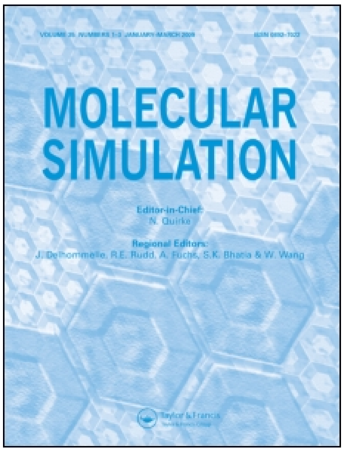

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MODELLING OF 3D RADIAL DISTRIBUTION FUNCTIONS WITH THE PROGRAM MATHEMATICA

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Using the program *Mathematica* 2.0 we have fitted the computer simulation data of the radial distribution function (RDF) for almost 700 states and five values of the Week-Chandler-Andersen (WCA) perturbative parameter for three-dimensional (3D) Lennard-Jones fluids. The fit has the form of the polynomial of tenth degree with respect to the interparticle distance. Applying the WCA theory to this fit we have calculated the difference between the pressures of the full and reference system. To test our fit we have compared the calculated differences with those ones obtained by molecular simulation data.

Keywords: 3D simple fluids; radial distribution function; WCA theory; program *Mathematica*

The structure of fluids with spherical particules may be conveniently described through the radial distribution function (RDF) [1]. It is very important to know its shape as it is the principal structural information used to calculate basic thermodynamic quantities of fluids.

In two (2D) or three-dimensional (3D) systems the RDF can be obtained from theoretical approximations as Percus-Yevick (PY), hypernetted-chain (HNC) theories, etc., or by computer simulations. In 3D case the RDF can be obtained also by scattering experiments. All these methods are mentioned in [2] and in references therein.

For realistic potential interactions description the Lennard-Jones (LJ) potential is used very frequently. It was reasonable to treat the LJ fluid by exploiting the results already existing for the hard sphere (HS) fluids, for which the basic thermodynamic properties have been described well enough. The principal idea, to treat the LJ system essentially as a HS system but perturbated by the attractive interaction, has been presented in several versions of the so-called perturbation theories. The versions most frequently used are those of Baker and Henderson [3] as well as WCA [4].

Using the WCA theory we have made computer simulations for 700 states in 3D case similarly as it was done in 2D case [2, 5]. We have obtained the values of the RDFs for different values of the pertubative parameters and also values of the difference between the pressures of the full LJ system and the reference one. In this work we present the modelling of the RDFs as the polynomials of tenth degree. Next we compare the difference of pressures obtained from molecular simulations with that one from the WCA theory with the use of our RDF model. We would like emphasize that this last test is more better than those ones for models considered earlier and obtained in different way [6–7]. Describing the reference system by Carnahan-Starling (CS) [8] model and Verlet-Weis hard sphere (HS) formula [9] permits us to create a simple and exact enough equation of state (EOS), which has not so many parameters (but the model of RDF must have a lot of parameters to be exact sufficiently). We note that although other EOSs for 3d and 2D LJ fluids have been published [10–13] despite their accuracy, they present by themselves two main problems: the lack of theoretical basis and/or their big size, making very difficult their mathematical handling. All modelling results presented in this paper have been done with the help of the program *Mathematica* 2.0 [14]. The figures also have been created by this program.

In the WCA theory [4], the full intermolecular potential is separated into a reference part U_0 and a perturbation part U_p. All the short-range repulsive forces are contained in U_0, and the perturbation part U_p contains all the long-range attractive forces. The intermolecular potential is written as

$$U(r) = U_0(r) + \lambda\, U_p(r), \tag{1}$$

where r is the interparticle distance and λ is a perturbation parameter which varies continuously from $\lambda = 0$ (reference system) to $\lambda = 1$ (full system). The WCA theory uses the Lennard-Jones (LJ) potential

$$u_{\mathrm{LJ}}(r) = 4\,(\,(1/r)^{12} - (1/r)^{6}), \tag{2}$$

for which

$$\begin{aligned} U_0(r) &= u_{\mathrm{LH}}(r) + 1 \qquad && r \leqslant r_m = 2^{1/6}, \\ &= 0 && r > r_m \end{aligned} \tag{3}$$

and

$$U_p(r) = -1 \qquad r \leqslant r_m,$$
$$= u_{\mathrm{LJ}}(r) \quad r > r_m. \tag{4}$$

In these equations the quantities are expressed in reduced LJ units. Henceforth all thermodynamic properties will be expressed in the reduced LJ form.

