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Comparison between integral equation method and molecular dynamics simulation for three-body forces: Application to supercritical argon

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The prediction of the structural and thermodynamic properties of supercritical argon has been carried out by two independent routes: semianalytical calculations and numerical simulations. The first one is based on the hybridized mean spherical approximation (HMSA) conjugated with an effective pair potential that incorporates multipole dispersion interactions. The second one uses a very recent numerical simulation technique, inspired by the Car–Parrinello method [van der Hoef et al., J. Chem. Phys. 111, 1520 (1999)], which contains an effective quantum-mechanical representation of the underlying electronic structure. The latter approach allows us to treat the contribution of the three-body effects as well, and to validate the use of an effective pair potential for them in the framework of the self-consistent integral equation method. For all the supercritical argon states studied, the results obtained with the semianalytical approach are in good agreement with the predictions of the numerical simulation. Here it is shown that HMSA remains competitive with molecular dynamics simulation when the triple-dipole and the dipole–dipole–quadrupole three-body terms are taken into account. © 2001 American Institute of Physics.

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I. INTRODUCTION

The aim of liquid theory is to describe, as accurately as possible, the molecular arrangement and the thermodynamic properties of a large variety of simple fluids. For certain systems, such as rare gases, empirical interatomic potentials, which must be considered more as a means to elucidate liquid properties rather than an end in itself, have been used very successfully in predicting a wide range of properties. Even if the statistical theory of the liquid state has been developed almost exclusively for pairwise additive forces, it is well known that many-body forces make a significant contribution to the structural and thermodynamic properties. For this reason the role of two- and three-body contributions has attracted much attention from theory, simulation, and experiment.

For describing the interactions in simple fluids, the classical way consists of modeling empirical effective potentials. Either the Lennard-Jones 12–6 potential or more complex potentials dealing with an increasing number of empirical parameters have been propounded in the literature to depict the dipole–dipole interactions. Their particular functional forms are chosen for purely pragmatic reasons, and must therefore be viewed only as accurate fitting functions. Three-body dispersion energy that describes the long-range triple-dipole interactions was developed initially by Axilrod–Teller and has been extended to many-body dispersion interactions in the expansion of the nonadditive third-order energy. However it is of interest to notice that the Lennard-Jones potential fitted to fluid data incorporates many-body effects which are known to modify the two-body interaction. The proof is indirect and based on the fact that the agreement between experiment and theory is obtained though many-body terms is ignored in the calculations.

Many-body effects can also be treated from an effective description of the electronic structure with an ab initio type of molecular dynamics approach. The advantage of these quantum-chemical calculations is that it is straightforward to include dispersion terms higher or equal to the triple-dipole interactions. Moreover, periodic boundary conditions can be treated in a way that is consistent with the treatment at the pair level.

In order to compare the classical expressions for the Bell three-body potentials with that obtained by simulation, we calculate the effective atomic structure of Ar with two approaches different in nature, i.e., the integral equation and a novel simulation approach developed in the spirit of the Car–Parrinello method. From the theoretical point of view, the atomic structure is closely related to a given interatomic potential by a formally exact integral equation or by numerical simulation calculations. During the last few decades, the art of deriving integral equations has been largely developed, and the approach based on the thermodynamically consistent integral equation provides a very accurate atomic structure over a wide range of temperature and density. Specifically, the hybridized mean spherical approximation (HMSA), with
suitable modifications to take the three-body forces into account, generates very good results compared to the low-temperature measurements for Ar.\textsuperscript{18} and also to the performant molecular dynamics calculations for Kr.\textsuperscript{19} Simultaneously, the novel simulation method, which permits direct treatment of the many-body effects, has been introduced recently\textsuperscript{1} to determine the energy, equation of state, and pair correlation function of Ar. Instead of using empirical parameters, the description of the many-body contributions at the quantum-mechanical level is useful to test the empirical pair- and three-body potentials as well as the reliability of the HMSA approximation. Thus, our primary statistical mechanics tools for treating the structure are the HMSA integral equation and a novel simulation model.

