Solution of the Percus-Yevick Equation for Linear Molecules Interacting through Either a Kihara or a Soft Repulsive Potential

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SOLUTION OF THE PERCUS–YEVICK EQUATION FOR LINEAR MOLECULES INTERACTING THROUGH EITHER A KIHARA OR A SOFT REPULSIVE POTENTIAL

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We have solved the Ornstein–Zernike equation with the Percus–Yevick closure for soft spherocylinders interacting through either a soft repulsive potential or a Kihara one. The used algorithm is the same we presented before in a previous paper for hard spherocylinders. Structural properties and a complete study of the behaviour of the pair correlation function with the orientation, density and elongation of the systems are presented. The pair correlation function directly obtained subsequently allows the few first coefficients of the expansion in spherical harmonics to be obtained and we have performed Monte Carlo simulation to compare them and make a check of the adequacy of the Percus–Yevick equation for these systems. Also thermodynamic properties such as the equation of state and internal energy have been calculated and we have compared some of these values with available simulation results. The conclusion is similar to that for hard spherocylinders: namely that the Percus–Yevick closure does not represent the orientational part of the pair correlation function very well for all the system studied. However, in obtaining the thermodynamic properties these errors are compensated, and the accuracy obtained is good.

KEY WORDS: Orientational correlations, equation of state, Monte Carlo simulation.

I INTRODUCTION

The theoretical study of molecular fluids has been greatly developed during the last decades[1]. Several non-central interaction models have been proposed, and we could affirm that among them, the multi-center interaction site model[2] (ISM) has received considerable attention. However, during the last few years, other potential models have appeared to study the convex bodies, namely Kihara[3] or Gaussian overlap[4] models.

For the Kihara model the potential function depends only on the shortest distance between molecules, and its greatest advantage is that complexity does not aggravate with number of atoms of the molecule as occurs with the ISM. However, it is not so simple to use and a big problem appears in calculating the shortest distance between convex bodies; this is the principal reason why until now it has not been

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commonly used in solving integral equations. Unfortunately, only scarce theoretical ways to evaluate the properties of soft convex bodies are available. Using severe approximations the average correlation function has been obtained[5-7], but not the pair correlation function. Also several perturbation theories have been developed for these models by Boublik[8,9] and more recently by Padilla and Lago[10] where the structure of the reference system is calculated using different approaches. So we have considered it advantageous and interesting to study thoroughly these models, and due to the fact that the properties of the reference system, both structural and thermodynamical must be known in a perturbation scheme, these systems are also of great interest.

In a series of previous papers[11,12], we have presented a method of solving the Percus–Yevick equation[13] (PY) for systems consisting of hard spherocylinders. Hard spherocylinders can be thought as the parallel convex bodies to a rectilinear segment which forms the axis of the cylindrical part of the spherocylinder. Comparison of our results with Monte Carlo simulation showed a nice agreement for not very large elongations but also important shortcomings, and conclusions were in agreement with those of Perera and Patey[14] who using a different algorithm, have also solved the PY equation for longer hard spherocylinders. Our particular solution method is based in using a fast algorithm to calculate shortest distances between the cylindrical axes[15,16]. Thus, our algorithm could be applied not only to hard spherocylinders but also to any other system interacting through a more general intermolecular potential. In this paper we study the repulsive branch of Kihara potential, named reference potential in a WCA[17]-like division of the Kihara potential, and the full Kihara. The main purpose of this paper is to find out how the PY equation can explain the structural and thermodynamic properties of systems of soft spherocylinders and those of systems interacting with a realistic potential.

The general experience for simple fluids is that the PY equation yields good results for soft repulsive spherical potentials[15] and we are interested now in finding out which features of the agreement are kept for soft anysotropic systems. Quite luckily, Vega and Frenkel[19] and Kantor and Boublik[20] have recently performed some simulations of these systems with two different elongations for the repulsive and also for a complete Kihara potential. Moreover, we ourselves have carried out some additional Monte Carlo simulations. We show here all the results allowing a complete picture of the behaviour of the PY equation for different orientations, elongations and densities using the cited repulsive and complete Kihara potential. For one of the repulsive systems, two different temperatures have been used. So the paper schedule is as follows: we shall shortly review in Section II the basis of the used algorithm, emphasising the differences with the case of hard spherocylinders. Section III is devoted to show our results for the pair correlation function (PCF) for some selected mutual orientations. Section IV shows the few first spherical harmonic coefficients in the expansion of the PCF comparing them with the available simulations. In Section V, the results for the thermodynamic functions directly obtainable from the PCF, namely internal energy and virial pressure, are shown and also compare with available simulation. Lastly, Section VI is devoted to a general discussion of the adequacy of the method for these systems.

