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Abstract
Understanding the interatomic interactions in noble gases remains one of the fundamental problems not completely solved to date. From small-angle neutron scattering experiments it is well-known that three-body forces exist and cannot be neglected. On the theoretical side, semi-analytic and simulation methods have been used to reveal the nature of these many-body interactions. The purpose of the present work is to provide an overview of the different three-body contributions to the interactions and their relative importance in describing the structural and thermodynamic properties for noble gases by means of the integral equation theory and molecular dynamics simulations. We examine the relevance of the effective state-dependent pair potential in this framework, as well as the self-consistency problem that we are faced with in the integral equation theory.

1. Introduction

Neutron scattering experiments [1–5] in vapour and liquid states of noble gases have confirmed the presence of additional interactions at large distance, which can be associated with many-body contributions. In simple fluids, the particles are spherically symmetric and constitute a non-polar medium. Therefore the potential energy function for noble gases can be written as a sum of many-body potentials

$$U_N(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \sum_{i<j}^{N} u_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_{i<j<k}^{N} u_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k). \tag{1}$$

According to Barker and Henderson [6], the terms beyond the three-body one can be neglected due to their smallness. Three-body interactions arise because the electron clouds in two molecules near to one another readjust in response to a third molecule coming into their neighbourhood and, while they are much smaller than the two-body contribution, they cannot be neglected for most non-polar fluids.

In choosing specific forms for the two-body potential u_2 and the three-body potential u_3 to model noble gases in the fluid state, some problems arise: (i) the uniqueness, (ii) the transferability and (iii) the representability of the potentials. Strictly speaking, the uniqueness is never achieved since, to date, no general method exists to derive such potentials. Different functional forms (e.g. the Lennard-Jones potential) can be stated, with several parameters fitted on experimental or *ab initio* data over the wider possible domain of thermodynamic states. The transferability of a potential reflects its capability of being valid in an environment different than that for which it has been built. In the majority of cases, the potentials are restricted to the thermodynamic domain in which they are fitted. Finally, a potential has the property of representability if it is capable of describing all the physical properties of the real system it models. The inclusion of the relevant contributions in a potential (e.g. the exchange repulsion terms at short distance and the dispersion attraction terms at long distance) should improve its representability.

One of the questions of importance, which has been raised by several authors [7, 8] recently, is the validity of the approach that consists in using an effective pair potential that captures the essential features of the three-body contributions to the interactions in noble gases. It is seen that such an effective potential depends on density as well as temperature [9], and therefore it is called state dependent. In molecular dynamics simulations, the two- and three-body potentials and forces can be tackled readily [10]. Such a coarse-grained procedure, that intends to simplify equation (1) and reduce it to a sum of pair potentials, is the cornerstone in the framework of the liquid state theory to determine the physical properties of the system.

However, the problems of uniqueness, transferability and representability mentioned above are even more acute in the case of density-dependent potentials. For noble gases, these problems are revealed in particular in the calculation of the thermodynamic properties. In fact, the expressions of the internal energy, virial pressure and isothermal compressibility, for instance, have to be written with a different effective pair potential to take the three-body contributions into account correctly [9].

In this paper, we raise the following issues:

 (i) the description of the potential functions u_2 and u_3 that are relevant to represent the interatomic interactions (from the literature it appears that the two-body potential of Aziz–Slaman (AS) [11] plus the Axilrod–Teller (AT) triple-dipole three-body potential [12] alone is a good representation of the interatomic interactions for noble gases over a wide range of thermodynamic states),
 (ii) the formalism of the integral equation theory to determine the thermodynamic and structural properties,
(iii) the comparison of the integral equation and molecular dynamics results with experiment for low- and high-density liquid Kr to test the effective state-dependent pair potentials.

Finally, we discuss our results and we consider some perspectives.

2. Interactions in noble gases

The potential energy function given by equation (1) contains the two- and three-body potentials. Although several choices are possible for the two-body potential u_2 of noble gases, rather more realistic is the AS [11] model

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

where $x_{ij} = r_{ij}/r_{\mathrm{m}}$ is the reduced distance and r_{m} is the position of the minimum of the potential. Since the asymptotic form of the dispersion terms diverges for small distance it is damped by the function $F(x_{ij})$ in order to take the neglect of charge overlap effects, that become appreciable as distance decreases, into account:

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

All the coefficients in equations (2) and (3), known with some degree of precision by fitting experimental data, are listed in the paper of Aziz and Slaman [11]. Concerning the reliability of the pair potential in noble gases, Marcelli and Sadus [13] have shown that the potentials of AS and Barker, Fisher and Watts (BFW) [14] yield similar results in describing the liquid–vapour coexistence curve.

