Relationships between three-body and two-body interactions in fluids and solids

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Molecular dynamics data are reported for two-body and three-body interactions in noble gases at densities covering the gas, liquid, and solid phases. The data indicate that simple relationships exist between three- and two-body interactions in both fluid and solid phases. The relationship for liquids has a simple density dependence with only one external parameter. In contrast, the solid phase relationship depends both on density and on the square of density and requires the evaluation of two parameters. The relationships are tested for both system-size and temperature dependences. The values of the relationship parameters are only sensitive to system size when a small number of atoms are involved. For 500 or more atoms, they remain nearly constant. The relationships are valid for both subcritical and slightly supercritical temperatures. A practical benefit of the relationships is that they enable the use of two-body intermolecular potentials for the prediction of the properties of real systems without the computational expense of three-body calculations. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2353117]

I. INTRODUCTION

In principle, the molecular simulation[1] of materials could involve the calculation of all interatomic interactions involving two-, three-, and other higher-body terms, which represent an infinite number of calculations. Fortunately, the diminishing magnitude[1–3] of successive many-body contributions and their alternate signs means that the combination of two- and three-body interactions is a very good approximation for either the total force or total energy. However, the addition of three-body interaction remains computationally prohibitive[3] even for simulations involving only a few hundred atoms. To overcome this difficulty, effective multibody potentials such as the Lennard-Jones potential are used that only involve calculating interactions between pairs of atoms. Nonetheless, for atomic systems, such as the noble gases, it is possible to determine accurate two-body potentials. Originally, the development[2] of two-body potentials[4,5] required very accurate experimental data such as molecular beam collision data and second virial coefficient measurements, which could be unambiguously attributed to two-body interactions alone. More recently, developments in theory mean that accurate two-body potentials can be obtained from *ab initio* calculations.[6–8]

Despite their theoretical merit, two-body potentials[4–8] cannot be used to accurately predict the physical properties of real fluids because the contribution of other-body interactions, most notably three-body interactions, is missing. It is currently impossible[8] to accurately determine three-body interactions from *ab initio* calculations. This means that the application of either *ab initio*[6–8] or empirical[4,5] two-body potentials to the properties of real materials requires the addi-tional calculation of three-body interactions. Calculations involving empirical two-body potentials[3,9] or *ab initio* potentials[6–8] with the Axilrod-Teller[10] three-body term have yielded accurate predictions of the vapor-liquid phase coexistence of pure fluids. Of course, including three-body interactions comes with a great computational cost, which renders such an approach impractical for routine situations. To remedy this problem, Marcelli and Sadus[11] found that the contribution of three-body interactions to the energy of the fluid (E_3) could be obtained from the two-body energy (E_2) via the following simple relationship involving density ($\rho = N/V$, where N is the number of atoms and V is the volume) and parameters for the depth of the two-body intermolecular potential (ε), the two-body impenetrable collision diameter (σ), and a nonadditive coefficient (ν):

$$E_3 = -\frac{\lambda_a \nu \rho E_2}{\varepsilon \sigma^6}. \tag{1}$$

In Eq. (1), λ_a is a constant based on the optimal fit of the equation to the two- and three-body simulation data. Marcelli and Sadus reported[11] that very good agreement was obtained when $\lambda_a = 2/3$. The significance of Eq. (1) is that it allows us to use two-body potentials to accurately predict the properties of real fluids without incurring the computational cost of three-body calculations. Existing Monte Carlo or molecular dynamics codes can be easily modified with the intermolecular potential (u) given by[12]

$$u = u_2 \left(1 - \frac{\lambda_a \nu \rho}{\varepsilon \sigma^6}\right), \tag{2}$$

where u_2 is the two-body intermolecular potential. The only other change is that the calculation of pressure (p) must account for the density dependence in the intermolecular potential.[13]

Equation (1) was originally obtained from the results of Monte Carlo Gibbs ensemble[14] calculations. Therefore, the available simulation data were limited to a narrow range of vapor and liquid densities with considerable statistical uncertainties in both the densities and the energies. The aims of this work are (a) to test Eq. (1) with accurate molecular dynamics data, (b) extend its scope to cover the entire fluid range, and (c) determine an equivalent relationship for solids.

