

Three-body interactions in fluids from molecular simulation: Vapor–liquid phase coexistence of argon

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Gibbs-ensemble molecular simulations are reported for the vapor–liquid phase coexistence of argon using the two-body Lennard-Jones potential. During the simulation, the possible effect of three-body interactions on the pressure and configurational energy of the vapor and liquid phases is estimated by performing calculations with three-body potentials. The intermolecular potentials used for the three-body calculations incorporate the influence of both three-body-dispersion and three-body-repulsion interactions. The results show that three-body repulsion makes a significant contribution to three-body interactions in the liquid phase. The effect of three-body dispersion is offset substantially by three-body repulsion. © 1996 American Institute of Physics. [S0021-9606(96)51312-5]

I. INTRODUCTION

Fluid-phase transitions are a direct consequence of intermolecular interactions. Historically, however, prediction of vapor–liquid equilibria has relied almost exclusively on approximate theoretical models or on empirical equations of state rather than on rigorous models for intermolecular interaction at high fluid densities. The advent of new molecular simulation techniques¹ such as the Gibbs ensemble method² provides an opportunity to apply directly our knowledge of intermolecular potentials to the prediction of phase equilibria of fluids. The advantage of molecular simulation over other predictive methods is that comparison of simulation results with experimental data provides an unambiguous test for the accuracy of theory, particularly for the intermolecular potential used in the simulation. For a one-component fluid, the only assumption made concerning molecular interactions is the choice of intermolecular potential.

It is commonly assumed that the outcome of molecular interactions can be adequately attributed to the effect of two-body interactions alone. Accurate two-body potentials have been developed³ for some of the noble gases and the influence of three- or more-body interactions has been incorporated as “density effects” in some models.⁴ Consequently, the role of three- or more-body interactions is inadequately documented. Calculations using three-body interactions are typically limited to those based on the triple–dipole dispersion term of Axilrod and Teller;⁵ those calculations commonly contribute 5%–10% of the pairwise additive energy of the liquid phase. These results suggest that pairwise calculations alone cannot fully account for the effects of intermolecular interactions. Several simulation studies⁶ for phase coexistence of both one-component and two-component fluids using pairwise potentials are available but no work on deviations from pairwise additivity has been reported.

The purpose of this work is to examine the role of three-

body interactions on the vapor–liquid coexistence of simple fluids. The Gibbs ensemble² is used to simulate vapor–liquid coexistence for argon and the results are compared with experimental data. Vapor–liquid coexistence is simulated using the conventional Lennard-Jones pairwise potential. However, during the simulation the effect of three-body interactions on the pressure and configurational energy of the fluid is estimated by calculations using three-body potentials. The effect of three-body dispersion interactions are calculated using the Axilrod–Teller term.⁵ The contribution of repulsive three-body interactions is also included using an electrostatic distortion potential developed by Sherwood *et al.*⁷

II. INTERMOLECULAR POTENTIALS AND CALCULATION DETAILS

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

$$u(ij) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right], \quad (1)$$

where the ϵ and σ parameters are characteristic of the strength of intermolecular interaction and molecular size, respectively. The parameters ($\epsilon/k = 119.8$ K, $\sigma = 0.341$ nm) for argon used in this work are not “effective” parameters for dense argon. Instead, they are based on analysis of gas-phase virial coefficient data.⁸ More accurate pair-potentials for argon are available.³ However, the Lennard-Jones potential is simple to implement and it can be used to predict² accurately the coexistence curve of argon with the exception of the near-critical region.

Two contributions to three-body interactions were used in the simulations. The Axilrod–Teller term⁵ accounts for the contribution of three-body-dispersion interactions:

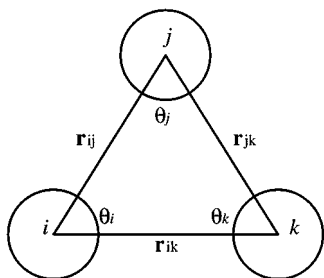


FIG. 1. Triplet configuration of atoms i , j , and k in Eqs. (2) and (3).

$$u^{\text{disp}}(ijk) = \nu \frac{(1 + 3 \cos \theta_i \cos \theta_j \cos \theta_k)}{(r_{ij} r_{ik} r_{jk})^3}, \quad (2)$$

where θ refers to the inside angles of a triangle formed by three molecules i , j , and k (see Fig. 1) and ν is the nonadditive coefficient. This potential is negative for near-linear configurations and positive for acute triangular arrangements. Accurate values of the nonadditive coefficient ν are available⁹ for all of the pure noble gases and many combinations of the noble gases. For argon, $\nu = 7.3382 \times 10^{-90}$ J cm⁹.