For the three-body potential u_3, several contributions can be considered. What can be taken into account are the dispersion terms whose the number depends on the number of configurations for the multipole moments (dipole d, quadrupole q, octupole o, etc) as well as on the order at which the multipole expansion is truncated

$$u_{3\text{disp}} = u_{\text{ddd}} + u_{\text{ddq}} + u_{\text{dqq}} + u_{\text{qqq}} + u_{\text{ddo}} + u_{\text{ddd4}}. \tag{4}$$

The first five terms come from third-order perturbation theory while the last one is fourth-order. The main contribution to $u_{3\text{disp}}$ is the third-order triple-dipole term u_{ddd} derived by AT [12]

$$u_{\text{ddd}}(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) = \nu \frac{1 + 3\cos\theta_i \cos\theta_j \cos\theta_k}{r_{ij}^3 r_{ik}^3 r_{jk}^3}, \tag{5}$$

which corresponds to an irreducible potential between three closed shell atoms. θ_i, θ_j and θ_k denote, respectively, the angles at vertex i, j and k of the triangle (i, j, k) 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 other multipolar potentials have been determined within the perturbation theory [15–17] and the expressions for evaluating each contribution have been taken from Doran and Zucker [18]. Note that the ddo contribution is difficult to calculate because of the lack of value for the interaction constant.

The three-body exchange interaction can also be used in some circumstances. For this purpose, the expression of Bruch and McGee [19] can be considered, which has been extensively used by Loubeyre [20] to investigate the thermodynamic properties of solid rare gases. However, this potential decays exponentially with respect to either distance of three nearby atoms and its influence is only observable at high density, as shown by Bukowski and Szalewicz [21], so that exchange interactions have been neglected for thermodynamic states of krypton under study here.

It has been evidenced that the dqq and qqq contributions have only a small influence even in the liquid state, whereas the ddq and ddd4 potentials have a non-negligible contribution, though they compensate each other. This has also been observed by Marcelli and Sadus [13] and by Bukowski and Szalewicz [21] in their *ab initio* simulations of argon for the liquid–vapour equilibria and pure phases. Therefore, the three-body contributions are well represented by the dominant contribution only, the ddd triple-dipole interaction $u_3 = u_{\text{ddd}}$.

3. Thermodynamic properties

From the potential energy function given by equation (1), it is possible to derive an exact expression for the internal energy in terms of the pair potential $u_2(r)$ and correlation

function $g_2(r)$ as well as the three-body potential $u_3(\mathbf{r}_{12}, \mathbf{r}_{23})$ and triplet-correlation function $g_3(\mathbf{r}_{12}, \mathbf{r}_{23})$:

$$\frac{E}{\langle N \rangle} = \frac{3}{2\beta} + \frac{E_2}{\langle N \rangle} + \frac{E_3}{\langle N \rangle} \tag{6}$$

with

$$\frac{E_2}{\langle N \rangle} = \frac{\rho}{2} \int u_2(r_{12}) g_2(r_{12}) \, d\mathbf{r}_{12}, \tag{7}$$

$$\frac{E_3}{\langle N \rangle} = \frac{\rho^2}{6} \int u_{\mathrm{ddd}}(\mathbf{r}_{12}, \mathbf{r}_{23}) g_3(\mathbf{r}_{12}, \mathbf{r}_{23}) \, d\mathbf{r}_{12} \, d\mathbf{r}_{23}, \tag{8}$$

where ρ is the number density and $\beta = (k_B T)^{-1}$ is the inverse temperature. Similarly, the virial pressure reads

$$P = \frac{\rho}{\beta} + P_2 + P_3, \tag{9}$$

with

$$P_2 = -\frac{\rho^2}{6} \int r_{12} \frac{d u_2(r_{12})}{d r_{12}} g_2(r_{12}) \, d\mathbf{r}_{12}, \tag{10}$$

$$P_3 = -\frac{\rho^3}{18} \int \left\{ r_{12} \frac{\partial}{\partial r_{12}} + r_{23} \frac{\partial}{\partial r_{23}} + r_{13} \frac{\partial}{\partial r_{13}} \right\} u_{\mathrm{ddd}}(\mathbf{r}_{12}, \mathbf{r}_{23}) g_3(\mathbf{r}_{12}, \mathbf{r}_{23}) \, d\mathbf{r}_{12} \, d\mathbf{r}_{23}. \tag{11}$$