II. THEORY

A. Intermolecular potentials

Details of the intermolecular potentials have been discussed elsewhere[1,3,5] 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.[5] The BFW potential is the same potential that was originally[11] used to formulate Eq. (1). It provides an accurate description of the two-body only contribution to the phase equilibria and pVT properties of fluids. It can also be modified[15] to account for two-body forces in both krypton and xenon. Marcelli and Sadus[11] established that Eq. (1) was equally valid for argon, krypton, and xenon. Therefore, calculations for argon were mainly conducted as part of this work.

Different types of interaction are possible depending on the distribution of multipole moments between the atoms.[16–19] The contributions from third-order interactions involving dipoles and quadrupoles in addition to the fourth-order triple dipole contribution have been evaluated previously.[3] The results demonstrate[3] 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 was evaluated from the formula proposed by Axilrod and Teller (AT).[10] The AT potential has only one interatomic parameter, namely, the nonadditive coefficient ν, which is also included in Eq. (1). The total intermolecular potential is the sum of the Barker-Fisher-Watts and Axilrod-Teller terms (BFW+AT). As summarized elsewhere[3] values of the nonadditive term and the parameters for the BFW potentials are available in the literature.[5,20,21]

B. Simulation details

NVT molecular dynamics[1] simulations were performed for 108, 256, 500, and 864 atoms at different temperatures and reduced densities ranging from 0.03 to 1.3. 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 equilibrate the system, and a further 200 000 time steps were carried out to calculate average values. Adopting the common practice of molecular simulation, the temperature $(T^* = k_B T/\varepsilon)$, density $(\rho^* = \rho\sigma^3)$, and energy $(E^* = E/\varepsilon N)$ are reported in reduced units relative to the intermolecular parameters of the BFW potential. It is also convenient to define a reduced nonadditive coefficient $(\nu^* = \nu/\varepsilon\sigma^9)$.

Periodic boundary conditions were applied. 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[1] that, for periodic systems involving pairwise interactions, the cutoff distance for the simulation must not exceed half of the box length. However, as discussed elsewhere,[3] 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 energy were obtained accurately. The standard errors in the energies were typically less than 0.1%.

III. RESULTS AND DISCUSSION

A. Fluid phase relationship

For interactions involving two-body interactions, 500 atoms are usually sufficient to minimize the influence of system size to within the statistical uncertainties of the simulation. However, it has been recently observed[22] that system-size dependences are more significant in three-body interactions because the size of the system limits the number of triplets that will be observed for interatomic separations within the cutoff distance of the AT potential. In particular, a simulation involving a small number of atoms may not generate a sufficient number of atomic triplets in comparison to atomic pairs to accurately reflect the relative contribution of three-body interactions to two-body interactions.

The system-size dependency of the ratio of three- and two-body energies at reduced densities of 0.03–1.3 is illustrated in Fig. 1(a) at $T^* = 0.9914$. From Fig. 1(a), we observe that the ratio is sensitive to the size of the system. In particular, the results for 108 atoms deviate substantially from the results obtained with 256, 500, and 864 atoms. At moderate to high densities, the results for 256 atoms also display a significant departure from the data obtained for both 500 and 864 atoms. In contrast, the results for 500 and 864 atoms are in reasonable agreement with each other at all densities. A discontinuity in the data is also apparent from Fig. 1(a), which occurs in the vicinity of the solid-liquid phase transition. Therefore, Eq. (1) does not apply to the solid phase, which requires the formulation of a separate relationship.

