An accurate expression for radial distribution function of the Lennard-Jones fluid

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Abstract

A simple and accurate expression for radial distribution function (RDF) of the Lennard-Jones fluid is presented. The expression explicitly states the RDF as a continuous function of reduced interparticle distance, temperature, and density. It satisfies the limiting conditions of zero density and infinite distance imposed by statistical thermodynamics. The distance dependence of this expression is expressed by an equation which contains 11 adjustable parameters. These parameters are fitted to 353 RDF data, obtained by molecular dynamics calculations, and then expressed as functions of reduced distance, temperature and density. This expression, having a total of 65 constants, reproduces the RDF data with an average root-mean-squared deviation of 0.0152 for the range of state variables of $0.5 \leqslant T^* \leqslant 5.1$ and $0.35 \leqslant \rho^* \leqslant 1.1$ ($T^* = kT/\varepsilon$ and $\rho^* = \rho\sigma^3$ are reduced temperature and density, respectively). The expression predicts the pressure and the internal energy of the Lennard-Jones fluid with an uncertainty that is comparable to that obtained directly from the molecular dynamics simulations.

1. Introduction

The radial distribution function (RDF) acts as a bridge for relating macroscopic thermodynamic properties to interparticle interactions of substances. The RDF is a key quantity in statistical mechanics because it characterizes how the particles correlations in a substance decay with increasing separation. The knowledge about RDF is important for several reasons: First of all, knowledge of the RDF is sufficient information to calculate thermodynamic properties, particularly the isothermal compressibility. It could be sufficient for pressure and internal energy calculations, also, if we assume pairwise additivity of intermolecular potential energy function is sufficient [1–3]. Second, information about RDF will allow us to calculate direct correlation function integrals which are the basis of the fluctuation theory of mixtures [4]. Third, the RDF is the best characteristic of the nature of substances, specially liquids and knowledge about it could reveal the peculiarities of fluids and fluid mixtures [1–3]. One of the attractive approaches to the theory of liquids is the fact that we can calculate its RDF's from the first principles, having assumed a suitable form for the intermolecular potential, such as the Lennard-Jones potential. This module permits the RDF to be calculated for the Lennard-Jones fluid over a desired and wide range of intermolecular distances, temperatures and densities. Furthermore, availability of the RDF and equation of state of the Lennard-Jones fluid may help the development of a new class of perturbation and variational theories of liquid state wherein the reference state is assumed to be the Lennard-Jones fluid [5]. The importance of these theories lies in their applications to a vast variety of liquids and solutions. For example, these theories have been recently applied to research the density

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and temperature dependence of the effective intermolecular pair potentials of fluids and mixtures [6].

Since the limited RDF data in the literature [7] which are produced through molecular dynamics simulations are available only in the form of tables which are inconvenient to use, the presentation of an explicit expression as a function of $r^* = r/\sigma$, $T^* = (kT)/\varepsilon$, $\rho^* = \rho\sigma^3$ seemed necessary, where r^* is the reduced interparticle distance and k, σ, ε, r, T, and ρ are the Boltzmann constant, length parameter of the Lennard-Jones potential function, energy parameter of the Lennard-Jones potential function, interparticle distance, absolute temperature, and density, respectively.

The main goal of the present work is to introduce a simple and accurate expression for RDF of the Lennard-Jones fluid as a continuous function of reduced interparticle distance, temperature, and density.

2. The expression

The first step for presentation of an expression capable of stating the RDF $g(r^*,T^*,\rho^*)$ as a function of reduced interparticle distance, temperature, and density is to write an equation describing the distance dependence of this expression. This equation should satisfy the following limiting condition:

$$\lim_{r^* \to \infty} g(r^*, T^*, \rho^*) = 1.$$

Such equation in the first place should fairly fit to the RDF's, and secondly it should not have exceedingly large number of parameters. Too large a number of parameters not only makes the application of the resulting equation difficult, but also causes the determination of functionality of these parameters with temperature and density to be accompanied with high deviations. To achieve this, we propose the following simple equation involving 11 adjustable parameters:

$$g(r^*, T^*, \rho^*)$$
$$= 1 + (r^*)^{-2} \exp[-(ar^* + b)] \sin[(cr^* + d)]$$
$$+ (r^*)^{-2} \exp[-(gr^* + h)] \cos[(kr^* + l)], \quad r^* > 1,$$
$$(1a)$$

$$g(r^*, T^*, \rho^*) = s \exp[-(mr^* + n)^4], \quad r^* \leqslant 1, \quad (1b)$$

where a, b, c, d, g, h, k, l, m, n, and s are the adjustable parameters being functions of temperature and density themselves. The term $\exp[-(mr^* + n)^4]$ provides for the decay of the first peak, while the terms $\exp[-(ar^* + b)]\sin[(cr^* + d)]$ and $\exp[-(gr^* + h)]\cos[(kr^* + l)]$ give an oscillating-decaying shape to the function as the RDF need to have.

