Beyond Traditional Effective Intermolecular Potentials and Pairwise Interactions in Molecular Simulation

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Abstract. Molecular simulation methods such as Monte Carlo simulation and both equilibrium and nonequilibrium molecular dynamics are powerful computational techniques that allow the exact calculation of molecular properties with minimal approximations. The main approximations are the choice of intermolecular potential and the number of particles involved in each interaction. Typically, only pairwise interactions are counted using a simple effective intermolecular potential such as the Lennard-Jones potential. The use of accurate two-body potentials and calculations that explicitly include three or more body interactions are rare because of the large increase in computational cost involved. Here, we report recent progress in the use of both genuine two-body potentials and calculations involving three-body interactions. We show that in some cases, the contribution of three-body interactions can be accurately estimated from two-body interactions without the increase in computational cost involved in explicitly accounting for three-body interactions. As an example of the benefit of including three-body interactions, the improvement in the prediction of vapour-liquid equilibria is examined.

1 Introduction

Molecular simulation [1] is a generic term that encompasses both Monte Carlo (MC) and molecular dynamics (MD) algorithms. The appeal of molecular simulation is that it provides a means of predicting the properties of matter by evaluating the underlying intermolecular interactions. Unlike other computational techniques, the calculations are exact and require very few simplifying assumptions or approximations. The main assumptions are the choice of intermolecular potential and how many atoms or molecules are involved in each interaction. The heart of a molecular simulation is the evaluation of intermolecular energy (MC simulation) or forces (MD simulation). For example, in the absence of external influences, the potential energy of N interacting particles can be obtained from:

$$E_{pot} = \sum_i \sum_{j>i} u_2(r_i, r_j) + \sum_i \sum_{j>i} \sum_{k>j>i} u_3(r_i, r_j, r_k) + \dots, \quad (1)$$

where the summations are performed for all distinct particle interactions, u_2 is the potential between pairs of particles, u_3 is the potential between particle triplets etc. An analogous expression can be written in terms of force, which is simply the derivative of the potential with respect to intermolecular separation.

The point of truncation of Eq. (1) determines the overall order of the algorithm. Including pair, three-body and four-body interactions result in algorithms of ON^2 , ON^3 and ON^4 , respectively. It should be noted that computation saving strategies [2] have been developed that mean that these theoretical limits are rarely approached in practice. Nonetheless, the large increase in computing time involved when three or more body interactions are involved has meant that, until recently, it has only been computationally feasible to calculate pair interactions. In a molecular simulation Eq. (1) is typically truncated after the first term and the two-body potential is replaced by an effective potential:

$$E_{pot} = \sum_i \sum_{j>i} u_{eff}(r_i, r_j). \quad (2)$$

Therefore, only pairwise interactions are calculated and the effects of three or more body interactions are crudely incorporated in the effective intermolecular potential.

Many intermolecular potentials have been proposed [1,3], but molecular simulations are overwhelmingly performed using the Lennard-Jones potential:

$$u_{eff}(r_i, r_j) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (3)$$

where ϵ_{ij} is the potential minimum and σ_{ij} is the characteristic diameter between particles i and j . The use of the Lennard-Jones potential is not confined only to atoms. It is also widely used to calculate the site-site interactions of molecules and it is the non-bonded contribution of molecular force fields such as AMBER [4] and CHARMM [5].

The use of effective intermolecular potentials and confining the calculations to pairwise interactions makes molecular simulation computationally feasible for a diverse range of molecules. Effective intermolecular potentials generally yield good results. However, the use of effective intermolecular potentials also means that the effects of three-body interactions remain hidden. It has recently become computationally feasible to perform molecular simulations involving three-body interactions. Here, we examine the consequences of these calculations and show how the contribution of three-body interactions can be obtained from two-body intermolecular potentials.

2 Simulation Details

2.1 Simulation Algorithms

The simulations discussed in this work are the result of implementing two different algorithms. Simulations of vapour-liquid coexistence equilibria were obtained using the Gibbs Ensemble algorithm [6] as detailed elsewhere [7]. Nonequilibrium molecular dynamics (NEMD) calculations used the SLLOD algorithm [8] as discussed recently [9].

