PHYSICAL REVIEW E **74**, 031203 (2006)

Three-body interactions and solid-liquid phase equilibria: Application of a molecular dynamics algorithm

Liping Wang and Richard J. Sadus[*]
Centre for Molecular Simulation, Swinburne University of Technology, PO Box 218 Hawthorn, Victoria 3122, Australia

(Received 20 June 2006; published 15 September 2006)

The effect of three-body interactions on the solid-liquid phase boundaries of argon, krypton, and xenon is investigated via a novel technique that combines both nonequilibrium and equilibrium molecular dynamics. The simulations involve the evaluation of two- and three-body forces using accurate two-body and three-body intermolecular potentials. The effect of three-body interactions is to substantially increase the coexistence pressure and to lower the densities of liquid and solid phases. Comparison with experiment indicates that three-body interactions are required to accurately determine the total pressure. In contrast to vapor-liquid phase equilibria, the relative contribution of three-body interactions to the freezing pressure exceeds the contribution of two-body interactions at all temperatures.

DOI: 10.1103/PhysRevE.74.031203 PACS number(s): 61.20.Ja, 64.70.Dv, 71.15.Pd, 82.20.Wt

I. INTRODUCTION

The phase behavior of both pure systems and binary mixtures has been widely studied by molecular simulation [1], using techniques such as the Gibbs ensemble [2], Gibbs-Duhem [3], or histogram reweighing [4] algorithms. The common aim of many of these investigations is to accurately predict the phase diagram using effective intermolecular potentials, most notable the Lennard-Jones potential. In contrast, other studies [5–11] have used molecular simulation techniques, in conjunction with genuine two- and three-body intermolecular potentials [12–14], to determine the influence of various intermolecular interactions on phase behavior. These studies have concluded that three-body interactions have a significant influence on phase behavior. Three-body interactions decrease the density of the liquid phase of pure fluids [5–7,9] and they contribute significantly [6] to the vapor-liquid critical point. In binary mixtures [10,11], three-body interactions are required to obtain good agreement between theory and experiment for the pressure-composition behavior. There is also some evidence [15] that three-body interactions have a pivotal role in the transition between the different global phase behavior types of binary mixtures.

Previous investigations of three-body interactions on phase equilibria have been confined largely to fluids. In contrast, the aim of this work is to determine the role of three-body interactions on the solid-liquid phase transition. Theortetical studies have been reported [16–22] which indicate three-body interactions are important in solid phases. However, the direct molecular simulation of solid-liquid equilibria [23–25] for both pure fluids and mixtures has mainly focused on predicting phase coexistence using an effective intermolecular potential.

The solid-liquid phase transition is difficult to determine accurately using traditional molecular simulation techniques. The high densities mean that it is not practical to use the Gibbs ensemble [2] because of the difficulty of exchanging particles between the phases. Although this limitation is avoided by the Gibbs-Duhem [3] technique, it is not self-starting, which means it requires prior knowledge of one pair of coexistence data. Therefore, its ability to predict the phase boundary largely depends on the accuracy of the starting point data. In this work, we employed a novel approach [26] for locating the solid-liquid phase boundary which combines elements of both equilibrium and nonequilibrium molecular dynamics techniques. The approach yields reliable calculations and it avoids the problems encountered in both Gibbs ensemble and Gibbs-Duhem methods.

II. THEORY

A. Intermolecular potentials

Details of the intermolecular potentials have been discussed in considerable detail elsewhere [6,11] and therefore only a very brief outline is given here. The two-body interactions of argon are well represented by the Barker-Fisher-Watts (BFW) potential [12]. The BFW potential was specifically determined [12] from low-density data, which are only affected by two-body interactions. The data included molecular beam data and second virial coefficients. It provides an accurate description of the two-body only contribution to the phase equilibria and pressure-temperature-volume (pVT) properties of fluids. The advantage of using the BFW potential is that it can also be modified [27] to account for two-body forces in both krypton and xenon. Different types of interaction are possible depending on the distribution of multipole moments between the atoms [28–30]. The contributions from third-order interactions involving dipoles and quadrapoles in addition to the fourth-order triple dipole contribution have been evaluated previously [6,31]. The results demonstrate [6,31] that 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, which were evaluated from the formula proposed by Axilrod and Teller [14] (AT). The AT potential

---

[*]Corresponding author. Email address: RSadus@swin.edu.au

has only one interatomic parameter, namely, the nonadditive coefficient v. The total intermolecular potential is the sum of the Barker-Fisher-Watts and Axilrod Teller terms (*BFW* +*AT*). As summarized elsewhere [6], values of the nonadditive term and the parameters for the BFW potential for argon, krypton, and xenon are available in the literature [12,27,31,32]. It should be noted that this model only includes the long-range asymptotic part of three-body interactions and it does not include shorter range contributions.

