

## A simple expression for radial distribution functions of pure fluids and mixtures

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(Received 9 January 1995; accepted 5 June 1995)

A simple expression for the radial distribution function (RDF) of pure fluids and mixtures is presented. It satisfies the limiting conditions of zero density and infinite distance imposed by statistical thermodynamics. The equation contains seven adjustable parameters; they have been fitted to extensive literature data of RDF's for a Lennard-Jones fluid at different values of temperature and density. These in turn have been expressed as functions of reduced temperature and density, thus allowing a complete parametrization with respect to these variables using 21 parameters altogether with fairly good accuracy. The values of the reduced pressure and internal energy calculated by numerical integration of the completely parametrized equation compare fairly with literature molecular dynamics simulation results. The capability of the expression to fit to RDF's of mixtures has been checked against some of the extensive RDF simulation data of binary mixtures of Lennard-Jones fluids with different diameters available in the literature. Data pertaining to different molar fractions as well as to different  $\epsilon_{AA}/\epsilon_{BB}$  ratios have been considered, and the agreement between calculated and simulation curves has resulted satisfactory. The proposed expression can be used to calculate by integration related quantities such as compressibility, internal energy, pressure and, using the Kirkwood–Buff theory, the chemical potentials and partial molar volumes of the components of mixtures for which RDF data are available. © 1995 American Institute of Physics.

THE  
JOURNAL OF  
CHEMICAL  
PHYSICS

### INTRODUCTION

Radial distribution (pair correlation) functions (RDF) are the primary linkage between macroscopic thermodynamic properties and intermolecular interactions of fluids and fluid mixtures. In the canonical ensemble of statistical mechanics, where the temperature,  $T$ , the volume,  $V$ , and the number of particles of each component in the system,  $N_i$ , are fixed, the radial (pair) distribution function,  $g_{ij}(r, \rho, T)$ , is given by

$$g_{ij}(r, \rho, T) = V^2 (1 - \delta_{ij}/N_j) \times \int e^{-\Phi/kT} d\mathbf{r}_3 \cdots d\mathbf{r}_N / Z_c(T, V, \mathbf{N}). \quad (1)$$

In this equation,  $\rho$  is the number density,  $\delta_{ij}$  is the Kronecker delta,  $\mathbf{N}$  is the set of number of molecules,  $N_1, N_2, \dots, N_c$ ,  $\Phi$  is the total potential energy of the system,  $k$  is Boltzmann constant,  $\mathbf{r}_i$  is the position vector of molecule  $i$ , and  $Z_c(T, V, \mathbf{N})$  is the configurational integral,

$$Z_c(T, V, \mathbf{N}) = \int \cdots \int e^{-\Phi/kT} d\mathbf{r}_1 \cdots d\mathbf{r}_N \cdots \quad (2)$$

The relations between  $g_{ij}$  and the internal energy  $u$  and pressure  $p$ , assuming pairwise additivity of intermolecular potential energy function, are the following:<sup>1</sup>

$$u = u_{ig} + \frac{1}{2} N \rho \sum_{i=1}^c \sum_{j=1}^c x_i x_j \int_0^\infty \phi_{ij}(r) g_{ij}(r) 4\pi r^2 dr, \quad (3)$$

$$p = kT\rho - \rho^2/6 \sum_{i=1}^c \sum_{j=1}^c x_i x_j \int_0^\infty r \phi'_{ij}(r) g_{ij}(r) 4\pi r^2 dr, \quad (4)$$

where  $\phi'$  is the derivative of the potential function with respect to the distance  $r$ .

Modern theories of fluid and fluid mixtures have benefited a great deal from the concept of radial distribution function. The RDF theories have been quite successful in describing the behavior of simple liquids and liquid mixture,<sup>1-7</sup> although have been able to provide RDF analytic expressions only for very simple model fluids such as the hard spheres and hard rods.<sup>7,8</sup> Moreover, the validity of Eqs. (3) and (4) is limited to spherically symmetric potentials, and therefore their application to polar nonspherical fluids is impossible. On the other hand, the Kirkwood–Buff theory<sup>9</sup> provides equations valid for any kind of molecular shapes which allow the calculation of thermodynamic properties of mixtures such as compressibility, partial molar volumes and chemical potentials only requiring the knowledge of the integrals over the distance of the radial (center to center) distribution functions (Kirkwood–Buff integrals,  $G_{ij}$ ):

$$G_{ij} = \int_0^\infty [g_{ij}(r) - 1] 4\pi r^2 dr. \quad (5)$$

Although in recent years several studies have been carried out to calculate the Kirkwood–Buff integrals of real mixtures from thermodynamic properties by the inverted equation of the theory,<sup>6</sup> no extensive study is available at our knowledge to calculate these quantities directly from Eq. (5),