Deriving the pressure with respect to ρ yields the isothermal compressibility χ_T to be

$$\frac{1}{\chi_T} = \rho \frac{\partial P}{\partial \rho}\bigg|_T = \frac{\rho}{\beta} + B_2 + B_3, \tag{12}$$

with

$$B_2 = -\frac{\rho^2}{3} \int r_{12} \frac{d u_2(r_{12})}{d r_{12}} \left\{ g_2(r_{12}) + \frac{\rho}{2} \frac{\partial g_2(r_{12})}{\partial \rho} \right\} d\mathbf{r}_{12}, \tag{13}$$

$$B_3 = -\frac{\rho^3}{6} \int \left\{ r_{12} \frac{\partial}{\partial r_{12}} + r_{23} \frac{\partial}{\partial r_{23}} + r_{13} \frac{\partial}{\partial r_{13}} \right\} u_{\mathrm{ddd}}(\mathbf{r}_{12}, \mathbf{r}_{23})$$
$$\times \left\{ g_3(\mathbf{r}_{12}, \mathbf{r}_{23}) + \frac{\rho}{3} \frac{\partial g_3(\mathbf{r}_{12}, \mathbf{r}_{23})}{\partial \rho} \right\} d\mathbf{r}_{12} \, d\mathbf{r}_{23}. \tag{14}$$

For the AT interaction given by equation (5), which is a homogeneous function of the variables r_{12}, r_{13} and r_{23}, the Euler theorem $\left(\sum_{i>j} r_{ij} \frac{\partial u_{\mathrm{ddd}}}{\partial r_{ij}} = -9 u_{\mathrm{ddd}} \right)$ can be applied to simplify some terms of the virial pressure and isothermal compressibility such as

$$P_3 = 3\rho \frac{E_3}{\langle N \rangle}, \tag{15}$$

$$B_3 = 3P_3 + \frac{\rho^4}{2} \int u_{\mathrm{ddd}}(\mathbf{r}_{12}, \mathbf{r}_{23}) \frac{\partial g_3(\mathbf{r}_{12}, \mathbf{r}_{23})}{\partial \rho} \, d\mathbf{r}_{12} \, d\mathbf{r}_{23}. \tag{16}$$

To actually carry out the calculation of equations (15) and (16), the superposition approximation of Kirkwood [22]

$$g_3(\mathbf{r}_{12}, \mathbf{r}_{23}) = g_2(r_{12}) g_2(r_{23}) g_2(r_{13}) \exp\{-\beta u_{\mathrm{ddd}}(\mathbf{r}_{12}, \mathbf{r}_{23})\}, \tag{17}$$

has to be done to estimate the triplet-correlation function $g_3(\mathbf{r}_{12}, \mathbf{r}_{23})$, which leaves unchanged the virial pressure and isothermal compressibility to third order in density. If the bipolar

coordinates are now used to perform the three-dimensional integrals, the thermodynamic properties can be evaluated by the following expressions

$$\frac{E_2}{\langle N \rangle} = 2\pi\rho \int_0^\infty u_2(r_{12}) g_2(r_{12}) r_{12}^2 \, dr_{12}, \tag{18}$$

$$\frac{E_3}{\langle N \rangle} = \frac{4\pi^2\rho^2}{3} \int_0^\infty g_2(r_{12}) r_{12} \, dr_{12} \int_0^\infty g_2(r_{13}) r_{13} \, dr_{13}$$
$$\times \int_{|r_{12}-r_{13}|}^{r_{12}+r_{13}} u_{\text{ddd}}(r_{12}, r_{13}, r_{23}) g_2(r_{23}) \exp(-\beta u_{\text{ddd}}) r_{23} \, dr_{23}, \tag{19}$$

$$P_2 = -\frac{2\pi\rho^2}{3} \int_0^\infty \frac{du_2(r_{12})}{dr_{12}} g_2(r_{12}) r_{12}^3 \, dr_{12}, \tag{20}$$

$$P_3 = 3\rho \frac{E_3}{\langle N \rangle}, \tag{21}$$

$$B_2 = 2P_2 - \frac{2\pi\rho^3}{3} \int_0^\infty \frac{du_2(r_{12})}{dr_{12}} \frac{\partial g_2(r_{12})}{\partial\rho} r_{12}^3 \, dr_{12}, \tag{22}$$

$$B_3 = +3P_3 + 4\pi^2\rho^4 \int_0^\infty r_{12} \, dr_{12} \int_0^\infty r_{13} \, dr_{13}$$
$$\times \int_{|r_{12}-r_{13}|}^{r_{12}+r_{13}} u_{\text{ddd}}(r_{12}, r_{13}, r_{23}) \frac{\partial g_3(r_{12}, r_{13}, r_{23})}{\partial\rho} r_{23} \, dr_{23}. \tag{23}$$

These expressions, which are formally exact, contain explicitly the pair and triplet correlation functions. In practice, it is necessary to approximate the triplet correlation function in terms of the pair correlation function. However, it should be emphasized that, even if this approximation were neglected ($g_2(r_{12})g_2(r_{23})g_2(r_{13}) \sim 1$), the effect of the three-body potential would be felt through the pair correlation function. In addition, equations (21) and (23) show that the triple-dipole contributions to the thermodynamic properties are simply related together. These expressions are not new, but they contribute to facilitate the numerical evaluation of the virial pressure and isothermal compressibility and to perform a comprehensive study of the influence of the three-body interactions in noble gases.