Marcelli and Sadus reported[11] that the conclusions reached for argon also applied equally to both krypton and xenon. To verify this, we performed identical molecular dynamics simulations for krypton and xenon using appropriate modifications[15] of the BFW potential and intermolecular parameters previously used[3] for these atoms. The results for argon, krypton, and xenon at subcritical temperatures are compared in Fig. 1(b). The comparison illustrates that the ratio of three-body to two-body interaction is almost identical for the three systems. Therefore, subsequent calculations were restricted exclusively to argon.
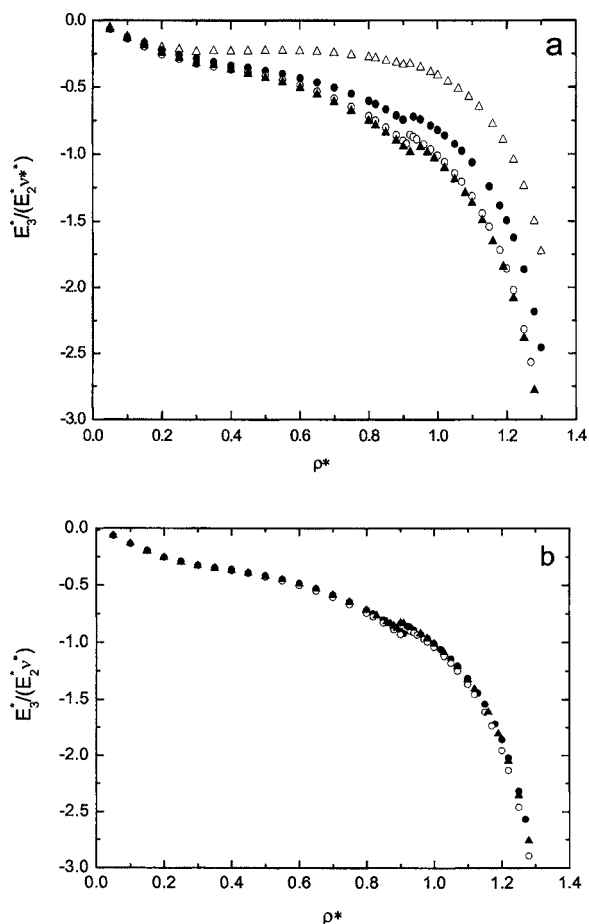
FIG. 1. (a) Ratios of three-and two-body potential energies obtained in this work for ensembles with different numbers of argon atoms ($\triangle$ 108, $\bullet$ 256, $\bigcirc$ 500, and $\blacktriangle$ 864) at different densities and $T^* = 0.9914$. (b)Comparison of calculations for 500 atoms of argon ($\bullet$, $T^* = 0.9914$), krypton ($\bigcirc$, $T^* = 1$), and xenon ($\blacktriangle$, $T^* = 0.9252$) at subcritical temperatures.

FIG. 2. (a)Comparison of the predictions of Eq. (1) at normal liquid densities, using values of λ_a summarized in Table I, with simulation data obtained in this work for different numbers of argon atoms ($\triangle$ 108, $\star$ 200, $\bullet$ 256, $\bigcirc$ 500, and $\blacktriangle$ 864). (b)The system-size dependence of the λ parameter in Eq. (1).

The simulation data in the normal liquid range of reduced densities between 0.4 and 0.8 were fitted to Eq. (1) to obtain values of λ_a for the different system sizes. Reduced densities both below 0.4 and above 0.8 were excluded to avoid metastable states in the two-phase vapor-liquid region and two-phase solid-liquid region, respectively. It is evident from Fig. 2(a) that the linear relationship is a very good approximation in all cases, particularly for systems of 256 or more atoms. The values of λ_a vary from 0.38 (108 atoms) to 0.85 (864 atoms). The value of $\lambda_a = 0.65$ attributed to 200 atoms was obtained from analyzing the Gibbs ensemble data reported previously.[11] It should be noted that although these calculations were reported for 500 atoms, they were distributed between two phases. This means that, on average, the liquid phase contained only 200 atoms. It is apparent from Fig. 2(b) that the value of λ_a does not increase linearly with system size, but instead rapidly reaches a plateau. Therefore, the value of $\lambda_a = 0.85$ is probably a good approximation of the infinite atom limit. This is in contrast to the value of $\lambda_a = 2/3$ reported previously[11] from Gibbs ensemble data. It should be noted that this relationship is not valid in the low-density region, where two-phase separation is likely to occur.
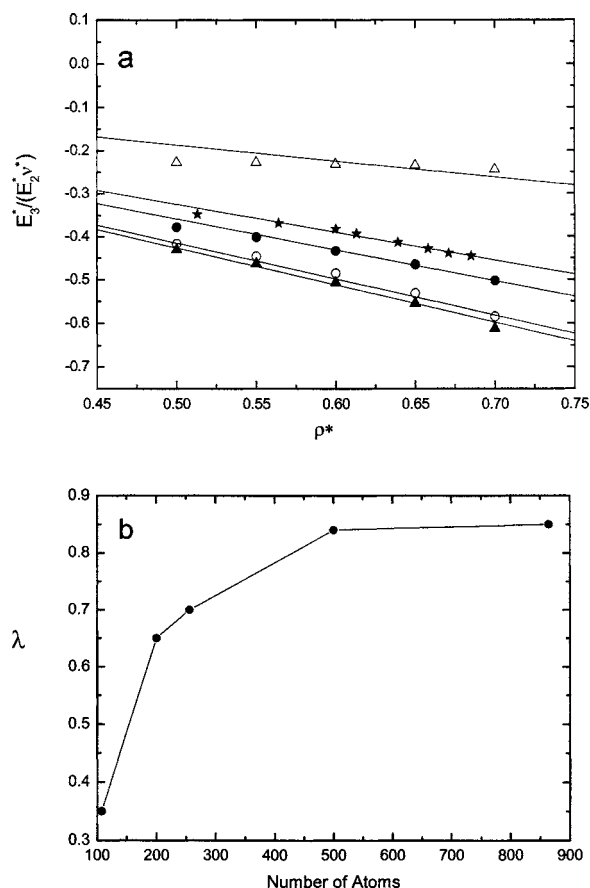
B. Solid phase relationship

