

Effect of three-body interactions on the vapor-liquid phase equilibria of binary fluid mixtures

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Gibbs-Duhem Monte Carlo simulations are reported for the vapor-liquid phase coexistence of binary argon+krypton mixtures at different temperatures. The calculations employ accurate two-body potentials in addition to contributions from three-body dispersion interactions resulting from third-order triple-dipole interactions. A comparison is made with experiment that illustrates the role of three-body interactions on the phase envelope. In all cases the simulations represent genuine predictions with input parameters obtained independently from sources other than phase equilibria data. Two-body interactions alone are insufficient to adequately describe vapor-liquid coexistence. In contrast, the addition of three-body interactions results in very good agreement with experiment. In addition to the exact calculation of three-body interactions, calculations are reported with an approximate formula for three-body interactions, which also yields good results. © 2006 American Institute of Physics. [DOI: 10.1063/1.2275309]

I. INTRODUCTION

The physical properties of fluids are governed overwhelmingly¹ by interactions involving pairs of molecules. However, it has also been documented²⁻⁴ that three-body interactions can make a small but significant contribution to the energy of liquids. The vapor-liquid phase transition represents an important property, which is sensitive to intermolecular interactions. Typically, the vapor-liquid equilibria of both pure substances and mixtures have been modeled⁵ using effective intermolecular potentials, which do not distinguish between the different many-body contributions to interactions between molecules. Molecular simulation⁶ is an ideal tool to investigate the role of intermolecular interactions because, unlike conventional theoretical methods, the contributions from intermolecular potentials can be evaluated rigorously. Historically, molecular simulation⁶ studies have also been confined largely to the evaluation of pairwise interactions using effective intermolecular potentials such as the Lennard-Jones potential. However, recent work⁷⁻¹² has been reported using either an accurate two-body+three-body potential^{7,8} or *ab initio* intermolecular potentials.⁹⁻¹²

Molecular simulation of the phase behavior of pure fluids⁷⁻⁹ has consistently shown that three-body interactions have a significant influence on vapor-liquid coexistence. For example, studies^{7,8} using either the two-body Aziz-Slaman¹³ (AS) or Barker-Fisher-Watts¹⁴ (BFW) potentials with the three-body Axilrod-Teller¹⁵ (AT) term indicate that three-body interactions are required to accurately determine the coexistence densities of the liquid phase. In contrast, the role of three-body interactions on the phase behavior of binary

mixtures is less well documented. Marcelli and Sadus¹⁶ reported preliminary results, which indicated that the main influence of three-body interactions in binary mixtures was to slightly alter the coexistence densities whereas the pressure-composition behavior was not significantly affected. In contrast, more recent work¹⁴ using an *ab initio* potential has indicated that three-body interactions affect the pressure-composition behavior of binary mixtures. Unlike pure component systems, binary mixtures introduce the complication of accounting for interactions between dissimilar molecules which can potentially generate a diverse range of phase behavior.⁵ This diversity of behavior has practical implications for processes such as the storage and transportation of fluids, the design of plant and equipment, and scientific investigations of the properties of mixtures. The aim of this work is to determine the influence of three-body interactions on the vapor-liquid equilibria of binary mixtures

II. THEORY

A. Intermolecular potentials

Details of the intermolecular potentials have been discussed elsewhere⁸ and therefore only a brief outline is given here. The two-body interactions of argon are well represented by the BFW potential¹⁴ which is a linear combination of the Barker-Pompe¹⁷ (u_{BP}) and Bobetic-Barker¹⁸ (u_{BB}) potentials,

$$u_2(r) = 0.75u_{BB}(r) + 0.25u_{BP}(r), \quad (1)$$

where the potentials of Barker-Pompe and Bobetic-Barker have the following form:

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TABLE I. Summary of the intermolecular potential parameters used in this work.