4. Pair correlation function

From equations (18)–(23) it appears that the thermodynamic quantities of fluids can be calculated when the interatomic potential is reasonably well characterized and the pair correlation function is known as a consequence of the superposition approximation. In this work, we use first the large-scale molecular dynamics (MD) simulation to determine the pair correlation function, against which our results issued from the integral equation (IE) theory can be tested, because making direct comparison between IE theory and experiment does not allow us to judge the quality of the interatomic potential independent of its treatment. Contrary to the IE theory, in molecular dynamics the three-body forces are exactly and explicitly considered so that the effect of the triple-dipole contribution to the pair correlation function can be observed without ambiguity.

4.1. Large-scale molecular dynamics

Although the presence of the three-body interactions in noble gases are rather inferred by comparing a physical property calculated by two different theories, a valuable comparison can be also achieved between the MD and experimental structure factors at small angle scattering

accessible to simulation for large systems. In order to reduce the CPU time required to carry out the runs and to cope with a large number of atoms [24, 25], the classical molecular dynamics code [23] has been parallelized and the long-range corrections to the thermodynamic quantities for two- and three-body contributions have been included.

Since the knowledge of the two- and three-body forces is needed to perform a simulation, for the AS potential the force acting on particle i from particle j is taken to be

$$\mathbf{F}_{ij}(r_{ij}) = \left\{ A \exp(-\alpha x_{ij} + \beta x_{ij}^2)(-\alpha + 2\beta x_{ij}) \right. \tag{24}$$

$$\left. - F(x_{ij}) \left[\sum_{p=0}^{2} \frac{(2p+6)C_{2p+6}}{x^{2p+7}} - \frac{2D(D - x_{ij})}{x_{ij}^3} \sum_{p=0}^{2} \frac{C_{2p+6}}{x^{2p+6}} \right] \right\} \mathbf{e}_{ij}, \tag{25}$$

where $\mathbf{e}_{ij}$ is a unit vector in the $\mathbf{r}_{ij}$-direction. For the AT potential, the force acting on particle i from particles j and k reads

$$\mathbf{F}_{i,jk}(r_{ij}, r_{jk}, r_{ik}) = \frac{\partial u_3}{\partial r_{ij}} \mathbf{e}_{ij} + \frac{\partial u_3}{\partial r_{ik}} \mathbf{e}_{ik}, \tag{26}$$

while the forces acting on j and k are respectively

$$\mathbf{F}_{j,ik}(r_{ij}, r_{jk}, r_{ik}) = -\frac{\partial u_3}{\partial r_{ij}} \mathbf{e}_{ij} + \frac{\partial u_3}{\partial r_{jk}} \mathbf{e}_{jk},$$

$$\mathbf{F}_{k,ij}(r_{ij}, r_{jk}, r_{ik}) = -\frac{\partial u_3}{\partial r_{ik}} \mathbf{e}_{ik} - \frac{\partial u_3}{\partial r_{jk}} \mathbf{e}_{jk}. \tag{27}$$

The expressions of the three partial derivatives of u_3 can be found in the paper of Hoheisel [26]. From Newton's third law, we have $\mathbf{F}_{ij} = -\mathbf{F}_{ji}$ for the two-body forces and $\mathbf{F}_{i,jk} = -\mathbf{F}_{j,ik} - \mathbf{F}_{k,ij}$ for the three-body forces. Consequently, the forces can be calculated in reducing the computational time both for pair-and three-body forces. Equations (25)–(27) yield simple analytical forms that are very convenient for our computational purposes. The procedures of the MD simulations used here to predict the small-q structure factor can be found in previous papers [25, 31, 10]. For computational purposes, a cut-off $r_c = 2.5r_m$ of the interactions is used for the two- as well as the three-body potential. For the latter, it is worth noting that with this value of r_c, configurations in which one pair of a triplet are separated up to $5r_m$ are taken into account [26]. As shown in [10], an influence of the cut-off is seen only below $q = 2.5$ nm^{-1} on the structure factor $S(q)$, or on the direct correlation function $c(q)$ $(=(1 - 1/S(q))/\rho)$. Consequently, in this region, the q^3 component of the low-q expansion of $c(q)$ is absent (e.g. see relations (20) and (21) of [31]) and the effects of the different interaction terms cannot be discussed.