Pursuant to above, all parameters $P_i = a$, b, c, d, g, h, k, l, m, n, and s are to be expressed as functions of reduced temperature and density. The final expression of

RDF $g(r^*,T^*,\rho^*)$ should fulfill the following limiting conditions:

At zero density it must reduce to its ideal gas limit of unity:

$$\lim_{\rho \to 0} g(r^*, T^*, \rho^*) = 1.$$

Our calculations have demonstrated that the parameters $P_i = b$, d, h, and l are functions of density only and the parameter $P_i = n$ is a function of temperature only and the remaining parameters are functions of temperature and density. The following functional forms for the parameters are proposed:

$$P_i = q_{1,i} + q_{2,i} \exp[-q_{3,i}T^*] + q_{4,i} \exp[-q_{5,i}T^*] + \frac{q_{6,i}}{\rho^*}$$
$$+ \frac{q_{7,i}}{(\rho^*)^2} + \frac{q_{8,i} \exp[-q_{3,i}T^*]}{(\rho^*)^3} + \frac{q_{9,i} \exp[-q_{5,i}T^*]}{(\rho^*)^4}, \quad (2)$$

for $P_i = a(T^*,\rho^*), g(T^*,\rho^*)$,

$$P_i = q_{1,i} + q_{2,i} \exp[-q_{3,i}T^*] + q_{4,i}\rho^* + q_{5,i}(\rho^*)^2$$
$$+ q_{6,i}(\rho^*)^3 + q_{7,i}(\rho^*)^4 + q_{8,i}(\rho^*)^5, \quad (3)$$

for $P_i = c(T^*,\rho^*), k(T^*,\rho^*)$,

$$P_i = q_{1,i} + q_{2,i} \exp[-q_{3,i}\rho^*], \quad (4)$$

for $P_i = b(\rho^*), h(\rho^*)$,

$$P_i = q_{1,i} + q_{2,i} \exp[-q_{3,i}\rho^*] + q_{4,i}\rho^*, \quad (5)$$

for $P_i = d(\rho^*), l(\rho^*)$,

$$P_i = \left(q_{1,i} + q_{2,i}\rho^* + \frac{q_{3,i}}{T^*} + \frac{q_{4,i}}{(T^*)^2} + \frac{q_{5,i}}{(T^*)^3}\right)$$
$$\times (q_{6,i} + q_{7,i}\rho^* + q_{8,i}(\rho^*)^2)^{-1}, \quad (6)$$

for $P_i = s(\rho^*,T^*)$,

$$P_i = q_{1,i} + q_{2,i} \exp[-q_{3,i}T^*] + \frac{q_{4,i}}{T^*} + q_{5,i}\rho^* + q_{6,i}(\rho^*)^2,$$
$$(7)$$

for $P_i = m(\rho^*,T^*)$ and

$$P_i = q_{1,i} + q_{2,i} \exp[-q_{3,i}T^*], \quad (8)$$

for $P_i = n(T^*)$.

These functions have been selected in such a manner as to satisfy the above limiting conditions.

3. Results and discussion

In order to check the capability of Eqs. (1a) and (1b) to reproduce the RDF data, these equations have been fitted to 353 RDF data obtained by using molecular dynamics calculations for the range of state variables $0.5 \leqslant T^* \leqslant 5.1$ and $0.35 \leqslant \rho^* \leqslant 1.1$. The molecular dynamics calculations have been performed using MOLDY software [8] for 2000 argon atoms interacting via the Lennard-

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Jones potential ($\sigma = 3.405$ Å, $\varepsilon/k = 119.8$ K) and then re-sults have been converted to reduced format. MOLDY is a highly portable C program for performing molecular dynamics simulations of solids and liquids. The model system is completely specified in an input file and may contain atoms, molecules or ions in any mixture. Mole-cules are treated in the rigid-molecule approximation. Potential function of Lennard-Jones, 6-exp and MCY forms are supported and the code is structured to give a straightforward interface to add a new functional form.

For each RDF data, the distance between the points from 0.0 to 2.4 and from 2.4 to 5 has been considered 0.04 and 0.2 respectively (as presented by Verlet [9]). To test the accuracy of our computations many of the already available Verlet simulation data were repro-duced using the MOLDY software.