II THEORY AND SYSTEMS STUDIED

In this work the PY equation has been solved for a system of linear molecules modelled by linear segments, namely rods, of length L whose intermolecular interactions are given by:

$$u^0(\rho) = \begin{cases} 4\varepsilon[(\sigma/\rho)^{12} - (\sigma/\rho)^6 + \tfrac{1}{4}] & \text{if } \rho < 2^{1/6}\sigma \qquad (1a) \\ 0 & \text{if } \rho > 2^{1/6}\sigma \qquad (1b) \end{cases}$$

for the soft repulsive system; and by a Kihara potential determined by:

$$u(\rho) = 4\varepsilon[(\sigma/\rho)^{12} - (\sigma/\rho)^6] \qquad (2)$$

in the realistic system.

In the above equations ρ is the shortest distance between rods modelling molecules. For two molecules i and j it depends on the shortest distance between molecular centers and on the relative orientation, that in our case are determined by polar coordinates R_{ij}, θ_{ij}, and ϕ_{ij} and the two orientational angles α_{ij} and β_{ij} all described in Ref. 11. Magnitudes σ and ε are potential parameters with dimensions of length and energy respectively.

We defined the reduced magnitudes $L^* = L/\sigma$, the packing fraction $\eta = nv_\sigma$, where n is the numerical density of the system and v_σ is the volume of a spherocylinder of length L and diameter σ. The reduced temperature $T^* = T/(\varepsilon/k)$ being k the Boltzmann constant and T the absolute temperature. In general we reduce length magnitudes by σ and energy magnitudes by ε.

The PCF of this system can be obtained solving the Ornstein–Zernike[21] equation (OZ):

$$h(R_1, \omega_1, \omega_2) = c(R_{12}, \omega_1, \omega_2) + (n/\Omega^2)$$

$$\times \int h(R_{23}, \omega_2, \omega_3)c(R_{13}, \omega_1, \omega_3)dR_{13}d\omega_1d\omega_3 \qquad (3)$$

where $h(R_i, \omega_i, \omega_i)$ is the total correlation function, and $c(R_{ij}, \omega_i, \omega_j)$ is the direct correlation function; Ω is a normalization integral whose value for linear molecules, as is our case, is 4π. Finally R_{ij} and ω_i are positional and orientational coordinates respectively.

An additional closure relation is also required and we have chosen the PY closure defined as:

$$y(R_{12}, \omega_1, \omega_2) = h(R_{12}, \omega_1, \omega_2) - c(R_{12}, \omega_1, \omega_2) \qquad (4)$$

where

$$y(R_{12}, \omega_1, \omega_2) = (h(R_1, \omega_1, \omega_2) + 1)\exp(\beta u(\rho)) \qquad (5)$$

here β is as usual $(kT)^{-1}$.

Finally, the PCF, $g(R_{ij}, \omega_i, \omega_j)$, is defined in terms of the total correlation function $h(R_{ij}, \omega_i, \omega_j)$, as:

$$g(R_{12}, \omega_1, \omega_2) = h(R_{12}, \omega_1, \omega_2) + 1 \qquad (6)$$

Our particular solution method for solving equation (3) using (4) as closure requires:

1) Computation of ρ_{ij} as a function of R_{ij}, θ_{ij}, ϕ_{ij}, α_{ij} and β_{ij}.

2) Calculation of the position and orientation of the molecule 2 respect molecule 3, assumed known the position and orientation of molecule 1 respect molecule 2 and of molecule 3 respect molecule 1.

3) The use of a good expression for the interpolation of the PCF as depending on the angles.

4) The use of a good initial approximation for the PCF.

5) An algorithm guaranteeing the convergence of the solution through the different iterations.

Every detail of the solution of the integral equation is similar to that of the solution of the equation for hard spherocylinders models, and has been described elsewhere[11]. The integration algorithm of the PY equation have been that of Conroy[22] using 6044 grid points. Curves have been smoothed down using a plines subroutine, so maximum error can be estimated in a 5%. The PCF has been obtained for four selected relative orientations, namely head-to-tail, parallel, crossed and T respectively.

