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Three-body dispersion contributions to the thermodynamic properties and effective pair interactions in liquid argon

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The contributions of three-body triple dipole and dipole-dipole-quadrupole dispersion interactions to the thermodynamic properties of liquid argon are examined, using a recently introduced simulation scheme which contains an explicit, quantum mechanical representation of the underlying electronic structure [Mol. Phys. **94**, 417 (1998)]. The experimental pressure and energy at a series of liquid densities are shown to be quite accurately reproduced by a combination of the best available pair potential (Aziz) plus these three-body terms. The extent to which these many-body effects can be encompassed by an effective pair potential is then discussed. The nonuniqueness of such an effective potential is reiterated. It is shown that in the dense liquid, the three-body contribution to the effective pair potential ($\phi(r)$) varies approximately linearly with density and is almost temperature independent. It is shown how the addition of $\phi(r)$ to the Aziz pair potential moves the latter toward the widely used Lennard-Jones (12-6) potential. © 1999 American Institute of Physics. [S0021-9606(99)50527-8]

I. INTRODUCTION

The rôle of many-body contributions to the interatomic potential in determining the properties of atomic fluids is a subject which has attracted much attention over a long period of time, from theory,¹⁻⁸ simulation⁹⁻¹² and experiment.¹³⁻¹⁵ Foremost among the many-body terms are the three-body contributions to the dispersion interactions, for which the Axilrod-Teller (AT) expression¹⁶ gives the lowest-order (triple dipole, or DDD) contributions:

$$u_{123}^{\text{DDD}} = C_9(1 + 3 \cos \gamma_1 \cos \gamma_2 \cos \gamma_3) r_{12}^{-3} r_{13}^{-3} r_{23}^{-3}, \quad (1)$$

where γ_1 , γ_2 , and γ_3 are the interior angles of the triangle formed by atoms 1, 2, and 3 and r_{ij} is an interatomic separation. Other many-body effects include higher-order dispersion terms (dipole-dipole-quadrupole, or DDQ, etc.) as well as many-body contributions which enter on the range of the overlap of the electron densities of the constituent atoms. Explicit expressions for the higher-order dispersion terms do exist, but become increasingly complicated,¹⁷⁻¹⁹ and their effect on liquid-state properties has not been characterized. Very little is known about the short-range terms; in part these must “damp” the asymptotic expressions for the dispersion interactions at short-range,²⁰ but other effects must occur in the repulsive interaction between a collection of three or more atoms.

Recently, we introduced a novel simulation method which allows the dispersion effects to be represented. In it the dispersion interaction is not modeled via the classical expressions for the pair- and three-body potential (e.g., the London and Axilrod-Teller formulas), but from an explicit description of the electronic structure in the spirit of the

Car-Parrinello method.²¹ The advantage of treating dispersion interactions in this way, rather than by use of the analytical expression, is that the description at the quantum mechanical level allows for proper treatment of both dispersion damping and periodic boundary conditions at the *three*-body level. The latter makes this method suitable for performing simulations of bulk system with full three-body interactions, whereas the use of an explicit three-body potential, like the AT, always introduces problems of truncating the interactions.

In the present paper, we apply this method to the classical problem of the many-body dispersion contributions to the properties of argon. In it we will examine these contributions to the energy, equation-of-state (EoS) and radial distribution function (RDF). We will then also consider how the many-body potential terms contribute to a (temperature and density dependent) *effective pair potential* and, ultimately, discuss how the combination of this with the “exact”²² pair potential compares with the much studied Lennard-Jones pair potential.

A partial motivation for this first application of the code is to validate it on a well-studied problem. However, compared to previous studies our work contains a number of additional features. First, we characterize the significance of the DDQ terms, in addition to the DDD ones and thereby hint at the convergence of the three-body dispersion terms at the level of properties. Second, we are using a liquid structure which is fully consistent with the implicit many-body potential we are using, rather than evaluating the three-body effects using structures deduced with a pair potential, or doing a perturbation calculation. Third, we evaluate the effec-

tive pair potentials at a wider range of temperature and density than has been done previously. We note that, although the problem has been much studied, there remains a great deal of ignorance about what has been learned from these studies. For example, although it is well-recognized that an effective potential must depend on the thermodynamic state, it is little appreciated that there is no such thing as *the* effective pair potential at a given state point—two different pair potentials are required to reproduce energy and EoS. In the face of this, perhaps some repetition of long-standing results can be tolerated.

II. SIMULATIONS OF THE TWO- AND THREE-BODY DISPERSION EFFECTS

A. The simulation model

In this section, we will briefly describe the simulation model that is being used: for full details we refer to Ref. 19

The method rests on a simplified representation of the internal electronic structure of the atoms by a *single* quantum particle in an effective three-level system: an *s*-type ground state, three *p*-type excited states, and five *d*-type excited states. This system is then handled in a fully quantum mechanical way, using an *N*-atom wave function which is expanded (configuration interaction) about the noninteracting ground state over all possible pairs of excited states, where the *N*-atom functions are constructed from the single atom states by simple product. If combined with an electronic Hamiltonian containing all dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions, we may derive an analytical expression for the energy $e^{\text{CPA}}(\{c\}, \{\mathbf{r}\})$ depending on all the coefficients $\{c\}$ in the expansion of the wave function, and all the coordinates $\{\mathbf{r}\}$ of the atoms, in the so-called Coupled-Pair Approximation (CPA).²³ It has been shown numerically that the minimum of e^{CPA} with respect to the coefficients, provides the correct two- and three-body dispersion energy, up to triple-quadrupole. With this simple model of the electronic structure, known values for the pair- and three-body dispersion of a wide range of atoms can be reproduced with the choice of a few parameters.