The Helmholtz free energy (HEF) per particle for a system where molecules interact according to the intermolecular potential given by (1) is,

$$A = A_0 - \rho\alpha(T,\rho) \tag{5}$$

A and A_0 being the HFE for the full LJ and of the reference system, respectively, T the temperature, ρ the density, and $\alpha(T,\rho)$ a function given by ([15])

$$-\alpha(T,\rho) = \frac{1}{2}\int U_p(r)g_0(r)d\vec{r} + \frac{1}{2}\int_0^1 d\lambda \int U_p(r)\,[g_\lambda(r) - g_0(r)]d\vec{r}, \tag{6}$$

where $g_\lambda(r)$ and $g_0(r)$ are the RDF of the perturbed ($\lambda \neq 0$) and reference ($\lambda = 0$) systems, respectively, and $d\vec{r} = 4\pi r^2 dr$ for 3D case. The physical meaning of $\alpha(T,P)$ is that it gives the contribution of the attractive forces, represented by the function $U_p(r)$, to the HFE. Differentiating Eq. (5) with respect to ρ we obtain the equation of state (EOS) [15]

$$P = P_0 + \Delta P, \tag{7}$$

where P and P_0 are the pressures of the full and reference systems respectively, and

$$\Delta P = -\rho^2\alpha(T,\rho) - \rho^3\partial\alpha(T,\rho)/\partial\rho, \tag{8}$$

As we have told earlier, since the pressure of the reference systems can be modelled very well by the Carnahan-Starling model and Verlet-Weis HS formula [8–9] then the next part of this paper we shall be concerning in the modelling of the RDF and its application to the calculation of ΔP.

Molecular dynamics (MD) calculations were carried out to obtain the RDFs, as well as other thermodynamic quantities, e.g. ΔP for 700 states corresponding to the supercritical, vapour and liquid regions for a 3D LJ fluids composed by 504 particules [6–7]. Each thermodynamical state was simulated during 5000 time-steps and for five values of $\lambda = 0, 0.25, 0.5, 0.75, 1$ with the step $\Delta r = 0.02$ units of the reduced interparticle distance we have obtained the RDF by the formula

$$g_\lambda(r) = \frac{n_\lambda(r)}{4\pi r^2 \Delta r \rho}, \tag{9}$$

where $n_\lambda(r)$ is the time-averaged number of particles situated at a distance $r \pm \Delta r$ from a given particle, when the interparticle potential is given by Eq. (1) [2]. In MD computer simulations the potential is cut off at the reduced interparticle distance of 2.5. The statistical error of the obtained values of RDF was estimated to be of the order of 1%. We have observed that for all $r \leqq 0.96$ the every RDF can be considered to be equal to zero and for $r \geqslant 2.5$ can be considered to be equal to one. Moreover, the difference $g_\lambda(r) - g_0(r)$ has the almost linear behaviour with respect to λ (Fig. 1).

Fog $\lambda = 0$, 0.25, 0.5, 0.75, 1 we have prepared data files involving the computer simulation data for RDF such that every line has presented: ρ, T, r, $g_\lambda(r)$, where $r \in \langle 0.96, 2.5 \rangle$ with the considered step. To fit this data we have had an intention to use the instruction **Fit** from the program *Mathematica* 2.0. The instruction **Fit** [*data,funs, vars*] finds a least-squares fit to a list of data

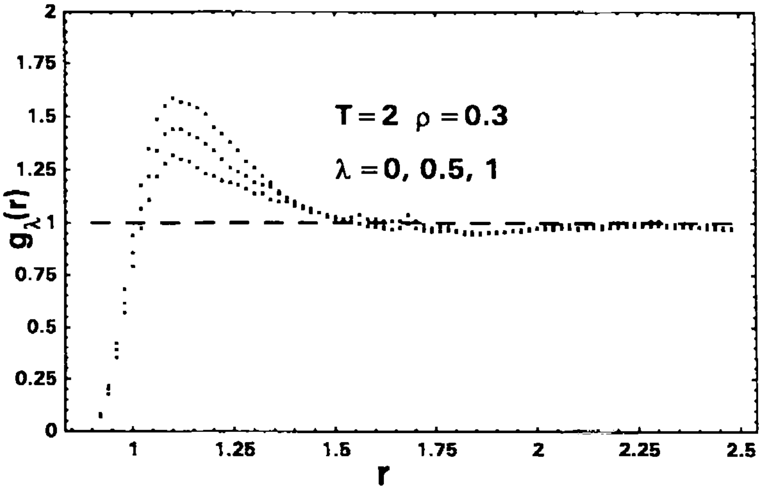


FIGURE 1 RDF obtained from computer simulations at $T = 2$ and $\rho = 0.3$ for $\lambda = 0, 0.5$ and 1.