A total of six systems interacting with a soft repulsive potential given by Eq. (1) have been studied. Five of them correspond to a soft repulsive system modelling N_2, where the parameters used are[23] $L = 0.93$ Å, $\sigma = 3.207$ Å and $\varepsilon/k = 117$ K. The last system correspond to a longer one. The corresponding packing fractions and parameters are given in the first three columns of Table 1.

Table 1

T^*	L^*	η	Theory		Simulation	
			U/NkT	PV/NkT	U/NkT	PV/NkT
1.075	0.2899	0.2	0.150	1.43	0.150	2.54
1.35	0.2899	0.2	0.164	1.45	—	—
1.35	0.2899	0.1	0.057	1.16	—	—
1.35	0.2899	0.4	0.812	3.05	—	—
1.35	0.2899	0.3	0.405	2.08	—	—
1.35	1.0	0.3	0.170	1.99	0.271	—

Values of the thermodynamic properties of the systems studied that interact with the soft repulsive part of a Kihara potential.

For systems whose intermolecular interactions corresponds to a Kihara potential given by Eq. (2) the packing fractions and parameters are shown in Table 2. Two of them correspond to a realistic model of N_2 with the same parameters cited before and the last one corresponds to a more elongated system which has been simulated by Kantor[20].

Table 2

T^*	L^*	η	Theory		Simulation	
			U/NkT	PV/NkT	U/NkT	PV/NkT
1.35	0.2899	0.1	-0.88	0.87	—	—
1.35	0.2899	0.2	-1.66	0.85	-1.67	0.63
1.0	1.0	0.3351	-3.48	1.08	-3.43	0.98

Values of the thermodynamic properties of the systems studied that interact with a Kihara potential. Simulations of last row correspond to Ref. 20.

III RESULTS OF THE PAIR CORRELATION FUNCTION (PCF)

The studied systems allow us to make a complete description of the behaviour of the PCF with the orientation in all the thermodynamic conditions. For every orientation the study has been made with density and elongation for soft repulsive systems and with the density for the real systems.

In all the cases irrespective of the potential or the thermodynamic conditions the PCF is a continuous curve with a first maximum at a distance close to $R_{ij} = 2^{1/6}\sigma$ for parallel and crossed position, $2^{1/6}\sigma + (L/2)$ for T position and $2^{1/6}\sigma + L$ for head-to-tail. That corresponds to the depth well of the potential for every orientation and it has very different PCF value for every one. A second maximum is observable in some systems but this is always much more smaller than the first one and in contrast to this has almost the same value for all the possible orientations and systems, although it can be remarked than in the cases of the Kihara potential, it is higher than in the cases with the truncated one.

We begin to describe the behaviour of the soft repulsive systems. Figure 1 shows the values of the PCF for the four principal relative orientations and one of the systems of the Table 1; according to this figure the maximum value corresponds to the parallel position closely followed by crossed and head-to-tail and T positions form a second group. This behaviour is common to all the systems, and the differences between both the two groups increases with the density or elongation. We have found already for hard spherocylinders the separation of the PCF in these two groups[11,12], and it has not disappeared for soft potentials.