We have incorporated this quantum mechanical scheme into a conventional molecular dynamics program via a Car–Parrinello type approach; in this, the coefficients are treated as extra degrees of freedom, which are updated in the simulation from time t to $t+dt$ by integrating the corresponding forces on the coefficients, in complete analogy with the update of the “real” degrees of freedom (i.e., the coordinates), and with the same timestep. Such a scheme requires the “coefficient” forces, which are calculated as minus the derivative of e^{CPA} with respect to the coefficient, and an inertia parameter, which connects the forces to the accelerations. Under suitable simulation conditions, the coefficients remain close to the adiabatic ground state (provided they were in this state initially), thereby avoiding a minimization procedure every timestep in the simulation.

The average dispersion energy and pressure can be evaluated as the average over e^{CPA} and a corresponding virial functional w^{CPA} , respectively, during the course of a simulation run:

$$U_{\text{disp}} = \langle e^{\text{CPA}} \rangle_{\rho, T}, \quad 3P_{\text{disp}} V = \langle w^{\text{CPA}} \rangle_{\rho, T}. \quad (2)$$

B. Simulation details

We have performed simulations of argon at densities ranging from $\rho^* = 0.1$ to $\rho^* = 0.9$ and at temperatures $T^* = 1.1$, $T^* = 1.6$ and $T^* = 2.0$, where we have used reduced LJ units ($\epsilon/k = 119.8$ K, $\sigma = 0.3412$ nm) to indicate the state point. We stress that this is purely for convenience, as no corresponding state relations hold in the presence of three-body forces.

The purpose of the calculations is to characterize the effects of the three-body interactions, with respect to the structure and properties predicted for the *true* pair potential, as represented by the Aziz HFD-B potential.²² In practice, we have used a simpler form:

$$u(r_{12}) = a \exp(-br_{12}) + C_6 r_{12}^{-6} + (C_8 + c)r_{12}^{-8} \quad (3)$$

with $a = 400.1$, $b = 1.927$, $c = 1454$, $C_6 = 64.3$, $C_8 = 1169.9$ (all values in atomic units), where the C_6 and C_8 coefficients were set equal to the best literature values,²⁴ and the other three parameters (a , b and c), where chosen such that $u(r)$ fits the Aziz potential for all relevant distances.

The dispersive parts of the two- and three-body interactions were taken care of by the two-level quantum mechanical model described in Sec. II A. The remaining part of the potential ($a \exp(-br) + cr^{-8}$) was added as a classical potential in the molecular dynamics simulation. Four parameters, $\alpha_1, \alpha_2, u_1, u_2$, determine the magnitude of the various dispersion terms (see Ref. 19). They were determined from values of the classical dispersion parameters C_6, C_8, C_9 [Eqs. (1) and (3)] and C_{11} (the coefficient of the classical DDQ term^{17–19}) by means of relations (23) and (30) in Ref. 19. Values for C_6 and C_8 are given above, and a value for C_9 of 518.3 a.u. was found by Kumar and Meath.²⁴ The coefficient C_{11} was chosen equal to 668.16 au, which follows from the best estimates for the C_6 and C_8 coefficients and the dipole and quadrupole polarizabilities (see Ref. 19). This value was found to be within a few percent of the best literature value from Ref. 25. The resulting values of α_1, α_2, u_1 and u_2 were 10.748, 48.2, 0.742 and 0.5067 a.u., respectively, yielding the proper numerical values for C_6, C_8, C_9 and C_{11} by means of relations (23) and (30) in Ref. 19. Test runs showed that the DQQ and QQQ contributions are negligible compared to the DDD and DDQ, and therefore we did not consider any interaction beyond DDQ.

The systems studied contained 125 particles, and we used a timestep of 2.5 fs, which is about 4 times smaller than in conventional Lennard-Jones simulations. After equilibration the total production runs lasted 30 000 timesteps, during which pressure, energy and RDFs were measured, as well as the effective pair interactions discussed in Sec. III.

C. Results for the pressure, energy and $g(r)$

We begin by showing in Fig. 1 results for the RDF at three different reduced densities (0.1, 0.3, 0.8) and at a reduced temperature of 1.1. RDFs have been calculated for the full simulation model, including the three-body DDD and DDQ terms, and for a simulation with the Aziz pair potential