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and then to use these to obtain thermodynamic properties. These calculations are linked to the availability of an analytical expression that could be used to represent the RDF's of fluids and their mixtures. As we will see later on, due to different reasons, previous RDF expressions are not appropriate to the general purpose of our research, consisting in the calculation through the Kirkwood–Buff theory of the chemical potentials and the partial molar volumes of the components of binary mixtures of Lennard-Jones fluids first and of more complex substances afterward. In this work we elaborate on the asymptotic conditions required by statistical thermodynamics and on less rigorous geometrical and spatial considerations to provide a parametric equation for RDF of Lennard-Jones fluids and mixtures which can be used to comply with the first part of our research.

## RDF OF PURE FLUIDS

The radial distribution function  $g(r, \rho, T)$  of a pure fluid must satisfy the following asymptotic relations.

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

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

Similarly, at large intermolecular distances it must reduce to unity,

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

As the temperature goes toward infinity, the RDF must become independent of temperature as is the case with the hard-sphere fluid RDF,  $g^{hs}$ :

$$\lim_{T \rightarrow \infty} g(r, \rho, T) = g^{hs}(r, \rho).$$

In addition, the equation representing the RDF must be continuous over all distances and the first maximum should occur at the contact distance  $d$ , with  $d = h\sigma$ ,  $\sigma$  being the distance parameter of the Lennard-Jones potential function, and  $h$  an adjustable variable with value very near to unity.

Considering the above features regarding the general shape of the pure fluid RDF and the above boundary conditions, we propose the following dimensionless functional form for the radial distribution function:

$$g(y) = 1 + y^{-m} [g(d) - 1 - \lambda] + [(y - 1 + \lambda)/y] \\ \times \{ \exp[-\alpha(y - 1)] \cos[\beta(y - 1)] \}, \\ m \geq 1, \quad y \geq 1, \quad (6a)$$

$$g(y) = g(d) \exp[-\theta(y - 1)^2], \quad y < 1, \quad (6b)$$

where  $y = r/d$  is the dimensionless intermolecular distance, and  $h = d/\sigma$ ,  $m$ ,  $\lambda$ ,  $\alpha$ ,  $\beta$ ,  $\theta$ ,  $g(d)$  are adjustable parameters. The terms  $y^{-m}$  and  $\exp[-\theta(y - 1)^2]$  provide for the decay of the first peak, while the factor  $\exp[-\alpha(y - 1)] \cos[\beta(y - 1)]$  has the scope to give an oscillatory-decaying shape to the function as the RDF must have. Parameter  $h$  supports the deviation of  $d$  from  $\sigma$ , and  $\lambda$  provides some flexibility in the section in between the first and second peaks, allowing the

curve to deviate from a strict exponential oscillatory decay. The other terms guarantee continuity of the function at  $r = d$ .

In order that the RDF equation may be capable to include temperature and density dependence, all parameter  $p_i = h, \theta, m, g(d), \lambda, \alpha, \beta$ , are to be expressed as function of the reduced temperature and density,  $T^* = kT/\epsilon$ ,  $\rho^* = \rho\sigma^3$ ,  $\epsilon$  being the energy parameter. The following functional forms are proposed:

$$p_i = [q_{1,i} + q_{2,i} \exp(-\epsilon/kT)] \exp[q_{3,i}(\rho\sigma^3)], \quad (7)$$

for  $p_i = \theta, g(d), \lambda, \beta$ , and  $h'$ , with  $h' = 1000(h - 1)$ ; and

$$p_i = [q_{1,i} + q_{2,i} \exp(-\epsilon/kT)] [(\rho\sigma^3)^2 + q_{3,i}] / (\rho\sigma^3), \quad (8)$$

for  $p_i = m$  and  $\alpha$ . They have been chosen to satisfy the limiting condition of RDF above outlined.