The functionality of the 11 parameters of Eqs. (1a) and (1b) with respect to the reduced temperature and density has been determined using Eqs. (2)–(8). Table 1 gives the set of the 11 parameters, q_i, values and root-mean-squared deviations (rmsd) of the fit related to them.

Eqs. (1a) and (1b), together with Eqs. (2)–(8) and the entries in Table 1, constitutes our expression for the RDF of a Lennard-Jones fluid. As an example, compar-isons have been made in Fig. 1 between RDF's pre-sented by this expression and those obtained using molecular dynamics calculations.

We have used this expression to reproduce 353 RDF's. The rmsd's for our fits, Eqs. (1a), (1b), (2)–(8) and the constants in Table 1, have been calculated. The range of these deviations is 0.0038–0.076 and the average rmsd is 0.0152. It is observed that the deviations increase with increasing density and decreasing temperature.

We have compared the expression for the RDF pre-sented in this paper with the two previously important expressions. Since both papers have been used the molecular dynamics data of RDF reported by Verlet [9] to check the capability of their expressions, we have also performed such calculations. Table 2 shows the rmsd's between our predicted (Eqs. (1a), (1b), (2)–(8) and the constants in Table 1) and reported RDF's of Verlet. The average rmsd for 25 RDF's is 0.025.

First, we consider the expression presented by Gold-man [10]. Since this expression has 108 constants and is mathematically complicated, its usage is quite difficult. This expression reproduces 25 of Verlet's data with an average rmsd of 0.034 while our expression which in-volves 65 constants, reproduces 25 Verlet's data with an average rmsd of 0.025.

Fig. 1. Calculated and molecular dynamics RDF results. The points are molecular dynamics data. The curves were obtained from Eqs. (1a), (1b), (2)–(8) and the constants in Table 1. From top to bottom, the figures represent RDF's for $\rho^* = 0.9$, $T^* = 1.5$ and $\rho^* = 0.55$, $T^* = 4.5$, respectively.

Table 1
Constants q_i for Eqs. (2)–(8) and rmsd's of the fit related to each constant

	q_1	q_2	q_3	q_4	q_5	q_6	q_7	q_8	q_9	rmsd
a	9.24792	−2.64281	0.133386	−1.35932	1.25338	0.45602	−0.326422	0.045708	−0.0287681	0.02
b	−8.33289	2.1714	1.00063							0.002
c	−0.0677912	−1.39505	0.512625	36.9323	−36.8061	21.7353	−7.76671	1.36342		0.0345
d	−26.1615	27.4846	1.68124	6.74296						0.0106
g	0.663161	−0.243089	1.24749	−2.059	0.04261	1.65041	−0.343652	−0.037698	0.008899	0.0048
h	0.0325039	−1.28792	2.5487							0.0015
k	16.4821	−0.300612	0.0937844	−61.744	145.285	−168.087	98.2181	−23.0583		0.0074
l	−6.7293	−59.5002	10.2466	−0.43596						0.008
s	1.25225	−1.0179	0.358564	−0.18533	0.0482119	1.27592	−1.78785	0.634741		0.0392
m	−5.668	−3.62671	0.680654	0.294481	0.186395	−0.286954				0.0096
n	6.01325	3.84098	0.60793							0.002

Table 2
Root-mean-squared deviations for the fitted (Eqs. (1a), (1b), (2)–(8) and the constants in Table 1) versus the molecular dynamics RDF data of Verlet

ρ^*	0.880	0.880	0.880	0.850	0.850	0.850	0.850	0.850	0.850
T^*	1.095	0.936	0.591	2.888	2.202	1.273	1.127	0.880	0.786
rmsd	0.0209	0.0279	0.0439	0.0130	0.0164	0.0211	0.0212	0.0281	0.0296
ρ^*	0.850	0.850	0.824	0.750	0.750	0.750	0.750	0.650	0.650
T^*	0.719	0.658	0.820	2.845	1.304	1.070	0.827	3.669	1.827
rmsd	0.0319	0.125	0.0268	0.011	0.0145	0.0188	0.0363	0.0156	0.0185
ρ^*	0.650	0.650	0.650	0.500	0.450	0.450	0.450		
T^*	1.584	1.036	0.900	1.360	2.934	1.710	1.552		
rmsd	0.0095	0.015	0.0177	0.016	0.0077	0.0184	0.0144		

In 1995, Matteoli and Mansoori [11] proposed a simpler expression for RDF's than. Their expression has 21 constants which is advantageous. First, they presented equations for the expression of distance dependence of RDF which reproduced 25 RDF's of Verlet with an average rmsd of 0.053. These equations have seven adjustable parameters. Second, they only used 25 RDF's data of Verlet to obtain the functionality of these parameters with reduced temperature and density. Since the number of Verlet's data is not sufficient for determining the functionality of these parameters, their final expression could not provide an acceptable prediction of pressure and internal energy (see Table 2 and Fig. 4 of [11]).