In Figure 2 we can estimate the variation of the PCF with the density for parallel orientation; qualitative analogue graphs have been obtained for the other orientations and we can say that extremes become more manifest when the density increases, being this effect more pronounced for the most favourable situations. To corroborate this point we can compare the differences of the values of the PCF corresponding to the first maximum for two different densities from the figure, between $\eta = 0.2$ and $\eta = 0.1$ we have $(g_p)_{max}^{0.2} - (g_p)_{max}^{0.1} = 0.66$, between $\eta = 0.3$ and $\eta = 0.2$ we have $(g_p)_{max}^{0.3} - (g_p)_{max}^{0.2} = 1.50$ and finally, between $\eta = 0.4$ and $\eta = 0.3$ we have $(g_p)_{max}^{0.4} - (g_p)_{max}^{0.3} = 1.89$; similar numbers for the same differences have been obtained for crossed orientation. Whereas the results of the PCF give for head-to-tail $(g_p)_{max}^{0.2}$
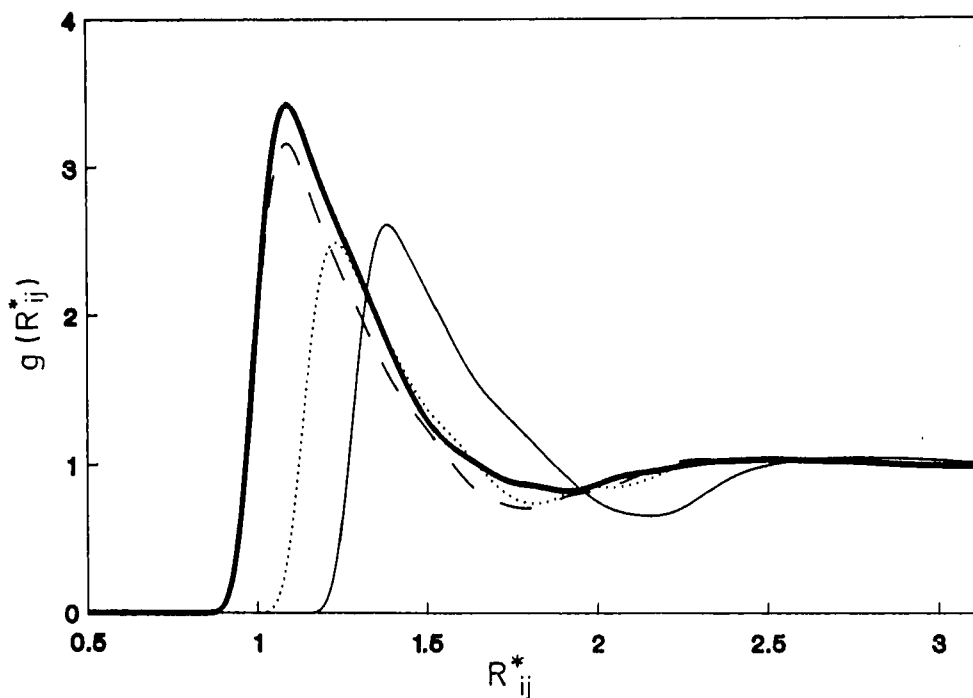
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Figure 1   Values of the PCF for systems interacting with a soft repulsive potential, $T^* = 1.35$, $L^* = 0.2899$, $\eta = 0.03$. Gross line parallel, dashed line crossed, dotted line T position, solid line head-to-tail.

$- (g_p)^{0.1}_{max} = 0.42$; $(g_p)^{0.3}_{max} - 1.00$, and finally $(g_p)^{0.4}_{max} - (g_p)^{0.3}_{max} = 1.47$, and similar values are obtained for T orientation.

