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Simulation results for a fluid with the Axilrod-Teller triple dipole potential

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Simulations are performed for a fluid whose atoms interact with the Lennard-Jones pair potential and the Axilrod-Teller three-body potential, and results are tabulated for the internal energy and for the virial pressure. The triple dipole potential is effectively repulsive, as is well known, making the internal energy less negative and the pressure more positive than for the underlying Lennard-Jones fluid. For the relatively low polarizabilities examined, $\nu/3\epsilon\sigma^9 \approx 0.03$, the perturbation approximation of Barker, Fisher, and Watts [Mol. Phys. **21**, 657 (1971)] is shown to be essentially exact, and the hypernetted-chain approximation of Attard [Phys. Rev. A **45**, 3659 (1992)] is quantitatively accurate at low densities, but only qualitatively correct for the liquid state.

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I. INTRODUCTION

This paper is concerned with establishing some benchmark results for a fluid that interacts with a three-body potential. Most studies of the macroscopic properties of matter assume that the microscopic interaction potentials are pairwise additive, and that higher-order many-body contributions can be neglected. In an important series of papers, Barker and co-workers [1–3] showed that a pair potential plus the Axilrod-Teller triple dipole potential were necessary and sufficient to describe argon. Their conclusions were based on a perturbation approximation, which, although plausible for the parameters used, has not been tested against exact calculations. Since the form of the intermolecular potential is crucial to a statistical-mechanical description of matter, it seems desirable to quantitatively assess the validity of the perturbation approximation. Further, the data may be used to test future approximations for fluids with three-body potentials.

Simulation results for the internal energy and for the virial pressure are reported for a Lennard-Jones plus Axilrod-Teller fluid. This model potential is sufficient for testing theoretical approximations. Although the choice was certainly motivated by reality, it is not intended to apply the results to any real fluid since it is too simple to describe an actual intermolecular potential over the whole range of separations. The choice of potential parameters approximately reflect the properties of argon, but again the highly idealized model serves only to establish some benchmark results against which approximate theories may be tested. Two such approximations are examined here: the perturbation approach used by Barker and co-workers [1–3], and the hypernetted-chain closure for fluids with three-body potentials recently given by Attard [4]. For the relatively low polarizability $\nu/3\epsilon\sigma^9 \approx 0.03$, which is essentially the ratio of the strengths of the three- and two-body potentials, it is shown that the perturbation approximation [1–3] is very accurate, and that the closure approximation of Attard [4] is most reliable at low densities.

II. THEORY

A. Model fluid

The Hamiltonian for the fluid consists of two- and three-body terms,

$$H_N = \sum_{\substack{i,j=1 \\ (i<j)}}^{N} u_2(r_{ij}) + \sum_{\substack{i,j,k=1 \\ (i<j<k)}}^{N} u_3(\mathbf{r}_i,\mathbf{r}_j,\mathbf{r}_k) \ . \tag{1}$$

The Lennard-Jones pair potential is

$$u_2(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] \ , \tag{2}$$

and the Axilrod-Teller triple dipole potential is [5]

$$u_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = \nu \frac{r_{12}^2 r_{13}^2 r_{23}^2 + 3(\mathbf{r}_{12}\cdot\mathbf{r}_{13})(\mathbf{r}_{21}\cdot\mathbf{r}_{23})(\mathbf{r}_{31}\cdot\mathbf{r}_{32})}{r_{12}^5 r_{13}^5 r_{23}^5} \ . \tag{3}$$

To be definite, values of the parameters that effectively describe the properties of argon may be chosen, even though the Lennard-Jones potential is too simple to represent the interaction potential between a pair of argon atoms over the whole range of separations [6]. As mentioned above, the results for this model fluid are only to be used to test approximate theories, and they have little relevance to any experiment performed on argon. However, since one would like to test a theory in a region near its eventual application, there is some motivation for choosing this model potential with the following parameters. In this work a core diameter of $\sigma = 3.405$ Å, and a well depth of $\epsilon/k_B = 120$ K are used for most cases. These correspond to the measured position and depth of the argon potential well, but they overestimate the van der Waals dispersion contribution at long range [6]. The same core and a value of $\epsilon/k_B = 75.3$ K give the exact asymptote at long range, and some results are also presented for this case. The Axilrod-Teller triple dipole potential is the leading many-body correction to the pair potential at long range, and for argon $\nu=7.32\times10^{-108}$ J m^9 [2,7]. At small separations the intermolecular potential is likely dominated by the repulsion between pairs of atoms, and so other triplet contributions [8] besides the Axilrod-Teller asymptote are not considered here.