## RDF OF BINARY MIXTURES

Equations (6a) and (6b) can be slightly modified so as to be applied to binary mixtures. A proper mixture RDF equation should take into account the variation in the position of the peaks and in their separation distance as the composition of the mixture changes. From the observation of the shapes of the RDF's obtained by molecular dynamics simulations of pure compounds and of binary mixtures, the following two general features as regards position of the peaks and their separation distance can be identified for the three RDF's  $g_{AA}, g_{BB}, g_{AB}$  of a mixture of two Lennard-Jones fluids,  $A$  and  $B$ , with diameters  $\sigma_A$  and  $\sigma_B$ .<sup>7,10</sup> These features are based on spatial considerations only; the influence on the RDF shape due to the energy parameters,  $\epsilon_{ij}$ , is taken into account *a posteriori* by means of the parametrization Eq. (8).

(i) The contact distance  $d$ , where the first peak appears, is determined by the diameters of the components of the mixture independently of the molar fractions:

$$d = h(\sigma_A + \sigma_B)/2, \quad (9)$$

where  $h$  ( $h \approx 1$ ) accounts for deviations of the value of  $d$  from the average molecular diameter.

(ii) Each subsequent maximum is located at a distance  $\Delta r_M$  from the previous one that depends on the composition.

Simulation experiments indicate that the location of the second peak is mainly determined by the size of the particles which play the major role in filling the space in between the pair of molecules under observation, and these are the molecules of that species which is the most concentrated and/or the largest in size.<sup>7</sup> So, if  $A$  and  $B$  have similar diameters,  $\sigma_A \cong \sigma_B$ , at molar fraction  $X_A = 0.9$ , the space is filled mainly by  $A$  molecules, whereas at  $X_A = 0.1$  it is the  $B$  particles which occupy most of the space, and consequently the second peak maximum will be located in the two cases at a distance approximately equal to  $\sigma_A$  and  $\sigma_B$ , respectively, from the 1st maximum. If  $\sigma_A \gg \sigma_B$ , even at  $X_A = 0.5$ , the molecules of species  $A$  will occupy most of the space, so that  $\Delta r_M \approx \sigma_A$ . All this is independent of the pair of molecules under observations,  $A-A$ ,  $A-B$ , or  $B-B$ . We introduce this feature in our equation by assuming that  $\Delta r_M$  is given by a weighted arithmetic mean of  $\sigma_A$  and  $\sigma_B$  according to

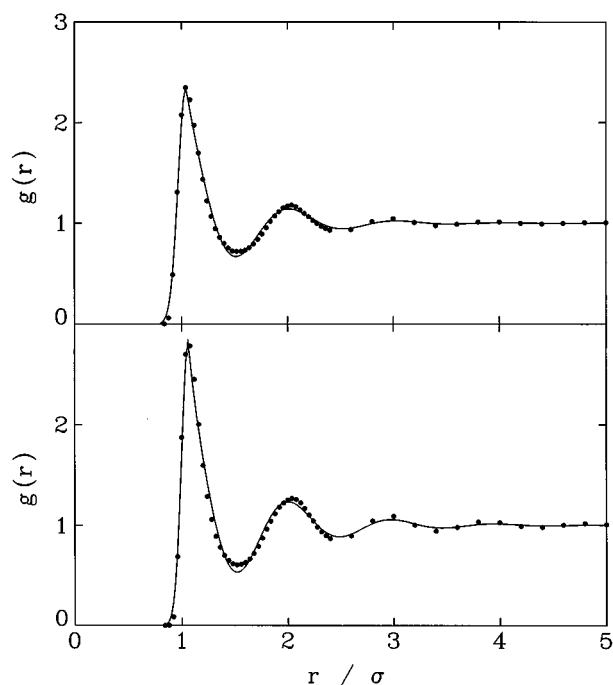


FIG. 1. Plot of radial distribution function,  $g(r)$ , vs the reduced distance,  $r/\sigma$ . (●), molecular dynamics simulation data,<sup>11</sup> (—), best fitting curves [Eqs. (6a),(6b) with parameters of Table I]. From bottom to top, the figures represent data of the 1st and 5th lines of Table I, respectively.

$$\Delta r_M = h(X_{VA}\sigma_A + X_{VB}\sigma_B), \quad (10)$$

where  $X_{VA}$  and  $X_{VB}$  are the volume molar fractions of the components  $A$  and  $B$  in the mixture, respectively.

