

On the relationship between two-body and three-body interactions from nonequilibrium molecular dynamics simulation

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Nonequilibrium molecular dynamics (NEMD) simulations are performed for argon at different strain rates using accurate two-body and three-body intermolecular potentials. The contributions of two- and three-body interactions to the configurational energy of argon at different strain rates are reported. The NEMD data indicate that there is the same simple relationship between two- and three-body interactions as reported previously [Marcelli and Sadus, *J. Chem. Phys.* **112**, 6382 (2000)] from equilibrium Monte Carlo simulations. The relationship is largely independent of strain rate. NEMD calculations using this relationship for shear viscosity at different strain rates indicate good agreement with full two-body+three-body calculations. This means that the effect of three-body interactions on transport properties might be achieved in a conventional two-body NEMD simulation without incurring the computational penalty of three-body calculations. © 2001 American Institute of Physics. [DOI: 10.1063/1.1413971]

I. INTRODUCTION

Despite the considerable increase in computing performance and improvements in algorithms in recent decades, molecular simulation¹ is typically confined to calculating interactions between pairs of molecules. However, genuine pair-potentials such as the BFW² or Aziz–Slaman³ potentials are used only rarely. Instead, common practice is to use an effective many-body potential such as the Lennard-Jones potential. Effective potentials are very useful for coarse grain simulations but their use can hide subtle intermolecular influences. For example, it was recently reported^{4,5} that the vapor–liquid equilibria of fluids are significantly influenced by three-body interactions. These important three-body effects have previously remained undetected because earlier work was confined to effective potentials. It has also been established^{4,5} that pair-potentials alone are insufficient for quantitatively accurate calculations. Instead, to obtain quantitative agreement with experiment, pair-potentials must be used in conjunction with three-body interactions.

There are many contributions to three-body interactions but the available evidence⁵ indicates that the triple-dipole term of Axilrod and Teller⁶ alone is an excellent approximation. Nonetheless, the need for three-body calculations in addition to pair calculations represents a considerable computational impediment. Recently, Monte Carlo simulations have been reported⁷ which indicate that there is a simple and accurate relationship between the two-body (E_2) and three-body (E_3) configurational energies of a fluid:

$$E_3 = -\frac{2\nu\rho E_2}{3\epsilon\sigma^6}, \quad (1)$$

where ν is the nonadditive coefficient,⁸ 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). The significance of this relationship is that it allows us to obtain an accurate overall intermolecular potential (u) solely in terms of pair contributions (u_2) and well-known intermolecular parameters:

$$u = u_2 \left(1 - \frac{2\nu\rho}{3\epsilon\sigma^6} \right). \quad (2)$$

Therefore, the effect of three-body interactions can be incorporated into a simulation involving pair-interactions without any additional computational cost. Comparison⁷ of this approach with a full two-body plus three-body calculation indicates that there is no significant loss of accuracy.

The transport properties of fluids, such as shear viscosity, is an aspect of fluid behavior that could potentially benefit from the use of accurate pair-potentials and three-body interactions. In common with other applications of molecular simulation, the transport properties of fluids have largely been investigated using effective potentials, although some work involving three-body potentials has been reported^{9–12} for shear viscosity. The aim of this work is to determine whether Eq. (1) is also valid for fluids far from equilibrium. In particular, it is of interest to determine the effect of different strain rates on the validity of Eq. (1).

II. SIMULATION DETAILS

The details of the simulation have been discussed extensively elsewhere.^{5,11} Therefore, only an outline of the main details is given here.

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A. Intermolecular potentials

For the pair-interactions of argon, we used the Barker–Fisher–Watts (BFW)² potential, which has the following functional form:

$$u_2(r) = \epsilon \left[\sum_{i=0}^5 A_i (x-1)^i \exp[\alpha(1-x)] - \sum_{j=0}^2 \frac{C_{2j+6}}{\delta + x^{2j+6}} \right]. \quad (3)$$

In Eq. (3), $x = r/r_m$ where r_m is the intermolecular separation at which the potential has a minimum value 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 values of these parameters were taken from the literature² and they have also been recently summarized elsewhere.⁷

The contribution from three-body interactions was evaluated from the triple-dipole potential proposed by Axilrod and Teller:⁶

$$u_3 = \frac{\nu(1 + 3 \cos \theta_i \cos \theta_j \cos \theta_k)}{(r_{ij} r_{ik} r_{jk})^3}, \quad (4)$$

where ν is the nonadditive coefficient, and the angles and intermolecular separations refer to a triangular configuration of atoms. The nonadditive coefficient for argon (518.3 a.u.) was taken from the literature.⁸

B. NEMD simulation details

The NEMD simulations were performed by applying the standard SLLOD equations of motion for planar shear flow,¹³ using a Gaussian thermostat multiplier to keep the kinetic temperature of the fluid constant. In previous work,^{11,12} such simulations have been used to report the energy, pressure, and shear viscosity. The focus of this work is to determine the relative contributions to energy of two-body (E_2) and three-body (E_3) interactions at different strain rates ($\dot{\gamma}$), and to show if this relationship is useful for NEMD simulations.