B. Monte Carlo

The simulation was performed with the Hamiltonian, Eq. (1), using the standard metropolis algorithm. A cubic box was used, with periodic boundary conditions, minimum image convention, and a potential cutoff of half the box length. The minimum-image convention has to be modified slightly for the case of a three-body potential (and also to calculate the three-particle distribution function [9]), because an ambiguity that leads to physically unrealizable triangles can occur; the distance between the closest images of particles j and k with respect to particle i is not necessarily the minimum-image distance of j to k. The situation can be resolved generally by defining the x component of the lattice translation vectors,

$$t_{ij}=[(x_i-x_j)/L]L\ ,\quad t_{ik}=[(x_i-x_k)/L]L\ , \tag{4}$$

where l is the box length and $[x]$ means the closest integer to x. One takes the x component of the separation vectors to be

$$\begin{aligned} x_{ij}&=x_i-x_j-t_{ij}\ ,\\ x_{ik}&=x_i-x_k-t_{ik}\ ,\\ x_{jk}&=x_j-x_k+t_{ij}-t_{ik}\ , \end{aligned} \tag{5}$$

and similarly for the y and z components. For most cases x_{jk} is the same as given by the standard minimum-image convention, but for those times when the usual approach corresponds to an unrealizable triangle, this method gives an acceptable result.

The cutoff convention sets the triplet potential to zero if any side of the triangle has a length greater than $L/2$ (and similarly for the pair potential). Configurations with ambiguous nearest images do not contribute to the three-body part of the Hamiltonian because the actual triangle yielded in this case by the minimum-image algorithm above has at least one side greater than $L/2$.

The internal energy and the pressure were evaluated as ensemble averages of the Hamiltonian and of the virial, respectively, apart from the three-body pressure term which was found from the energy via Euler's theorem for homogeneous functions [2]. A tail correction for the $L/2$ cutoff was added to the two-body term. No tail correction was added to the three-body term, although a method for this has been suggested [2]. Most of the simulations were carried out with 108 particles. At a density of $\rho=0.5\sigma^{-3}$, this corresponded to a potential cutoff of $L/2=3\sigma$. After equilibration, some two million configurations were generated, and statistics were collected every four moves per particle. The entire simulation was divided into 20 blocks, and the standard deviation of these blocks was estimated. The statistical uncertainty quoted in the tables is this number divided by the square root of 20.

C. Perturbation approximation

The perturbation approach used by Barker, Fisher, and Watts [2] consists of the linearization of the exponential of the Hamiltonian with respect to the three-body potential. This procedure is arguably valid when the strength of the Axilrod-Teller triple dipole potential is small compared to the well depth of the pair potential. For the present fluids, $\nu/\epsilon\sigma^9\approx0.1$, and one expects the approximation to be accurate.

In the perturbation theory [2], the internal energy is written as an ensemble average of the pair and of the triplet potential and of their product in the reference fluid, which interacts only with the pair potential, and similarly for the virial pressure. In the present case the reference system is the pure Lennard-Jones fluid. Simulations were performed using the metropolis algorithm, with 108 particles in a cubic box, periodic boundary conditions, the standard minimum-image convention, and a potential cutoff of half the box length. For the ensemble averages, the three-body minimum-image convention described above was used. A tail correction for the two-body term was added. After equilibration, some seven million configurations were generated, and the ensemble averages were collected every ten moves per particle. The statistical error was estimated as described above, from the fluctuations in 20 subaverages.