There are two different behaviours of the PCF with the elongation of the spherocylinder for the orientations studied. Figure 3 shows variation of parallel and T position that represent the two behaviours. While for parallel and crossed the PCF decreases when elongation does it; for head-to-tail and T the PCF increases when elongation decreases. For the longer elongation the values corresponding to the first maximum of the PCF are very different for every orientation, these values become similar when the elongation decreases, and the dependence with the orientation tends to disappear. Also the order in the magnitude of this value varies from one elongation to the other, while for $L^* = 1.0$ we can say that $(g_p)_{max} > (g_{cr})_{max} > (g_T)_{max} > (g_{ht})_{max}$ this classification for $L = 0.2899$ is $(g_p)_{max} > (g_{cr})_{max} > (g_{ht})_{max} > (g_T)_{max}$, anyway we can continue establishing two different groups for the PCF, one for parallel and crossed orientation and the other for head-to-tail and T orientation. This peculiar conduct was already found in hard systems, and it is not surprising at all. We have to comment that for all the cases we obtain different values for g_p and g_{cr}, which is a better result than that obtained from zero and first order RAM perturbation theories[24] that suppose the PCF independent of polar angle ϕ_{ij}.
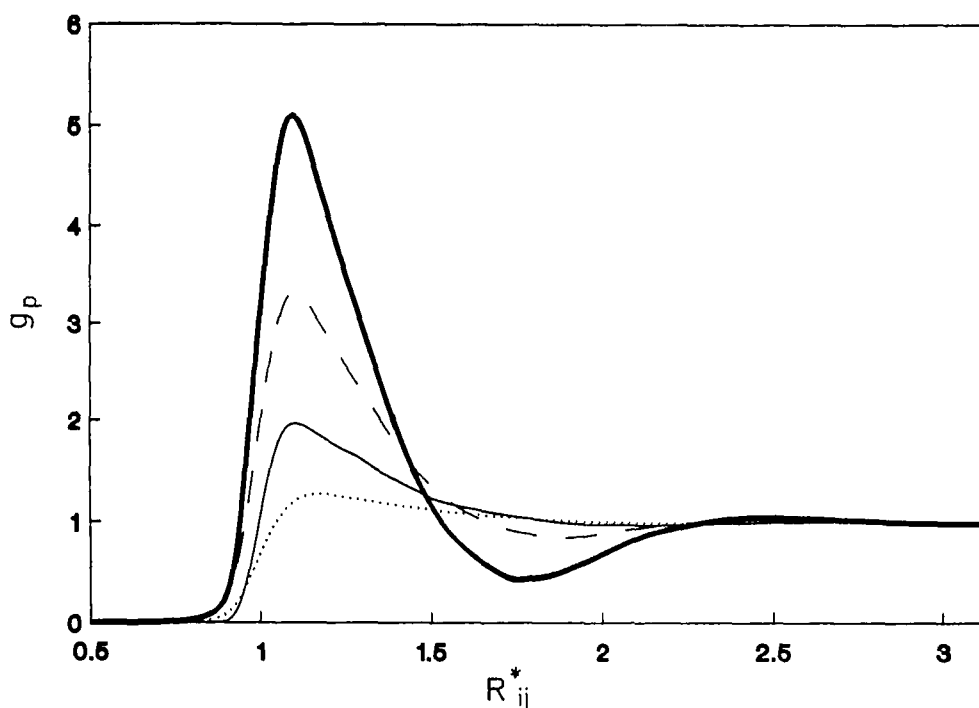
Figure 2   Values of the parallel PCF for systems interacting with a soft repulsive potential, $T^* = 1.35$, $L^* = 0.2899$. Gross line $\eta = 0.4$, dashed line $\eta = 0.3$, solid line $\eta = 0.2$, dotted line $\eta = 0.1$.

Results for different temperatures in the system with $L^* = 0.2899$ and $\eta = 0.2$ give no significant different values for the PCF between both temperatures. In the four relative positions differences with the temperature have the same order as our algorithm error, so we cannot establish its influence in these systems. This may be due to the fact that influence of temperature is always smaller than that of density or elongation and working with a small density, as is our case, the differences cannot be detected with our algorithm.

Respect to the realistic potential results are not too different, Figure 4a shows results for the largest system and 4b for N_2 system. The PCF for the N_2 model presents only one remarkable maximum and minimum for every orientation and every density. The differences between these two extremes increase with density, and similarly to soft repulsive potentials or hard systems the increment is bigger for parallel and crossed orientation, about ten times more than for the other two, and those are in any case the favourite. For the third system, the longest one, comments are similar, but a second noticeable maximum appears, even though relative to the first is almost contemptible.