	Argon ^a		Krypton ^b
ν_{DDD} (a.u.) ^c	518.3		1572
ε/k (K)	142.095		201.9
σ (Å)	3.3605		3.573
r_m (Å)	3.7612		4.006 7
	Barker-Pompe	Bobetic-Barker	
α	12.5	12.5	12.5
α'			12.5
δ	0.01	0.01	0.01
A_0	0.2349	0.292 14	0.235 26
A_1	-4.7735	-4.414 58	-4.786 86
A_2	-10.2194	-7.701 82	-9.2
A_3	-5.2905	-31.929 3	-8.0
A_4	0.0	-136.026	-30.0
A_5	0.0	-151.0	-205.8
P			-9.0
Q			68.67
C_6	1.0698	1.119 76	1.063 2
C_8	0.1642	0.171 551	0.170 1
C_{10}	0.0132	0.013 748	0.014 3

^aTwo-body parameters from Ref. 14.^bTwo-body parameters from Ref. 2.^cFrom Ref. 22.

$$u_2(r) = \varepsilon \left[\sum_{i=0}^5 A_i (z-1)^i \exp[\alpha(1-z)] - \sum_{j=0}^2 \frac{C_{2j+6}}{\delta + z^{2j+6}} \right]. \quad (2)$$

In Eq. (2), $z = r/r_m$, where r_m is the intermolecular separation at which the potential has a minimum value, and the other parameters are obtained by fitting the potential to experimental data for molecular beam scattering, second virial coefficients, and long-range interaction coefficients. The contribution from repulsion has an exponential dependence on intermolecular separation and the contributions to dispersion of the C_6 , C_8 , and C_{10} coefficients are included. The only difference between the Barker-Pompe and Bobetic-Barker potentials is that a different set of parameters is used in each case. These parameters¹⁴ are summarized in Table I.

Modifications² to Eq. (2) are required to obtain an optimal representation for other noble gases. For krypton, Barker *et al.*² determined a potential of the form

$$u_2(r) = u_0(r) + u_1(r), \quad (3)$$

where $u_0(r)$ is identical to Eq. (2) and $u_1(r)$ is given by

$$u_1(r) = \begin{cases} [P(z-1)^4 + Q(z-1)^5] \exp[\alpha'(1-z)], & z > 1 \\ 0, & z \leq 1, \end{cases} \quad (4)$$

and α' , P , and Q are additional parameters obtained by fitting data for differential scattering cross sections. In this work we have used Eq. (3) to predict the properties of krypton with the parameters² summarized in Table I. In the particular case when $\alpha' = \alpha$, Eq. (3) becomes

$$u_2(r) = \varepsilon \left[\sum_{i=0}^5 A'_i (z-1)^i \exp[\alpha(1-z)] - \sum_{j=0}^2 \frac{C_{2j+6}}{\delta + z^{2j+6}} \right],$$

$$A'_1 = A_1, \quad A'_2 = A_2, \quad A'_3 = A_3,$$

$$A'_4 = A_4 + P \quad \text{for } z > 1 \text{ and } A'_4 = A_4 \quad \text{for } z \leq 1,$$

$$A'_5 = A_5 + Q \quad \text{for } z > 1 \text{ and } A'_5 = A_5 \quad \text{for } z \leq 1. \quad (5)$$

Different types of interaction are possible depending on the distribution of multipole moments between the atoms.¹⁹⁻²¹ Marcelli and Sadus⁸ evaluated the contributions from third-order interactions involving dipoles and quadrupoles in addition to the fourth-order triple-dipole contribution. There is a high degree of cancellation of the multipole terms, which means that the third-order triple-dipole term alone is a good representation of three-body dispersion interactions. In view of this, we have only considered contributions from third-order triple-dipole interactions in this work.

The triple-dipole potential can be evaluated from the formula proposed by Axilrod and Teller,¹⁵

$$u_{DDD}(ijk) = \frac{\nu_{DDD}(ijk)(1 + 3 \cos \theta_i \cos \theta_j \cos \theta_k)}{(r_{ij} r_{ik} r_{jk})^3}, \quad (6)$$

where $\nu_{DDD}(ijk)$ is the nonadditive coefficient, and the angles and intermolecular separations refer to a triangular configuration of atoms. The nonadditive coefficients^{22,23} for argon and krypton are summarized in Table I.