In this paper, we present the results of the calculations of the structural and thermodynamic properties for Ar obtained owing to (i) the HMSA integral equation in combination with the reference Hartree–Fock dispersion (HFD-B2) pair potential\textsuperscript{10} corrected by a three-body potential, and (ii) the molecular dynamics simulation including the three-body effects by the quantum-mechanical approach. A comparison between simulation and integral equation demonstrates that the analytical forms for the three-body interactions employed in HMSA give an atomic structure that compares very well with simulation calculations, which incorporate the three-body dispersion forces in a fully quantum theoretical way. Computer simulation eliminates the uncertainty in the characterization of the real system so that one can assign any discrepancy between theory and controlled “simulation experiment” to some weakness either in the theory or in the interatomic potential. Since the adequacy of our baseline HMSA integral equation has already been tested against classical molecular dynamics,\textsuperscript{1} the goal of the present study is to compare the effect of the three-body forces used together with appropriate statistical mechanics tools and the effective description of the electronic structure at the three-body level.

\section{II. Interatomic Potential in Rare Gases}

We assume that the potential energy of a system of $N$ closed-shell entities can be developed in a cluster series depending on the true pair potential $u_2$ and the three-body potential $u_3$

$$U_N = \sum_{i<j}^N u_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_{i<j<k}^N u_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \cdots \quad (1)$$

In the standard statistical treatment of many physical phenomena, the first term on the right-hand side is kept in assuming pairwise additivity of the interactions. For rare gases, the reference pair potential, $u_2$, is often taken to be under the following form, continuously improved by Aziz and Slaman:\textsuperscript{10}

$$u_2(x_{ij}) = A \exp(-\alpha x_{ij} + \beta x_{ij}^2) - F(x_{ij}) \sum_{k=0}^{2} \frac{C_{2k+6}}{x_{ik}^{2k+6}}, \quad (2)$$

where $x_{ij} = r_{ij}/\sigma$ is the reduced distance, $\sigma$ being the position of the node of the potential, and

$$F(x_{ij}) = \begin{cases} \exp\left[-\left(\frac{D}{x_{ij}} - 1\right)^2\right] & \text{if } x_{ij} < D, \\ 1 & \text{if } x_{ij} \geq D, \end{cases} \quad (3)$$

is a switching function between the repulsive and attractive parts. The relevant parameters in Eqs. (2) and (3) are listed in the paper of Aziz and Slaman\textsuperscript{10} for Ar.

In Eq. (1), the second term, $u_3$, is the nonadditive potential between three isolated particles of which the definition is based on quantum-mechanical considerations.\textsuperscript{2} At third-order perturbation, three distinct mechanisms contribute to the three-body interaction: classical three-body induction, dispersion, and induction–dispersion interactions.\textsuperscript{20} For practical purpose, an explicit expression\textsuperscript{12} derived to third order is used for $u_3$ that reads within the original notation

$$u_3 = Z_{DDD} \cdot W_{DDD} + Z_{DDQ} \cdot W_{DDQ} + Z_{DQQ} \cdot W_{DQQ} + Z_{QQQ} \cdot W_{QQQ} \cdot (4)$$

Each term is the product of a constant $Z$, which depends on the atomic species involved in the interaction, and a geometrical function $W$ depending solely on the relative positions of the three atoms. The subscripts stand for the type of three-body terms, namely the dipole–dipole–dipole, dipole–dipole–quadrupole interactions, and so on. Additional expressions for higher-order many-body interactions exist too, but become more complicated\textsuperscript{21} and negligible. Since test runs performed with our simulation model showed that the $DQQ$ and $QQQ$ contributions are very small compared to the $DDD$ and $DDQ$, any interaction beyond $DDQ$ will be neglected in this work. According to Bell,\textsuperscript{12} the explicit forms for geometrical functions are, respectively,

$$W_{DDD} = \frac{3}{r_{ij} r_{ik} r_{jk}} \times (1 + 3 \cos \phi_i \cos \phi_j \cos \phi_k), \quad (5)$$

$$W_{DDQ} = \frac{3}{16 r_{ij} r_{ik} r_{jk}} \times \left[ (9 \cos \phi_k - 25 \cos 3 \phi_k) + 6 \cos(\phi_i - \phi_j)(3 + 5 \cos 2 \phi_k) \right], \quad (6)$$

where $\phi_i, \phi_j$, and $\phi_k$ denote the interior angles at the vertices $i, j$, and $k$ of the triangle with sides $r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$, $r_{ik} = |\mathbf{r}_k - \mathbf{r}_i|$, and $r_{jk} = |\mathbf{r}_k - \mathbf{r}_j|$. The constants $Z$ are given in terms of the polarizability factors $\alpha_1, \alpha_2$, and the excitation energies $u_1, u_2$ relatively to the atomic species with the prescription

$$Z_{DDD} = \frac{1}{r_{ij}^2} \alpha_1^2 u_1, \quad Z_{DDQ} = \frac{1}{4} \alpha_1^2 \alpha_2 u_1 u_2 (u_1 + u_2)^2. \quad (7)$$