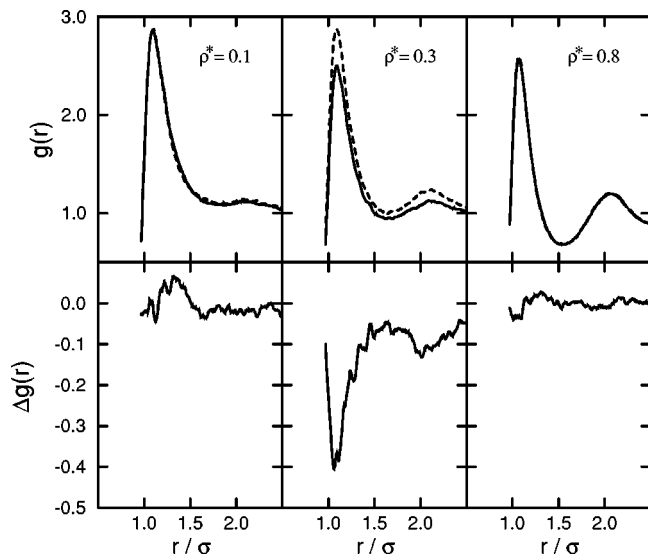


FIG. 1. Radial distribution function (RDF) of argon calculated at reduced densities of 0.1, 0.3 and 0.8 and a reduced temperature of 1.1. In the top figures the solid lines represent the RDF in the presence of full two- and three-body interactions ($g^{(3)}(r)$); the dashed lines (almost indistinguishable from the solid lines except at $\rho^*=0.3$) represent the RDF in the presence of the two-body Aziz potential only ($g^{(2)}(r)$). The difference $\Delta g(r) = g^{(3)}(r) - g^{(2)}(r)$ is shown in the bottom figures.

where these three-body terms are omitted; the differences, $\Delta g(r)$, between the RDFs of these calculations are shown in the bottom part of the figure. The results show that at the relatively low density of 0.3 (similar to the expected critical density), the three-body terms have a noticeable effect on the RDF. At the higher density of 0.8, close to the triple point density, and at the lowest density of 0.1, the difference between the RDFs obtained with and without the three-body effects is very small. At the high density, the liquid structure is dominated by packing effects,²⁶ and the dispersion terms are of little importance. At low density, the three-body contribution becomes small because of the relatively small number of three-atom encounters. The largest effects are found for densities around 0.3, which is in the vicinity of the critical density.

The reduction of the RDF by the three-body forces is still much larger than reported by Levesque and Weis¹¹ for krypton (which has stronger three-body effects than argon). They found that the RDF was reduced by about 0.02 in a small region about $r=1.1\sigma$, at a reduced density of 0.55. For this density, we find that the reduction is about 0.1 in this region of r .

Figure 2 shows the excess pressure and energy as a function of the density at a fixed temperature of 1.1.^{27,28} Results are shown for the full three-body potential, as well as for the Aziz pair potential, and for the usual argon Lennard-Jones pair potential. The results show that the three-body terms strongly modify the pressure and energy predicted with the true pair potential, bringing the predicted values into much closer agreement with experiment. The DDQ three-body terms are found to have a very small effect on the energy. Their effect on the pressure is small but nonnegligible, as shown in Table I.

The results obtained show that the energy and pressure

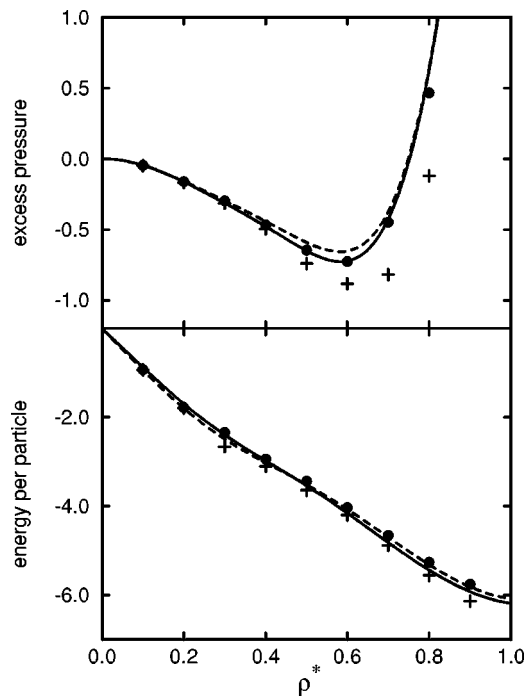


FIG. 2. Excess pressure and energy per particle of liquid argon, as a function of density, at a fixed temperature of $T^*=1.1$. All values are in (LJ) reduced units ($\epsilon/k=119.8$ K, $\sigma=0.3412$ nm). The symbols are the simulation results for the full three-body potential (black circles) and the two-body Aziz potential only (pluses); the solid and dashed lines are the results from the Lennard-Jones potential (Ref. 27) and experiment (Ref. 28), respectively.

predicted by combining the Aziz pair potential with the corresponding three-body dispersion terms are in good agreement with experiment. A similar agreement with experiment for Krypton was found by Barker,¹⁰ for a slightly different pair potential (K2 by Barker, Klein, Bobetic)²⁹ plus AT. In a more recent study by Meroni *et al.*⁷ the three-body AT terms were evaluated from a pair HNC theory for krypton. Although their results showed the same trend as in our simulations, the three-body contributions were not large enough to get the Aziz + AT results into good agreement with experiment. The conclusion from our simulations fully underscores Barker's statement in Ref. 10: "the net contribution of other many-body interactions to the properties of solid and dense fluid argon, krypton, xenon must be very small." A similar conclusion was drawn more recently by Anta *et al.*⁸ with regard to the phase-equilibrium properties of argon.

III. THE REPRESENTATION OF THREE-BODY EFFECTS IN AN EFFECTIVE PAIR POTENTIAL

A question of general interest is the way in which the three-body effects contribute to an effective pair potential which might be used in a simulation or theoretical calculation to reproduce some property of the simulated fluid exactly. It is not generally recognized that this requires a *different* potential for each property calculated. In order to emphasize this point, we begin by obtaining in a unified way the relationship between the effective potentials which repro-

TABLE I. Various contributions to the simulation results for the total energy per particle (u) and the total excess pressure (P_{ex}), at a temperature $T^* = 1.1$. $u^{(2)}$ and $P_{\text{ex}}^{(2)}$ are the contributions from the Aziz potential. All values are in LJ units, and are inclusive of a long-range correction.