Due to the fact that radial slices from simulations for the PCF exist only for hard spherocylinders we cannot compare directly our results. We can remark with reference to the PCF that for apolar systems and soft potentials favourite position
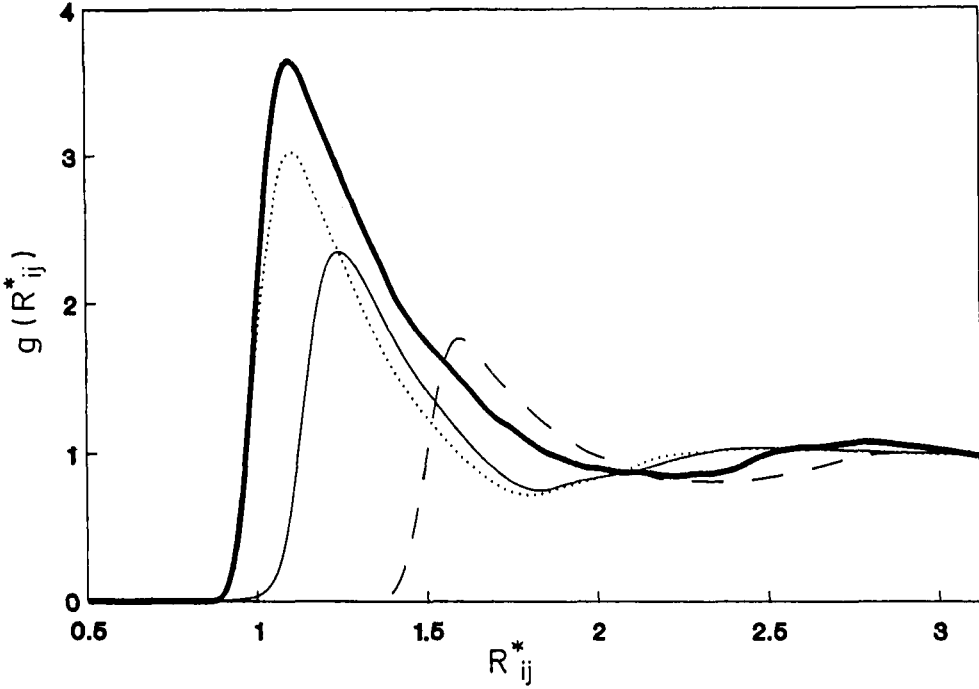
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Figure 3 Values of the PCF for systems interacting with a soft repulsive potential and $\eta = 0.03$. Solid line T position, $T^* = 1.35$, $L^* = 0.2899$. Dashed line T position, $T^* = 1.35$, $L^* = 1.0$. Gross line parallel, $T^* = 1.35$, $L^* = 1.0$. Dotted line parallel, $T^* = 1.35$, $L^* = 0.2899$.

is parallel as occurs in hard models[11], and was expected from the potential[23]. Also the values for the realistic systems are higher in every case than those interacting with a repulsive potential, this corroborate the role of the attractive forces in determining the structure of molecular fluids, as occurs for molecular mixtures[25], if we think in the range of low densities we study in this work.

IV RESULTS FOR THE SPHERICAL HARMONIC COEFFICIENTS OF THE PAIR CORRELATION FUNCTION (SHC)

The PCF calculated with Eq. (6) gives the expansion of the correlation function in spherical harmonic (SHC) using the formulae[26] for homonuclear molecules:

$$g_{1l'm}(R_{12}) = 4 \int_0^\pi \int_0^1 \int_0^1 g(R_{12}, \omega_1, \omega_2) Y_{1,-m}(\theta_1', 0) Y_{1',m}(\theta_2', \phi_{12}')$$

$$\times d \cos \theta_1' d \cos \theta_2' d\phi_{12}' \tag{7}$$

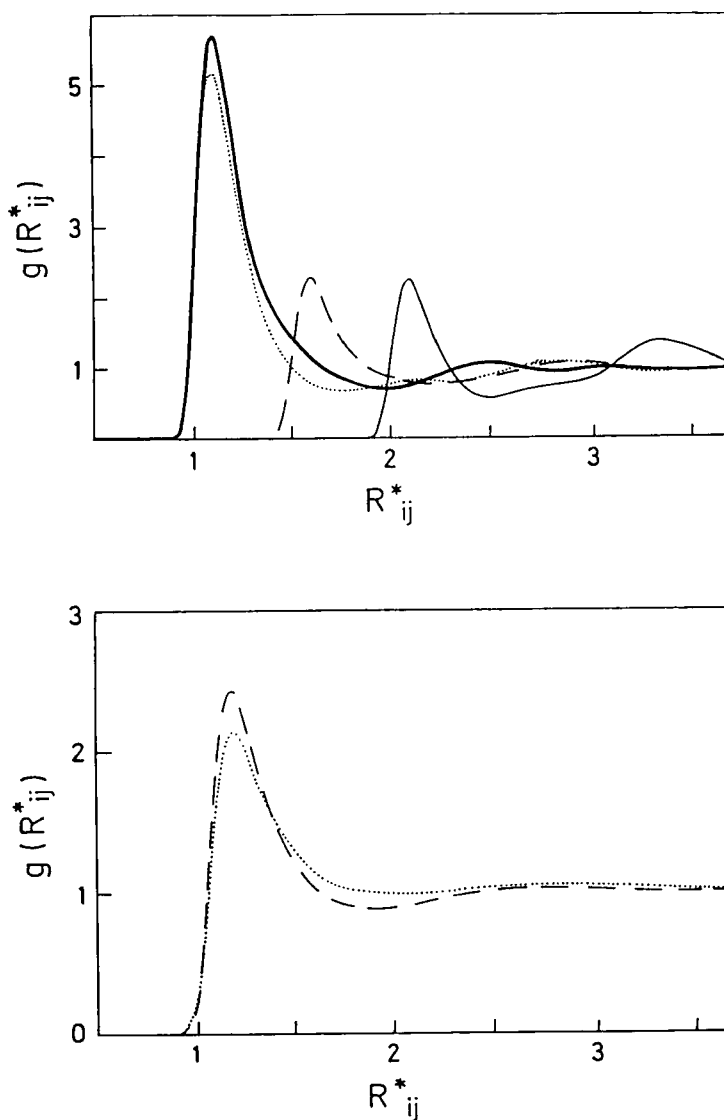where $\phi_{12}' = \phi_2' - \phi_1'$.