4.2. Self-consistent integral equation method

In the self-consistent integral equation method, the presence of three-body interactions raises a problem because the three-body potential has to enter as an effective state-dependent pair potential determined separately from the IE theory. According to the IE method, the pair-correlation function is obtained by means of the Ornstein–Zernike relation

$$g(r_{12}) - 1 = c(r_{12}) + \rho \int [g(r_{13}) - 1]c(r_{23}) \, d\mathbf{r}_3 \tag{28}$$

combined with the closure relation

$$g(r_{12}) = \exp[-\beta u_{\text{eff}}(r_{12}) + \gamma(r_{12}) + B(r_{12})], \tag{29}$$

where $g(r_{12})$ is the pair correlation function, $c(r_{12})$ is the direct correlation function, $\gamma(r_{12})$ $[=g(r_{12}) - 1 - c(r_{12})]$ is the indirect correlation function, $B(r_{12})$ is the bridge function and $u_{\mathrm{eff}}(r_{12})$ is the effective pair potential that will be approximated below.

There are a large number of possibilities from which to choose the bridge function $B(r_{12})$, but for our purposes we use that derived by Zerah and Hansen [27] (HMSA) because it allows us to achieve the thermodynamic consistency owing to a parameter being adjusted by requiring that the long-wavelength limit of the structure factor,

$$S(0) = \left[1 - \rho \int \mathrm{d}\mathbf{r}_{12} c(r_{12})\right]^{-1}, \tag{30}$$

is equal to $\frac{\rho}{\beta} \chi_{\mathrm{T}}$, where the isothermal compressibility χ_{T} is calculated with equation (12). It has been shown [28], with a more complete set of thermodynamic relations involving virial pressure and energy routes, that the thermodynamic consistency is obtained accurately if the above-mentioned criteria are considered. In addition, Caccamo and Pellicane [29] have shown recently that the thermodynamic consistency achieved with those criteria is correct for potentials such as those studied here. In contrast, for potentials having shorter range, a global consistency dealing with the virial pressure might be set up instead of the isothermal compressibility. In addition, the problem of thermodynamic consistency for complex systems, which has been raised recently by Tejero [30], is still not fully understood.

4.3. Effective state-dependent pair potential

In the case of fluids with only two-body potentials, the effective potential to be used in equation (29) is the genuine pair potential. But if three-body interactions are present, they must be transformed into a sum of effective pair potentials to be tractable within the integral equation theory. As in our previous works [31, 32], we use the expression for the effective pair potential proposed by Sinanoglu [33] as well as Rushbrooke and Silbert [34] that reads

$$u_{\mathrm{eff}}(r_{12}) = u_2(r_{12}) + \langle u_3(r_{12})\rangle, \tag{31}$$

with

$$\langle u_3(r_{12})\rangle = -\frac{\rho}{\beta} \int g(r_{13}) g(r_{23}) [\exp\{-\beta u_{\mathrm{ddd}}(\mathbf{r}_{12}, \mathbf{r}_{23})\} - 1]\,\mathrm{d}\mathbf{r}_3. \tag{32}$$

This way of treating the three-body interactions has proven to be efficient for describing the pair-correlation function in noble gases [36–38]. While $u_2(r_{12})$ and $u_3(\mathbf{r}_{12}, \mathbf{r}_{23})$ are independent of the thermodynamic state, it is clear from equation (32) that the effective pair potential is explicitly density and temperature dependent. Practically, we use a cut-off of $u_{\mathrm{ddd}}(\mathbf{r}_{12}, \mathbf{r}_{23})$ identical to the MD one in the numerical evaluation of equation (32).

An interesting question, related to the use of equation (32), is whether or not it is possible to calculate diverse physical properties with the same effective pair potential. Since the pioneering work of Casanova et al [9] (see also [7]), we know that a unique effective state-dependent pair potential cannot be used for the calculation of every thermodynamic property. Then, the internal energy has to be calculated by

$$\frac{E}{\langle N\rangle} = \frac{3}{2\beta} + 2\pi\rho \int g(r)\left[u_2(r) + \frac{1}{3}\langle u_3(r)\rangle\right] r^2\,\mathrm{d}r \tag{33}$$

while, for the virial pressure, the following expression has to be used

$$P = \frac{\rho}{\beta} - \frac{2\pi\rho^2}{3} \int g(r)\frac{\mathrm{d}}{\mathrm{d}r}\left[u_2(r) + \frac{2}{3}\langle u_3(r)\rangle\right] r^3\,\mathrm{d}r. \tag{34}$$

It should be stressed that using equation (31) to determine the internal energy and virial pressure of the noble gases instead of exact expressions leads to a too large estimation of the three-body effects. This actually poses the problem of the representability of the effective pair potential since it can be different in different applications. In the following, one of our intentions is to compare the results of equations (33) and (34) with those of equations (6) and (9).