B. Combining rules

The above intermolecular potentials can be applied directly to binary mixtures by assuming suitable combining rules for the intermolecular parameters. In general if we denote an energylike parameter such as ε or ν of an atom of identity i by the symbol W_{iii} , the contribution of interacting pairs and triplets of atoms can be calculated from

$$W_{ijk} = (W_{iii} W_{jjj} W_{kkk})^{1/3}, \quad (7)$$

$$W_{ij} = (W_{ii} W_{jj})^{1/2}.$$

In general if we denote distance-related parameters such as σ , A , C_6 , etc., by the symbol Y , the contribution of interacting pairs of atoms can be calculated from

$$Y_{ij} = \frac{Y_{ii} + Y_{jj}}{2}. \quad (8)$$

C. Simulation details

The vapor-liquid properties of mixtures of argon and krypton at different temperatures were obtained using the Gibbs-Duhem algorithm.²⁴ The Gibbs-Duhem algorithm is not self-starting: it requires *a priori* knowledge of a coexistence point. In this work, a convenient choice for the initial starting point was the vapor-liquid equilibrium point of pure krypton. For each temperature, we first evaluated the vapor-liquid coexistence of krypton using the Gibbs ensemble²⁵ for 500 atoms. Typically 1500 cycles are used for equilibration

and a further 1500 cycles are used to calculate ensemble averages. Each cycle consisted of 500 attempted displacements, an attempted volume change, and 500 atom exchange attempts.

The semigrand ensemble version²⁴ of the Gibbs-Duhem algorithm was used for the simulation of the argon+krypton binary mixtures because of the similarity of the two components. The system size was 512 atoms in each phase. Before commencing the Gibbs-Duhem algorithm, the initial ratios of fugacity and Henry's constant for the starting coexistence point were obtained by performing *NPT* Monte Carlo simulations for 10 000 preequilibration and 10 000 postequilibration cycles. Each cycle typically involved 512 attempted displacements, an attempted volume change, and 512 "fake" identity exchange attempts.

The Gibbs-Duhem Monte Carlo simulations were as follows. Starting from the initial point, 20 simulations were performed according to Clapeyron equations at different fugacity fractions. The reduced step size for the fugacity fractions was $\Delta\xi=0.05$. Each step involved 10 000 cycles: 8000 cycles for equilibration and further 2000 cycles to accumulate ensemble averages. Each cycle involved 512 attempted displacements, an attempted volume change, or 512 attempted identity exchanges. The phase and the type of move were chosen at random. Periodic boundary conditions were applied. The two-body potentials were truncated at half the box length and appropriate long-range correction terms were evaluated to recover the contribution to pressure of the full intermolecular potential. The three-body simulations were truncated at a quarter of the box length as described previously.⁸

III. RESULTS AND DISCUSSION

Two-body interactions are undoubtedly the dominant influence on the properties of fluids. Therefore, an accurate description of two-body interactions is required before any conclusions concerning the influence of three-body interactions can be made reliably. This important precondition severely limits the scope of mixtures that can be investigated. In practice, it means that we are limited to mixtures of noble gases for which accurate two-body potentials are available. As simple atoms, the noble gases are also free of additional complexity of shape, bonding, etc., that occur in molecules. However, the vapor-liquid equilibria of noble gases such as helium and neon introduce the additional uncertainty of quantum corrections. This leaves argon, krypton, and xenon as candidates for the formation of binary mixtures. Experimental data for the vapor-liquid equilibria of mixtures involving xenon and either argon or krypton are either scarce or nonexistent which further limits the comparison to the argon+krypton binary mixture. We used the BFW potential (described above) because previous experience⁸ had demonstrated that it was an accurate representation of two-body interactions and it could be applied to both argon and krypton.

We performed simulations at temperatures of 143.15, 148.15, 153.15, 158.15, 163.15, and 177.38 K. These temperatures were chosen to enable a direct comparison with