The changes to be introduced in Eqs. (6a) and (6b) for these to become valid also for mixtures should take into account the variation of both  $d$  and  $\Delta r_M$  according to the mixture composition and to the  $i$ - $j$  couple as expressed in Eqs. (9) and (10), and at the same time preserving continuity of the function at  $r=d$  and as the composition changes gradually from one pure compound to the mixtures to the other pure compound. This can be accomplished by taking different functional forms for  $y$  according to whether  $r < d$  or  $r > d$ :

$$r < d, \quad y = r/d; \quad (11)$$

$$r > d, \quad y = (r - d + \Delta r_M)/\Delta r_M. \quad (12)$$

By introducing these conditions and expressions for  $y$  in Eqs. (6a) and (6b), we obtain a RDF expression which can be used for all three  $g_{ij}$  functions of a binary mixture. Similarly to pure fluids, the dependence on temperature and pressure is taken into account by expressing parameters according to Eqs. (7) and (8). Moreover, it can be realized that the mixture equations tend to the pure fluid ones when the concentration of one component goes to zero; i.e., if  $X_{VB} \rightarrow 0$  then  $X_{VA} \rightarrow 1$ , and, looking at Eqs. (9) and (10), we have  $d = \Delta r_M = h\sigma_A$ .

## RESULTS AND DISCUSSION

### Pure fluids

In order to check the capability of Eqs. (6a) and (6b) to reproduce the actual behavior of the RDF's, we have considered the MD simulation data reported by Verlet.<sup>11</sup> They are quite appropriate for this study because extend to  $r$  values of

TABLE I. Parameters of the RDF equation determined by best-fitting of data of Ref. 11.<sup>a</sup>

s.d. · 10 <sup>2</sup>	$h$	$m$	$g(d)$	$\lambda$	$\alpha$	$\beta$	$\theta$
6.81	1.065	13.42	2.830	0.9310	1.579	6.886	135.9
6.84	1.070	13.51	2.920	0.9818	1.518	6.924	146.7
9.91	1.088	16.31	3.220	1.1010	1.470	7.212	159.5
4.70	1.036	9.369	2.220	0.6795	1.957	6.391	88.52
4.55	1.043	9.680	2.350	0.7879	1.935	6.449	104.3
5.30	1.062	12.01	2.680	0.8696	1.713	6.667	130.4
5.55	1.065	12.02	2.760	0.9184	1.651	6.737	144.5
6.57	1.075	13.30	2.880	0.9438	1.582	6.840	148.4
7.16	1.080	13.83	2.940	1.0320	1.596	6.947	150.1
7.80	1.085	14.75	3.000	1.0420	1.587	7.016	149.0
9.13	1.088	10.06	3.080	1.3950	1.568	7.003	200.9
6.60	1.082	13.29	2.840	0.9534	1.649	6.853	142.4
3.95	1.045	6.601	2.030	0.7118	2.340	6.038	86.19
4.52	1.072	9.370	2.380	0.8082	1.990	6.382	117.8
4.77	1.082	10.49	2.480	0.8289	1.921	6.515	119.1
5.23	1.090	11.63	2.620	0.8930	1.876	6.597	135.5
3.42	1.045	4.537	1.780	0.5984	2.654	5.567	72.79
3.48	1.070	6.030	2.020	0.7146	2.397	5.901	96.46
3.81	1.075	6.436	2.080	0.7474	2.375	5.978	99.78
4.31	1.095	10.08	2.320	0.6957	2.160	6.288	107.7
4.78	1.102	11.37	2.430	0.6986	2.051	6.480	108.5
4.40	1.102	7.015	1.980	0.5596	2.640	6.006	81.18
2.96	1.070	6.000	1.620	0.3084	2.817	5.186	70.90
4.05	1.097	4.367	1.850	0.6614	3.175	5.597	74.92
4.52	1.105	1.910	1.860	0.8383	3.405	5.531	70.80

<sup>a</sup>Parameters of Eqs. (6a) and (6b). The lines correspond in the order to the 25 RDF curves for a Lennard-Jones fluid of Table IV of Ref. 11. Here s.d. is the standard deviation of the fit.

TABLE II. Coefficients of the parametrization equations.<sup>a</sup>

	$q_1$	$q_2$	$q_3$	s.d.	EQ.
$h'^b$	403.5	-371.7	-1.552	1.20	7
$m$	22.79	-17.54	-0.0508	1.10	8
$g(d)$	1.708	-0.8569	0.8196	0.0370	7
$\lambda$	0.5644	-0.3057	0.8579	0.0834	7
$\alpha$	0.2411	0.1387	4.216	0.156	8
$\beta$	5.289	-1.180	0.3996	0.0858	7
$\theta$	71.44	-46.68	1.100	5.20	7

<sup>a</sup>Eqs. (7) and (8) of text applied to data of Table I.