as a linear combinations of the functions *funs* of variable *vars*. We have tried to find the fit of RDF in the following form

$$g_\lambda(r) = \sum_{i=0}^{10} C_i^\lambda r^i, \tag{10}$$

where

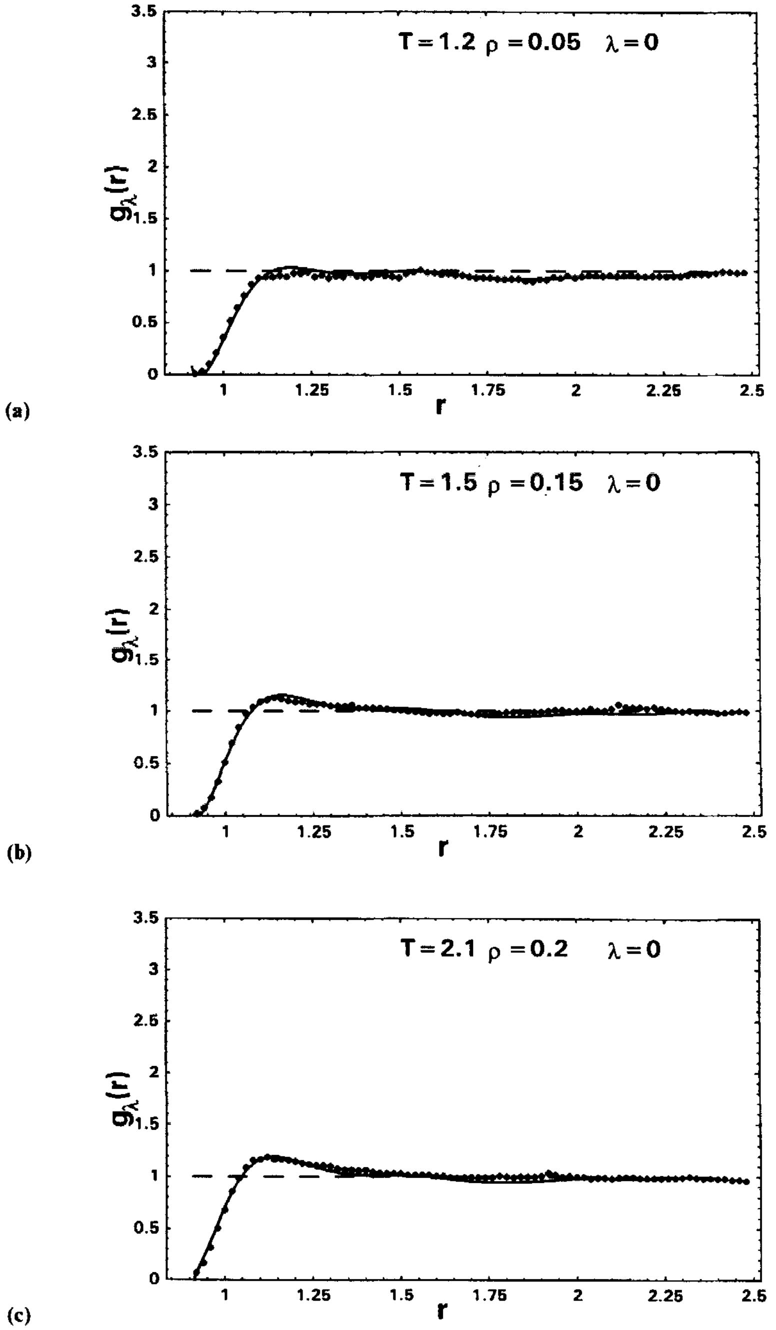
$$C_i^\lambda = D_{i1}^\lambda + D_{i2}^\lambda T + D_{i3}^\lambda T^2 + D_{i4}^\lambda T^3 + (D_{i5}^\lambda + D_{i6}^\lambda T + D_{i7}^\lambda T^2 + D_{i8}^\lambda T^3)\rho \tag{11}$$

for $i = 0, \ldots, 10$. First we have applied the instruction **Fit** to the prepared file for all considered thermodynamic state to find the fit presented above. But without any success. The file has been too large for the program *Mathematica*. We have changed the strategy. For fixed λ and for every thermodynamic state we have fitted RDF to the form (10) and have prepared 11 files such that every line has had the form: ρ, T, C_i^λ $(i = 0, \ldots, 10)$. Next using again the instruction **Fit** we have fitted C_i^λ $(i=0,\ldots,10)$ to the form given by (11). In this manner we have fitted RDFs for $\lambda = 0$ and 1. Having in mind our earlier observations we have defined the fit for any $\lambda \in \langle 0, 1 \rangle$ by the formula