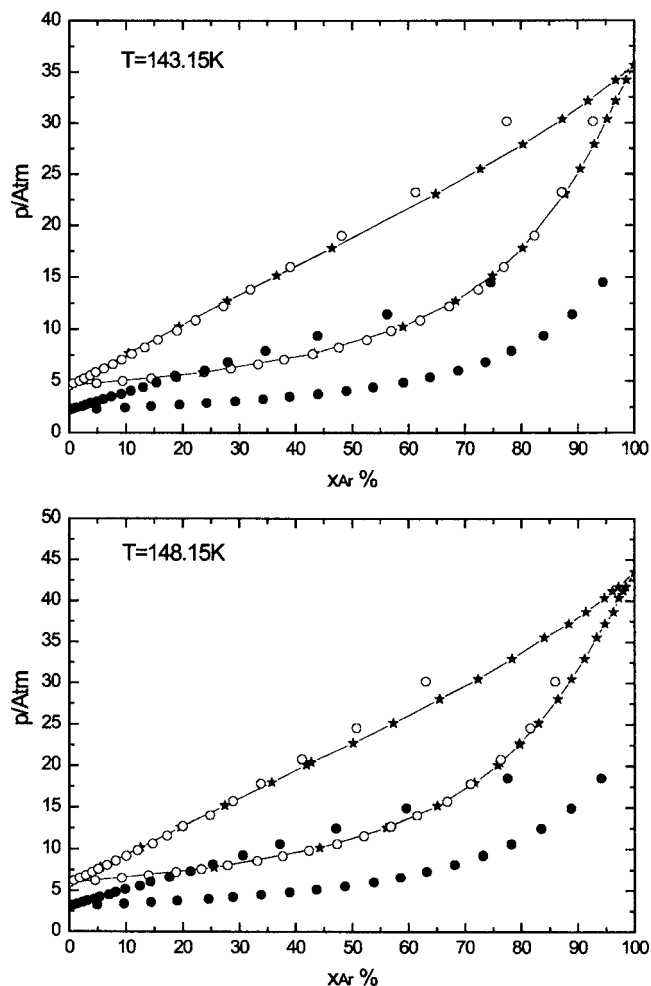


FIG. 1. Vapor-liquid equilibria of argon+krypton binary mixtures at temperatures of 143.15 and 148.15 K. Experimental data (Ref. 26) (\star -) are compared with two-body (\bullet) and two-body+three-body simulations (\circ) reported in this work.

experimental data²⁶ and to examine three-body influences over a reasonable range of temperatures. In all cases, two distinct simulations were performed. The phase envelope was determined using only two-body interactions and two-body+three-body interactions. The comparison of simulation with experiment (Figs. 1–3) indicates that two-body interactions alone fail to adequately describe the pressure-composition behavior of the argon+krypton binary mixtures. In particular, at low temperatures (Fig. 1) there is hardly any overlap between the experimental and simulation data. In contrast, the simulations, which include three-body interactions, yield very good agreement with the experimental data in all cases. The agreement with experiment is particularly noteworthy along the vapor branch.

These good results were achieved by using simple combining rules [Eqs. (7) and (8)] for all the contributions to the intermolecular potential parameters from interactions between dissimilar atoms. The simulations represent genuine predictions, which do not use any arbitrarily fitted combining rule parameters. However, the use of alternative combining rules could possibly further improve the agreement between theory and experiment. Delhommelle and Millie²⁷ have concluded that the Lorentz-Berthelot combining rules overesti-