B. Simulation details

At any given temperature, the pressure and coexistence densities of the liquid and solid phases were obtained using the novel approach reported by Ge *et al.* [26]. The procedure combines aspects of both nonequilibrium and equilibrium molecular dynamics. At a given temperature and density, the pressure at different strain rates was determined using nonequilibrium molecular dynamics. In the absence of a freezing transition, these isothermal isochors exhibit a near constant value of pressure irrespective of the strain rate. In contrast, at densities equal or greater to the freezing point, there is an abrupt increase in pressure between the zero-strain rate (equilibrium) case and the first nonzero strain rate (nonequilibrium value). As illustrated elsewhere [26], the sharp abruptness of this transition makes it easy to identify the freezing pressure and density with considerable accuracy. The freezing point determined in this way is equivalent to that obtained from equilibrium simulations. The nonequilibrium method is relatively simple to implement and it provides a computationally efficient [26] alternative to conventional equilibrium techniques. Having identified the coexistence pressure, temperature, and the freezing density in this way, conventional *NVT* molecular dynamics simulations are performed to obtain the isothermal pressure-density behavior of the solid curve. Therefore, the density of the melting point can be simply obtained by locating the point at which the constant coexistence pressure "tie-line" touches the solid curve.

The nonequilibrium molecular dynamics simulations were performed using the standard *sllod* [33] algorithm and Lees-Edwards [26,33] periodic boundary conditions. The equilibrium *NVT* molecular dynamics simulations were performed using conventional cubic periodic boundary conditions [1]. In both cases the starting structure was a face centered cubic lattice. The equations of motion were integrated by a fourth-order Gear predictor-corrector scheme [1] with a reduced integration time step of 0.001. The first 50 000 time steps of each trajectory were used to obtain either a steady state or to equilibrate the system, and a further 200 000 time steps were carried out to calculate average ensemble values. In both cases a system size of 500 atoms and was used.

The BFW two-body potential was truncated at half the box length and long-range corrections were used to recover the full contribution to the intermolecular potential. A cutoff distance of a quarter of the box length was used for three-body interactions from the AT potential. It is very well known that, for periodic systems involving pairwise interactions, the cutoff distance for the simulation must not exceed half the box length. However, as discussed elsewhere [6], when three-body interactions are involved the cutoff distance for the three-body term must not exceed a quarter of the box length. If this distance is exceeded, the triplets obtained will not be correctly imaged. A feature of the calculations reported here is that contributions of two- and three-body interactions to both energy and pressure were obtained accurately. The standard errors in the energies and pressures were typically both less than 0.1%.

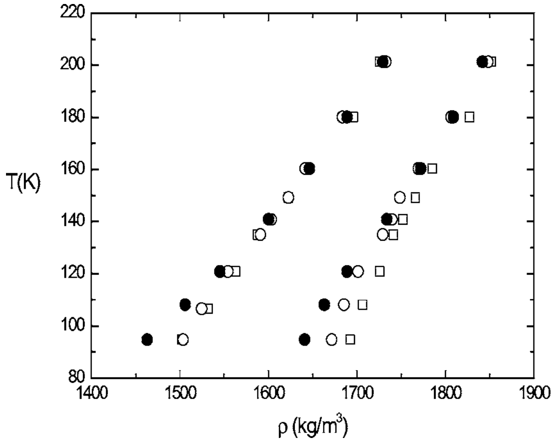

FIG. 1. Comparison of theory with experiment (●) [34] for the liquid and solid coexistence densities of argon obtained using two-body (□) and two-body+three-body (○) interactions.