$$g_\lambda(r) = g_0(r) + \lambda(g_1(r) - g_0(r)) \tag{12}$$

The average percentage mean deviation (APMD) between values of the RDFs obtained from computer simulations and those ones obtained from (12) for all states (about 700) and all λ (5 values) is about 3.6%. The most large errors (about 10%) are for $r < 1$ and for the liquid zone nearby the triple point. Figures 2–3 present some examples of the RDFs obtained from simulations (points) and their fits with formula (10)–(11) (continuous line). Perhaps the considered errors seem to be large enough but we must take into account that the basic thermodynamic properties are not obtained directly with the use of the point values of the RDFs but only by integrals involving RDFs. Because of this to check our fit it is better to compare, for example, the ΔP from computer simulation with that one by the proposed fit. First step to this test is to calculate α from the formula (6). Because of the form of U_p given by (4) we have calculate every integral in (4) as the sum of two integrals first one to r_m and the second one from r_m to 2.5. For the calculations we have used the instruction **Integrate**[f, $\{r, r\max, r\min\}$] which gives the definite integral $\int_{r\min}^{r\max} f dr$. The final form of α is as follows

$$\alpha(T,\rho) = \alpha_1(T) + \alpha_2(T)\rho, \tag{13}$$



FIGURES 2a–h Examples of RDFs obtained from simulations (points) and their fits with the formulas (10)–(11) (continuous line) for $\lambda = 0$.

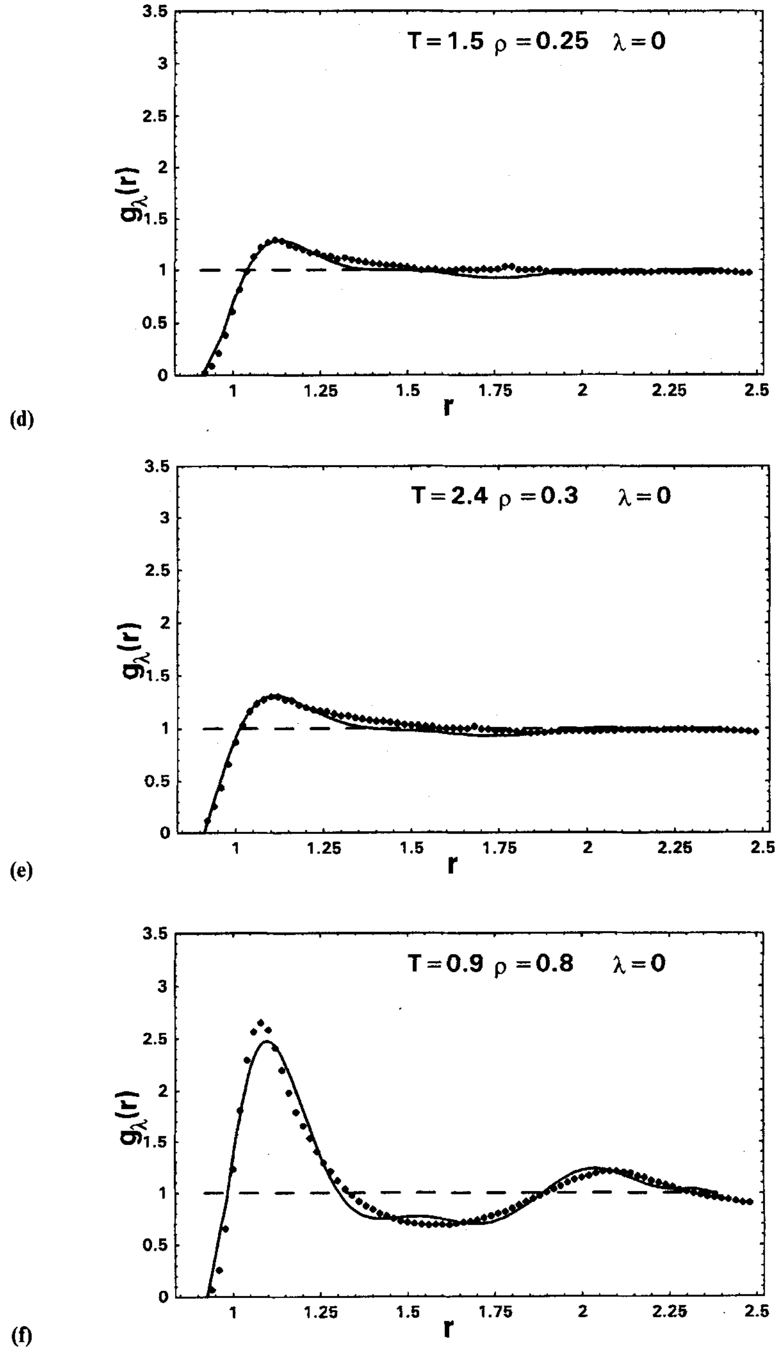
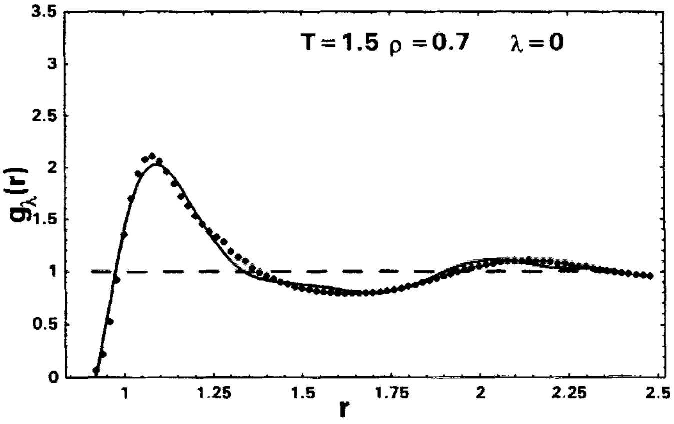
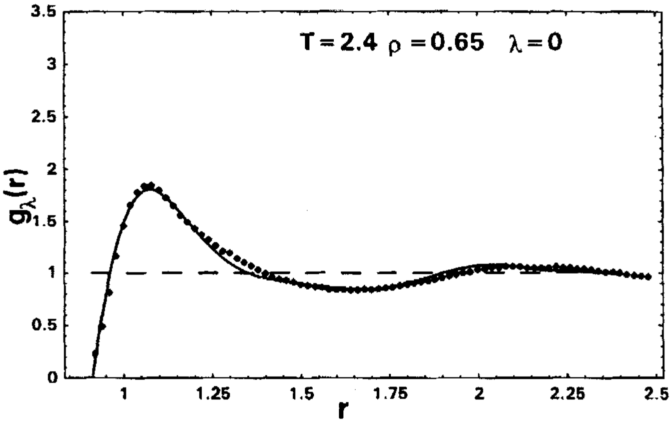