With the values of the parameters $\alpha_1, \alpha_2, u_1, u_2$ taken from van der Hoef and Madden,\textsuperscript{15} the resulting values of the interaction constants for Ar are $Z_{DDD} = 2.524 \times 10^{-27}$ J nm$^3$ and $Z_{DDQ} = 2.719 \times 10^{-29}$ J nm$^4$. These constants, which determine the strength of the interaction, depend on the electronic configuration of the atoms but their evaluation, subject
to uncertainty, is not easy. However, our values are in reasonable agreement with those of Bell\textsuperscript{12} estimated to 2.476 \times 10^{-27} \text{J nm}^2 and 3.243 \times 10^{-29} \text{J nm}^1, respectively. In addition, it is worth mentioning that the lowest-order (DDD) contribution to the three-body interaction \( u_3 \) corresponds exactly to the Axilrod–Teller\textsuperscript{11} expression, with the familiar parameter \( \nu \) formally equal to 3\( Z_{DDD} \).

### III. ATOMIC STRUCTURE

#### A. Approximative self-consistent integral equation

The low symmetry of triangular configurations compared with that of the pair configurations makes the situation complicated in allowing significantly less simplification of the calculations. In practice, this drawback is overcome owing to the basic assumption of any integral equation that reduces the \( N \)-body potential energy [Eq. (1)] to a sum of effective pair potentials.\textsuperscript{22,23} It is worth noting that there are two possible expressions for the three-body contribution, depending on whether it is deduced from the potential energy or from the pressure.\textsuperscript{24} In fact, it has been shown\textsuperscript{16,3} that both forms of the effective potential differ just by the numerical factor of 3, so that either \( \langle 3u_3 \rangle \) or \( \langle u_3 \rangle \) can be used as a three-body effective potential. In the following, as in our previous work,\textsuperscript{1} we consider the quantity \( \langle u_3 \rangle \), relevant for the pressure, to treat the first two terms corresponding to \( DDD \) and \( DDQ \), so that the explicit form of the effective potential is

\[
u(r_{ij}) = u^2_{ij}(r_{ij}) + \langle u_3(r_{ij}) \rangle \tag{7}\]

with

\[
g(r_{ij}) = \exp[-\beta u^R_{ij}(r_{ij})] \left[ 1 + \frac{\exp[f(r_{ij})(g(r_{ij}) - 1 - c(r_{ij}) - \beta u^A(r_{ij})]) - 1}{f(r_{ij})} \right]. \tag{10}\]

Here, the assumption is made that the full effective potential [Eq. (7)] may be split into its repulsive short-range part, \( u^R_{ij}(r_{ij}) \), and its weak, attractive long-range part, \( u^A_{ij}(r_{ij}) \), according to the prescription of Weeks et al.\textsuperscript{25}

\[
u^R_{ij}(r_{ij}) = \begin{cases} u(r_{ij}) - u(r_m), & \text{if } r_{ij} < r_m, \\ 0, & \text{if } r_{ij} > r_m, \end{cases} \tag{11}\]

\[
u^A_{ij}(r_{ij}) = \begin{cases} u(r_m), & \text{if } r_{ij} < r_m, \\ u(r_{ij}), & \text{if } r_{ij} > r_m, \end{cases} \tag{12}\]

where \( r_m \) is the position of the principal minimum of the effective pair potential. The quantity \( f(r_{ij}) \) is a mixing function whose expression is used by Bretonnet and Jakse,\textsuperscript{17} and which has the merit to ensure the thermodynamic self-consistency by requiring the equality between the compressibilities coming from the virial equation of state and from the grand-canonical ensemble, namely

\[
\rho k_B T \chi_T = S(0), \tag{13}\]

where \( S(0) \) is the long-wavelength limit of the structure factor. Therefore, the set of Eqs. (9) to (13), supplemented by Eqs. (7) and (8), is solved in a thermodynamically self-consistent manner by a classical algorithm proposed by Libik et al.\textsuperscript{26} which consists of solving the nonlinear set of equations by the Newton–Raphson method in combination with the traditional iterative technique.\textsuperscript{17} A good compromise is to represent the functions by a grid size of 1024 with a step of 0.02.