5. Application to krypton

We come now to the presentation of our results for gaseous and liquid krypton in order to test the theoretical background displayed in previous sections. Our aim is two-fold:

 (i) to test the representability of the interatomic potential combining the two-body potential of AS with the triple-dipole contribution, and
 (ii) to test the ability of an effective state-dependent pair potential to represent the three-body contribution in the framework of the IE theory.

In a previous work [10], we have shown, using MD simulations, that the main influence of the three-body potential on the structure factor $S(q)$ is only seen at small q. At large q, the IE results presented here are in excellent agreement with the MD ones. This shows that the large-q part of $S(q)$ is not very sensitive to the triple-dipole potential whatever the method used. Therefore, the comparison of the small-q part of $S(q)$ calculated by MD simulation with the experimental one represents a stringent test for the three-body interactions, and that of the MD simulation with the IE method one allows us to check if the effective state-dependent pair potential represents properly the triple-dipole interaction. Since it has been shown that the self-consistent IE considered here is very efficient for two-body potentials alone [27, 35], in this work we focus only on the IE results from the effective pair potential that contains the triple-dipole contribution.

In figures 1–3, we display the small-q part of the $S(q)$ for the gas phase ($T = 297$ K and $\rho = 1.52, 1.97, 2.42$ and 4.277 nm^{-3}), the liquid phase ($T = 169$ K and $\rho = 14.57$ nm^{-3}) and in the vicinity of the triple point ($T = 130$ K and $\rho = 16.83$ nm^{-3}), respectively. When the MD results are compared to the experimental data, very good agreement is found in the vapour phase [3] and in the liquid state [5] at $T = 169$ K. However, near the triple point, a slight overestimation appear with respect to the experiment. It should be mentioned that no experimental data for small angle neutron scattering exist for the latter thermodynamic state, to the best of our knowledge. Since MD simulation involves no approximation, our results suggest that higher-order three-body interactions are improperly neglected, unless there is some systematic error of unknown origin in the experimental data. Therefore, we conclude that the interatomic potential that combines the AS two-body potential with the AT three-body potential is a good representation for the interactions of Kr in the vapour and liquid phases at low densities. At higher densities, such as those characteristic of liquids near the triple point, it is suspected that the overlap corrections to the dispersion and exchange interactions are not completely negligible. This holds for the thermodynamic properties such as the pressure with an effect of the three-body exchange interaction estimated at about 20% in magnitude of the AT contribution with the same sign [10].

We turn now to our IE results which concerns the use of the effective state-dependent pair potential given by equation (32). As pointed out for the first time by Casanova *et al* [9] and revisited by van der Hoef and Madden [7] in connection with *ab initio* MD simulation, there are additional consequences to the thermodynamic properties when one wishes to determine them by means of an effective potential. As a matter of fact, the internal energy and the virial pressure have to be calculated using equations (33) and (34), revealing the non-uniqueness of
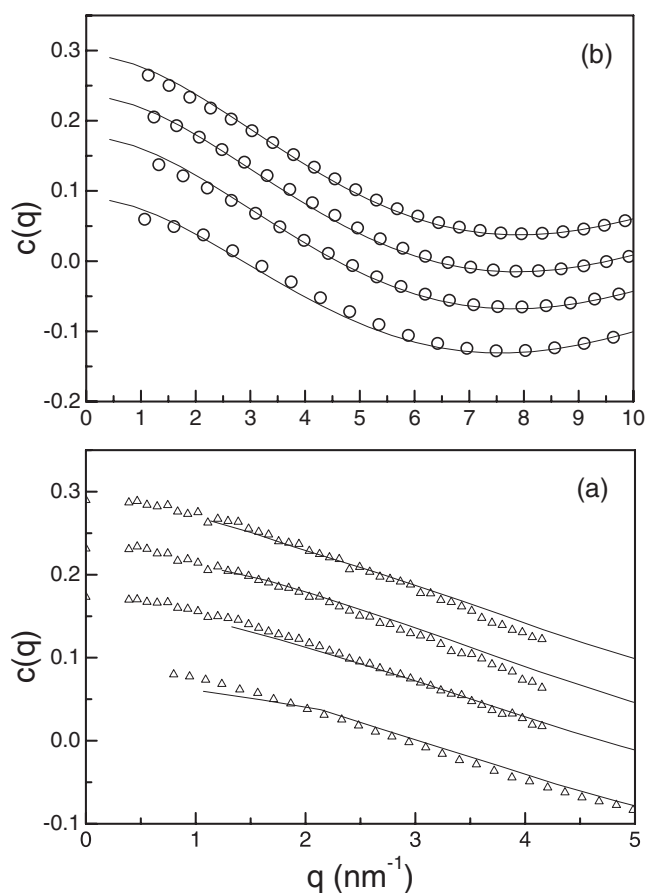
Figure 1. Fourier transform of the direct correlation function $c(q)$ at $T = 297$ K and $\rho = 1.52$, 1.97, 2.42 and 4.277 nm^{-3} from the top to the bottom (the curves for $\rho = 1.52$, 1.97 and 2.42 nm^{-3} are shifted upwards by an amount of 0.05, 0.1 and 0.15, respectively): (a) comparison between molecular dynamics [25] (solid lines) and experiments [3, 5] (up triangles); (b) comparison between the integral equation method (solid curves) and molecular dynamics [25] (open circles). Note that the function $c(q)$ is drawn, which is related to the structure factor $S(q)$ by the simple relation $S(q) = (1 - \rho c(q))^{-1}$. The up triangles at $q = 0$ stand for the PVT data of [39].

