

A link between the two-body and three-body interaction energies of fluids from molecular simulation

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Molecular simulation data are reported that indicate that there is a simple empirical relationship between two-body and three-body interaction energies. The significance of this relationship is that three-body interactions can be estimated accurately from two-body interactions without incurring the computational penalty of three-body calculations. The relationship is tested by performing Gibbs ensemble simulations for the vapor–liquid equilibria of argon. The results are in good agreement with calculations that explicitly evaluate all three-body interactions. © 2000 American Institute of Physics. [S0021-9606(00)50413-9]

I. INTRODUCTION

Advances in molecular simulation algorithms¹ coupled with rapid growth in the calculation speed of modern high performance computers, provide unprecedented opportunities to investigate natural phenomena from a molecular perspective. Molecular simulation has been applied to the design of beneficial pharmaceutical products,² the optimization of important industrial processes,² and to the resolution of fundamental scientific questions.^{3,4} Despite the use of high performance computing, molecular simulation is confined largely to the calculation of two-body interactions using “effective” intermolecular potentials. The inclusion of three- or more-body interactions remain computationally prohibitive. In this work, we report molecular simulation data that indicate there is a simple empirical relationship between two-body and three-body interaction energies for noble gas atoms. The significance of this relationship is that three-body interactions can be estimated accurately from two-body interactions without incurring the computational penalty of three-body calculations. The relationship has the potential of improving both the accuracy and predictive value of molecular simulation.

The appeal and usefulness of molecular simulation is that it often allows an accurate calculation of natural phenomena without the plethora of approximations and assumptions that limit the usefulness of conventional theoretical approaches to prediction and estimation. The key theoretical assumptions of molecular simulation are the following: the choice of intermolecular potential used to calculate interactions between molecules; and how many molecules contribute to the intermolecular interaction. It is commonly assumed that intermolecular interactions are confined to pairs of molecules, and contributions involving three, four, or more atoms are ignored. When this assumption is invoked, the molecular properties are assumed to be “pair-additive.” Generally, interactions between pairs⁵ of molecules make the

overwhelming contribution to the overall intermolecular interaction. However, it is also documented⁶ that three-body interactions can make a significant contribution to intermolecular interactions in liquids. Despite this, molecular simulations rarely account rigorously for the effect of three-body interactions.^{7–13} Instead, the typical molecular simulation assumes pair additivity, and uses a simple “effective” intermolecular potential in which many-body effects are said to be included in the values of the intermolecular parameters.

The use of “effective” intermolecular potentials is a source of considerable inaccuracy and uncertainty in molecular simulations. For example, recent calculations¹² have shown that three-body interactions contribute significantly to the phase behavior of fluids, whereas this effect had been hidden previously by the use of effective intermolecular potentials. The agreement between experiment and theory for the phase envelope was improved considerably by explicitly accounting for three-body interactions. However, accounting for three-body interactions requires considerably more computing resources than simple pair interactions. In the worst case, the computing time of a system of N molecules scales in proportion to N^2 for pair interactions, compared with N^3 for three-body interactions. Although computation-time saving algorithms have been developed¹ to avoid the worst case scenario, accounting for three-body interactions typically requires at least one order of magnitude more computing time than simple pair calculations. This means that such calculations are far from routine, even with today’s high performance computers. However, because of the importance of three-body interactions, it is highly desirable to include them in molecular simulations.

II. THEORY

A. Intermolecular potentials

The Barker–Fisher–Watts¹⁵ (BFW) potential was used for the pair interactions of argon, and the potentials reported by Barker *et al.*¹⁶ were used to represent the pair interactions

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

	Argon ^a		Krypton ^b	Xenon ^c
ν (a.u.) ^d	518.3		1572	5573
ϵ/k (K)	142.095		201.9	281.0
σ (Å)	3.3605		3.573	3.890
r_m (Å)	3.7612		4.0067	4.3623
	Barker–Pompe	Bobetic–Barker		
α	12.5	12.5	12.5	12.5
α'			12.5	12.5
δ	0.01	0.01	0.01	0.01
A_0	0.2349	0.292 14	0.235 26	0.2402
A_1	−4.7735	−4.414 58	−4.786 86	−4.8169
A_2	−10.2194	−7.701 82	−9.2	−10.9
A_3	−5.2905	−31.9293	−8.0	−25.0
A_4	0.0	−136.026	−30.0	−50.7
A_5	0.0	−151.0	−205.8	−200.0
P			−9.0	59.3
Q			68.67	71.1
C_6	1.0698	1.119 76	1.0632	1.0544
C_8	0.1642	0.171 551	0.1701	0.1660
C_{10}	0.0132	0.013 748	0.0143	0.0323

^aTwo-body parameters from Ref. 15.