III. RESULTS AND DISCUSSION

We determined the solid-liquid coexistence properties of argon, krypton, and xenon. The choice of these systems was largely based on the availability of accurate two-body intermolecular potentials, molecular simplicity, and the availability of experimental data. Two-body forces govern the properties of fluids overwhelmingly, with three-body interactions having an important secondary role. Therefore, using accurate two-body intermolecular potentials is important to minimize the risk of incorrectly attributing properties to three-body interactions that in fact arise from a weakness in our understanding of two-body interactions. This important consideration restricts the analysis to argon, krypton, and xenon, which, as atoms, are also free of the additional complexities involved in molecular interactions. Indeed, it should be noted that the additional uncertainties of quantum effects currently greatly inhibits a similar investigation of helium and neon. The simulations reported here represent genuine predictions using intermolecular parameters [6] obtained independently from other sources.

The densities of the coexisting liquid and solid phases calculated for argon are compared with experiment [34] in Fig. 1. It is apparent from this comparison that the calculations involving only two-body interactions result in both liquid and solid phase densities that are higher than the experimental data, particularly at low temperatures. The addition of three-body interactions results in lower coexistence densities and an improved agreement with experiment. This lowering of densities is similar to the effect of three-body

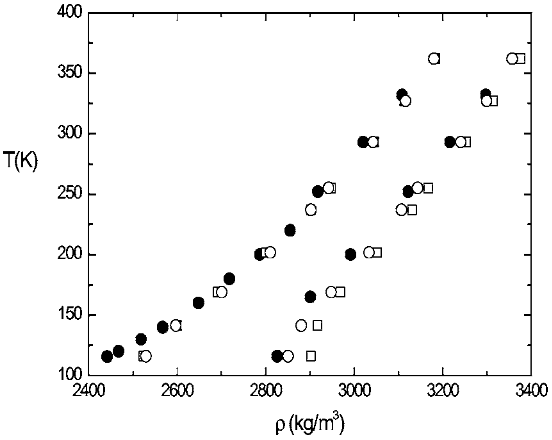

FIG. 2. Comparison of theory with experiment (●) [19,34,35] for the liquid and solid coexistence densities of krypton obtained using two-body (□) and two-body+three-body (○) interactions.

interactions on vapor-liquid equilibria [6,7]. The improvement in the agreement with experiment is most noticeable at temperatures above 120 K. In contrast, at temperatures below 120 K, the addition of three-body interactions alone is not sufficient to obtain accurate agreement with experiment, which might indicate that other factors, for example, quantum effects, are affecting the phase behavior. This observation is at slight variance with an analysis of the melting curve reported elsewhere [19], which indicated that two- and three-body interactions alone were sufficient for good agreement at all temperatures. It should be noted that, in general, the coexisting density is more prone to experimental error than either the temperature or the pressure.

Calculations for the coexisting liquid and solid densities of krypton are illustrated in Fig. 2. Comparing the data in Fig. 2 with that of Fig. 1, it appears that for both argon and krypton, the coexisting liquid phase densities are largely uninfluenced by three-body interactions. The agreement with experiment for krypton at low temperatures is noticeably better than can be achieved for argon. In contrast, three-body interactions have a greater impact on solid densities. Comparison with experimental data [19,34,35] indicates that the addition of three-body interactions considerably improves the agreement with experiment.

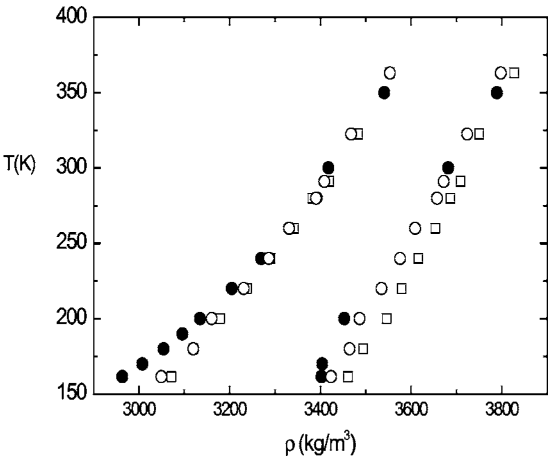

FIG. 3. Comparison of theory with experiment (●) [19,34,35] for the liquid and solid coexistence densities of xenon obtained using two-body (□) and two-body+three-body (○) interactions.

