of argon in the liquid phase is illustrated in Fig. 2. Typically, three-body repulsion can be expected to represent 45% of the contribution of Axilrod-Teller interactions. The failure to account for three-body repulsion is a possible explanation for the inaccuracy of the Lennard-Jones + Axilrod-Teller potential. The comparison of simulation with experimental data supports the hypothesis that three-body repulsion must also be included in any accurate description of three-body interaction. In the absence of a potential which includes both three-body repulsion and attraction, a two-body potential alone is likely to be more accurate.

CONCLUSIONS

Generally, the Lennard-Jones + Axilrod-Teller potential is not a more accurate alternative to the Lennard-Jones potential. This does not imply a failure per se of the Axilrod-Teller potential. Instead, it indicates that the accurate modelling of three-body interactions must also include other aspects of three-body interactions, most notably, three-body repulsion. The effect of three-body repulsion is to largely offset the contribution of Axilrod-Teller interactions. Consequently, in the absence of an accurate description of three-body interactions which include contributions from both repulsion and attraction, a two-body potential is an accurate alternative.

LIST OF SYMBOLS

A fitting parameter in Eq. (5)
B fitting parameter in Eq. (5)
C fitting parameter in Eq. (4)
c critical property
E configurational energy
k Boltzmann’s constant
N number of molecules
P pressure
Pr \( P^*/P^* \)
r intermolecular distance
T temperature
Tr \( T^*/T^* \)
u intermolecular potential

Greek Alphabet

\( \varepsilon \) Lennard-Jones energy parameter
\( \sigma \) Lennard-Jones distance parameter
\( \rho \) number density
\( \rho_r \) \( \rho^*/\rho^*_c \)
\( \theta \) intramolecular angle
\( \mu \) chemical potential
\( \nu \) nonadditive coefficient
Subscripts and Superscripts
* reduced property
AT Axilrod-Teller
disp dispersion
i, j, k molecule i, j or k
LJ Lennard-Jones
l liquid
v vapour

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REFERENCES