The simulations typically involved 500 particles and conventional periodic boundary conditions and long-range corrections were applied. It should be noted that simulations involving three-body interactions require additional care to maintain the spatial invariance of three particles with respect to periodic boundary conditions [10].

2.2 Intermolecular Potentials

A feature of the simulations discussed here is that Eq. (1) is truncated after the three-body term. Therefore, expressions for both u_2 and u_3 are required. Several accurate two-body potentials for noble gases are available in the literature [1]. In addition, some recent work has also been reported on ab initio potentials [11,12]. However, the focus of our examination is the Barker-Fisher-Watts (BFW) potential [13] which has the following functional form:

$$u_2 = \varepsilon \left[\sum_{i=0}^5 A_i (x-1)^i \exp[\alpha(1-x)] - \sum_{j=0}^2 \frac{C_{2j+6}}{\delta + x^{2j+6}} \right]. \quad (4)$$

In eq. (4), $x = r/r_m$, where r_m is the intermolecular separation at which the potential passes through a minimum 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 contribution to dispersion of the C_6 , C_8 and C_{10} coefficients are included.

The main contribution to three-body dispersion can be obtained from the triple-dipole term determined by Axilrod and Teller [14]:

$$u_3 = \frac{\nu (1 + 3 \cos \theta_i \cos \theta_j \cos \theta_k)}{(r_{ij} r_{ik} r_{jk})^3}, \quad (5)$$

where ν is the non-additive coefficient, and the angles and intermolecular separations refer to a triangular configuration of atoms.

3 Results and Discussion

At the outset it should be noted that calculations of the effect of three-body interactions have been performed in the past. For example Barker et al. [13] estimated the three-body energy of argon, Monson et al. [15] investigated three-body interactions in diatomic molecules, Rittger [16] analyzed thermodynamic data for the contribution of three-body interaction and Sadus and Prausnitz [17] estimated the three-body contribution to energy on the vapour-liquid coexistence curve. Typically, in these early reports the contributions of three-body interactions were periodically estimated during the course of an otherwise conventional pairwise simulation. However, recently [9-12] three-body interactions have actually been used to determine the outcome of the simulation by contributing to the acceptance criterion

for each and every step of a Markov chain in a MC simulation or contributing to every force evaluation in a MD simulation.

The atomic noble gases have provided the focus of most of the work on three-body interactions because they are free from the additional complexities of molecular shape and polar interactions. The contributions to three-body dispersion for atomic systems are documented [18,19]. In addition to the triple-dipole term (Eq. (5)) contributions can be envisaged from dipole-dipole-quadrupole (DDQ), dipole-quadrupole-quadrupole (DQQ), triple-quadrupole (QQQ), dipole-dipole-octapole (DDO) and fourth-order triple-dipole (DDD4) interactions.

The phase behaviour of fluids is likely to be very susceptible to the nature of intermolecular interactions. Simulations [1] with the Lennard-Jones potential indicate good agreement for the vapour-liquid phase envelope except at high temperatures resulting in an overestimate of the critical point. In Fig. 1, a comparison is made between experiment and simulations of the vapour-liquid phase envelope of argon in the reduced temperature ($T^* = kT/\epsilon$, k is Boltzmann's constant) – reduced density ($\rho^* = \rho\sigma^3$) projection. It is apparent from Fig. 1 that the BFW potential alone cannot be used for accurate predictions. However, when the BFW potential is used in conjunction with contributions from three-body terms (DDD + DDQ + DDQQ + QQQ + DDD4), very good agreement with experiment is obtained. In particular, the improved agreement for the liquid phase densities can be unambiguously attributed to the importance of three-body interactions. A similar conclusion can be made for the other noble gases [10].