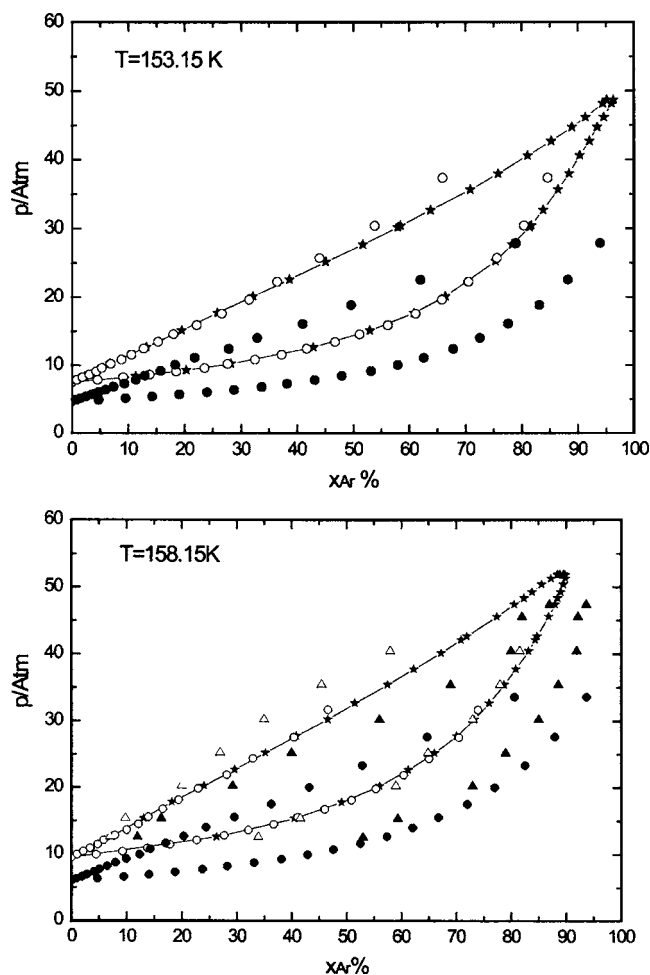


FIG. 2. Vapor-liquid equilibria of argon+krypton binary mixtures at temperatures of 153.15 and 158.15 K. Experimental data (Ref. 26) (\star) are compared with two-body (\bullet) and two-body+three-body (\circ) simulations reported in this work. For mixtures at 158.15 K, a comparison is also made with simulation data reported previously (Ref. 12) using two-body *ab initio* (\blacktriangle) and two-body *ab initio* + AT (\triangle) potentials.

mate the properties of the noble gases. Improved agreement for the phase equilibria of binary molecular systems has also been reported²⁸ using alternative combining rules. However, these investigations involved either the Lennard-Jones potential or the exponential-six potential rather than the genuine two- and three-body potentials used in this work. Conclusions reached regarding the appropriateness of combining rules are almost invariably affected by the choice of intermolecular potential. An analogous situation arises in the conventional calculation^{5,29} of phase equilibria for which the choice of equation of state directly affects the magnitude of combining rule parameters. This means that there is no *a priori* prescription for the choice of combining rules that is likely to be equally valid for all intermolecular potentials. It should be noted that the main aim of this work was to examine the role of three-body interactions on vapor-liquid equilibria in binary mixtures. Although it is likely that the use of superior combining rules would improve quality of agreement between theory and experiment, this would not significantly affect the conclusions reached regarding the relative contribution of two- and three-body interactions.

It is reasonable to infer from these comparisons that

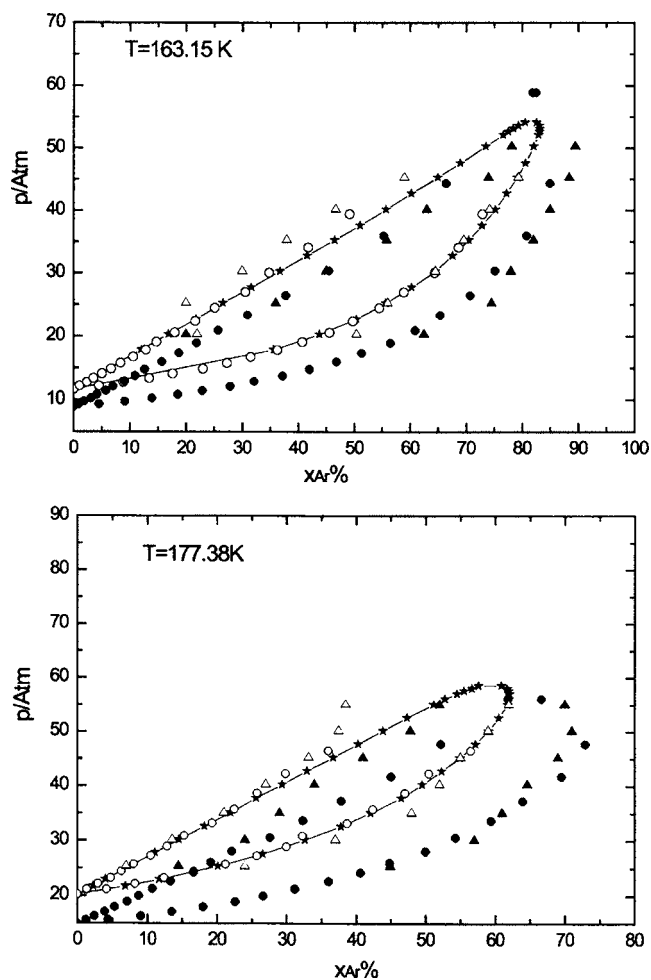


FIG. 3. Vapor-liquid equilibria of argon+krypton binary mixtures at temperatures of 163.15 and 177.35 K. Experimental data (Ref. 26) (\star) are compared with two-body (\bullet) and two-body+three-body (\circ) simulations reported in this work. Comparison is also made with simulation data reported previously (Ref. 12) using two-body *ab initio* (\blacktriangle) and two-body *ab initio* + AT (\triangle) potentials.