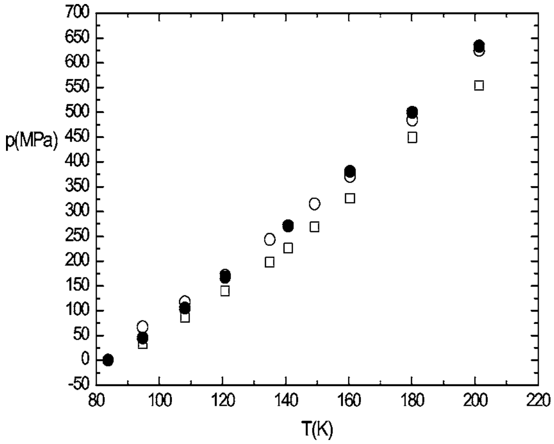

FIG. 4. Comparison of theory with experiment (●) [19,34,35] for solid-liquid coexistence pressure of argon obtained using two-body (□) and two-body+three-body (○) interactions.

Figure 3 illustrates the effect of two- and three-body interactions on the coexisting liquid and solid densities of xenon. In common with both argon and krypton, the addition of three-body interactions does not significantly affect the liquid phase densities of xenon and the agreement with experimental data at low temperatures is not perfect, i.e., temperatures below 200 K. The main influence of three-body interactions is to significantly lower the density of the solid phase, which results in very good agreement with experiment.

The solid-liquid coexistence pressure of argon at different temperatures is illustrated in Fig. 4. It is apparent that in the absence of three-body interactions, the coexistence pressure at any temperature would be significantly underestimated. The addition of three-body interactions improves the agreement with experiment [19,34,35], although the pressure is slightly overestimated at lower temperatures. These overestimations can be partly attributed to the failure to correctly predict the liquid densities at lower temperatures (Fig. 1). It should be noted that the absolute magnitude of the three-

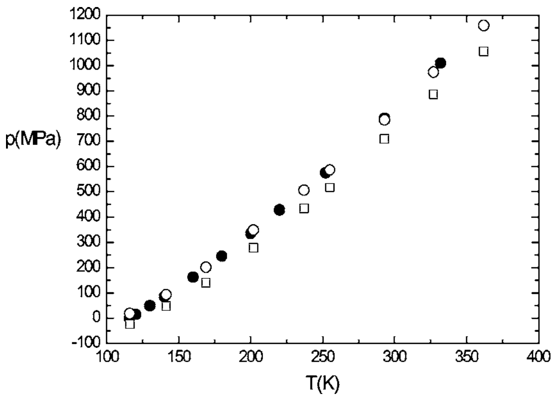

FIG. 5. Comparison of theory with experiment (●) [19,34,35] for the solid-liquid coexistence pressure of krypton obtained using two-body (□) and two-body+three-body (○) interactions.

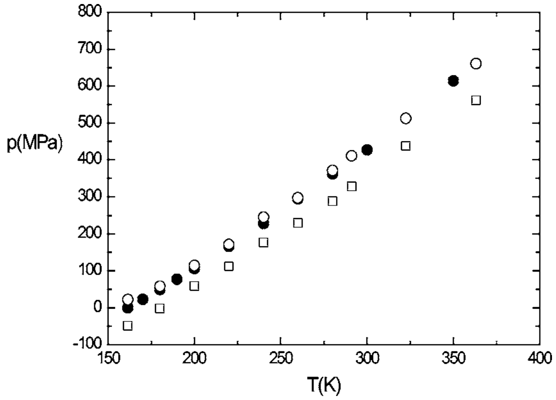

FIG. 6. Comparison of theory with experiment (●) [19,34,35] for solid-liquid coexistence pressure of xenon obtained using two-body (□) and two-body+three-body (○) interactions.

body contribution is significant. For example, at a temperature of 210.32 K, the addition of three-body interactions increases the pressure by 71.49 MPa.

The pressure-temperature behavior of krypton and xenon are illustrated in Figs. 5 and 6, respectively. The trends observed are broadly similar to those observed for argon. However, it is also apparent that three-body interactions play an increasingly important role in determining the pressure of argon, krypton, and xenon. At low temperatures, it is apparent from either Fig. 5 or 6 that in the absence of three-body interactions, the overall pressure would be negative.