The calculation of pressure and internal energy may provide a critical test of the accuracy of our expression for RDF's. We have calculated the reduced pressure and internal energy of the Lennard-Jones fluid by the following equations [1]:

$$P^*(\rho^*, T^*) = \rho^* T^* - 16\pi(\rho^*)^2 \int_0^\infty g(r^*, \rho^*, T^*)$$
$$\times [(r^*)^{-4} - 2(r^*)^{-10}] dr^*, \tag{9}$$

$$u^*(\rho^*, T^*) = 8\pi\rho^* \int_0^\infty g(r^*, \rho^*, T^*) \times [(r^*)^{-10} - (r^*)^{-4}] dr^*, \tag{10}$$

where $P^*(\rho^*, T^*)$ and $u^*(\rho^*, T^*)$ are the reduced pressure and internal energy, respectively. Fig. 2 demonstrates comparisons between the values of reduced pressure and internal energy obtained by molecular dynamics simulations [12] and those calculated using our expression. As it is observed, our expression predicts pressure and internal energy of the Lennard-Jones fluid with an uncertainty that is comparable to that obtained directly from molecular dynamics results.

4. Conclusions

We have presented a simple and accurate expression for the Lennard-Jones fluid RDF. This expression involves 11 adjustable parameters each of which is ex-
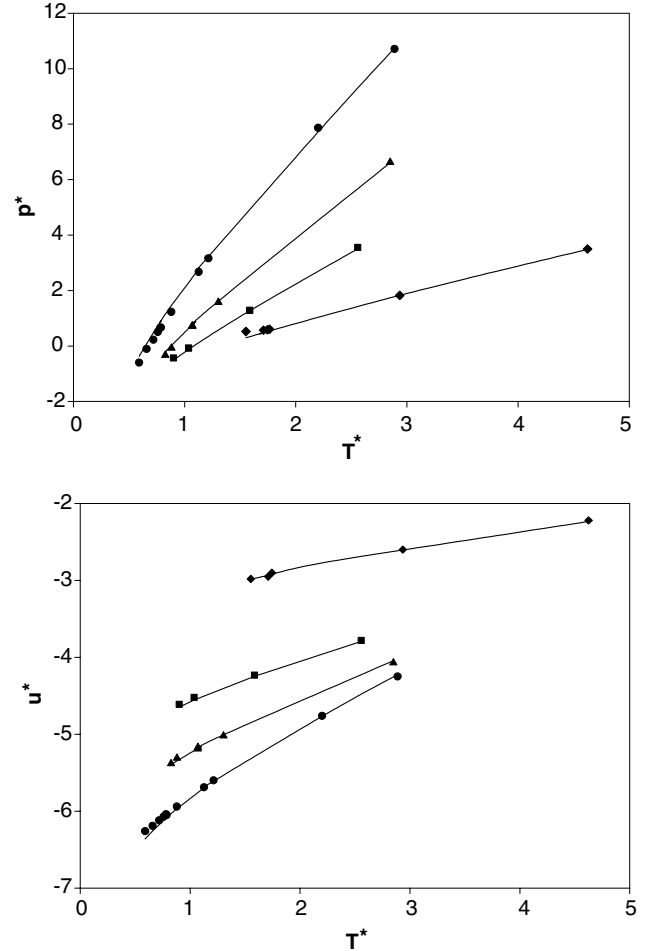

Fig. 2. Comparisons between values of reduced pressure and internal energy obtained by molecular dynamics simulations in [9] (full point) and those calculated by Eqs. (9) and (10) using our expression (solid lines). (●), $\rho^* = 0.85$; (▲), $\rho^* = 0.75$; (■), $\rho^* = 0.65$; (♦)$\rho^* = 0.45$.

pressed as functions of temperature and density. In comparison with other previous expressions, this expression is capable of producing a balance between the number of parameters (65 constants altogether) and the accuracy needed for reproducing the Lennard-Jones fluid RDF, is able to predict the thermodynamic properties in an efficient and reliable way.

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