Sherwood *et al.*⁷ recognized that three-body repulsions are significant at small interatomic separations. They developed two approximate models for three-body-repulsive interactions at small interatomic separations. Their electrostatic distortion model is particularly suitable for our simulations because both the angle-dependent terms and the pair separations are already evaluated in calculation of the Axilrod–Teller term. For a one-component fluid, we have

$$u^{\text{rep}}(ijk) = \frac{4\epsilon\sigma^{21}}{9} \left[\frac{\cos 2\theta_i}{(r_{ij}r_{ik})^9 r_{jk}^3} + \frac{\cos 2\theta_j}{(r_{ij}r_{jk})^9 r_{ik}^3} + \frac{\cos 2\theta_k}{(r_{ik}r_{jk})^9 r_{ij}^3} \right], \quad (3)$$

where ϵ and σ are the Lennard-Jones parameters. Equation (3) was obtained⁷ by considering the effect of a third body on the repulsion between the pairs of atoms that constitute the triplet illustrated in Fig. 1. The different contributions to Eq. (3) represent the effect of a third atom on the repulsion experienced by the three pairs of atoms. The contribution⁷ of three-body repulsion to the nonadditivity of the third virial coefficient may be equivalent to 45% of the magnitude of the Axilrod–Teller term. The contribution from Eq. (3) was evaluated for each triplet of atoms which had at least one pair-separation $< \sigma$. The total contribution of three-body interactions becomes

$$u(ijk) = u^{\text{disp}}(ijk) + u^{\text{rep}}(ijk). \quad (4)$$

The energy (E) and pressure (P) were evaluated using

$$E = \langle E_2 \rangle + \langle E_3 \rangle, \quad (5)$$

$$E_2 = \sum_i \sum_{j>i} u(ij), \quad (6)$$

$$E_3 = \sum_i \sum_{j>i} \sum_{k>j>i} u(ijk), \quad (7)$$

$$P = kT \langle \rho \rangle + \langle P_2 \rangle + \langle P_3 \rangle, \quad (8)$$

$$P_2 = -\frac{1}{3V} \sum_{i<j} \left(\frac{r_{ij} \partial}{\partial r_{ij}} \right) u(ij), \quad (9)$$

$$P_3 = -\frac{1}{3V} \sum_{i<j<k} \left(\frac{r_{ij} \partial}{\partial r_{ij}} + \frac{r_{ik} \partial}{\partial r_{ik}} + \frac{r_{jk} \partial}{\partial r_{jk}} \right) u(ijk), \quad (10)$$

where T , V , ρ , and k denote temperature, volume, density and the Boltzmann constant, respectively. Subscripts 2 and 3 refer to the contribution of two-body and three-body interactions, respectively, and the angle brackets indicate ensemble averages. The chemical potential was determined during attempted particle interchanges using the formula proposed by Smit *et al.*¹⁰

$$\mu_i = -kT \ln \left\langle \frac{V_I}{N_{I,i} + 1} \exp(-\beta \Delta U_{I_i}) \right\rangle, \quad (11)$$

where ΔU_{I_i} is the configurational energy change of region I during attempted particle transfers, N is the number of particles in the region.

III. SIMULATION DETAILS

The NVT-Gibbs ensemble² was used to simulate the coexistence of liquid and vapor phases. Three-hundred molecules were partitioned between two boxes to simulate the vapor and liquid phases. The temperature of the entire system is held constant and surface effects are avoided by placing each box at the centre of a periodic array of identical boxes. Equilibrium is achieved by attempting molecular displacements (for internal equilibrium), volume fluctuations (for mechanical equilibrium) and particle interchanges between the boxes (for material equilibrium). The Gibbs-ensemble method has recently been reviewed.⁶

The simulations were performed in cycles with each cycle typically consisting of 300 attempted displacements, a single volume fluctuation and 10–2000 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 40 000 cycles (approximately between 20 and 80 million configurations) and a further 40 000 cycles were used to accumulate the averages. The calculations were truncated at intermolecular separations greater than half the box length and appropriate long-range corrections¹ 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. The configurational properties were updated after each successful move.