ρ^*	$u^{(2)}$	u^{DDD}	u^{DDQ}	u (total)	$P_{\text{ex}}^{(2)}$	$P_{\text{ex}}^{\text{DDD}}$	$P_{\text{ex}}^{\text{DDQ}}$	P_{ex} (total)
0.1	-0.930	0.007	0.002	-0.921	-0.048	0.002	0.000	-0.046
0.2	-1.795	0.010	0.006	-1.780	-0.168	0.004	0.003	-0.160
0.3	-2.658	0.306	0.009	-2.342	-0.315	0.011	0.008	-0.296
0.4	-3.103	0.148	0.014	-2.941	-0.496	0.012	0.017	-0.468
0.5	-3.640	0.187	0.018	-3.435	-0.740	0.066	0.027	-0.646
0.6	-4.205	0.151	0.026	-4.029	-0.884	0.114	0.046	-0.724
0.7	-4.881	0.183	0.037	-4.660	-0.820	0.294	0.077	-0.449
0.8	-5.557	0.243	0.053	-5.261	-0.119	0.463	0.125	0.469
0.9	-6.135	0.307	0.075	-5.753	1.730	0.693	0.200	2.624

duce the energy and EoS of the liquid with the full many-body potential, as has previously been done by Barker,³ and Rowlinson and co-workers,⁴ among others.

A. Nonuniqueness of the effective pair potential

We start from the exact expressions for the potential energy U and the excess pressure P_{ex} in a fluid at a particular state point (ρ, T) , where the particles interact via a two-body potential $u_{12} = u(r_{12})$ and a three-body potential $u_{123} = u(r_{12}, r_{13}, r_{23})$:

$$U = \frac{1}{2} \rho^2 \int \int d\mathbf{r}_1 d\mathbf{r}_2 g_{12} u_{12} + \frac{1}{6} \rho^3 \int \int \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 g_{123} u_{123}, \quad (4)$$

$$3P_{\text{ex}}V = \frac{1}{2} \rho^2 \int \int d\mathbf{r}_1 d\mathbf{r}_2 g_{12} w_{12} + \frac{1}{6} \rho^3 \int \int \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 g_{123} w_{123}, \quad (5)$$

with

$$w_{12} = -r_{12} \frac{\partial u_{12}}{\partial r_{12}}, \quad (6)$$

$$w_{123} = - \left(r_{12} \frac{\partial}{\partial r_{12}} + r_{13} \frac{\partial}{\partial r_{13}} + r_{23} \frac{\partial}{\partial r_{23}} \right) u_{123},$$

and where $g_{12} = g(r_{12})$ and $g_{123} = g(r_{12}, r_{13}, r_{23})$ are the pair- and three-body radial distribution functions, respectively. By writing g_{123} in the following form (which defines g'_{123})

$$g_{123} = g_{12} g_{13} g_{23} g'_{123}, \quad (7)$$

we can evaluate the three-body part of Eq. (5) as

$$3 \times \frac{1}{6} \rho^3 \int \int d\mathbf{r}_1 d\mathbf{r}_2 g_{12} r_{12} \frac{-\partial}{\partial r_{12}} \left[\int d\mathbf{r}_3 g_{13} g_{23} g'_{123} u_{123} \right], \quad (8)$$

where the factor of 3 follows from the three terms which constitute w_{123} . As a final result, we may write the excess pressure in the following form:

$$3P_{\text{ex}}V = \frac{1}{2} \rho^2 \int \int d\mathbf{r}_1 d\mathbf{r}_2 g_{12} r_{12} \frac{-\partial}{\partial r_{12}} [u_{12} + \varphi_{12}], \quad (9)$$

with

$$\varphi_{12} = \varphi(r_{12}; \rho, T) = \rho \int d\mathbf{r}_3 g_{13} g_{23} g'_{123} u_{123}. \quad (10)$$

In same way we can rewrite the potential energy Eq. (4) as

$$U = \frac{1}{2} \rho^2 \int \int d\mathbf{r}_1 d\mathbf{r}_2 g_{12} [u_{12} + \phi_{12}] \quad (11)$$

with

$$\phi_{12} = \phi(r_{12}; \rho, T) = \frac{1}{3} \rho \int d\mathbf{r}_3 g_{13} g_{23} g'_{123} u_{123}. \quad (12)$$

From Eqs. (9) and (11) follows that we may define *two* effective pair potentials $u_{12} + \varphi(r; \rho, T)$ and $u_{12} + \phi(r; \rho, T)$, where the corrections to the true pair potential differ by a factor of 3:

$$\varphi(r; \rho, T) = 3\phi(r; \rho, T), \quad (13)$$

and yield the correct three-body pressure and energy, respectively. In other words, the effective pair potential deduced from three-body interactions is not a unique quantity. In the following we will consider the three-body contribution to the effective pair potential, ϕ , relevant for the energy. Note that such terms are defined as an average over the radial distribution functions and are therefore *state dependent*. In the limit of $r \rightarrow \infty$, the AT form may be used to show that $\phi^{\text{DDD}}(r; \rho, T)$ can be written as an explicit function of the distance and density:^{2,4,30}

$$\lim_{r \rightarrow \infty} \phi^{\text{DDD}}(r; \rho, T) = f(r; \rho) = \frac{8\pi}{9} C_9 \rho r^{-6}. \quad (14)$$