^bTwo-body parameters from Ref. 16.

^cTwo-body parameters from Ref. 16.

^dFrom Ref. 19.

of krypton and xenon. The BFW potential 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:

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

In Eq. (2), ϵ is the depth of the potential; $x = r/r_m$, where r_m is the intermolecular separation at which the potential has a minimum value. 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 δ parameter is a small correction term. The parameters of Eq. (2) are obtained by fitting the potential to experimental data for molecular beam scattering, second virial coefficients, and long-range interaction coefficients. The values of the parameters used in this work were obtained from the literature¹⁵ and they are summarized in Table I.

For krypton and xenon, the Barker *et al.*¹⁶ potential has 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

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

and α' , P , and Q are additional parameters obtained by fitting data for differential scattering cross sections. The parameters for this potential were obtained from the literature¹⁶ (Table I).

The contribution from three-body interactions was obtained from the triple-dipole formula proposed by Axilrod and Teller,²⁰

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

where ν is the nonadditive coefficient, and the angles and intermolecular separations refer to a triangular configuration of atoms. Values of the nonadditive coefficients were obtained from the work of Leonard and Barker¹⁹ (Table I). It should be noted that although there are other contributions from three-body interactions, recent work¹² confirms that they largely cancel each other, and that the Axilrod–Teller term alone is an excellent approximation for the total three-body interaction. A recent review of intermolecular potentials is available.¹

B. Simulation details

We performed NVT Monte Carlo¹ and NVT Gibbs ensemble¹⁴ simulations for 500 atoms of argon, krypton, and xenon. The simulations were performed in cubic boxes, and the conventional periodic boundary conditions were applied.¹ For pair interactions, long-range corrections were used to recover the full contribution to the intermolecular potential, whereas three-body interactions were assumed to be zero at separations greater than a quarter of the box length.¹² For the NVT simulations, a total of 40 000 cycles were used, with averages being accumulated after 20 000 cycles. The run length for the NVT Gibbs ensemble calculations was 3000, with averages being accumulated after 1500 cycles. Each cycle of the Gibbs ensemble simulation involved 500 attempted displacements, one volume interchange, and 500 interchange attempts. The two-body energy (E_2) was obtained by averaging the contribution of the pair potential over all distinct pairs of atoms, whereas the three-body energy (E_3) is the average of the Axilrod–Teller²⁰ potential for all distinct triplets of atoms. The three-body simulations require typically 20 and 12 CPU hours on the Fujitsu VP300 and NEC SX-4/32 supercomputers, respectively.

III. RESULTS AND DISCUSSION

The ratio of three-body (E_3) to two-body (E_2) energies obtained from the NVT simulations is shown in Fig. 1 as a function of reduced number density ($\rho^* = \rho\sigma^3$, where $\rho = N/V$, N is the number of atoms, V is the volume, and σ is the molecular diameter). The temperatures used covered the temperature range for vapor–liquid coexistence of a pure fluid. It is apparent that the ratio is a linear function of density that is consistent with theoretical considerations.^{21–23} Furthermore, within the statistical uncertainties of the simulation, the results for argon, krypton, and xenon appear to obey the same relationship. A least-squares fit of the simu-

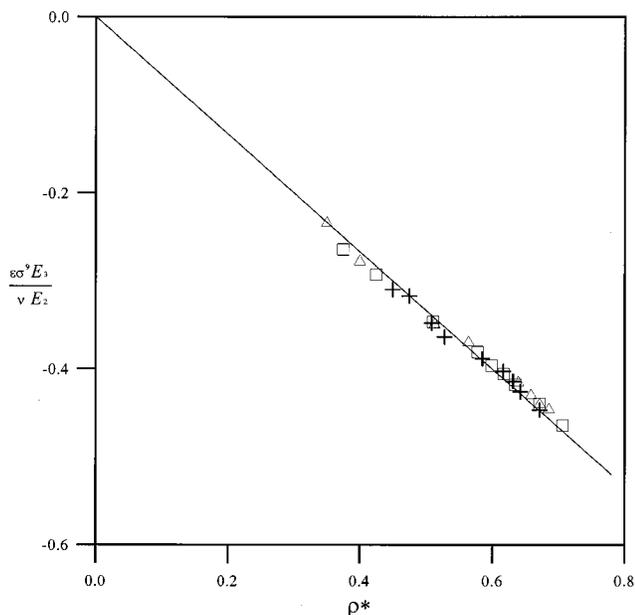


FIG. 1. The ratio of three-body and two-body energies obtained from molecular simulation at different reduced densities. Results are shown for argon (Δ), krypton (+), and xenon (\square). The line through the points was obtained from Eq. (6).