Figure 4 Values of the PCF for realistic systems interacting with a Kihara potential. a) $T^* = 1.0$, $L^* = 1.0$, $\eta = 0.3351$. Gross line parallel. Dotted line crossed. Dashed line T position. Solid line head-to-tail. b) Parallel orientation PCF. $T^* = 1.35$, $L^* = 0.2899$. Dashed line $\eta = 0.2$. Dotted line $\eta = 0.1$.

The angular coordinates in Eq. (7) are related with those used in this work by

$$\theta'_1 \equiv \theta_{12} \tag{8}$$

$$\phi'_{12} \equiv \beta_{12} \tag{9}$$

$$\cos \theta'_2 \equiv \cos \beta_{12} \cos(\theta_{12} + \alpha_{12}) \tag{10}$$
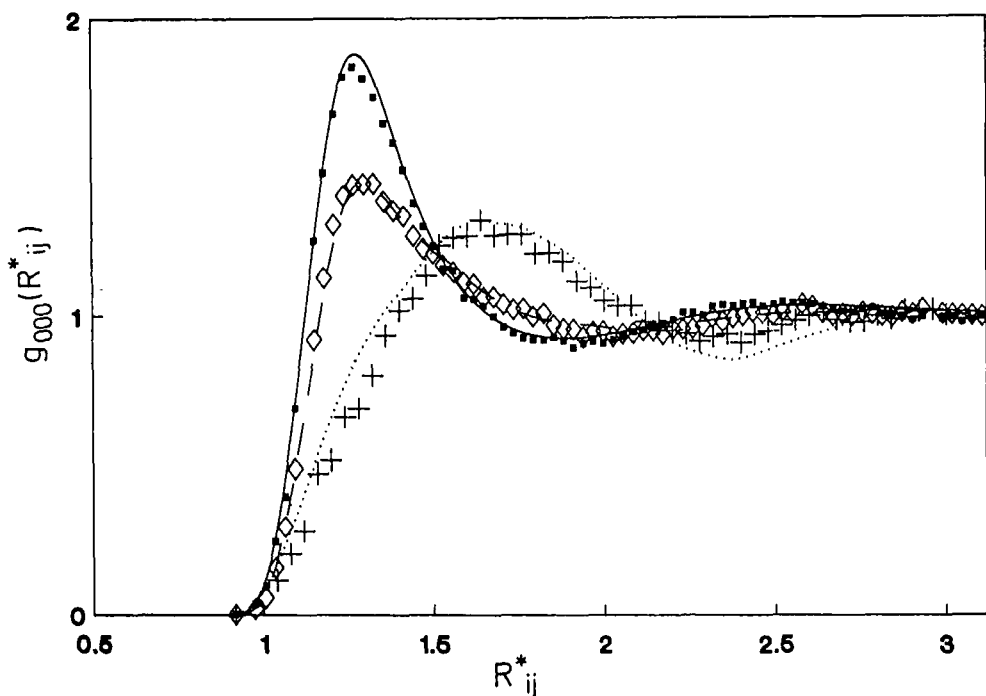
Figure 5   Comparison between simulation (dots) and theory (lines) for $g_{000}(r)$. Solid line realistic potential, $T^* = 1.35$, $L^* = 0.2899$, $\eta = 0.2$. Dashed line soft repulsive potential, $T^* = 1.35$, $L^* = 0.2899$, $\eta = 0.2$. Dotted line soft repulsive potential, $T^* = 1.35$, $L^* = 1.0$, $\eta = 0.3$.