B. Effective pair potentials from the simulation

In Ref. 19 it is shown that the dispersion energy e^{CPA} in our simulation model can be written in the following way:

$$e^{\text{CPA}}(\{c\}, \{\mathbf{r}\}) = \sum_{ij} e_{ij}^{(2)} + \sum_{ij} e_{ij}^{(3)}, \quad (15)$$

where $\sum_{ij} e_{ij}^{(2)}$ is a two-body type energy, and $\sum_{ij} e_{ij}^{(3)}$ is a three-body type energy. From Eq. (15) we can thus evaluate the three-body contributions to an effective pair potential in the simulation:

$$\phi'(r; \rho, T) = \left\langle \frac{1}{2} \sum_{ij} \delta(r - r_{ij}) e_{ij}^{(3)} \right\rangle_{\rho, T, 3B}, \quad (16)$$

where the subscript $3B$ indicates that this average is obtained over the course of an MD simulation in the presence of full three-body forces. We have to add a small correction $\Delta\phi$ to this term because of the fact that a strict separation into pure two- and three-body terms as indicated in Eq. (15) cannot be made in our variational equations, due to the CPA normalization factor which appears both in two- and three-body type terms; a detailed comparison with perturbation theory shows that also $e_{ij}^{(2)}$ contains some (small) three-body contributions. The corresponding correction $\Delta\phi$ can be estimated from a comparison with a true two-body run, i.e., by evaluating

$$\Delta\phi(r;\rho,T) = \left\langle \frac{1}{2} \sum_{ij} \delta(r-r_{ij}) e_{ij}^{(2)} \right\rangle_{\rho,T,3B} - \left\langle \frac{1}{2} \sum_{ij} \delta(r-r_{ij}) e_{ij}^{(2)} \right\rangle_{\rho,T,2B}. \quad (17)$$

The final three-body contribution to the effective pair potential measured is then given by

$$\phi(r;\rho,T) = \phi'(r;\rho,T) + \Delta\phi(r;\rho,T). \quad (18)$$

We note that the RDF is measured in the simulation via $g(r) = \langle \sum_{ij} \delta(r-r_{ij}) \rangle / 2\pi\rho^2 N$, from the same data as Eq. (16); therefore, by construction ϕ yields the exact three-body energy, when integrated over the radial distribution function, and is therefore directly comparable with the effective pair potential defined by Eq. (11). As shown in Ref. 19, DDD, DDQ appear as separate terms in $e_{ij}^{(3)}$ so the corresponding effective pair potentials measured via Eq. (16) might also be specified as

$$\phi = \phi^{\text{DDD}} + \phi^{\text{DDQ}}. \quad (19)$$

C. Results for the effective pair potential

In Fig. 3 we show results for the three-body correction to the effective pair potential at several densities and fixed temperature of 1.1. The results show ϕ normalized by the asymptotic form $f(r;\rho) = (8\pi/9)C_9\rho r^{-6}$ and indicates a nontrivial density dependence due to the changing local liquid structure. The results may be compared with theoretical estimates of ϕ^{DDD} obtained by use of

$$\beta\phi_{12} = -\frac{1}{3}\rho \int d\mathbf{r}_3 [\exp(-\beta u_{123}) - 1] g_{13} g_{23} \quad (20)$$

which (without the factor 1/3) yields the correct RDF to linear order in the density.^{1,2} Note that to lowest order in the expansion of the exponential, Eq. (20) is equivalent to Eq. (11), if the Kirkwood superposition approximation ($g'_{123} = 1$) is used. Applications of (20) can be found in the literature, using approximate expressions for the pair distribution function. In Refs. 2,4, $g(r)$ is estimated from $g(r) = \exp(-\beta u_{12}(r))$, i.e., the lowest density approximation. The resulting ϕ^{DDD} (dashed line) is compared with the simulation results in the figure, and seen to agree well with them at sufficiently low density ($\rho \sim 0.1$). In Ref. 6, $g(r)$ is calculated from a pair-hypernetted chain approximation. The re-

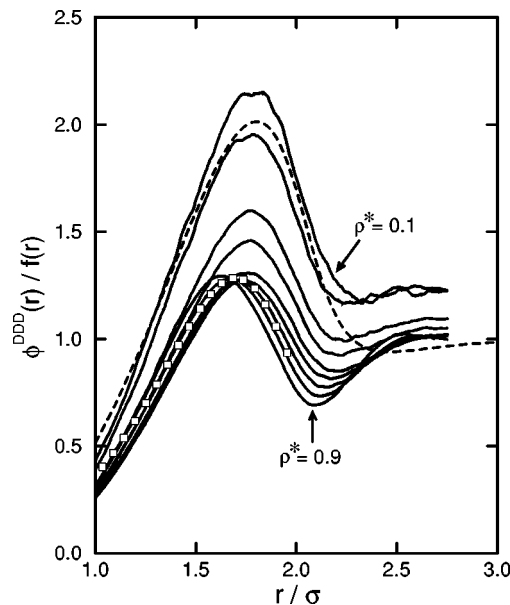


FIG. 3. Effective DDD pair potential $\phi^{\text{DDD}}(r)$ normalized by its functional form at infinity $f(r) = \frac{8}{9}\pi C_9 \rho r^{-6}$, at a reduced temperature of 1.1. Solid lines: simulation results for densities ranging from 0.1 (top curve) to 0.9 (bottom curve), with an increment of 0.1. Dashed line: theoretical result obtained from Eq. (20) with the low-density estimate $g(r) = \exp(-\beta u^{\text{rel}}(r))$ for the RDF (Ref. 4); open squares: theoretical result where the RDF is estimated from a pair HNC approximation at density 0.7 (Ref. 6).

sult of this approximation at $\rho = 0.7$ (open squares) compares very well with the simulation results at the corresponding density.