A total system size of 500 atoms was used. The simulations were performed in a cubic box and the conventional periodic boundary conditions¹ were applied. 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.⁵ The equations of motion are integrated by a fourth order Gear predictor-corrector scheme¹⁴ with a reduced integration time step ($t^* = t\sqrt{\epsilon/m\sigma^2}$, m is the mass) of 0.001. A single nonequilibrium simulation trajectory is typically run for 250 000 time steps. Averages are taken over five independent trajectories, each starting at a new configuration. To equilibrate the system, each trajectory is first run without a shearing field. After the shearing field is switched on, the first 50 000 time steps of each trajectory are ignored, and the fluid is allowed to relax to a nonequilibrium steady-state. Therefore, every energy datum point represents a total run length of $5 \times 200\,000 = 10^6$ time steps. The three-body simulations re-

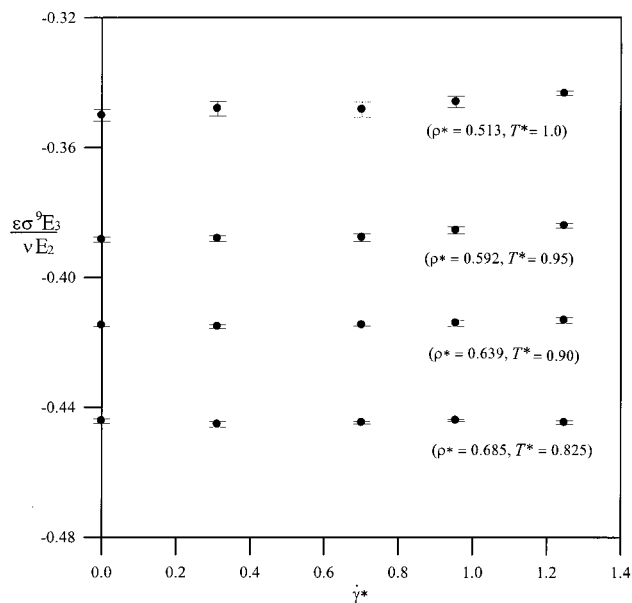


FIG. 1. The ratio of three-body and two-body energies of argon obtained from NEMD at different state points and different strain rates.

quire typically 20 and 12 CPU hours on the Fujitsu VPP300 and NEC SX-4/32 supercomputers, respectively. In contrast, two-body only simulations under the same conditions, run at least an order of magnitude faster.

III. RESULTS AND DISCUSSION

Equation (1) is a remarkably simple result that allows us to incorporate the effect of three-body interactions during a pairwise additive simulation. Equation (1) can be applied to both Monte Carlo and molecular dynamics simulations. In the latter case, the forces between molecules can be evaluated from the overall intermolecular potential defined by Eq. (2). However, prior to this work, the validity of such a simple relationship for NEMD was uncertain because of the added influence of factors such as variation in the strain rate.

The ratio of three-body to two-body energies for argon at different reduced densities ($\rho^* = \rho\sigma^3$) and reduced temperatures ($T^* = kT/\epsilon$, k is Boltzmann's constant) is shown in Fig. 1 as a function of reduced strain rate ($\dot{\gamma}^* = \dot{\gamma}\sigma\sqrt{m/\epsilon}$). The temperatures and densities represent different state points on the liquid-phase branch of the vapor–liquid coexistence curve of pure argon. Irrespective of the state point, it is apparent that the ratio of the energies is largely independent of the strain rate. The dependence of the energy ratio on density is illustrated in Fig. 2. The values predicted by Eq. (1) are also illustrated for comparison. This simple relationship fits the NEMD simulation data with an average absolute deviation of 2.3%. This is close to the same quality of agreement (2%) that was obtained⁷ for the Monte Carlo study of equilibrium properties.