Our analysis of the simulation data for the solid phase indicated that the ratio of three-body to two-body energies changes not only with density but also with the square of the density, i.e.,

$$E_3 = \frac{\nu E_2}{\varepsilon \sigma^6}(\lambda_a \rho - \lambda_b \sigma^3 \rho^2). \tag{3}$$

The accuracy of this relationship is illustrated in Fig. 3(a) and the values of λ_a and λ_b are summarized in Table I. Figure 3(a) indicates that Eq. (3) is reasonably accurate in all cases. The main deviation from this relationship occurs at a reduced density of 1.1, which can probably be attributed to the fact that the system has some metastable character at this density. The sensitivity of λ_a and λ_b to system size is illustrated in Fig. 3(b), which indicates that both values reach a plateau for 500 atoms. Therefore, $\lambda_a = 5.5$ and $\lambda_b = 6$ probably represent a very good approximation of the values for an infinite system.

C. The effect of temperature on the relationships

Originally,[11] Eq. (1) was obtained from Gibbs ensemble simulation at different temperatures, which indicates that the relationship should be valid over a reasonably wide range of
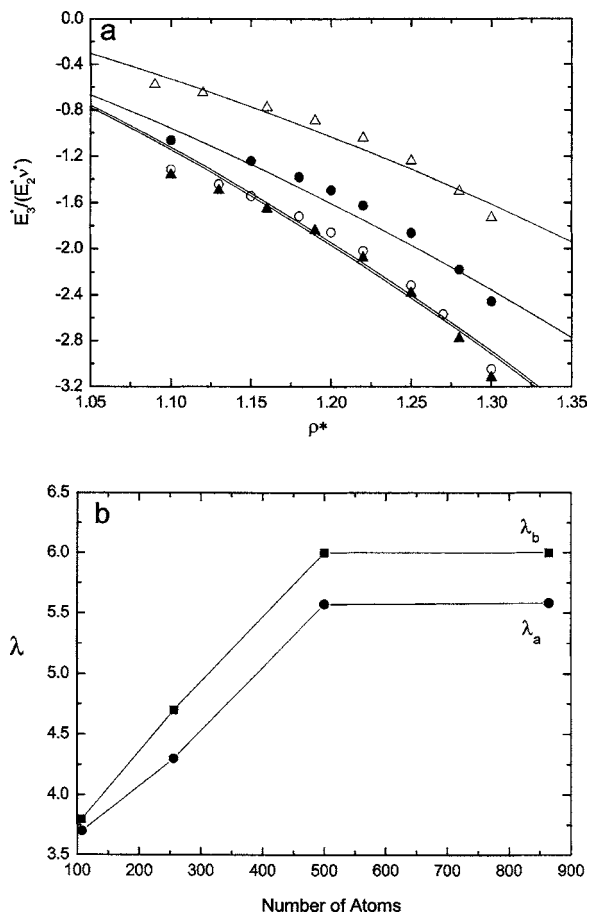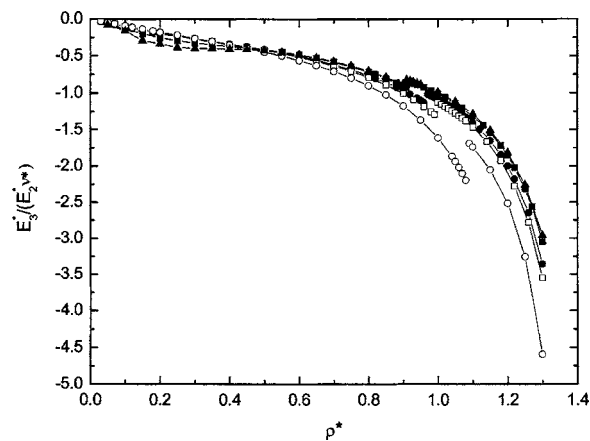
FIG. 4. The ratio of three- and two-body energies as a function of density at different temperatures. Molecular simulation data obtained in this work are shown for subcritical [$T^*=0.9$ (▲), $T^*=0.9914$ (■)], near critical [$T^*=1.2678$ (●)], and supercritical [$T^*=1.4168$ (□), $T^*=2.0$ (○)] temperatures.