FIGURE 2 (Continued)



(g)



(h)

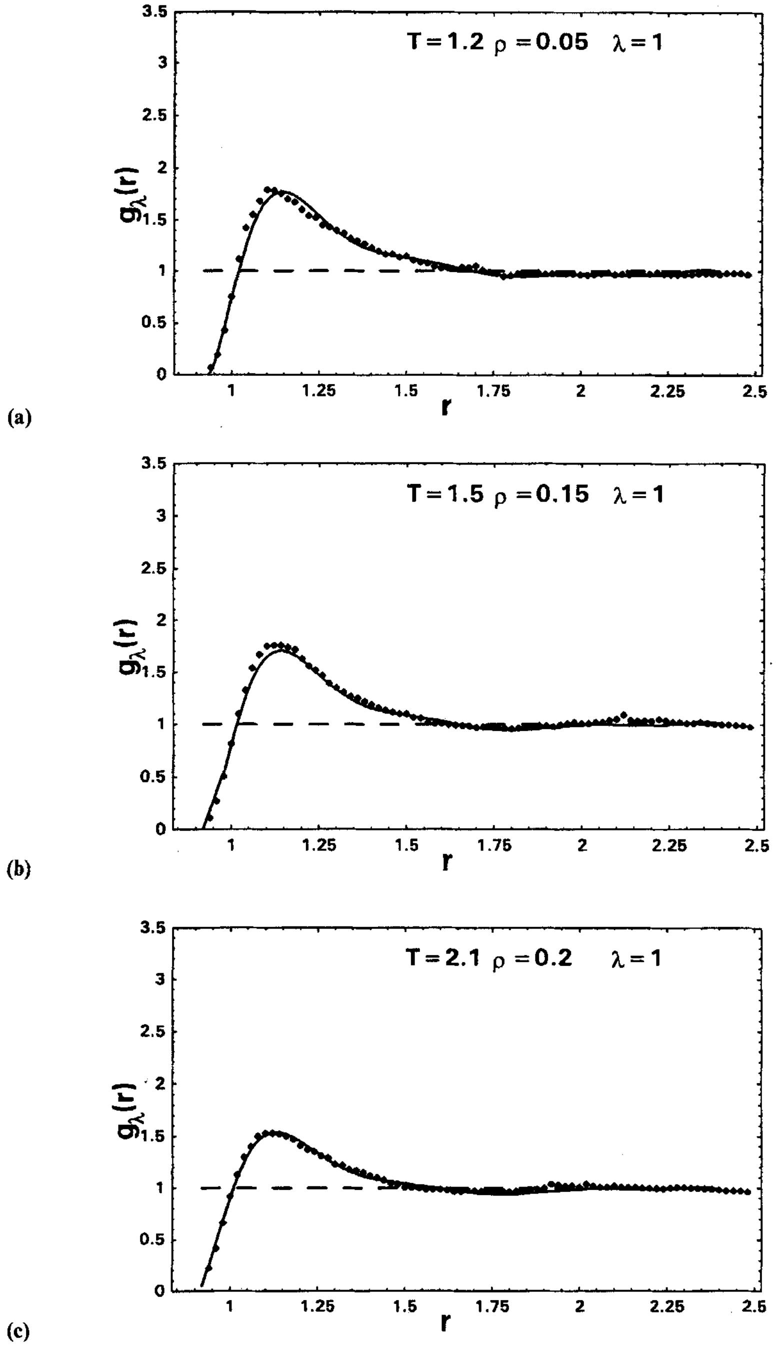
FIGURE 2 (Continued).