lation data for argon, krypton, and xenon yields the following empirical relationship between two-body and three-body energies:

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

As E_2 is generally negative, E_3 is positive, which is consistent with simulation data. The above equation is a remarkably simple result that fits all the simulation data with an average absolute deviation of 2.0%. The only constants in Eq. (6) are the well-known parameters (ϵ and σ) that characterize all pair potentials, and a nonadditive coefficient (ν). The relationship is independent of temperature for the range of densities at which the fluid is normally a liquid.

The benefit of Eq. (6) is that an accurate estimate of the three-body energy for fluid densities can be obtained from two-body calculations alone. To test the accuracy of this relationship, we performed Gibbs ensemble¹⁴ simulations for the phase equilibria of argon with the energies calculated from the BFW potential plus the contribution from Eq. (6). The Gibbs ensemble calculations were performed by first determining the contribution of two-body interactions. The two-body contribution was used in Eq. (6) to determine the contribution of three-body interactions. The combined two-body and three-body energies were then used to determine the acceptance of the Monte Carlo move. The results of these calculations are compared in Fig. 2 with both experimental data²⁴ and the full two-body+three-body calculation reported elsewhere.¹² The comparison indicates that the results obtained using Eq. (6) are nearly identical to the full two-body+three-body calculations.

It should be noted that, strictly speaking, the validity of the relationship is tied to the pair and three-body potentials

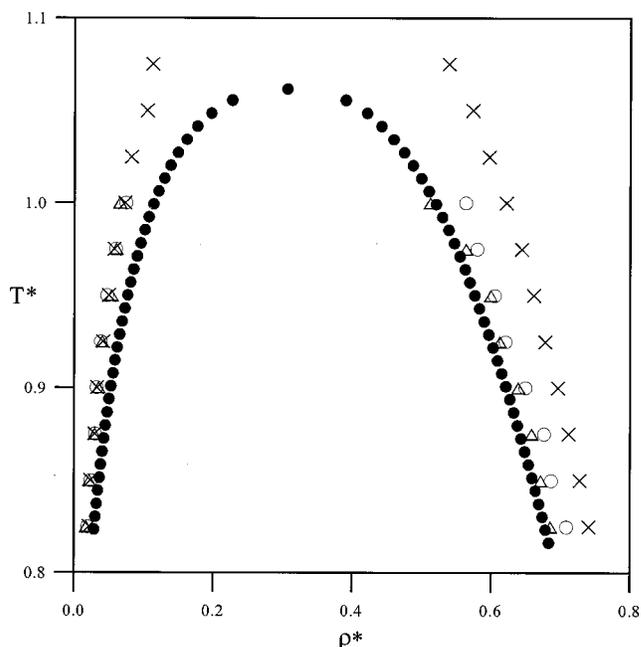


FIG. 2. A comparison of NVT Gibbs ensemble calculations with experiment²⁴ (\bullet) for the vapor-liquid equilibria of argon in the reduced temperature-density projection. Results are shown for the BFW potential¹² (\times), the BFW+Axilrod-Teller potential¹² (Δ), and the BFW+three-body contribution from Eq. (6) potential (\circ).

used in the simulations, and only three different atoms were considered. However, if these potentials genuinely reflect the contribution of two-body and three-body interactions, the result could be valid generally. We emphasize that the relationship should not be used for effective potentials such as the Lennard-Jones potential. The accuracy of the single relationship for argon, krypton, and xenon may also indicate that the result is valid for other atoms.

IV. CONCLUSIONS

Molecular simulation data indicate that there is a simple relationship between two-body and three-body energies. Therefore, the contribution to the energy of three-body interactions can be estimated accurately from two-body contributions without incurring the computational penalty of three-body calculations. The relationship has the potential of improving both the accuracy and predictive value of molecular simulation.

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