liquid region. In contrast, temperature has a much more significant influence in the solid phase, particularly at $T^*=2.0$.

The predictions of Eqs. (1) and (3) are compared with data at subcritical and slightly supercritical temperatures in Figs. 5(a) and 5(b), respectively. It is apparent from these comparisons that the relationships remain valid for these

FIG. 3. (a)Comparison of the predictions of Eq. (3), at solidlike densities, using values of λ_a and λ_b summarized in Table I, with simulation data obtained in this work for different numbers of argon atoms (△ 108, ● 256, ○ 500, and ▲ 864). (b)The system-size dependence of the λ parameters in Eq. (3).

temperatures, i.e., temperatures between the triple point and the critical point of the fluid. To investigate the influence of temperature on the relative contributions of two-body and three-body interactions, we performed molecular dynamics simulations at subcritical ($T^*=0.9$ and $T^*=0.9914$), near critical ($T^*=1.4168$), and supercritical temperatures ($T^*=1.2678$ and $T^*=2$). The results for these temperatures are compared in Fig. 4. It is apparent that the ratio of two- and three-body energies is only slightly influenced by temperature in the normal liquid range ($0.4 > \rho^* < 0.8$). It should be noted that the dip observed at low densities for $T^*=0.9$ corresponds to metastable states in the two-phase vapor-

TABLE I. Summary of the λ parameters of Eqs. (1) and (3) obtained for systems with different numbers of atoms.

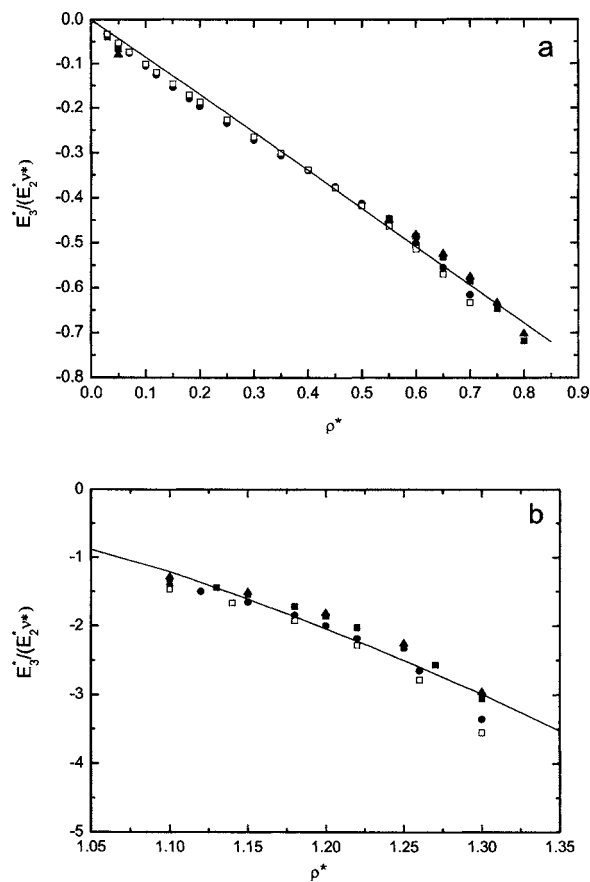|	Eq. (1)	Eq. (3)	
Number of atoms	λ_a	λ_a	λ_b
108	0.38	3.7	3.8
200	0.65		
256	0.72	4.3	4.7
500	0.83	5.57	6.0
864	0.85	5.58	6.0