Figure 4 illustrates the temperature dependence of ϕ^{DDD} , which is seen to be very low at liquid densities and only to become appreciable at low densities where the temperature dependence of the liquid structure becomes noticeable.

D. A thermodynamically consistent EPP

For simulation or theory it might be of interest to construct an effective pair potential $\bar{\phi}^{\text{DDD}}$ which is thermodynamically consistent, i.e., a single effective potential which reproduces both the correct three-body energy and three-

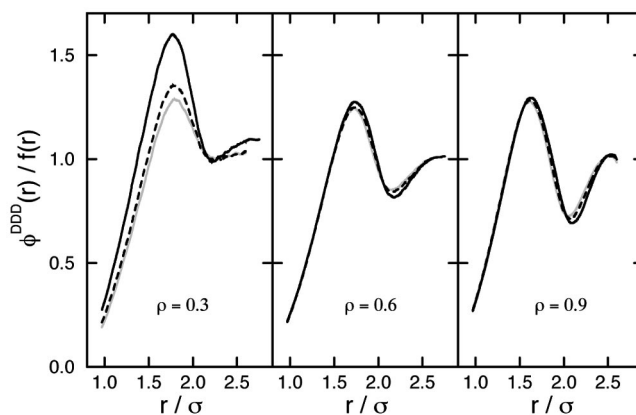


FIG. 4. Simulation results for the effective DDD pair potential $\phi^{\text{DDD}}(r)$ normalized by its functional form at infinity $f(r) = \frac{8}{9}\pi C_9 \rho r^{-6}$, at reduced temperatures of 1.1 (solid lines), 1.6 (dashed lines) and 2.0 (gray lines), at reduced densities 0.3 (left), 0.6 (middle) and 0.9 (right).

TABLE II. Ratio of the value of the C_N^{eff} coefficient obtained from the pressure equation (22), to the value obtained from the energy equation (23), as a function of the power N for three different densities, at a reduced temperature of $T^* = 1.1$. For all densities studied, the two values coincide at $N=9$, indicating the an effective pair potential of the form r^{-9} would give a consistent three-body energy and pressure.

Power N	$C_N^{\text{eff},P}/C_N^{\text{eff},U}$		
	$\rho^* = 0.3$	$\rho^* = 0.6$	$\rho^* = 0.9$
6	1.495	1.487	1.484
7	1.288	1.282	1.278
8	1.128	1.123	1.120
9	1.003	0.999	0.996
10	0.903	0.899	0.896
11	0.821	0.817	0.815
12	0.752	0.749	0.747

body pressure, at the DDD level. As was suggested by Barker,¹² such a potential should be a homogeneous function of the same degree (-9) in the coordinates as the Axilrod-Teller energy, i.e., we should try a potential

$$\bar{\phi}^{\text{DDD}}(r; \rho, T) = C_9^{\text{eff}}(\rho, T) r^{-9} \quad (21)$$

and determine the C_9^{eff} coefficient such that

$$U^{\text{DDD}} = \frac{1}{2} \rho^2 \int \int d\mathbf{r}_1 d\mathbf{r}_2 g_{12} C_9^{\text{eff}} r_{12}^{-9}, \quad (22)$$

$$3P_{\text{ex}}^{\text{DDD}} V = \frac{1}{2} \rho^2 \int \int d\mathbf{r}_1 d\mathbf{r}_2 g_{12} 9 C_9^{\text{eff}} r_{12}^{-9}. \quad (23)$$

If the potential is thermodynamically consistent, the C_9^{eff} coefficient determined from Eqs. (22) should be equivalent to the one determined from Eq. (23). This was found to be true for all densities and temperatures studied, as shown in Table II, in which we show the ratio of the coefficients of an effective potential of the form r^{-N} determined both from the total DDD pressure ($C_N^{\text{eff},P}$) and the total DDD energy ($C_N^{\text{eff},U}$), as a function of the power N , for various reduced densities and temperature 1.1. It is shown that the two coefficients coincide at $N=9$, which was also found for all other densities and temperatures studied.

In Fig. 5 we show the resulting C_9^{eff} determined from Eq. (22) [or Eq. (23)] as a function of the reduced density, for temperatures $T^* = 1.1$, $T^* = 1.6$ and $T^* = 2.0$. An extensive range of simulations would be required to determine a fit of the functional form of $C_9^{\text{eff}}(\rho, T)$; still, from the figure a simple estimate of the coefficient could be obtained in the density range $[0.0-1.0]$ and the temperature range $[1.0-2.0]$.