<sup>b</sup>In this case the parametrization equation produces  $h'$ , defined as  $h' = 1000(h - 1)$ .

5, refer to relatively wide ranges of temperature and density, and the number of points for each curve is sufficient to describe its shape accurately. By means of a nonlinear least-square routine, parameters  $p_i$  of Eqs. (6a) and (6b) have been adjusted to reproduce all 25 RDF curves there reported. As an example, to illustrate the performance of Eqs. (6a) and (6b), in Fig. 1 a comparison between simulation points and calculated curves for a couple of cases is shown.

In Table I the values of the parameters and the standard deviation of the fit are reported. We can observe that the standard deviation of the fit is in most cases less than 5%. In the few instances where less accuracy of fitting is achieved, the shape of the simulation curves in the  $r > d$  section presents anomalies such as discontinuities and sharp edges that our equation, as well as any other function which is continuous and has continuous derivatives, cannot reproduce. The parameters have then been fitted to Eqs. (7) and (8). Due to the very small deviations of parameter  $h$  from unity, the quantity  $h' = 1000(h - 1)$  instead of  $h$  was adjusted to Eq. (7). The set of  $q_i$  values obtained are reported in Table II, and in Fig. 2 the reproduction by Eqs. (7) and (8) of  $h$  and

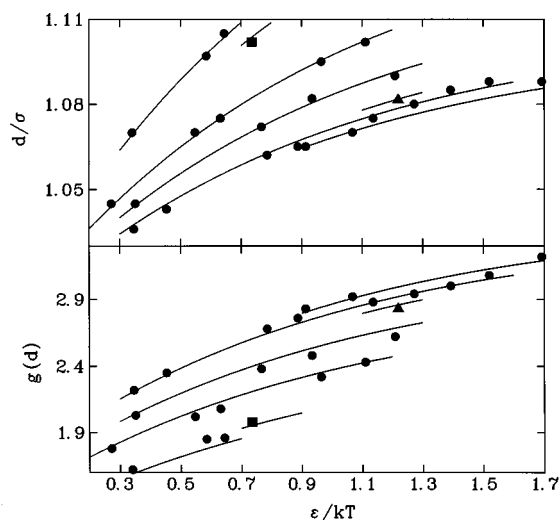


FIG. 2. Plot of the reproduction of parameters  $h = d/\sigma$  and  $g(d)$  by the parametrization Eq. (7). Points are best-fitting parameter values of Table I, the curves describe the trends of  $h$  and  $g(d)$  as calculated by Eq. (7) at constant reduced density  $\rho^*$ ,  $\rho^* = \sigma^3 \rho$ . From top to bottom,  $\rho^* = 0.88, 0.85, 0.824, 0.75, 0.65, 0.5, 0.45$ .

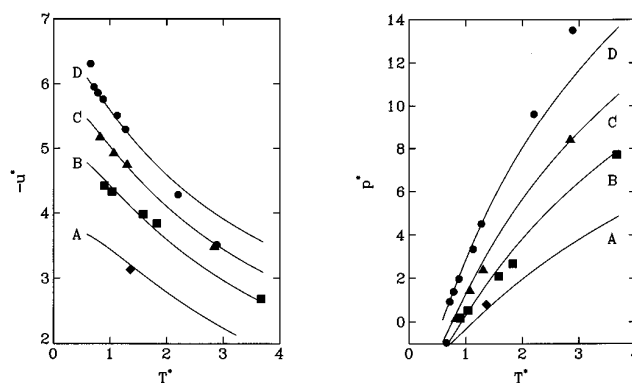


FIG. 3. Comparison between values of reduced internal energy,  $u^* = (u - u_{ig})/N\epsilon$ , and pressure,  $p^* = p\sigma^3/\epsilon$ , obtained by numerical integration of the RDF equation [Eqs. 6(a) and (b)] using parameters of Table I (full points) with those calculated by integration of the fully parametrized RDF equation (solid lines), that is, with parameters expressed as function of the reduced density,  $\rho^* = \rho\sigma^3$ , and temperature,  $T^* = kT/\epsilon$ , according to Eqs. (7) and (8) and values of Table II. (A,  $\blacklozenge$ ),  $\rho^* = 0.5$ ; (B,  $\blacksquare$ ),  $\rho^* = 0.65$ ; (C,  $\blacktriangle$ ),  $\rho^* = 0.75$ ; (D,  $\bullet$ ),  $\rho^* = 0.85$ .