Fig. 1. Comparison of experiment (•) with Gibbs ensemble simulations using the BFW potential (Eq. (4)) (□), the Aziz-Slaman potential (×, [20]), the Aziz-Slaman + Axilrod-Teller (+, [20]) and the BFW + three-body (DDD + DDQ + DQQ + QQQ + DDD4) potentials (Δ) for the vapour-liquid coexistence of argon [10]

Anta et al. [20] also reported good agreement with experiment for the Aziz-Slaman [21] two-body potential in combination with only the Axilrod-Teller term (see Fig. 1). The signs of the various contributions to three-body interactions are different and it was believed [22] that a large degree of cancellation occurs. Figure 2, illustrates the contribution to energy of the various contributions at different densities along the liquid side of the coexistence curve of argon [10].

Fig. 2. Comparison of the contribution of the various three-body terms (DDD (+), DDQ ($\square$), DQQ ($\circ$), QQQ ($*$) and DDD4 ($\times$)) to the reduced configurational energy ($E^* = E/\epsilon$) at different reduced densities ($\rho^* = \rho/\rho^s$) of the liquid-phase of argon obtained from Gibbs ensemble simulations [10]

The third order multipole interactions (DDQ + DQQ + QQQ) contribute approximately 32% of the triple-dipole term. However, it is apparent from Fig. 2 that there is an approximately equal contribution (26 % of DDD) from DDD4 interactions of opposite sign. Therefore the Axilrod-Teller term alone is a very good approximation of three-body dispersion interactions.

The above analysis does not address the effect of intermolecular repulsion. Theoretical models of three-body repulsion are less well developed than our understanding of three-body dispersion. There is evidence [22] that suggests that three-body repulsion may offset the contribution of Axilrod-Teller interaction by as much as 45%. However, this conclusion is based on approximate models [23]. Very recently [24], ab initio calculations for noble gases have been reported which explicitly account for three-body repulsion. It was observed that the effect of repulsion is also offset by other influences, leaving the Axilrod-Teller term alone as a very good approximation of the overall three-body interaction.

Irrespective of the fact that the Axilrod-Teller term alone is a very good approximation of three-body simulations, using it for routine simulations is computationally prohibitive. For example on a vector computer such as the NEC SX-5, the two-body calculations of the phase coexistence typically require 1 CPU hour per point to obtain meaningful results. In contrast, the same calculations involving three-body interactions require 12 CPU hours. Furthermore, to achieve the figure of 12 CPU hours, the code must be optimized to take advantage of the vector architecture as detailed elsewhere [25]. These impediments are magnified further if we attempt to incorporate three-body interactions for molecular systems. Another consequence of this computational impediment is that genuine two-body potentials have little role in molecular simulation because they alone cannot be used to accurately predict fluid properties. To make use of two-body potentials, a computationally expedient means of obtaining the three-body contribution is required.

Fig. 3. The ratio of three-body and two-body energies obtained from molecular simulation at different reduced densities. Results are shown for argon (Δ), krypton (+) and xenon ($\square$). The line through the points was obtained from Eq. (6) [26]

Responding to this need, Marcelli and Sadus [26] analyzed molecular simulation data and obtained the following simple relationship between the two-body (E_2) and three-body (E_3) configurational energies of a fluid:

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

where v is the non-additive coefficient, ϵ is the characteristic depth of the pair-potential, σ is the characteristic molecular diameter used in the pair-potential and $\rho = N/V$ is the number density obtained by dividing the number of molecules (N) by the volume (V). As illustrated in Fig. 3, this simple relationship predicts the three-body energy with an average absolute deviation of 2%.

A useful consequence of Eq. (6) is that it can be used to derive an effective potential from any two-body potential via the relationship:

$$u_{eff} = u_2 \left(1 - \frac{2v\rho}{3\epsilon\sigma^6} \right).$$
(7)

The results of Gibbs ensemble simulations [26] for the vapour-liquid equilibria of argon using Eq. (7) in conjunction with the BFW potential are compared with experiment in Fig. 4. It is apparent from Fig. 4 that Eq. (7) yields very good agreement. This is significant because it means that two-body intermolecular potentials can be usefully used in molecular simulations. Equation (7) only involves the evaluation of pairwise interactions, so the computational impediment of three-body calculations is removed.