It should be stressed, however, that such a potential would only reproduce the exact three-body energy and pressure if averaged over the RDF of the *full three-body system*. In order to see how well this effective pair potential would reproduce the structure of the 3B-fluid, we have performed a simulation with a potential obtained by combining the Aziz and the effective r^{-9} potential discussed above, at density $\rho^* = 0.3$ and temperature $T^* = 1.1$, and compared (Fig. 6) the result with those obtained from the Aziz potential alone and from the full three-body simulation (both as in Fig. 1). It can be seen that the Aziz + effective r^{-9} potential repro-

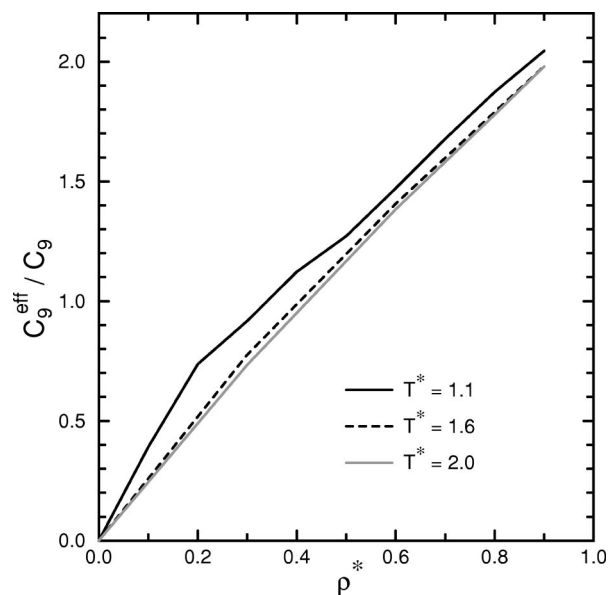


FIG. 5. Density and temperature dependence of the C_9^{eff} coefficient of an r^{-9} representation of the effective DDD pair potential, normalized by the C_9 Axilrod-Teller coefficient. The C_9^{eff} is constructed such as to yield the correct three-body DDD energy and pressure.

duces the full three-body RDF very well, a much larger discrepancy is found with the pure Aziz potential. Nevertheless, the small difference in structure causes the three-body energy and pressure from this simulation to be slightly different from those of the full three-body calculation. In principle, the C_9^{eff} coefficient could be re-evaluated in the two-body simulation via Eq. (22), the value of which could then be used in a new two-body simulation, etc., until convergence is

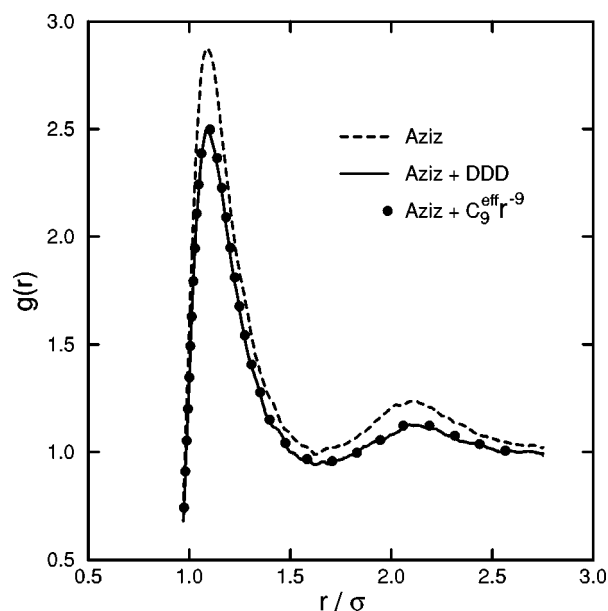


FIG. 6. RDF from a simulation with an Aziz + $C_9^{\text{eff}} r^{-9}$ potential (circles) compared with those from a simulation with the Aziz potential only (dashed curve) and with the full three-body potential (solid curve) at density 0.3 and temperature 1.1; it is shown that the $C_9^{\text{eff}} r^{-9}$ potential gives a good representation of the “true” structure from full three-body forces.

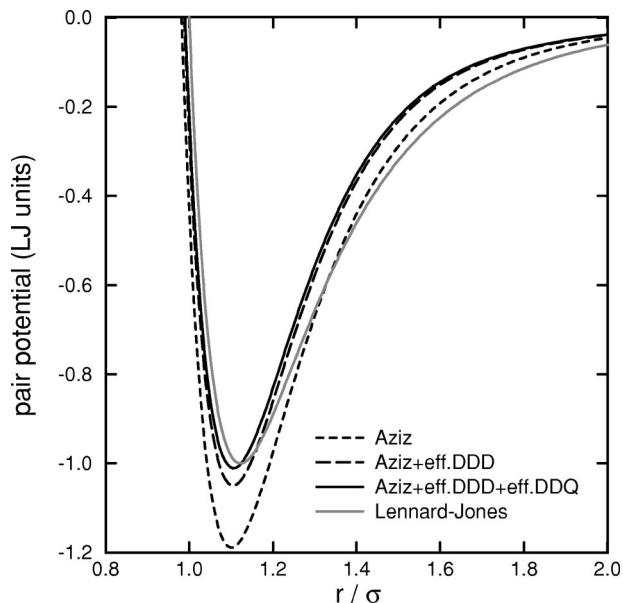


FIG. 7. A comparison of the true pair potential (Aziz), the Lennard-Jones potential and the effective pair potentials at the DDD and DDD+DDQ levels for argon at $\rho^*=0.9$ and $T^*=1.1$.

reached; the difference with the present estimate for the C_9^{eff} coefficient is expected to be small, however.