$g(d)$ , the most important parameters of our RDF equation, is shown.

Some years ago, Goldman<sup>12</sup> proposed an expression for the RDF of pure fluids which was able to reproduce Verlet's data somewhat more accurately than the present equation; the standard deviation averaged over all 25 RDF curves amounts to  $5.3 \cdot 10^{-2}$  for our equation and to  $3.3 \cdot 10^{-2}$  for his fitting. However, his model equation requires 108 parameters, and this makes its use quite difficult; moreover, the possibility of its extension to mixtures does not appear trivial. In contrast, the simplicity of our model, which only requires 21 parameters on the whole, and its validity also for mixtures, makes it quite affordable for further applications and studies.

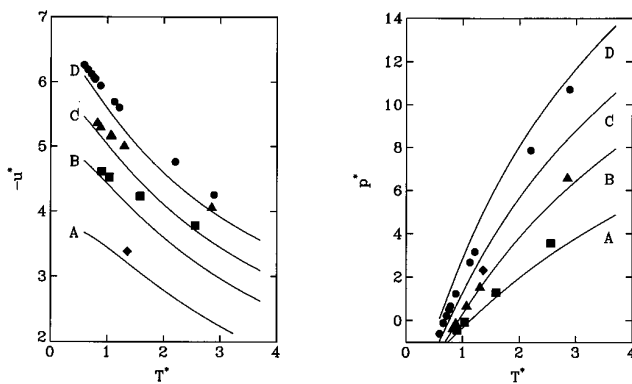


FIG. 4. Comparison between values of reduced internal energy,  $u^* = (u - u_{ig})/N\epsilon$ , and pressure,  $p^* = p\sigma^3/\epsilon$ , obtained by molecular dynamics simulation experiments in Ref. 14 (full points) and those calculated by numerical integration of the RDF equation [Eqs. (6a) and (6b)] with parameters expressed as function of the reduced density,  $\rho^* = \rho\sigma^3$ , and temperature,  $T^* = kT/\epsilon$ , according to Eqs. (7) and (8) and values of Table II (solid lines). (A,  $\blacklozenge$ ),  $\rho^* = 0.5$ ; (B,  $\blacksquare$ ),  $\rho^* = 0.65$ ; (C,  $\blacktriangle$ ),  $\rho^* = 0.75$ ; (D,  $\bullet$ ),  $\rho^* = 0.85$ .

TABLE III. Parameters of the RDF mixture equation resulting from best-fitting of selected simulation data of  $g_{ij}$  of Lennard-Jones mixtures.<sup>a</sup>

$g_{ij}$	$ij$	$x_A$	$\rho^*$	s.d. $\cdot 10^2$	$h$	$m$	$g(d)$	$\lambda$	$\alpha$	$\beta$	$\theta$
1	AA	0.5	0.164	6.72	1.070	5.0	2.100	1.38	4.473	5.16	66.9
1	AB	0.5	0.164	5.93	1.075	5.0	2.340	1.41	3.688	5.32	93.8
1	BB	0.5	0.164	5.55	1.082	10.1	2.370	1.87	3.832	5.32	127
2	AA	0.5	0.190	9.70	1.095	15.0	3.850	6.72	9.332	5.50	110
2	AB	0.5	0.190	5.28	1.073	11.0	2.405	3.43	6.302	5.28	112
2	BB	0.5	0.190	5.78	1.040	10.0	2.380	1.50	3.514	6.17	112
3	AA	0.95	0.171	6.25	1.110	3.95	1.482	0.38	5.121	5.00	45.8
3	AB	0.95	0.171	5.98	1.110	5.24	1.570	-0.048	3.672	6.00	56.5
3	BB	0.95	0.171	4.25	1.105	4.00	1.535	-0.087	3.299	7.00	76.9
4	AA	0.95	0.274	5.53	1.100	5.94	1.760	0.326	3.696	6.00	66.5
4	AB	0.95	0.274	4.41	1.085	5.60	1.430	-0.005	3.323	7.00	60.8
4	BB	0.95	0.274	4.28	1.065	1.88	1.270	0.181	4.080	6.50	53.7

<sup>a</sup>The  $g_{ij}$  simulation data were taken from Ref. 10. For all  $g_{ij}$ 's,  $\sigma_B/\sigma_A=2$ . The values of  $\epsilon_{BB}/\epsilon_{AA}$  were 3, 0.5, 2.0, and 0.5 for the  $g_{ij}$ 's #1, 2, 3, and 4, respectively. For the  $g_{ij}$ 's #1 and 3,  $T^*=kT/\epsilon_{AA}=3.0$ ; for the  $g_{ij}$ 's #2 and 4,  $T^*=1.0$ , and 2.0, respectively.