the effective state-dependent pair potential in this framework. To test these expressions, we have gathered in table 1 the energy and pressure results for the three thermodynamic states of Kr under consideration. The values calculated using equations (33) and (34) are compared with those obtained with the exact relations, i.e. equations (6) and (9) respectively. The good agreement for all the states attests to the reliability of equations (33) and (34) since the departure does not exceed 0.2% for the internal energy, while the agreement is a little bit worse with the effective pair potential given by equation (31). Even for the pressure, which takes very small values, the agreement is excellent. When the comparison is made with the MD data taken as a reference, the agreement is of the same quality.

Finally, we focus our attention on the comparison between the IE and MD structure factors in order to see the importance of the effective state-dependent pair potential specifically built for the integral equation approach. It is worth mentioning, however, that the results of the MHNC integral equation [4, 5] are of the same quality at $T = 130$ K as those of the HMSA
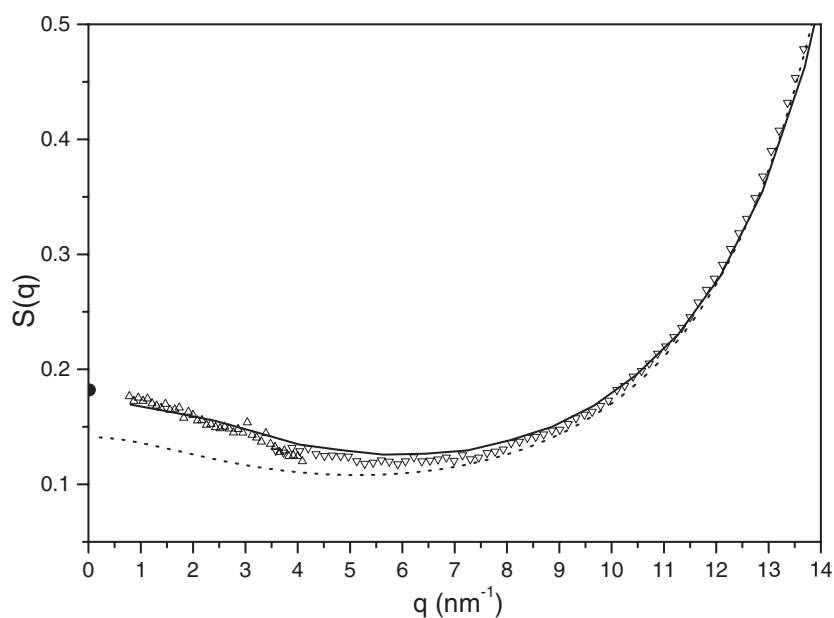
Figure 2. Small-q part of the structure factor $S(q)$ at $T = 169$ K and $\rho = 14.57$ nm^{-3}: small-angle neutron scattering experiments [5] (up triangles), large-q experiments [4] (down triangles), molecular dynamics simulations (solid curve), and integral equation method (dashed curve). The full circles stand for the PVT data of [39].
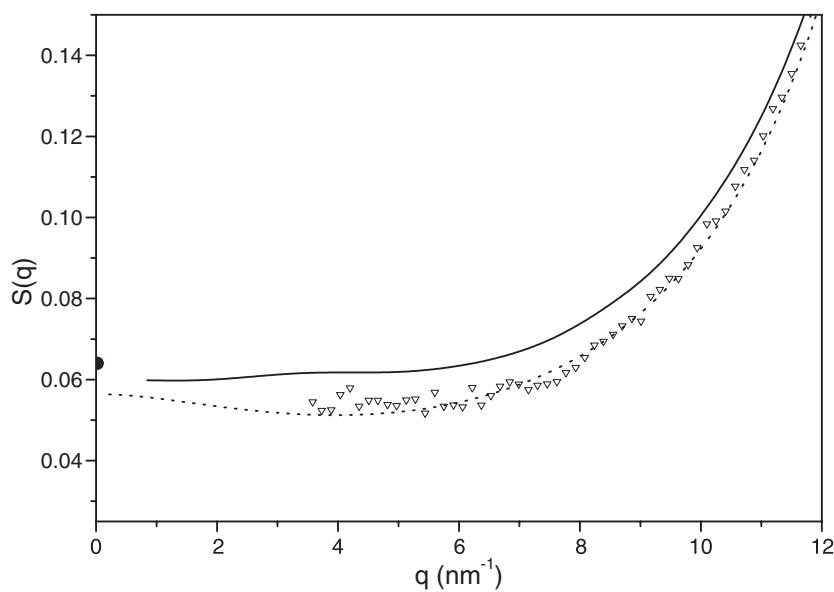