When the coexistence pressure for vapor-liquid equilibria is determined [6], the contribution of two-body interactions to the pressure is always negative, whereas three-body interactions always make a positive contribution to the pressure. The absolute magnitude of the three-body pressure of the liquid phase is typically less than half of the value of the two-body pressure. In contrast, for solid-liquid equilibria we normally observed a positive value for both two-body and three-body contributions to pressure. Figure 7 compares the relative contribution of three- and two-body interactions to the freezing pressure for argon, krypton, and xenon. In contrast to the case of vapor-liquid equilibria, the contribution of three-body interactions always exceeds that of two-body interactions. The relative contribution of three-body interactions is greatest at low temperatures, declining rapidly with increasing temperature.

IV. CONCLUSIONS

The algorithm proposed by Ge *et al.* [26] provides a computationally efficient method for determining solid-liquid coexistence that avoids the limitations of either the Gibbs ensemble or Gibbs-Duhem techniques. The data obtained from this simulation procedure indicate that three-body interactions lower the densities of the coexisting liquid and solid phases of argon, krypton, and xenon. However, the effect of three-body interaction is most significant on the density of the solid. Comparison with experiment indicates that the combination of two- and three-body interactions yields good agreement for the liquid phase densities at high temperatures. It is noteworthy that good agreement with experiment can be obtained without using higher body contributions. In contrast, the agreement is not perfect at lower temperatures, particularly in the vicinity of the triple point. This appears to suggest that factors other than two- and three-body interactions have an influence on the liquid phase density at low temperatures. The combination of two- and three-body interactions results in good agreement with experimental data for the coexistence pressure. In the absence of three-body

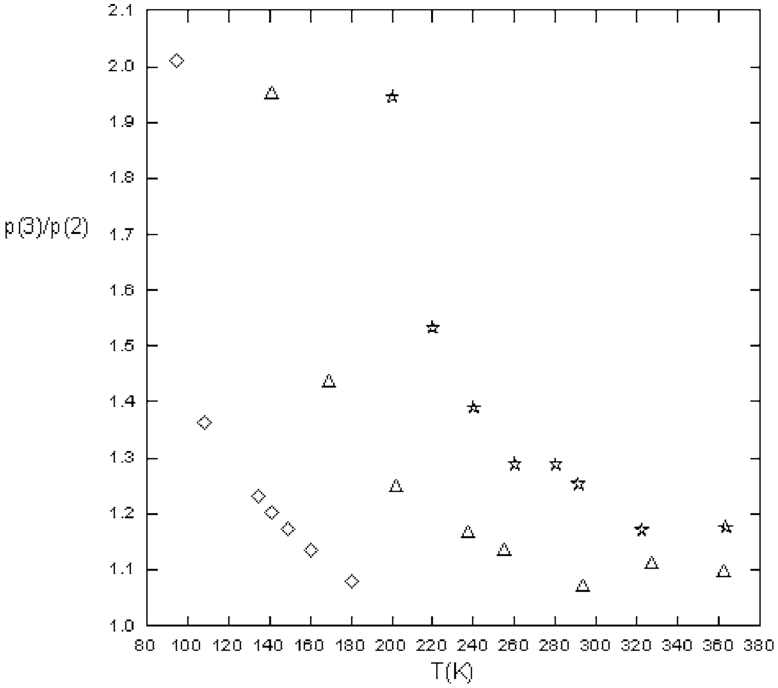

FIG. 7. Comparison of the relative contributions of three- and two-body interactions to the freezing pressure of argon (◇), krypton (△), and xenon (☆).

interactions, the pressure would be substantially underpredicted at all temperatures. The relative contribution of three-body interactions to the freezing pressure exceeds that of two-body interactions at all temperatures, whereas the reverse situation is observed for vapor-liquid equilibria.

ACKNOWLEDGMENTS

L.W. thanks the Australian government for financial support. The Australian Partnership for Advanced Computing provided a generous allocation of computer time.

[1] R. J. Sadus, *Molecular Simulation of Fluids: Theory, Algorithms and Object-Orientation* (Elsevier, Amsterdam, 1999).