To test the usefulness of this result, we performed NEMD simulations for the shear viscosity of argon using Eq. (2) in conjunction with the BFW two-body potential. The reduced shear viscosity ($\eta^* = \eta\sigma^2/\sqrt{m\epsilon}$), reduced configurational energy ($E_{\text{conf}}^* = E_{\text{conf}}/\epsilon$) and reduced configurational pressure ($P_{\text{conf}}^* = P_{\text{conf}}\sigma^3/\epsilon$) predicted by this relationship at

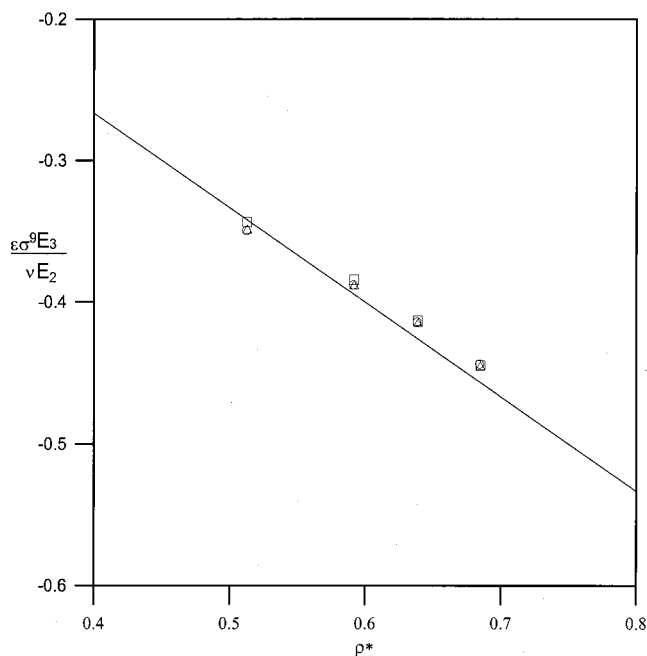


FIG. 2. The ratio of three-body and two body energies for argon obtained from NEMD at different strain rates [$\gamma^*=0$ (\circ), 0.702 (\triangle), 1.428 (\square)] as a function of density. The line through the points was obtained from Eq. (1).

different strain rates are illustrated in Fig. 3. In Fig. 3, a comparison is also made with calculations using the BFW+Axilrod-Teller potential.¹¹ It is apparent that, irrespective of strain rate, both the shear viscosity and configurational energy obtained from the simulations using Eq. (2) agree very well with the BFW+Axilrod-Teller calculations. Because the simulations using Eq. (2) do not involve explicitly evaluating three-body interactions, they only require the same amount of computer time as conventional two-body simulations.

In contrast to the accurate results for shear viscosity and configurational energy, calculations using Eq. (2) underestimated the two-body+three-body configurational pressure by typically 10%. To investigate the source of this discrepancy, we examined the effect of Eq. (2) on the pair-distribution function of the fluid. It is apparent from Fig. 4 that Eq. (3) only has a negligible effect on the pair-distribution function of the fluid, even at moderate to high strain rates. The two-body potential contribution to the pressure may be calculated from $g(r)$ as

$$p_u^{(2)} = (2/3)\pi\rho^2 \int_0^\infty g(r)r^3 \frac{\partial u^{(2)}(r)}{\partial r} dr. \quad (5)$$

A comparison of Eq. (5) with the directly calculated pressure via the standard Irving-Kirkwood expression¹⁵ for both the BFW+Axilrod-Teller potential and Eq. (2) yields excellent agreement to within the fourth decimal place. Equation (2) does not adversely affect the pair fluid structure normally expected from the full BFW+Axilrod-Teller potential. Therefore, the differences in the pressure results can only be due to differences in the three-body distribution functions as well as the *spatial derivatives* of the Axilrod-Teller potential