D. Closure approximation

A hypernetted-chain (HNC) closure for fluids with three-body potentials has been given by Attard [4]. Here the three-body potential is reduced to a state-dependent effective pair potential,

$$\beta\bar{u}(r_{12})\equiv-\rho\int\{-1+\exp[-\beta u_3(\mathbf{r}_{31},\mathbf{r}_{32})]\}\times g(r_{31})g(r_{32})d\mathbf{r}_3\ , \tag{6}$$

where $\beta=1/k_BT$, k_B being Boltzmann's constant and T the absolute temperature, where ρ is the number density, and where $g(r)=h(r)+1=\exp[-\beta w(r)]$ is the radial distribution function. The effective pair potential is the leading three-body contribution to the pair potential of mean force $w(r)$. Consequently, one can make the approximate closure

$$\beta w(r_{12})=\beta u_2(r_{12})+\beta\bar{u}(r_{12})-h(r_{12})+c(r_{12})-d(r_{12})\ , \tag{7}$$

where the total, $h(r)$, and the direct, $c(r)$, pair-correlation functions are related by the Ornstein-Zernike equation

$$h(r_{12})=c(r_{12})+\rho\int h(r_{13})c(r_{32})d\mathbf{r}_3\ . \tag{8}$$

The HNC approximation neglects the bridge function entirely,

$$d(r)=0\ , \tag{9}$$

while the reference hypernetted-chain closure approximates it by the bridge function of some reference fluid.

In this paper a hard-sphere fluid of the same density and core diameter was chosen, and the HNCP bridge function [10], which is the Padé approximant formed from the first two terms of the density expansion, is used to form the reference hypernetted-chain (RHNC) approximation

$$d(r)=\frac{\rho^2 d^{(2)}(r)}{1-\rho d^{(3)}(r)/d^{(2)}(r)} . \tag{10}$$

Finally, the internal energy and the virial pressure require an integral over the three-particle distribution function, and the Kirkwood superposition approximation is used for this

$$g_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=g(r_{12})g(r_{13})g(r_{23})\exp[-\beta u_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)] . \tag{11}$$

The numerical details of the calculations were as described previously [4]. The number of grid points used was 2^{12}, and the mesh in real space was $\Delta r=0.01\sigma$, giving a cutoff of 40σ. The integrals for the pressure, the energy, and the effective pair potential were evaluated using Gaussian quadratures with 75 nodes for the angular coordinate, and 250 nodes for the radial coordinate, and with a radial cutoff of 8σ. These multidimensional integrals were evaluated once every 20–100 iterations of the Ornstein-Zernike equation and closure. Up to five such cycles were sufficient for six-figure convergence of the various thermodynamic properties.

III. RESULTS

The various approximations are compared with simulation results for the energy and pressure of the fluid in Table I. The parenthetical quantity is the estimated error in the last digit, the standard deviation obtained as described above. The most exact approaches, the Monte Carlo (MC) and the molecular-dynamics (MD) [11] simulations, are in precise agreement for the internal energy per particle, and in reasonable agreement for the some-

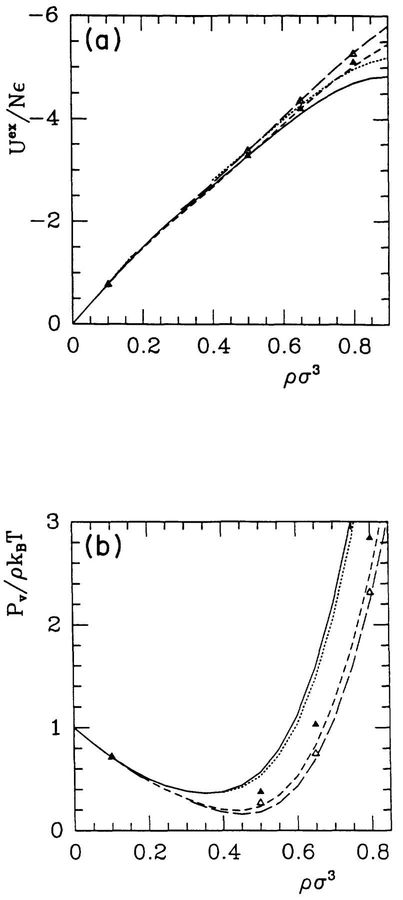

FIG. 1. The internal energy (A) and the virial pressure (B) of the fluids ($\sigma=3.405$ Å, $\epsilon/k_B=120$ K, and $\nu/\epsilon\sigma^9=0.072$ or $\nu=0$) at a reduced temperature of $k_BT/\epsilon=1.333$. The Axilrod-Teller fluid is described by the Monte Carlo simulations (solid symbols), the HNC (solid curve), and the RHNC (short-dashed curve). The Lennard-Jones fluid is described by the Monte Carlo simulations (open symbols), the HNC (dotted curve), and the RHNC (long-dashed curve).