FIG. 5. Comparison of the predictions of (a) Eq. (1) and (b) Eq. (3) for the fluid and solid regions, respectively, with simulation data obtained in this work for 500 argon atoms at different temperatures. Results are shown for subcritical [$T^*=0.9$ (▲), $T^*=0.9914$ (■)], near critical [$T^*=1.2678$ (●)], and supercritical [$T^*=1.4168$ (□), $T^*=2.0$ (○)] temperatures.
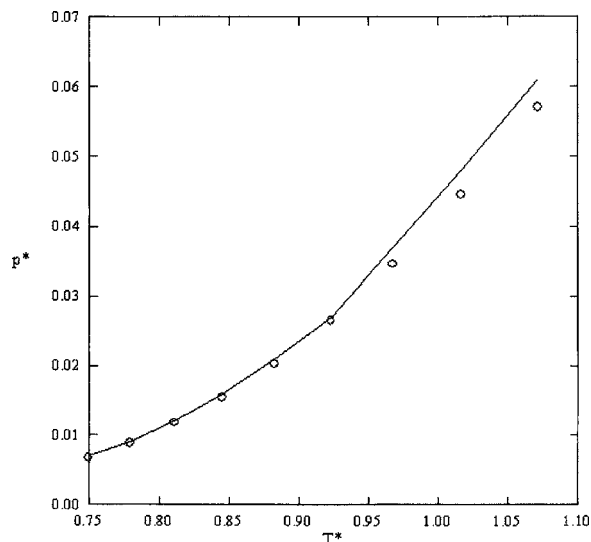
FIG. 6. Comparison of the vapor pressure curve of argon obtained using the BFW+AT potentials (—) with results obtained using the BFW potential + Eq. (1) (○).

temperatures. The reason for the relative insensitivity of Eqs. (1) and (3) to these temperatures is that the relationships were developed at temperatures at which the kinetic term makes a small contribution relative to the two-body term. However, as the temperature is increased, the kinetic contribution begins to dominate the two-body term. Therefore, the basis of the relationships becomes progressively weaker.

The value of these simple relationships is that they can be used to calculate all simulation quantities in a homogeneous phase with an accuracy similar to that obtained for the full two-body+three-body potentials. For example, previous Gibbs ensemble Monte Carlo[11] and nonequilibrium molecular dynamics[12] simulations have demonstrated that the relationship can be used to accurately obtain both the fluid phase envelope and shear viscosities at different strain rates, respectively. In addition to the energy, the pressure can also be accurately obtained[13] when the virial expression is suitably modified. The modification[13] to the virial expression for pressure arises because of the density-dependent nature of the intermolecular potential. Other issues regarding density-dependent potentials have been described in detail in the literature.[23] Figure 6 illustrates the accuracy of the relationship for the calculation of the vapor pressure curve of argon. At low temperatures, the pressures obtained are indistinguishable from results obtained using the full three-body potential, whereas at higher temperatures, the vapor pressure is slightly underpredicted. Details of the simulation method are the same as reported previously.[24] As noted above, a limitation of the approach is that it is not valid for inhomogeneous regions, which must be handled by other approaches.[25]

IV. CONCLUSIONS

Simple relationships exist between three- and two-body interactions in both the normal fluid region and solid phases of noble gases, and possibly other atoms. The relationship for liquids has a simple density dependence with only one parameter determined from simulation data. In contrast, the relationship for the solid depends both on density and on the square of density and requires two parameters to be evaluated. The values of these parameters are only sensitive to system size when a small number of atoms are involved. For a system size of 500 or more atoms, they remain constant. The relationships are valid for both subcritical and slightly supercritical temperatures. A practical benefit of the relationships is that they enable the use of two-body intermolecular potentials for the prediction of the properties of real systems without the computational expense of three-body calculations.

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