three-body interactions can be used to significantly improve the prediction of vapor-liquid equilibria of binary mixtures. In contrast, Marcelli and Sadus¹⁶ previously used the Gibbs ensemble to investigate the vapor-liquid equilibria of argon+krypton at 163.15 K without observing any significant influence of three-body interactions on the pressure-composition behavior. We attribute this to the relatively short simulation length and the small system size: only 3000 cycles were used and, on average, each phase contained less than 250 atoms.

Recently, Nasrabad *et al.*¹² reported calculations for the argon+krypton mixture using an *ab initio* two-body potential with the AT term. Their calculations are compared with our results in Figs. 2 and 3. At 158.15 K (Fig. 2), the *ab initio* two-body potential provides a better coverage of the phase envelope than the BFW potential. The addition of the AT term improves the agreement of theory with experiment for the vapor branch, which is consistent with our results. However, the pressure of the liquid branch is overpredicted whereas our results are in good agreement with experiment. At 163.15 K (Fig. 3), the BFW and *ab initio* potentials yield similar behavior. Once again, the addition of the AT term

improves the agreement with experiment for the vapor branch in both cases but the *ab initio*+AT combination overpredicts the pressure of the liquid branch. At 177.38 K (Fig. 3), our two-body+three-body calculations coincide reasonably close to the experimental data for both the vapor and liquid branches. Compared to the calculations at lower temperatures, agreement obtained for the liquid phase for the *ab initio*+AT calculations is somewhat better at this temperature. However, the improvement in accuracy appears to be at the expense of reduced accuracy for the vapor branch, which is now slightly underpredicted at most compositions. We note that the accuracy of the *ab initio* potential depends crucially on the quality of the fit of simulation data to an analytical expression. Therefore, future improvements in the accuracy of the data have the potential to improve the *ab initio*+AT results.

The calculation of three-body interactions is computationally prohibitive for routine application. In the worse case, the evaluation of three-body interactions for N atoms involves N^3 calculations compared with N^2 calculations for two-body interactions. However, it is apparent that two-body intermolecular potentials alone are not reliable for the accurate prediction of the properties of real fluids. This means that the simulation of real fluids must rely on the use of effective potentials such as the Lennard-Jones potential, which only involve pairwise interactions. To use genuinely two-body potentials, Marcelli and Sadus³⁰ proposed a simple formula to obtain the three-body contribution to energy (E_3) from the two-body energy (E_2):

$$E_3 = -\frac{2\nu\rho E_2}{3\varepsilon\sigma^6}, \quad (9)$$

where ρ is the number density, ε is the depth of the two-body intermolecular potential, σ is the two-body collision diameter, and ν is the three-body nonadditive coefficient. Equation (9) can be directly incorporated into a two-body simulation. The main modification is that the calculation of pressure (p) must account for the density dependence of the intermolecular potential:³¹

$$p = -\left\langle \sum_{i<j=1}^N \frac{1}{3V} \frac{du_2(r_{ij})}{dr_{ij}} r_{ij} \right\rangle + \left\langle \sum_{i<j=1}^N \frac{2\nu\rho}{9V\varepsilon\sigma^6} \frac{du_2(r_{ij})}{dr_{ij}} r_{ij} \right\rangle - \left\langle \frac{2\nu\rho^2}{3\varepsilon\sigma^6} E_2 \right\rangle. \quad (10)$$

Equation (9) works well for pure systems³⁰ but it has not been tested for mixtures.