TABLE I. Gibbs-ensemble simulation of the vapor–liquid phase coexistence of a one-component fluid (argon) using the Lennard-Jones potential.

T^*	Vapor				Liquid			
	ρ^*	P^*	E^*	μ^*	ρ^*	P^*	E^*	μ^*
1.25	0.128±0.015	0.096±0.005	-1.01±0.13	-3.64	0.507±0.014	0.096±0.007	-3.48±0.09	-3.69
1.20	0.099±0.020	0.077±0.008	-0.83±0.17	-3.67	0.560±0.017	0.081±0.017	-3.84±0.10	-3.66
1.15	0.081±0.005	0.064±0.003	-0.70±0.04	-3.66	0.612±0.012	0.067±0.012	-4.21±0.09	-3.64
1.10	0.057±0.002	0.047±0.001	-0.50±0.03	-3.72	0.641±0.005	0.055±0.016	-4.42±0.03	-3.72
1.05	0.041±0.003	0.035±0.002	-0.39±0.04	-3.78	0.671±0.009	0.034±0.020	-4.65±0.07	-3.76
1.0	0.028±0.004	0.024±0.003	-0.26±0.04	-3.89	0.701±0.007	0.028±0.030	-4.89±0.05	-3.92

Ideally, the contributions of both two-body and three-body interactions to the configurational energy of the fluid should be updated for each attempted move. However, it is currently not computationally feasible to include three-body interactions in the acceptance criterion because of the very large increase in computing time required to recalculate accurately triplet interactions. Consequently, only changes to two-body interactions contributed to the acceptance criterion and the predicted phase coexistence curve is not affected by three-body forces. Instead, the effect of three-body interactions to the energy and the pressure was estimated by recalculating their contribution periodically during the course of the simulation. Three-body effects were calculated at intervals of 100 cycles.

The uncertainties in the ensemble averages were calculated by dividing the post-equilibrium results into ten sections. The estimated errors represent the standard deviations of the section averages. A typical run required 2 h of CPU time on a CRAY C90 processor.

IV. RESULTS AND DISCUSSION

The coordinates of the coexistence curve for the Lennard-Jones fluid are given in Table I. The normal convention was adopted for the reduced density ($\rho^* = \rho\sigma^3$), temperature ($T^* = kT/\epsilon$), energy ($E^* = E/\epsilon$), chemical potential ($\mu^* = \mu/\epsilon$) and pressure ($P^* = P\sigma^3/\epsilon$). The data in Table I are generally in good agreement with previous work.² Figure 2 compares the simulation data with experimental density-temperature data¹¹ for argon. At low temperatures, both simulations agree well with experiment for both the vapor and liquid portions of the coexistence curve. Phase separation was not detected at temperatures greater than $T^* = 1.25$.

There are few examples in the fluid-phase literature of three-body calculations for dense fluids. The available simulation results are confined almost exclusively to those using the Axilrod–Teller potential. Barker *et al.*¹² demonstrated that the Axilrod–Teller potential makes a significant contribution (5%–10%) to the overall energy of liquid argon. Monson *et al.*¹³ reported that three-body interactions make a substantial contribution to the configurational energy of diatomic fluids; their calculations indicate that the nonadditive corrections for molecules such as chlorine are much larger than those for argon. Sherwood and Prausnitz¹⁴ have documented the contribution of the three-body-dispersion potential to the third virial coefficient. Later, Sherwood *et al.*⁷ re-

ported that the third virial coefficient is also sensitive to three-body repulsion interactions. Recently, Miyano¹⁵ used the Axilrod–Teller potential as the basis of an effective triplet potential and simulated the saturated vapor and liquid densities, enthalpies of vaporization and second virial coefficients of argon. The Axilrod–Teller potential has also been applied¹⁶ to the simulation of the shear viscosity of liquid argon. However, no simulations with three-body interactions have been reported for the phase coexistence of either pure fluids or fluid mixtures.