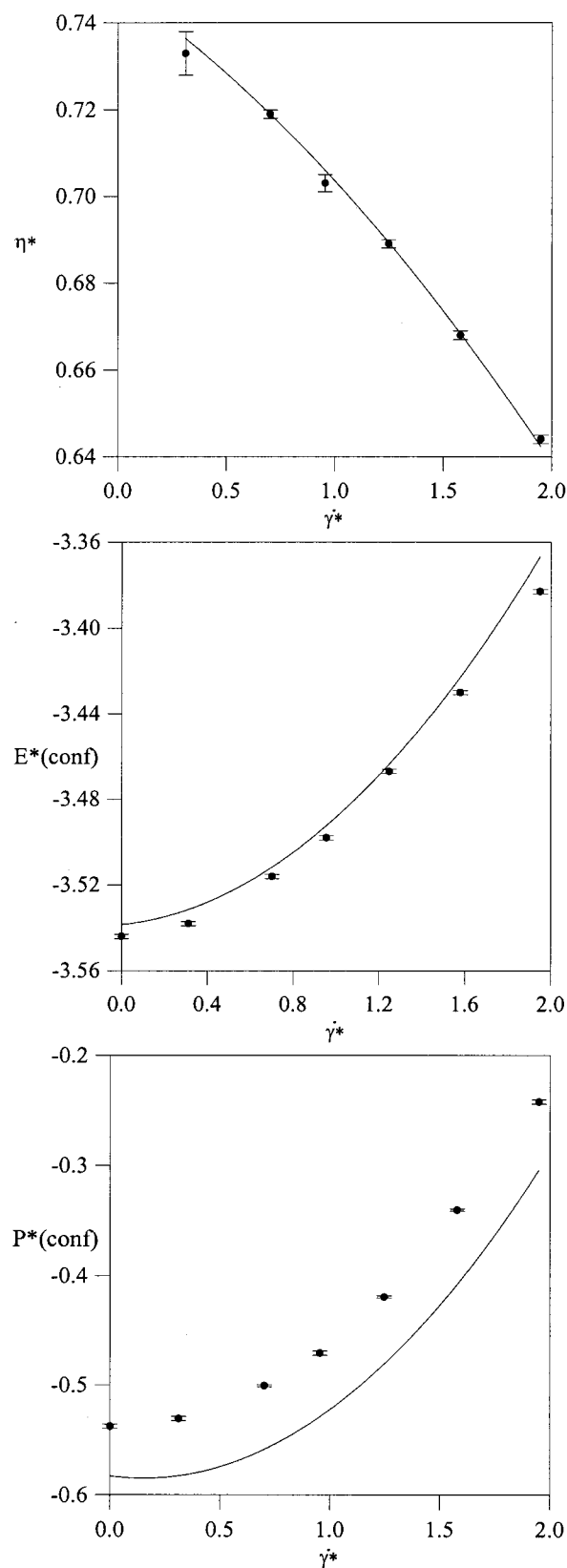


FIG. 3. Comparison of NEMD simulations for the shear viscosity, configurational energy and configurational pressure of argon using Eq. (2) (—) with data from simulations (Ref. 11) involving a full evaluation of BFW+Axilrod-Teller interactions (\bullet) ($T^*=0.95$, $\rho^*=0.592$). Long-range corrections have not been included.

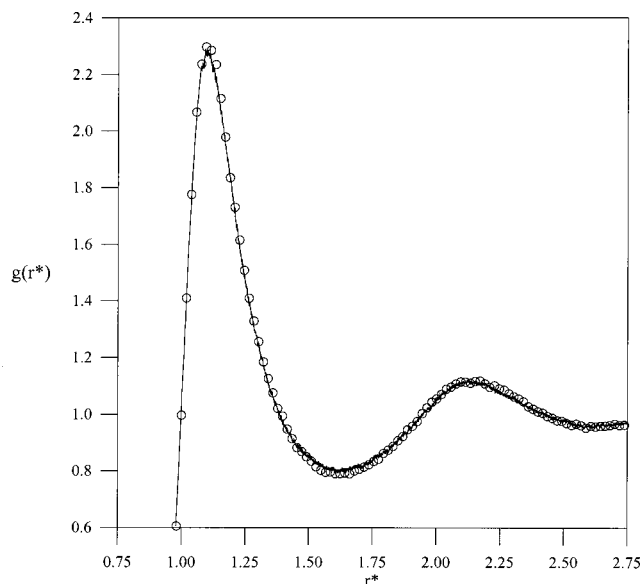


FIG. 4. Comparison of the pair-distribution function at different reduced intermolecular separations ($r^* = r/\sigma$) obtained using the BFW + Axilrod-Teller potential (\circ) and Eq. (2) (—). The reduced strain rate is 0.702.

function compared with the corresponding effective three-body term in Eq. (2).

IV. CONCLUSIONS

NEMD simulation data indicate that the simple relationship between two-body and three-body energies obtained from Monte Carlo simulations is also valid for shearing systems. The calculations at different strain rates indicate that the relationship is largely independent of strain rate. This relationship may be used to predict the shear viscosity at

different strain rates. Therefore, Eq. (2) is a reasonable approximation to a full two-body+three-body potential and could be used in NEMD simulations to incorporate the effect of three-body interactions without the computational cost of a full three-body calculation.

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