

# MOLECULAR SIMULATION OF THREE-BODY INTERACTIONS FOR VAPOR-LIQUID AND SOLID-LIQUID PHASE EQUILIBRIA

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

## 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 [5,6,7,9] 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 pure fluids. Theoretical 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 non-equilibrium molecular dynamics techniques. The approach yields reliable calculations and it avoids the problems encountered in both Gibbs ensemble and Gibbs-Duhem methods.

## Theory

### *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 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. In this work, three-body interactions were evaluated from the formula proposed by Axilrod and Teller [14] (AT). The total intermolecular potential is the sum of the Barker-Fisher-Watts and Axilrod Teller terms (BFW + AT).

### *Simulation Details*

The vapor-liquid equilibria of binary mixtures were evaluated using the Gibbs-Duhem technique [3]. In contrast, solid-liquid equilibria were determined using a novel molecular dynamics technique [26]. 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 non-equilibrium and equilibrium molecular dynamics. At a given temperature and density, the pressure at different strain rates was determined using non-equilibrium 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 non-zero state rate (non-equilibrium 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 non-equilibrium 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 non-equilibrium molecular dynamics simulations were performed using the standard *slod* [27].

## **Results and Discussion**

We [28] determined the solid-liquid coexistence properties of argon, krypton and xenon. The densities of the coexisting liquid and solid phases calculated for argon are compared with experiment in Figure 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 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. Similar conclusions apply to both krypton and xenon.

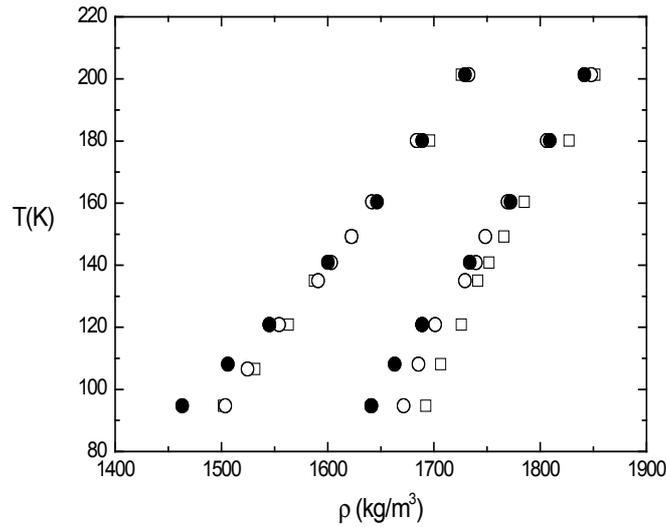


Figure 1. Comparison of theory with experiment (●) for the liquid and solid coexistence densities of argon obtained using two-body (□) and two-body + three-body (○) interactions [28].

The solid-liquid coexistence pressure of argon at different temperatures is illustrated in Figure 2. 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, 29, 30], 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 (Figure 2). It should be noted that the absolute magnitude of the three-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.

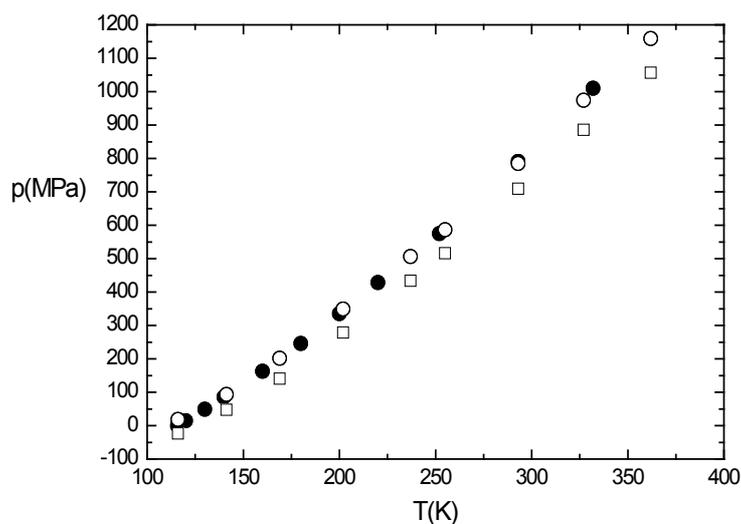


Figure 2. Comparison of theory with experiment (●) for solid-liquid coexistence pressures of krypton obtained using two-body (□) and two-body + three-body (○) interactions [28].