In the HMSA integral equation, the aim is to force thermodynamic consistency by forming a linear combination of isothermal compressibilities coming from the pressure and compressibility equations of state. Although this stratagem cannot be regarded as an advance in terms of physical understanding, it gives better results than other standard approximations and gains the advantage over them in determining the thermodynamic properties by necessity. When three-body forces are included, the internal energy, equation of state, and isothermal compressibility are given, respectively, by\textsuperscript{23}
\[ U = \frac{3}{2} \frac{N}{\beta} \int d\mathbf{r}_{ij} g(r_{ij}) u_2(r_{ij}) \]
\[ + \frac{\rho^2 N}{6} \int d\mathbf{r}_{ij} d\mathbf{r}_{ik} \Phi^{(3)}(\mathbf{r}_{ij}, \mathbf{r}_{ik}) u_3(\mathbf{r}_{ij}, \mathbf{r}_{ik}), \]

where \( \rho \) is the density of the system. This approximation is set.

The function \( g(r_{ij}) \) and \( \Phi^{(3)}(\mathbf{r}_{ij}, \mathbf{r}_{ik}) \) are the three-body potential. It is noticeable that the coefficients \( g(\mathbf{r}_{ij}) \) and \( \Phi^{(3)}(\mathbf{r}_{ij}, \mathbf{r}_{ik}) \) are a function of the three-body potential. It is noticeable that the coefficients are kept in their ‘minimum energy’ configuration. In principle, this would require a minimization procedure every time step of the simulation. This problem can be circumvented if we use an MD simulation method in which the expansion coefficients in the wave function are treated as additional degrees of freedom in the Car–Parrinello sense.27

Equations of motion for the expansion coefficients are derived from the Lagrangian formulation of classical mechanics, with the electronic energy \( e(c, \{ r \}) \) playing the role of a potential. To perform molecular dynamics, the coefficient equations of motion may be combined with equations of motion for the atomic positions and integrated simultaneously in time with the coefficients maintained at the adiabatic values, as in the standard Car–Parrinello method.28 This proved straightforward to implement. For full details, we refer to Ref. 15.

\[ \frac{\partial}{\partial t} \left[ \frac{\partial}{\partial \rho} \right] \frac{\partial}{\partial \rho} \]
three atoms is less than $\pi/2$ and negative for nearly linear configurations of the three atoms. As a consequence, the contribution $\langle u_3 \rangle$ is largely positive into the core of the atom, reinforcing the repulsion between two atoms and reducing the potential well depth. Since the repulsive part of the potential is mainly responsible for the structure and the attractive part for the thermodynamics, some consequences should be expected in the results of the pair correlation function and subsequent thermodynamic properties.

For the same thermodynamic states, we present (Fig. 2) the pair correlation functions $g(r)$ calculated by HMSA with the state-dependent effective potentials under consideration. Then, we compare the pair correlation functions $g(r)$ to those calculated by simulation, in Fig. 3. An overall agreement between the two approaches is observed for all the thermodynamic states. It should be stressed, however, that the DDQ contribution is found to have a quite negligible effect on $g(r)$ compared to the DDD contribution, both for HMSA and simulation: on the scale of the figure, there is no difference between the curves of $g(r)$ obtained with and without the DDQ contribution. The structure factor, $S(q)$, is not presented because the MD simulation is not well suited to study the low-$q$ region of $S(q)$, due to the small system size and statistical noise.

From the features of the pair potential, some deviations are expected in the region of the first peak of $g(r)$, the most sensitive region for the calculation of thermodynamic properties. The discrepancies on the height of the first peak (Fig. 2) remain weak but can reach 2% for certain densities. Such modifications attest that the three-body terms have a noticeable effect on the liquid structure. As in our previous works on Kr\(^1\) and Ar,\(^3\) the present results point out that the effect of the three-body interactions becomes especially visible at medium densities around the critical density. The interpretation can be sustained by physical reasons. First, it is quite clear that the three-body effects are small at low density due to the relatively small number of three-atom configurations. Then, even if the three-body effects increase with density, the packing effects involved in the liquid structure\(^29\) become so dominant at higher density that this completely masks the three-body effects. But, the overlapping between atoms can also be put forward. The exchange (or overlap) effects are already included in the HFD-B2 pair potential of Aziz and Slaman and, though substantially smaller than the DDD interaction and opposite in sign, their contributions increase with density,\(^30\) so that we may admit a fortuitous cancellation of the exchange effects and the DDD contributions making the three-body effects of little importance for higher densities. Incidentally, we mention the paper of Tau et al.\(^31\) considering the three-body effects on the structure of fluid Kr. Using a modified expression of DDD that takes into account the exchange interaction,\(^32\) the authors found that the combined effect of DDD and exchange interactions is smaller than that of the genuine DDD form. Also, the long-wavelength limit of the structure factor is not correct, so that they have to increase artificially the interaction constant $Z_{DDD}$ of 25% to recover the results of the pure DDD form.