[2] A. Z. Panagiotopoulos, N. Quirke, M. Stapleton, and D. J. Tildesley, Mol. Phys. **63**, 527 (1988).

[3] M. Mehta and D. A. Kofke, Chem. Eng. Sci. **49**, 2633 (1994).

[4] K. Kiyohara, K. E. Gubbins, and A. Z. Panagiotopoulos, Mol. Phys. **94**, 803 (1998).

[5] J. A. Anta, E. Lomba, and M. Lombardero, Phys. Rev. E **55**, 2707 (1997).

[6] G. Marcelli and R. J. Sadus, J. Chem. Phys. **111**, 1533 (1999).

[7] P. S. Vogt, R. Liapine, B. Kirchner, A. J. Dyson, H. Huber, G. Marcelli, and R. J. Sadus, Phys. Chem. Chem. Phys. **3**, 1297 (2001).

[8] G. Raabe and R. J. Sadus, J. Chem. Phys. **119**, 6691 (2003).

[9] A. E. Nasrabad and U. K. Deiters, J. Chem. Phys. **119**, 947 (2003).

[10] A. E. Nasrabad, R. Laghaei, and U. K. Dieters, J. Chem. Phys. **121**, 6423 (2004).

[11] L. Wang and R. J. Sadus, J. Chem. Phys. **125**, 074503 (2006).

[12] J. A. Barker, R. A. Fisher, and R. O. Watts, Mol. Phys. **21**, 657 (1971).

[13] R. A. Aziz and M. J. Slaman, Mol. Phys. **58**, 679 (1986).

[14] B. M. Axilrod and E. Teller, J. Chem. Phys. **11**, 299 (1943).

[15] R. J. Sadus, Ind. Eng. Chem. Res. **37**, 2977 (1998).

[16] J. A. Barker and M. L. Klein, Phys. Rev. B **7**, 4707 (1973).

[17] M. V. Bobetic and J. A. Barker, Phys. Rev. B **28**, 7317 (1983).

[18] J. A. Barker, Phys. Rev. Lett. **57**, 230 (1986).

[19] J. H. Kim, T. Ree, and F. H. Ree, J. Chem. Phys. **91**, 3133 (1989).

[20] H. Schlosser and J. Ferrante, Phys. Rev. B **43**, 13305 (1991).

[21] S. DiNardo and J. H. Bilgram, Phys. Rev. B **51**, 8012 (1995).

[22] R. Boehler, M. Ross, P. Söderlind, and D. B. Boercker, Phys. Rev. Lett. **86**, 5731 (2001).

[23] T. Tsang and H. T. Tang, Phys. Rev. A **18**, 2315 (1978).

[24] M. R. Hitchcock and C. K. Hall, J. Chem. Phys. **110**, 11433 (1999).

[25] M. H. Lamm and C. K. Hall, Fluid Phase Equilib. **194-197**, 197 (2002).

[26] J. Ge, G.-W. Wu, B. D. Todd, and R. J. Sadus, J. Chem. Phys. **119**, 11017 (2003).

[27] J. A. Barker, R. O. Watts, J. K. Lee, T. P. Schafer, and Y. T. Lee, J. Chem. Phys. **61**, 3081 (1974).

[28] W. L. Bade, J. Chem. Phys. **28**, 282 (1958).

[29] R. J. Bell, J. Phys. B **3**, 751 (1971).

[30] M. B. Doran and I. J. Zucker, J. Phys. C **4**, 307 (1971).

[31] M. A. van der Hoef and P. A. Madden, Mol. Phys. **94**, 417 (1998).

[32] P. J. Leonard and J. A. Barker, in *Theoretical Chemistry: Advances and Perspectives*, edited by H. Eyring and D. Henderson (Academic Press, London, 1975).

[33] D. J. Evans and G. P. Morriss, *Statistical Mechanics of Nonequilibrium Liquids* (Academic Press, London, 1990).

[34] G. K. Horton, in *Rare Gas Solids*, edited by M. L. Klein and J. A. Venables (Academic Press, London, 1976), Vol. 1.

[35] R. K. Crawford, in *Rare Gas Solids*, edited by M. L. Klein and J. A. Venables (Academic Press, London, 1977), Vol. 2.