being $\alpha_1(T)$ and $\alpha_2(T)$ the following functions:

$$\alpha_1(T) = B_1 + B_2T + B_3T^2 + B_4T^3$$

$$\alpha_2(T) = B_5 + B_6T + B_7T^2 + B_8T^3, \qquad (14)$$

and the coefficients B_i ($i=1,\ldots,8$) are given in the Table I. Obviously $\partial\alpha/\partial\rho = \alpha_2$. But to Eqs. (7) the asymptotic contribution $-1.6048\rho^2$ must be



FIGURES 3a–h Examples of RDFs obtained from simulations (points) and their fits with the formulas (10)–(11) (continuous line) for $\lambda = 1$.

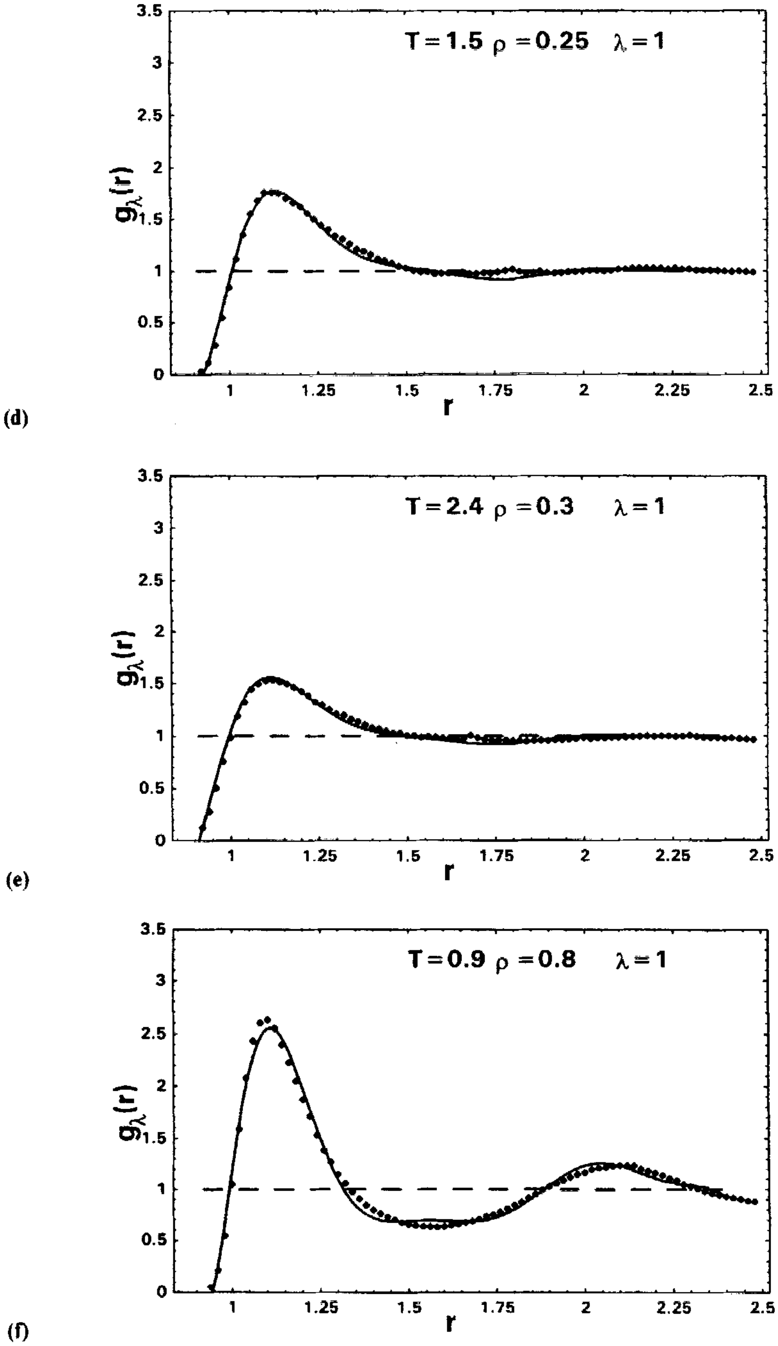
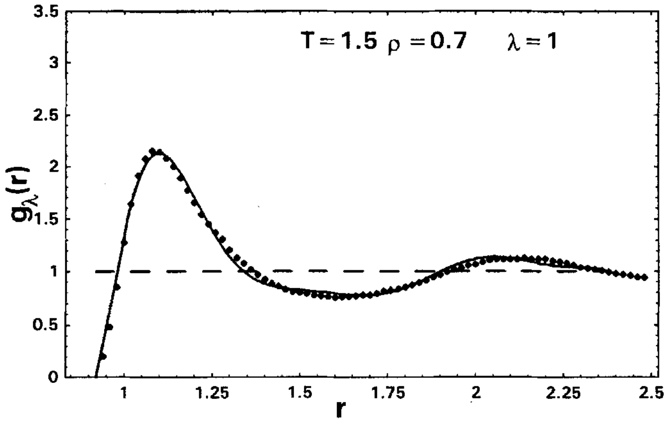
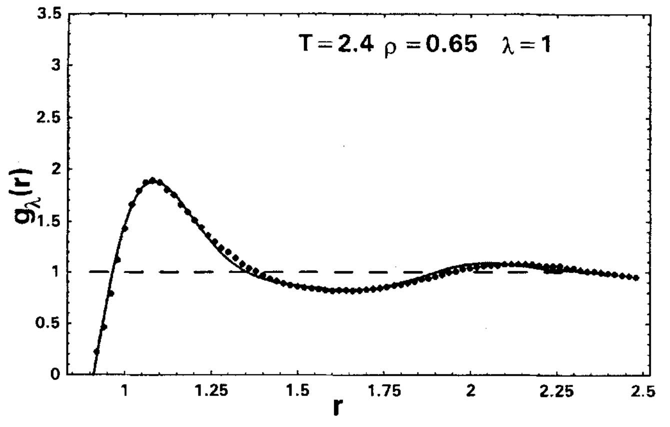