The relative role of the DDD and DDQ terms is shown in Table I, where the outcomes of the calculations of the thermodynamic properties obtained with the resultant distribution functions are compared. As expected, at fixed temperature the internal energy and isothermal compressibility decrease monotonously with the density, whereas the pressure increases. In contrast, at fixed density the internal energy and pressure increase with temperature, whereas the
isothermal compressibility decreases. The pressure and internal energy obtained with the \( \text{DDD} \) potential are larger compared to the pure AS pair potential, whereas the compressibility is smaller, which is not surprising since the AS potential is the most attractive. It is worth noting that the influence of the \( \text{DDD} \) contribution is somewhat larger at high densities for the pressure and energy, and at low densities for the compressibility. It can also be seen that the three-body forces have more influence when the temperature is decreasing. If we look at the influence of the \( \text{DDQ} \) interaction, roughly speaking we can say that its contribution reinforces the \( \text{DDD} \) one on the internal energy, pressure, and compressibility, at the rate of about 10%. Thus, our HMSA calculations show that the \( \text{DDQ} \) effect is small but non-negligible.

We also have investigated the comparison of the true effective potential with the Lennard-Jones (LJ) potential, for which a wealth of simulation data is available. In Table I we compare our values for the internal energy and pressure with the results of a recent equation of state proposed by Johnson et al.,\(^3\) which is based on the generic Benedict et al.\(^3\) equation with 33 parameters regressed from simulation. Traditionally, the pressure and internal energy are given in different reduced units connected to ours by the relations

![Diagram](image1)

**FIG. 3.** Pair correlation function \( g(r) \) corresponding to the AS+DDD +DDQ effective potential. Computations are done at reduced temperatures \( T^* = 1.6 \) (left curves) and \( 2 \) (right curves) and reduced densities \( \rho^* = 0.3, 0.6, \) and \( 0.9 \) from bottom to top. The solid lines stand for HMSA calculations and the open circles for molecular dynamics simulation.

![Diagram](image2)

**FIG. 4.** DDD effective potential normalized by its functional form at infinity \( f(r, \rho) = (8 \pi / 3) Z_{DDD} \rho \cdot r^{-6} \). Computations are done at reduced temperatures \( T^* = 1.6 \) (left curves) and \( T^* = 2 \) (right curves), and reduced densities \( \rho^* = 0.3, 0.6, \) and \( 0.9 \) from bottom to top. The solid lines stand for HMSA calculations and the open circles for molecular dynamics simulation.

<table>
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<th>( T^* )</th>
<th>( \rho^* )</th>
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<th>(\beta P/N)</th>
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<td>II</td>
<td>III</td>
<td>LJ</td>
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</table>

**TABLE I.** Thermodynamic properties calculated by HMSA, in using the AS pair potential alone (column I), the AS+DDD effective potential (column II), and the AS+DDD+DDQ effective potential (column III). The internal energy and pressure of the LJ fluid have also been shown for the sake of comparison.
\[ \frac{p \sigma^3}{\varepsilon} = \frac{\beta p}{\rho} (\rho \ast T') \]
\[ U = \frac{\beta U}{N} N^T. \]

From the comparison performed by van der Hoef and Madden\(^1\) between the LJ potential, the true AS pair potential, and the effective potential at the \( \text{DDD} \) and \( \text{DDD} + \text{DDQ} \) levels, it is seen that the depth of the LJ potential corresponds quite well with that of the effective potential containing the three-body effects. In contrast, the equilibrium position of the LJ potential is slightly shifted towards large distances and the shape of the curve is flatter than that of the effective potential, i.e., significantly deeper than the effective potential at larger distances and closer to the AS pair potential. Having the equation of state in view, the discrepancies are not as alarming as it might appear because, as shown in Table I, the pressure of the LJ fluid agrees well with that of the effective potential when the \( \text{DDD} \) contribution is included. However, the internal energy is in better agreement when the AS pair potential is used alone. Therefore, it is of interest to notice that the LJ fluid seems to incorporate implicitly the many-body effects and remains a good approximation for calculating the equation of state of Ar, although it is of course weakly density dependent.