The contributions of three-body interactions to the ensemble averages for pressure and configurational energy are summarized in Table II. Three-body interactions do not make a significant contribution to the energy of the vapor phase. The magnitude of both three-body dispersion and repulsion to the configurational energy increases with rising density. In the liquid phase, the three-body-repulsion energy ($E_{3\text{brep}}^*$) is typically 45% of the three-body-dispersion energy ($E_{3\text{bdisp}}^*$). This is consistent with previous estimates.⁷ The contribution from three-body repulsion is opposite to that of dispersion. Therefore, three-body repulsions substantially reduce the total three-body energy ($E_3^* = E_{3\text{bdisp}}^* + E_{3\text{brep}}^*$) of

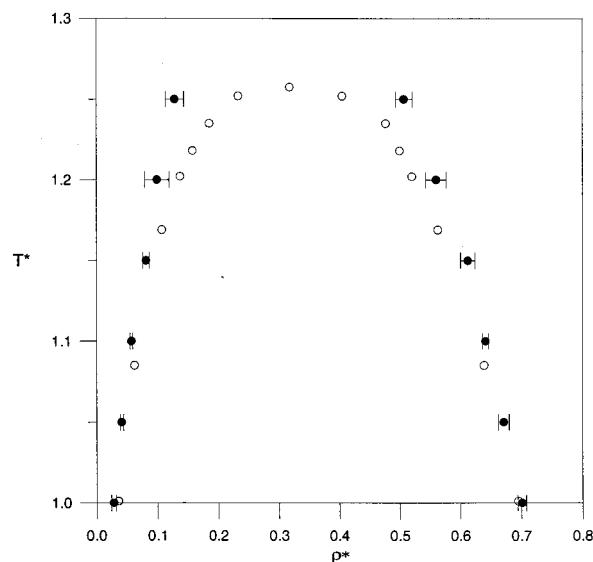


FIG. 2. Comparison of the experimental phase diagram for argon (○) with Gibbs-ensemble simulations (●).

TABLE II. The contribution of three-body interactions to the configurational energy and pressure of the coexisting vapor and liquid phases of a one-component fluid (argon).

T^*	$E_{3\text{disp}}^*$	$E_{3\text{rep}}^*$	$P_{3\text{disp}}^*$	$P_{3\text{rep}}^*$
Vapor phase properties				
1.25	0.043±0.003	-0.005±0.001	0.007±0.002	-0.006±0.002
1.20	0.0058±0.0008	-0.0017±0.0005	0.0017±0.0004	-0.0012±0.0005
1.15	0.0037±0.0008	-0.0010±0.0004	0.0009±0.0003	-0.0006±0.0002
1.10	0.0024±0.0003	-0.0008±0.0003	0.00041±0.00007	-0.0003±0.0001
1.05	0.0014±0.0001	-0.0004±0.0001	0.00017±0.00002	-0.00013±0.00002
1.0	0.00080±0.00009	-0.0003±0.0002	0.000074±0.000009	-0.00005±0.00004
Liquid phase properties				
1.25	0.094±0.024	-0.041±0.012	0.15±0.05	-0.15±0.05
1.20	0.129±0.004	-0.059±0.006	0.22±0.01	-0.24±0.03
1.15	0.145±0.004	-0.062±0.003	0.27±0.01	-0.27±0.01
1.10	0.169±0.003	-0.074±0.003	0.326±0.006	-0.33±0.01
1.05	0.186±0.002	-0.083±0.002	0.377±0.004	-0.39±0.01
1.0	0.205±0.003	-0.089±0.002	0.432±0.008	-0.44±0.01

the fluid. The contribution of three-body dispersion to pressure ($P_{3\text{disp}}^*$) is cancelled (within the uncertainty of the simulation) by the contribution of three-body repulsion ($P_{3\text{rep}}^*$).

The substantial degree of cancellation between three-body repulsion and three-body-dispersion interactions means that the overall contribution of three-body interactions to the fluid is small compared with two-body interactions. The total three-body energy (E_3^*) typically contributes <2.0% and <0.5% to the overall energy (E^*) of the liquid and vapor phases, respectively.

V. CONCLUSIONS

The contribution of both three-body-dispersion and repulsion interactions must be included to simulate accurately the effect of three-body interactions on the phase coexistence properties of simple fluids. A substantial number of triplets in the liquid phase have at least one intermolecular pair separation less than σ ; therefore, three-body repulsion is significant. In contrast, very few repulsive triplets are found in the vapor phase. Because the effect of three-body dispersion interaction is largely offset by three-body repulsion, reasonably accurate results can be obtained by only using two-body potentials. The accuracy of results using only two-body potentials is probably not because three-body interactions are unimportant, but because the effect of three-body dispersion and three-body repulsion cancel to a large extent.

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