We [31] performed simulations at temperatures of 143.15 K, 148.15 K, 153.15 K, 158.15 K, 163.15 K and 177.38 K for the vapor-liquid phase envelope of binary mixtures of argon + krypton. The results illustrated in Figure 3 are typical of all the mixtures studied. The comparison of simulation with experimental data [32] (Figure 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 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.

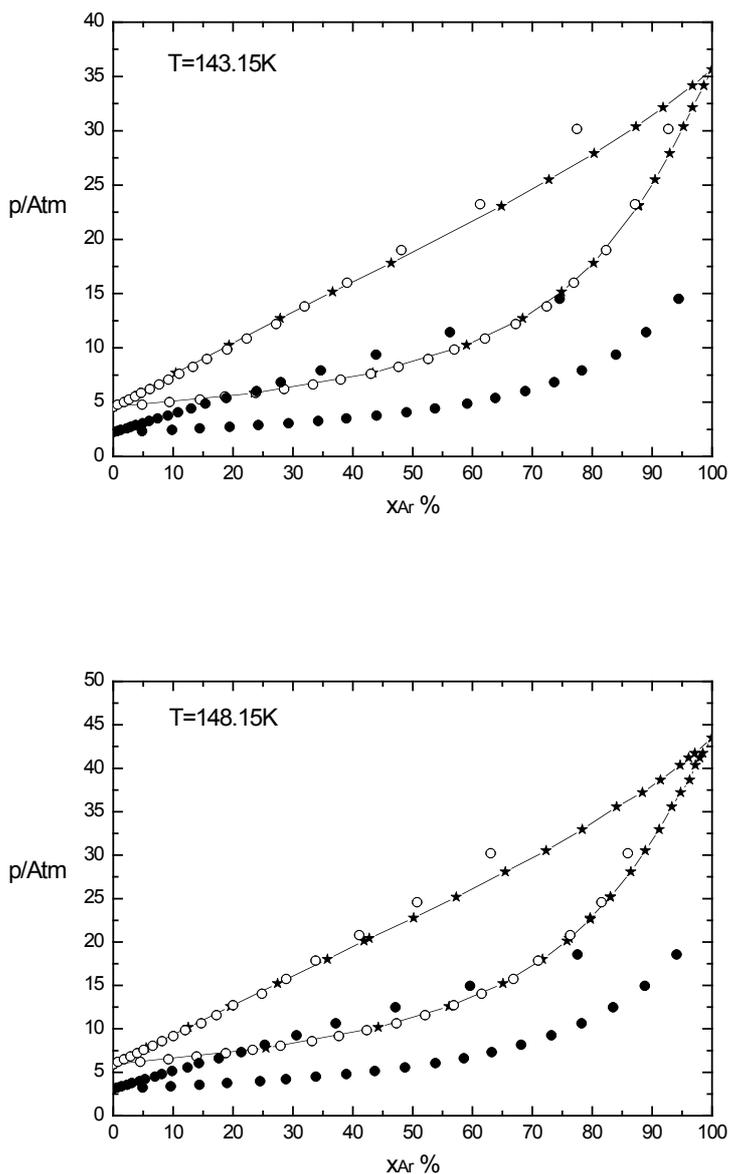


Figure 3. Vapor-liquid equilibria of argon + krypton binary mixtures at temperatures of 143.15 K and 148.15 K. Experimental data (-\*-) are compared with two-body (●) and two-body + three-body simulations (○) [31].

## 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. Three-body interactions also substantially influence the vapor-liquid equilibria of binary mixtures.

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