Fig. 4. Comparison of Gibbs ensemble calculations with experiment (●) for the vapour-liquid equilibria of argon in the reduced temperature-density projection. Results are shown for the BFW potential (×), the BFW + Axilrod-Teller potential (Δ) and Eq. (7) using the BFW potential (O) [26]

Although Eq. (7) was determined from Monte Carlo Gibbs ensemble simulation, it can also be used in MD. The forces required in MD are simply obtained from the first derivative of Eq. (7) with respect to intermolecular pair separation. Recently [27] it has been established that Eq. (7) can be used in NEMD [8,9] simulations of transport phenomena such as shear viscosity. As illustrated in Fig. 5, it was shown [27] that the ratio of two-body and three-body energies is largely independent of the reduced strain rate ($\dot{\gamma}^* = \dot{\gamma} \sigma \sqrt{m/\epsilon}$, m is the mass).

Fig. 5. The ratio of three-body to two-body energies for argon obtained from NEMD simulations at different strain rates and state points [27]

Furthermore, Eq. (6) can be used to predict the three-body energy obtained from NEMD simulations to average absolute deviation of 2.3%. This suggests that Eq. (7) can be used in an NEMD simulation to predict shear viscosities with a similar degree of accuracy as full two-body + three-body simulations. Some results [27] for the reduced shear viscosity ($\eta^* = \eta \sigma^2 / \sqrt{m\epsilon}$) are illustrated in Fig. 6, which confirm the usefulness of Eq. (7).

Fig. 6. Comparison of the reduced shear viscosity predicted by the BFW + Axilrod Teller potential (•) with NEMD simulations using Eq. (7) with the BFW potential (—) [27]

4 Conclusions

The results obtained from traditional effective intermolecular potentials can, in some cases, be misleading because the influence of three or more body interactions is not explicitly taken into account. Improved agreement between theory and experiment might be obtained by using two body potentials in conjunction with three-body interactions. The available evidence suggests that the Axilrod-Teller term alone is a good description of three-body interactions. There is also evidence that there is a simple relationship between two-body and three-body interaction energies, which can be used to formulate an effective potential from two-body potentials. This means that genuine two-body potentials can be used to accurately predict the properties of fluids.

References

1. Sadus, R. J.: *Molecular Simulation of Fluids: Theory, Algorithms and Object-Oriented*. Elsevier, Amsterdam (1999).
2. Frenkel, D., Smit, B.: *Understanding Molecular Simulation: From Algorithms to Applications*. Academic Press, San Diego (1996).
3. Stone, A. J.: *The Theory of Intermolecular Forces*. Clarendon Press, Oxford (1996).
4. Weiner, S. J., Kollman, P. A., Case, D. A., Singh, U. C., Ghio, C., Alagona, G., Profeta Jr, S., Weiner, P.: A New Force Field for Molecular Mechanical Simulation of Nucleic Acids and Proteins. *J. Am. Soc.* **106** (1984) 765-784.