FIGURE 3 (Continued).



(g)



(h)

FIGURE 3 (Continued).

added, because in the simulations the intermolecular potential was truncated at the distances $r > 2.5$. The APMD between the pressure ΔP from (8) and that one obtained from computer simulation is less than 1.5%. It is much more better than in the recently presented global model [7] obtained by the simultaneous fit of α and ΔP for which this error was 4.5%. Also errors for three phase: vapour, liquid and supercritical, are much more smaller than in the case of the model described in [7]. The Table IV gives the comparison of results. It means that our model of the RDFs is quite well to calculate basic thermodynamic properties for any density and for wide range of temperatures. Obviously it could be done easily thanks to the *Mathematica*.

TABLE I Coefficients for the model of the RDF presented by formulas (10) and (11) in the case of $\lambda = 0$

i	1	2
D^0_{0i}	21964.34897088740	7051.003302327661
D^0_{1i}	−139350.2241272747	−40710.49103867625
D^0_{2i}	387778.4882472590	110363.9289626783
D^0_{3i}	−623459.0143213843	−186295.4606747660
D^0_{4i}	641495.5112381789	215496.5368373153
D^0_{5i}	−441393.0193460656	−175817.4012575378
D^0_{6i}	205617.0574867199	100776.4164999647
D^0_{7i}	−63980.95443293702	−39541.85501013222
D^0_{8i}	12708.13047349101	10074.98292329295
D^0_{9i}	−1451.314381770914	−1497.607670733888
D^0_{10i}	72.07568195921478	98.37575439182680
i	3	4
D^0_{0i}	−8466.510617687440	1709.697829455704
D^0_{1i}	50512.03784547539	−10219.57664511407
D^0_{2i}	−136935.5491191491	27632.33352617905
D^0_{3i}	222841.3603538987	−44630.02202501774
D^0_{4i}	−241127.1454588677	47716.48312701808
D^0_{5i}	180850.5600202020	−35243.75008092502
D^0_{6i}	−94840.53305081700	18165.99740060937
D^0_{7i}	34183.51588167427	−6431.717600493810
D^0_{8i}	−8069.821601119140	1492.134114489146
D^0_{9i}	1122.726064671674	−204.2342808981310
D^0_{10i}	−69.71418372378688	12.49436814368750
i	5	6
D^0_{0i}	339343.8277135725	−372161.5241923337
D^0_{1i}	−2169188.811526466	2357621.928619326
D^0_{2i}	6152447.697563405	−6633487.290422976
D^0_{3i}	−10200513.31649033	10920696.41161123
D^0_{4i}	10952898.03395515	−11654208.45956504
D^0_{5i}	−7962351.108228733	8427160.287065650
D^0_{6i}	3970549.777617761	−4183181.024729627
D^0_{7i}	−1341707.276813420	1408087.665610213
D^0_{8i}	294158.1829499602	−307708.5570972950
D^0_{9i}	−37800.35109537907	39435.19984871939
D^0_{10i}	2162.937570722174	−2251.529986139590
i	7	8
D^0_{0i}	152148.8587326653	−22382.83485065755
D^0_{1i}	−961003.0603400970	141167.2177609763
D^0_{2i}	2697113.680580125	−395709.1998622871
D^0_{3i}	−4431006.912731200	649455.1211666364