To apply Eq. (9) to the mixtures, we propose a simple one-fluid approximation:⁵

$$E_3 = -\frac{2\rho E_2}{3\varepsilon_{11}\sigma_{11}^6} (x_1^2\nu_{111} + x_1x_2\nu_{112} + x_1x_2\nu_{221} + x_2^2\nu_{222}), \quad (11)$$

where x_i is the molar fraction of component i and ν_{ijk} is the three-body potential coefficient for the three different components i , j , and k . The above equation is based on the implicit assumption that the radial distribution functions of the

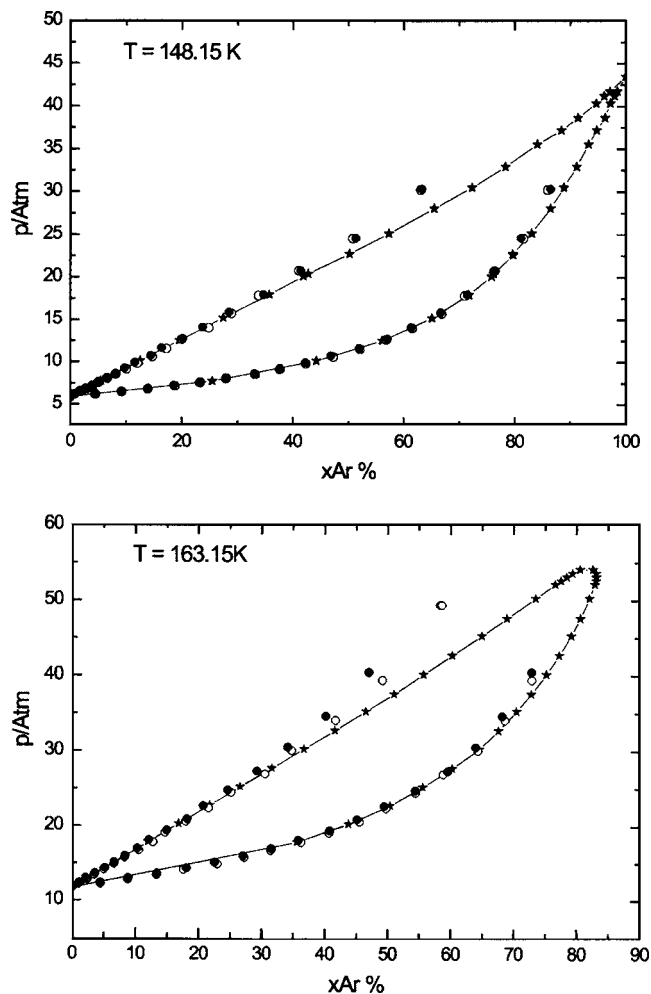


FIG. 4. Vapor-liquid equilibria of argon+krypton binary mixtures at temperatures of 148.15 and 163.15 K. Experimental data (Ref. 26) (★-) are compared with simulations obtained using a full two-body+three-body (○) calculations and the approximate three-body formula [Eq. (11)] (●).

component molecules are identical, and they both explicitly contain a contribution from interactions between dissimilar molecules.

To test the accuracy of this relationship, we performed Gibbs-Duhem simulations for argon+krypton mixtures at temperatures of 148.15 and 163.15 K. In these simulations, the contribution of three-body interactions was determined by Eq. (11). All other simulation details were identical to the full two-body+three-body calculations. Comparisons of experiment with simulation results using the two-body potential plus either the AT term or Eq. (11) are illustrated in Fig. 4. It is apparent from these comparisons that the calculations using Eq. (11) are almost the same as the results obtained from the full two-body and three-body calculations. This means that Eq. (11) provides a sufficiently accurate estimate of the contribution of three-body interactions to the energy of the binary mixture. The use of Eq. (11) reduces the overall computation time to that of a conventional two-body simulation.

IV. CONCLUSIONS

Molecular simulations using accurate two-body and three-body intermolecular potentials result in very good

overall agreement with experiment for the vapor-liquid equilibria of the argon+krypton binary mixture. Three-body interactions have an important role in determining vapor-liquid coexistence in binary mixtures. In the absence of three-body interactions, the pressure-composition behavior of binary mixtures is poorly predicted. The addition of three-body interactions provides near perfect agreement with experiment for the vapor branch of the coexistence curve while simultaneously improving the agreement with experiment on the liquid branch. A simple relationship between two- and three-body interactions can be used to incorporate the effect of three-body interactions without significant additional computational cost.

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