Figure 3. Small-q part of the structure factor $S(q)$ at $T = 130$ K and $\rho = 16.83$ nm^{-3}: large-q experiments [4] (down triangles), molecular dynamics simulations (solid curve), and integral equation method (dashed curve). The full circles stand for the PVT data of [39].

presented here, and slightly better at $T = 169$ K with respect to the experiment. Even if the agreement between IE theory and experiment seems to be better, the comparison between

Table 1. Excess internal energy $E^{ex}/N\varepsilon$ and pressure Pr_m^3/ε for gaseous and liquid Kr calculated using the IE method with equations (6) and (9), and calculated using equations (33) and (34) (subscript eff), respectively. The quantities with subscript MD correspond to the results of molecular dynamics simulations [10].

T (K)	ρ (nm^{-3})	$E^{ex}/N\varepsilon$	$E_{eff}^{ex}/N\varepsilon$	$E_{MD}^{ex}/N\varepsilon$	Pr_m^3/ε	$P_{eff}r_m^3/\varepsilon$	$P_{MD}r_m^3/\varepsilon$
130	16.83	−4.684	−4.675	−4.689	−0.124	−0.136	−0.12
169	14.57	−3.834	−3.919	−3.938	0.012	0.010	0.06
199	12.10	−3.198	−3.210	−3.232	0.082	0.097	0.11

IE and MD is obvious to test the state-dependent pair potential because the same three-body potential enters both approaches and just its treatment differs. In the vapour phase (figure 1) an excellent agreement is guaranteed between the IE method and the MD simulations. In the liquid state and near the triple point (figures 2 and 3), the concordance is still good since only slight deviations appear with respect to the MD curves. This shows the validity of the effective state-dependent pair potential constructed to be used in the specific context of the IE theory and emphasizes that the selected self-consistent integral equation is reliable in the vapour and liquid phases of Kr.

6. Conclusion

In this work, we have presented the formalism for practical calculation of thermodynamic and structural properties of noble gases when typical three-body interactions are taken into account. First, MD simulations were performed for large systems of atoms modelling gaseous and liquid Kr, at thermodynamic states for which small-angle neutron scattering experiments were recently reported in the literature. The objective of these simulations was to test the model for the interatomic potential in Kr. Compared to experimental structure factor, the findings strengthen our previous outcome [10] for the presence of three-body interactions in Kr satisfactory represented by the triple-dipole contribution at low and intermediate densities. At larger densities, a deviation appears on the small-q region ($q < 10$ nm^{-1}) of $S(q)$ that is the signature of missing three-body contributions. There is clear evidence that overlap corrections to the dispersion and exchange interactions increase for small interatomic distances and cannot be omitted in the analysis of the physical properties of dense noble gases at high density.

Second, the self-consistent integral equation theory has been used to investigate the role of the effective state-dependent pair potential in the calculation of the structural and thermodynamic properties. It is an important issue related to the uniqueness and representability of the interatomic potential capable of modelling conveniently the interactions in Kr and describing different physical properties on an equal footing. This work confirms that there is no unique effective state-dependent pair potential to represent the many-body interactions in simple liquids. As a matter of fact, the effective potential that correctly predicts the structure differs significantly from those derived to reproduce the internal energy or the virial pressure.

For high densities, the IE method slightly underestimates the small-q part of $S(q)$ relative to the MD simulation. A possible improvement in the IE approach could be to use a code of automatic differentiation to get exact density derivatives of the correlation functions and to refine the thermodynamic consistency. Further exploration of the IE theory in connection with the MD simulation and experiment is needed before the role of three-body forces in simple liquids can be well understood. Works proceeding towards this target are in progress.

Acknowledgments

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