TABLE I. The pressure and the internal energy of a fluid that interacts with the Lennard-Jones pair potential ($\epsilon/k_B=120$ K, $\sigma=3.405$ Å) and the Axilrod-Teller triple dipole potential ($\nu/\epsilon\sigma^9=0.072$) at two state points, as predicted by various theories. (pert. denotes perturbation.)

	$k_BT/\epsilon=1.033$, $\rho\sigma^3=0.65$		$k_BT/\epsilon=0.746$, $\rho\sigma^3=0.817$	
	$U^{ex}/N\epsilon$	$P/\rho k_BT$	$U^{ex}/N\epsilon$	$P/\rho k_BT$
MC	−4.366(2)	0.15(1)	−5.644(5)	0.56(4)
MD[a]	−4.36	0.10	−5.64	0.38
pert.	−4.363(1)	0.138(5)	−5.636(2)	0.62(1)
HNC	−4.2933	0.7723	−5.3944	2.6548
RHNC	−4.3573	−0.0253	−5.5845	0.8054
		Lennard-Jones ($\nu=0$)		
MC	−4.523(1)	−0.201(6)	−5.900(2)	−0.34(1)
MD[a]	−4.52	−0.11	−5.90	−0.20
HNC	−4.4678	0.6510	−5.6704	2.2619
RHNC	−4.5188	−0.1851	−5.8540	0.3568

[a] Reference [11].

what more sensitive virial pressure. A potential cutoff of 2.5σ was used in the molecular-dynamics simulations [11]. The perturbation approximation lies within the statistical uncertainty of the Monte Carlo simulations. This is an encouraging result considering that the fluid is a liquid at these high densities and low temperatures. The HNC approximation underestimates the magnitude of the internal energy, but is greatly improved by the inclusion of the hard-sphere bridge function in the RHNC approach. A similar improvement is seen in the case of the virial pressure.

Comparison with the Lennard-Jones fluid shows that the Axilrod-Teller triple dipole potential increases the internal energy and the pressure, as has been found previously [1–4]. One can see that a significant part of the error in the HNC approximations for the full fluid is already apparent at the pair level.

Table II contains simulation and perturbation results for the Axilrod-Teller fluid, and simulation results for the Lennard-Jones (LJ) fluid. Again, one sees that since the Axilrod-Teller triple dipole potential gives rise to an extra repulsion between the atoms via the effective pair potential [4], the energy and the pressure are increased with respect to the Lennard-Jones fluid [1–4]. The perturbation approximation agrees with the Monte Carlo simulation to within the statistical error, even for the relatively larger three-body contribution, $\nu/\epsilon\sigma^9=0.115$.

One simulation was performed with 256 atoms in order to test for finite-size effects. At the density of $0.65\sigma^{-3}$, this corresponded to increasing the potential cutoff from 2.8σ to 3.7σ. For the pure Lennard-Jones fluid, the internal energy was unaffected, but the pressure showed a statistically significant increase. The most obvious conclusion is that the tail correction to the pair terms works very well for the internal energy, but does not completely correct for the finite-size cutoff of the more sensitive virial pressure. For the Axilrod-Teller fluid, both the energy and the pressure were significantly more positive. Hence it appears that the neglect of the tails of the three-body terms is too crude an approximation, and that the superposition correction of Barker, Fisher, and Watts [2] may be well worth exploring. The limitation on the exact results reported here is probably the systematic errors due to finite-size effects, rather than statistical errors due to the finite number of configurations generated.