V. DISCUSSION AND CONCLUSION

This work is devoted to the structural and thermodynamic properties of supercritical argon. Concerning the structural properties, we have presented a comparative study of the pair distribution function for medium and high densities with the aid of a self-consistent integral equation and a new MD approach. To this end, we used as interatomic interactions those modeled by the two-body AS potential with the \( \text{DDD} \) and \( \text{DDD} + \text{DDQ} \) corrections for HMSA. Calculations have also been performed by MD simulation that allow us to evaluate numerically the respective contributions of the two-body and three-body potentials. It results from this work that a very good concordance is obtained for the \( \text{DDD} \) and \( \text{DDD} + \text{DDQ} \) contributions for the three-body forces. The agreement between the pair distribution function is obtained for the pair correlation function between HMSA and simulation for all the states under study. Such calculations also permit testing the validity of the use of an effective pair potential including three-body effects in the framework of the integral equation theory. Thus, HSA is a substantial improvement of the integral equation theory that remains competitive with MD simulation. After having compared the results obtained with the \( \text{DDD} \) and \( \text{DDD} + \text{DDQ} \) contributions, it turns out that the \( \text{DDD} \) and \( \text{DDQ} \) terms bring a mean positive contribution that reinforces the short-range part of the potential, the \( \text{DDQ} \) correction being about 10% of the \( \text{DDD} \) correction.

Though higher-order contributions to the three-body interaction \( u_3 \)—including three-body exchange—are smaller than the \( \text{DDD} \) contribution, they are believed to play a significant role in the explanation of many physical properties. Three-body interactions have been investigated by use of perturbation theory,\(^35\) MD simulation,\(^15\) liquid structure factor,\(^31,36\) and collision-induced light scattering,\(^37\) and it has been shown that they affect the equation-of-state. It should be mentioned that three-body exchange interactions can also be studied with the Slater–Kirwood form\(^22\) or by including a damping function in the expression \( Z_{\text{DDD}} W_{\text{DDD}} \) as in the Bulski and Chalanski paper.\(^38\)

To examine more thoroughly the role of the three-body force regardless of the exchange interaction, a useful way is to compare the \( \text{DDD} \) corrections obtained with HSA and MD simulation. The results displayed in Fig. 4 correspond to \( \langle u_3 \rangle \) normalized by its asymptotic form \( f(r, \rho) = (8 \pi / 3) Z_{\text{DDD}} \rho \cdot r^{-6} \). The agreement between HSA and MD results is particularly good for small distances and low densities. These curves reveal an oscillatory structure masked in \( \langle u_3 \rangle \) and a nonobvious density dependence due to the changing local liquid structure. A characteristic feature of the oscillation is the position of the first maximum, which is located between the first two peaks of \( g(r) \) and which decreases and moves to small distances when the density increases. Since \( \langle u_3 \rangle / f(r, \rho) \) is critically dependent on the density, we surmise that it may be deceptive to draw physical conclusions from its variation.

Concerning the thermodynamics, an important feature is to notice that the fluid under study becomes less compressible when the three-body effects are taken into account. Moreover, if compared to that of the LJ fluid, a significant improvement is observed for the pressure when the three-body contributions are present. In this connection, two papers\(^39,40\) have been published on the gas–liquid coexistence of Ar, in which the effect of the three-body interactions is partially included. More recently, Anta et al.\(^41\) have also assessed the influence of the three-body contributions in the problem of the phase coexistence by means of the hypenetered chain integral equation. While the LJ plus DDD system fails to reproduce the liquid branch of the phase diagram, the combination of Aziz’s potential with the DDD contribution leads to very accurate results for the thermodynamic and coexistence properties of Ar.

Simulating the contribution of the three-body forces rather than evaluating them in the framework of the integral equation theory is something very appealing because the liquid structure and thermodynamic properties are obtained in a manner fully consistent with the implicit many-body potential. The good concordance between both methods proves that the use of an effective pair potential added to the formalism of the integral equations remains valid when the three-body contributions are taken into account.

Three-body forces in supercritical Ar