5. Brooks, B. R., Bruccoleri, R. E., Olafson, B. D., States, D. J., Swaminathan, S., Karplus, M.: CHARMM: A Program for Macromolecular Energy, Minimization, and Dynamics Calculations. *J. Comput. Chem.* **4** (1983) 187-217.
6. Panagiotopoulos, A. Z.: Direct Determination of Phase Coexistence Properties of Fluids by Monte Carlo Simulation in a New Ensemble. *Mol. Phys.* **61** (1987) 813-826.
7. Panagiotopoulos, A. Z.: Direct Determination of Fluid Phase Equilibria by Simulation in the Gibbs Ensemble: A Review. *Mol. Sim.* **9** (1992) 1-23.
8. Evans, D. J. and Morriss, P.: *Statistical Mechanics of Nonequilibrium Liquids*. Academic Press, London (1990).
9. Marcelli, G., Todd, B. D., Sadus, R. J.: Analytic Dependence of the Pressure and Energy of an Atomic Fluid Under Shear. *Phys. Rev. E* **63** (2001) 021204.
10. Marcelli, G., Sadus, R. J.: Molecular Simulation of the Phase Behavior of Noble Gases Using Two-Body and Three-Body Intermolecular Potentials. *J. Chem. Phys.* **111** (1999) 1533-1540.
11. Vogt, P.S., Liapine, R., Kirchner, B., Dyson, A. J., Huber, H., Marcelli, G., Sadus, R. J.: Molecular Simulation of the Vapour-Liquid Phase Coexistence of Neon and Argon using Ab Initio Potentials. *Phys. Chem. Chem. Phys.* **3** (2001) 1297-1302.
12. Leonhard, K., Deiters, U.K.: Monte Carlo Simulations of Neon and Argon Using Ab Initio Potentials. *Mol. Phys.* **98** (2000) 1603-1616.
13. Barker, J. A., Fisher, R. A., Watts, R. O.: Liquid Argon: Monte Carlo and Molecular Dynamics Calculations. *Mol. Phys.* **21** (1971) 657-673.
14. Axilrod, B. M., Teller, E: Interaction of the van der Waals' Type Between Three Atoms. *J. Chem. Phys.* **11** (1943) 299-300.
15. Monson, A. P., Rigby, M., Steele, W. A.: Non-Additive Energy Effects in Molecular Liquids. *Mol. Phys.* **49** (1983) 893-898.
16. Rittger, E.: Can Three-Atom Potentials be Determined from Thermodynamic Data? *Mol. Phys.* **69** (1990) 867-894.
17. Sadus, R. J., Prausnitz, J. M.: Three-Body Interactions in Fluids from Molecular Simulation: Vapor-Liquid Phase Coexistence of Argon. *J. Chem. Phys.* **104** (1996) 4784-4787.
18. Bell, R. J.: Multipolar Expansion for the Non-Additive Third-Order Interaction Energy of Three Atoms. *J. Phys. B* **3** (1970) 751-762.
19. Bell, R. J. and Zucker, I. J. in Klein, M. L. and Venables, J. A. (Eds): *Rare Gas Solids*, Vol. 1., Academic Press, London (1976).
20. Anta, J. A., Lomba, E., Lombardero, M.: Influence of Three-Body Forces on the Gas-Liquid Coexistence of Simple Fluids: the Phase Equilibrium of Argon. *Phys. Rev. E* **55** (1997) 2707-2712.
21. Aziz, R. A., Slaman, M. J.: The Argon and Krypton Interatomic Potentials Revisited. *Mol. Phys.* **58**, (1986) 679-697.
22. Maitland, G. C., Rigby, M., Smith, E. B., Wakeham, W. A.: *Intermolecular Forces: Their origin and Determination*, Clarendon Press, Oxford (1981).
23. Sherwood, A. E., de Rocco, A. G., Mason, E. A.: Nonadditivity of Intermolecular Forces: Effects on the Third Virial Coefficient. *J. Chem. Phys.* **44** (1966) 2984-2994.
24. Bukowski, R., Szalewicz, K.: Complete Ab Initio Three-Body Nonadditive Potential in Monte Carlo Simulations of Vapor-Liquid Equilibria and Pure Phases of Argon. *J. Chem. Phys.* **114** 9518-9531 (2001).
25. Marcelli G.: The Role of Three-Body Interactions on the Equilibrium and Non-Equilibrium Properties of Fluids from Molecular Simulation. PhD Thesis, Swinburne University of Technology (2001), <http://www.it.swin.edu.au/staff/rsadus/cmsPage/>.
26. Marcelli, G., Sadus, R. J.: A Link Between the Two-Body and Three-Body Interaction Energies of Fluids from Molecular Simulation. *J. Chem. Phys.* **112** (2000) 6382-6385.
27. Marcelli, G., Todd, B. D., Sadus, R. J.: On the Relationship Between Two-Body and Three-Body Interactions from Nonequilibrium Molecular Dynamics Simulation. *J. Chem. Phys.* **115** (2001) 9410-9413.