The $C_9^{\text{eff}} r^{-9}$ potential is not the *true* three-body correction to the effective pair potential; the latter is shown in Fig. 3, and will not fit to a simple functional form; the r^{-9} potential should be viewed as a practical alternative for modeling three-body DDD interactions, reproducing the energy, pressure *and* RDF with reasonable accuracy. It should be emphasized that the r^{-9} potential has been fitted to *bulk* thermodynamic properties, and will fail at surfaces and interfaces, as has been shown by Barker.¹² In his paper, Barker demonstrated that the r^{-9} potential results in a surface free energy which disagrees by as much as 19% (argon) to 35% (xenon) with the experimental data. Inclusion of the full three-body interaction brought the disagreement down to 2%.

IV. DISCUSSION—RELATIONSHIP OF THE TRUE AND LENNARD-JONES PAIR POTENTIALS

We conclude by showing in Fig. 7 a comparison of the true pair potential [u_{12} , Eq. (3)], the much studied Lennard-Jones potential ($\epsilon/k=119.8$ K, $\sigma=0.3412$ nm) and the effective pair potentials $u_{12} + \varphi^{\text{DDD}}(r; \rho, T)$ and $u_{12} + \varphi^{\text{DDD}}(r; \rho, T) + \varphi^{\text{DDQ}}(r; \rho, T)$ at $\rho=0.9$ and $T=1.1$ (i.e., close to the triple point). Including the three-body effects

progressively reduces the depth of the effective pair potential with increasing density, without shifting the position of the minimum, so that in the dense fluid the depth of the effective pair potential corresponds quite well with that of the Lennard-Jones potential. The relative importance of the DDD and DDQ effects is illustrated by the figure, which indicates a rapid convergence of the multipole series for argon. Note that we have shown the effective pair potential for the *pressure*, which would lead to an overestimate of the three-body effects on the energy [cf. Eq. (13)]. The Lennard-Jones potential, which gives a reasonable compromise potential for the pressure *and* energy, while agreeing well with the effective potential in the region of the repulsive wall and the minimum, is significantly deeper than the effective potentials at larger r and closer to the pair potential there.

¹G. S. Rushbrooke and M. Silbert, *Mol. Phys.* **12**, 505 (1967).

²D. A. Copeland and N. R. Kestner, *J. Chem. Phys.* **49**, 5214 (1968); *Trans. Faraday Soc.* **33**, 8 (1937).

³J. A. Barker, D. Henderson, and W. R. Smith, *Mol. Phys.* **17**, 579 (1969).

⁴G. Casanova, R. J. Dulla, D. A. Jonah, J. S. Rowlinson, and G. Saville, *Mol. Phys.* **18**, 589 (1970).

⁵S. Celi, L. Reatto, and M. Tau, *Phys. Rev. A* **39**, 1566 (1989).

⁶P. Attard, *Phys. Rev. A* **45**, 3659 (1992).

⁷A. Meroni, L. Reatto, and M. Tau, *Mol. Phys.* **80**, 977 (1993).

⁸J. A. Anta, E. Lomba, and M. Lombardo, *Phys. Rev. E* **55**, 2707 (1997).

⁹J. A. Barker, R. A. Fisher, and R. O. Watts, *Mol. Phys.* **21**, 657 (1971).

¹⁰J. A. Barker, *Phys. Rev. Lett.* **57**, 230 (1986).

¹¹D. Levesque and J. J. Weis, *Phys. Rev. A* **37**, 3967 (1988).

¹²J. A. Barker, *Mol. Phys.* **80**, 815 (1993).

¹³P. G. Mikolaj and C. J. Pings, *Phys. Rev. Lett.* **15**, 849 (1965).

¹⁴M. Tau, L. Reatto, R. Magli, P. A. Egelstaff, and F. Barocchi, *J. Phys.: Condens. Matter* **1**, 7131 (1989).

¹⁵F. Formisano, C. J. Benmore, U. Bafile, F. Barocchi, P. A. Egelstaff, R. Magli, and P. Verkerk, *Phys. Rev. Lett.* **79**, 221 (1997).

¹⁶B. M. Axilrod and E. Teller, *J. Chem. Phys.* **11**, 299 (1943).

¹⁷R. J. Bell, *J. Phys. B* **3**, 751 (1970).

¹⁸R. J. Bell and I. J. Zucker, in *Rare Gas Solids*, edited by M. L. Klein and J. A. Venables (Academic, London, 1977).

¹⁹M. A. van der Hoef and P. A. Madden, *Mol. Phys.* **94**, 417 (1998).

²⁰A. J. Stone, *The Theory of Intermolecular Forces* (Clarendon, Oxford, 1996).

²¹R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985).

²²R. A. Aziz and M. J. Slaman, *Mol. Phys.* **58**, 679 (1986).

²³R. Ahlrichs and P. Scharf, *Adv. Chem. Phys.* **12**, 501 (1987).

²⁴A. Kumar and W. J. Meath, *Mol. Phys.* **54**, 823 (1985).

²⁵M. B. Doran, *J. Phys. B* **7**, 558 (1974).

²⁶J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic, London, 1986).

²⁷J. K. Johnson, J. A. Zollweg, and K. E. Gubbins, *Mol. Phys.* **78**, 591 (1993).

²⁸C. H. Twu, L. L. Lee, and K. E. Stirling, *Fluid Phase Equilibria* **4**, 35 (1980).

²⁹J. A. Barker, M. L. Klein, and M. V. Bobetic, *IBM J. Res. Dev.* **20**, 222 (1976).

³⁰H. Stenschke, *J. Chem. Phys.* **100**, 4704 (1994).