Also Li *et al.*<sup>13</sup> proposed an analytical formula for RDF's of fluids and fluid mixture. Their aim was to provide an expression, derived from the wave motion equation, which could reproduce the RDF's of Lennard-Jones fluids, and also predict the excess enthalpy of mixtures. As regards the former point, from the comparison they made with five curves of Verlet we have calculated an average standard deviation by  $20 \cdot 10^{-2}$ , against a value of  $5.2 \cdot 10^{-2}$  that we obtain with our equation for the same curves. This very large deviation is mostly due to the poor reproduction of the  $r < d$  section and, to a lesser extent, of the  $d < r < 2d$  section, and renders this equation unsuitable for its use in the calculation of thermodynamic properties through the Kirkwood–Buff theory.

To investigate how the fitting uncertainties reflect on calculated thermodynamic properties, we have calculated the reduced internal energy,  $u^*=(u-u_{ig})/N\epsilon$ , and pressure,  $p^*=p\sigma^3/\epsilon$ , by numerical integration of Eqs. (3) and (4) with parameters given by Eqs. (7) and (8). We have carried out this calculation at several values of the reduced temperature  $T^*$ ,  $T^*=kT/\epsilon$ , for each of four different values of the reduced density  $\rho^*$ ,  $\rho^*=\rho\sigma^3$ . In Fig. 3 these calculated curves are compared with the  $u^*$  and  $p^*$  values obtained by numerical integration of the RDF function with parameters of Table I. We can see that, except for the first and the last point at  $\rho^*=0.85$ , a fairly good reproduction is obtained, and this supports the validity of our parametrization equations.

In another paper, Verlet<sup>14</sup> reports the results of simulation experiments of thermodynamic properties of Lennard-Jones fluids. The data of  $u^*$  and  $p^*$  there obtained have been compared in Fig. 4 with the curves calculated as described above. The figure suggests that good agreement is found only limitedly to the trends; if we look at the single values, the simulation data are all lower than their corresponding curves, and the deviation is larger the higher the temperature. These discrepancies cannot be due only to inadequacy of our model equation or to inaccurate fitting (see Fig. 3); it may be possible that the simulation technique has some inconsistency in the ways of producing the thermodynamic properties and the RDF curves, and this drawback appears more effective at high  $T^*$  and leads to negative values of  $p^*$  at low  $T^*$ ; however, the maximum error admitted by Verlet<sup>11</sup> of 0.2 in the

compressibility factor,  $p/\rho kT$ , which at  $\rho^*=0.85$  corresponds to an average error of 0.17 on  $p^*$ , explains only a half of the difference between simulated  $p^*$  values and calculated curves. The uncertainty and dispersion in the simulated data is also evident if we compare  $p^*$  data with those obtained in a smaller range of  $T^*$  by Johnson and Gubbins<sup>15</sup>