Figure 1 shows the internal energy and the virial pressure for the Axilrod-Teller fluid and for the Lennard-Jones fluid at a reduced temperature of $k_BT/\epsilon=1.333$. The RHNC approximation is almost quantitatively correct for the internal energy, but for the pressure underestimates the additional repulsion due to the triple dipole potential. But the HNC and the RHNC theories indicate that this is a subcritical isotherm for the Lennard-Jones fluid, but a supercritical one for the Axilrod-Teller fluid. At low densities one can see that the effect of the triple dipole potential is small, as also follows from Eq. (6) which is linear in density to leading order. In this regime the HNC and the RHNC are exact.

IV. CONCLUSION

This paper reports some exact benchmarks for a fluid whose intermolecular potential includes a three-body term. The total potential employed here is a gross simplification of any real intermolecular potential, including the ones used previously to accurately describe argon [1–3,6]. However, it shares enough similarities with reality that any theory which describes this model accurately will be equally reliable when applied to the experimental system using more sophisticated potentials. In this paper

TABLE II. The pressure and the internal energy of the fluids ($\sigma=3.405$ Å).

	MC		pert.		LJ ($\nu=0$)	
$\rho\sigma^3$	$U^{ex}/N\epsilon$	$P/\rho k_BT$	$U^{ex}/N\epsilon$	$P/\rho k_BT$	$U^{ex}/N\epsilon$	$P/\rho k_BT$
		$\epsilon/k_B=120$ K, $\nu/\epsilon\sigma^9=0.072$, $k_BT/\epsilon=1.333$				
0.10	−0.764(3)	0.725(3)	−0.763(1)	0.723(1)	−0.775(1)	0.716(1)
0.50	−3.277(3)	0.38(1)	−3.274(1)	0.402(6)	−3.375(1)	0.267(6)
0.65	−4.203(2)	1.03(1)	−4.201(1)	1.028(6)	−4.357(1)	0.751(6)
0.80	−5.010(4)	2.85(2)	−5.014(2)	2.830(8)	−5.267(2)	2.314(8)
		$\epsilon/k_B=120$ K, $\nu/\epsilon\sigma^9=0.072$, $k_BT/\epsilon=1.166$				
0.50	−3.349(4)	0.06(1)	−3.342(1)	0.063(5)	−3.454(1)	−0.084(5)
0.65	−4.292(2)	0.60(1)	−4.287(1)	0.605(5)	−4.444(1)	0.299(5)
0.80	−5.146(4)	2.54(2)	−5.152(2)	2.423(9)	−5.404(2)	1.841(9)
		$\epsilon/k_B=75.3$ K, $\nu/\epsilon\sigma^9=0.115, k_BT/\epsilon=1.860$				
0.50	−3.047(2)	1.083(7)	−3.041(1)	1.105(4)	−3.185(1)	0.943(4)
0.65	−3.856(2)	1.931(7)	−3.853(2)	1.931(6)	−4.099(2)	1.604(6)
0.65[a]	−3.845(3)	1.968(9)	−3.844(1)	1.965(4)	−4.0992(9)	1.622(4)
0.80	−4.451(5)	3.75(2)	−4.458(3)	3.729(9)	−4.865(3)	3.133(9)

[a] 256 atoms.

the perturbation approximation used by Barker and coworkers [1–3] was tested and found to be virtually exact for this highly idealized model of argon. By the above argument, this observation lends some weight to the specific conclusions of those workers regarding the necessity and the sufficiency of the Axilrod-Teller triple dipole potential for calculating the macroscopic properties of argon. The accuracy of the perturbation approach for argon likely pertains to other fluids [12], at least those with low polarizabilities, $\nu/3\epsilon\sigma^9$. Since the simulation of the three-body fluid is one or two orders of magnitude more computationally demanding than that of a fluid which interacts only with pair potentials, the perturbation approach offers significant savings.

Complementary approaches for fluids that interact with three-body potentials are based on the Ornstein-Zernike integral equation. The HNC theory of Attard [4] was tested here and found to be accurate at low densities, but less reliable for the liquid state. The RHNC theory offered worthwhile improvements, even using the simplest prescription for the reference fluid. It is possible that procedures could be developed to optimize this choice. Alternatively, the methods developed to calculate the three-particle distribution function, such as the binodal chain approximation [13], could be adapted for fluids with three-body potentials, and tested against the benchmark results established here.

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