TABLE I (Continued)

D^0_{4i}	4720692.836740918	$-$691379.5223599440
D^0_{5i}	$-$3409067.816726714	498992.8096068663
D^0_{6i}	1690580.532427520	$-$247351.6681488236
D^0_{7i}	$-$568668.9725920300	83180.19542097360
D^0_{8i}	124216.2835467943	$-$18166.47241511953
D^0_{9i}	$-$15915.63388836851	2327.490289229561
D^0_{10i}	908.6459551012900	$-$132.8806036446879

TABLE II Coefficients for the model of the RDF presented by formulas (10) and (11) in the case of $\lambda = 1$

i	1	2
D^1_{0i}	95103.85325855910	$-$52241.23205058802
D^1_{1i}	$-$627856.9976829306	372465.5994083283
D^1_{2i}	1833293.664757011	$-$1160655.526308699
D^1_{3i}	$-$3119996.759606427	2087883.598163555
D^1_{4i}	3429678.535724768	$-$2407030.209071532
D^1_{5i}	$-$2546326.634933245	1862115.932206478
D^1_{6i}	1293992.669632037	$-$980722.5604065060
D^1_{7i}	444735.7227666087	347752.0092426598
D^1_{8i}	98998.48040882510	$-$79557.82570623545
D^1_{9i}	$-$12896.26496120698	10616.58024306630
D^1_{10i}	746.9964811457932	$-$628.1853557895447
i	3	4
D^1_{0i}	6387.951214577959	865.4048181090750
D^1_{1i}	$-$62175.94350390098	$-$1853.776480664667
D^1_{2i}	234376.6934339065	$-$4768.803855922879
D^1_{3i}	$-$480051.8140668182	23750.02712406246
D^1_{4i}	608186.0609975056	$-$41600.96077428380
D^1_{5i}	$-$505411.7946683082	41252.82472017156
D^1_{6i}	281518.2385309160	$-$25711.49443051481
D^1_{7i}	$-$104402.8702819005	10307.64985951463
D^1_{8i}	24775.47665423007	$-$2589.701074663967
D^1_{9i}	$-$3407.912532117026	372.0439040961961
D^1_{10i}	206.8371663473751	$-$23.36365311877603
i	5	6
D^1_{0i}	228550.5685659273	$-$253453.6313097043
D^1_{1i}	$-$1416362.929820584	1537848.595632371
D^1_{2i}	3892188.682781069	$-$4135265.166948975
D^1_{3i}	$-$6249538.171748497	6493985.339549923
D^1_{4i}	6497129.734632173	$-$6600141.402119380

TABLE II (Continued)

D^1_{5i}	−4572526.446258862	4539398.597929388
D^1_{6i}	2207515.037372377	−2141034.515757025
D^1_{7i}	−722295.4137127810	684232.1865349989
D^1_{8i}	153373.2749797466	−141879.0279738679
D^1_{9i}	−19094.96004919616	17246.28765720961
D^1_{10i}	1058.993338589289	−933.7288965834640
i	7	8
D^0_{1i}	108206.9773981747	−16791.78418570737
D^1_{1i}	−650405.4567340419	100583.8587806274
D^1_{2i}	1731331.545362507	−266732.1709703361
D^1_{3i}	−2689631.210097189	412655.7715630713
D^1_{4i}	2702366.914913617	−412752.4652938045
D^1_{5i}	−1836157.379141150	279097.8310982663
D^1_{6i}	855008.7591933430	−129291.4036145539
D^1_{7i}	−269588.9526335187	40541.93372656737
D^1_{8i}	55116.9526335187	−8240.209847912060
D^1_{9i}	−6601.444650208548	980.8242979478660
D^1_{10i}	351.9213473588027	−51.94399890824040

TABLE III Coefficients for the function α given by (13) and (14)

B_1	3.759033568203449
B_2	3.773975618183613
B_3	−2.193489640019834
B_4	0.388278247788549
B_5	4.561845630407334
B_6	−5.517716303467751
B_7	2.964387804269791
B_8	−0.516092101112008

TABLE IV The comparison of the APMD for the ΔP in three phases for the model obtained in this paper and for the fit presented in [7]

	Vapour	*Liquid*	*Supercritical*
Global fit	2.31%	6.09%	5.21%
Fit by RDFs	1.33%	0.68%	2.83%

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