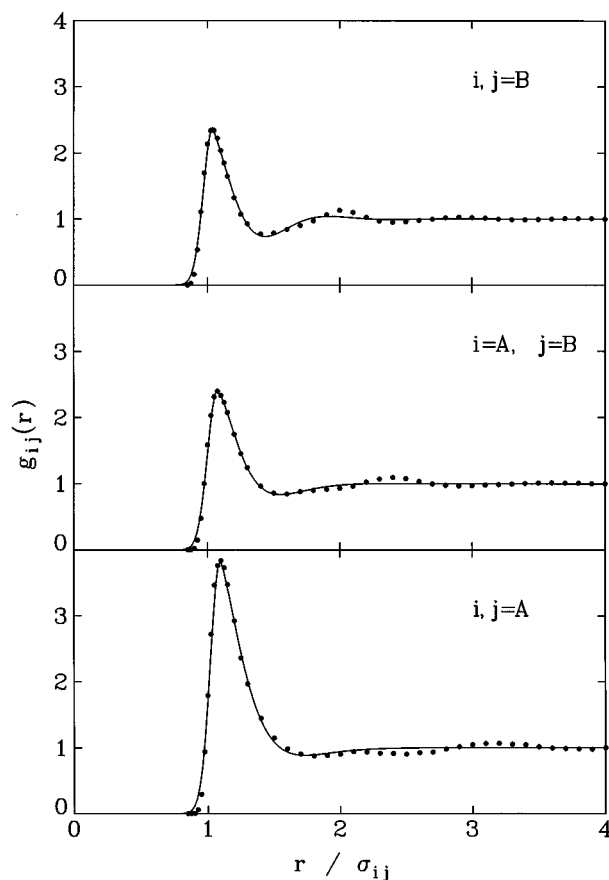


FIG. 5. Plot of  $g_{ij}$  ( $i, j=A, B$ ) vs reduced distance for a mixture of  $A+B$  with:  $\sigma_{AB}=(\sigma_A+\sigma_B)/2$ ,  $\sigma_B/\sigma_A=2$ ,  $X_A=0.5$ ,  $\epsilon_{BB}/\epsilon_{AA}=0.5$ ,  $T^*=kT/\epsilon_{AA}=1$ , and  $\rho^*=\rho\sigma_{AA}^3=0.190$  ( $g_{ij}$ #2 in Table III). (●), molecular dynamics computer simulation data;<sup>10</sup> (—), present calculations by Eqs. (6), (9)–(12) with parameters of Table III for  $g_{ij}$ #2.

in simulation experiments using the more accurate Nicholas equation of state.

### Binary mixtures

Ely and Huber<sup>10</sup> have obtained a large collection of very detailed simulation data of  $g_{ij}$  of binary mixtures of Lennard-Jones fluids. These data refer to  $\sigma_B/\sigma_A=2$  and to a variety of molar fractions, of  $\epsilon_{AA}/\epsilon_{BB}$ , of density and temperature. In order to examine the behavior of Eqs. (6a), (6b), (9)–(12) as to their capability of reproducing  $g_{ij}$  of mixtures, among Ely and Huber's data we have chosen some at  $X_A=0.5$  and  $X_A=0.95$ , and for each molar fraction two different sets corresponding to different  $\epsilon_{AA}/\epsilon_{BB}$  ratios. This choice allows a wide variation in the spectrum of the RDF shape here examined. To apply Eq. (10), the volume molar fractions were calculated through:

$$X_{VA} \cong X_A \sigma_A^3 / (X_A \sigma_A^3 + X_B \sigma_B^3) \quad (13)$$

which in turn allows calculation of  $\Delta r_M$  and hence of  $y$  in Eq. (12).

Table III collects the values of the parameters of Eqs. (6a) and (6b) for all 12  $g_{ij}$ 's considered, obtained by a least squares routine, as well as the standard deviation. The fairly good reproduction of the simulation data is evident from inspection of Fig. 5. Worth mentioning is also the fact that the  $\beta$  values of Table III are not very different from  $2\pi$ , which is the expected value if Eq. (10) were strictly obeyed.

The flexibility of Eqs. (6a), (6b), (9)–(12) guaranteed by the adjustable parameters should also allow their application to multicomponent mixtures, as long as appropriate conditions similar to Eqs. (9)–(12) are introduced. Extension of this treatment to all Ely and Huber's data is in progress, in order to get a full parametrization of the mixture RDF equation, and to determine possible relationships between these parameters and those of the single components. This subject will be covered in a future paper, together with an extensive calculation via Eq. (5) of the Kirkwood–Buff integrals of Lennard-Jones fluid mixtures, and from these, by means of the Kirkwood–Buff theory, of the chemical potential and partial molar volume, to be compared with those of real mixtures of apolar and polar compounds.

### CONCLUSIONS

It is shown that the simple parametric equation for RDF of fluids and fluid mixtures here proposed is able to reproduce the shape of the simulated RDF of Lennard-Jones fluids and mixtures at different values of the reduced temperature and density with good accuracy. The expression contains seven adjustable parameters, each of which can be expanded in terms of temperature and density by appropriate functional forms, each containing three additional parameters. By using a parametrization obtained from literature simulated RDF data of Lennard-Jones fluids, values of reduced internal energy and pressure calculated by integration agree fairly with literature data for the same type of fluids. Thanks to its good fitting capability, the expression lends itself to be used as a convenient tool for the calculation of relevant thermodynamic properties once a good reproduction of experimental or simulated RDF data has been obtained.

### ACKNOWLEDGMENT

This research is supported in part by the NSF Grant No. CTS-9108595.

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