The integration method for solving (7) was Conroy method, as used before, with 6044 grid points; integrals were truncated in 4σ taking the PCF as 1 beyond this limit irrespectively of the orientation as we have obtained before. Interpolation formulae for the PCF are the same used in the solution of the PY equation, even if we are conscious, from results of hard systems[12] that error in interpolating with this formulae may be important.

Results obtained for $g_{000}(r)$ and its comparison with simulation for three of the systems studied, are shown in Figure 5. Two of the systems correspond to a soft repulsive potential and the third one to a realistic potential.

Simulation has been carried out using Monte Carlo method[27], conditions are described in Ref. 19 for the N_2 models and in Ref. 12 for $L^* = 1.0$ system.

We can observe that concordance is qualitatively and quantitively good in all cases even for long elongations although interpolation formulae was not the best one. However, results for the second SHC $g_{200}(r)$ are not so good, they can be seen in Figure 6. In this case prediction is only qualitative if we consider qualitative to obtain
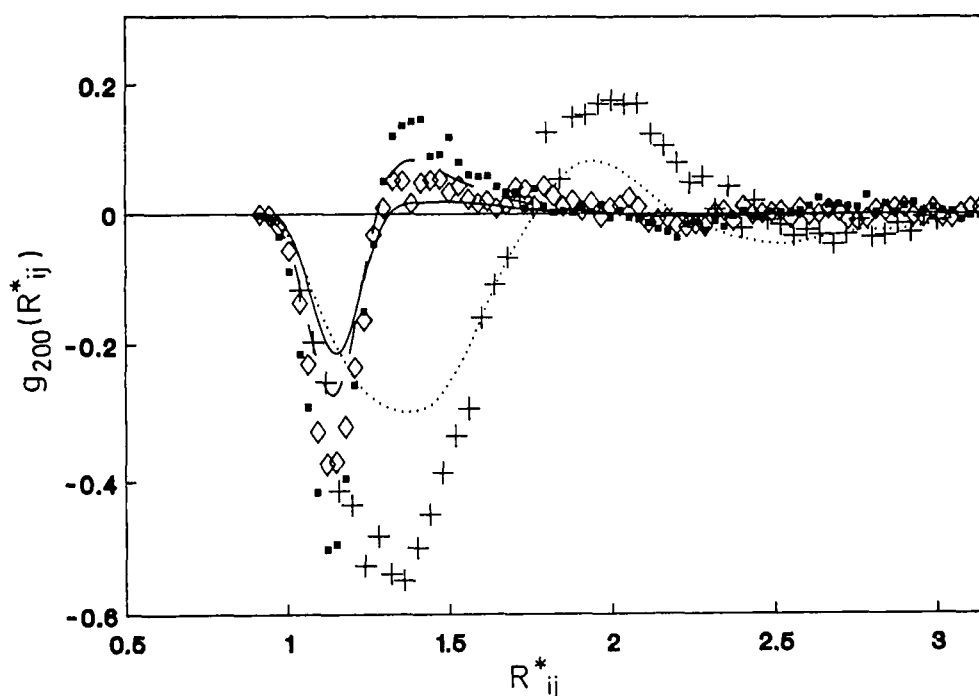
Figure 6 Comparison between simulation (dots) and theory (lines) for $g_{000}(r)$. Solid line realistic potential, $T^* = 1.35$, $L^* = 0.2899$, $\eta = 0.2$. Dashed line soft repulsive potential, $T^* = 1.35$, $L^* = 0.2899$, $\eta = 0.2$. Dotted line soft repulsive potential, $T^* = 1.35$, $L^* = 1.0$, $\eta = 0.3$.

the position and relative order of the extremes but not the absolute value. For the third SHC, $g_{220}(r)$, we have obtained results whose concordance is also qualtitative uniquely. From this we can evidence as for hard spherocylinders[12,14] that orientational part of the potential is not well represented by the PY equation, although we also have to take into account the influence of the approximations used for solving the integral equation.

The aspect and behaviour of $g_{000}(r)$ for soft repulsive and realistic potential is presented in Figures 7 and 8 respectively. We observe that the value of the first maximum decreases when elongation increases and when density decreases, this means that positional structure becomes less important when elongation increases, oppositly orientational structure becomes more important, because extremes of the next SHC become more pronounced when elongation increases. We can say, then, that PY is more accurate to represent not long molecules, where positional structure is more important than the orientational one.
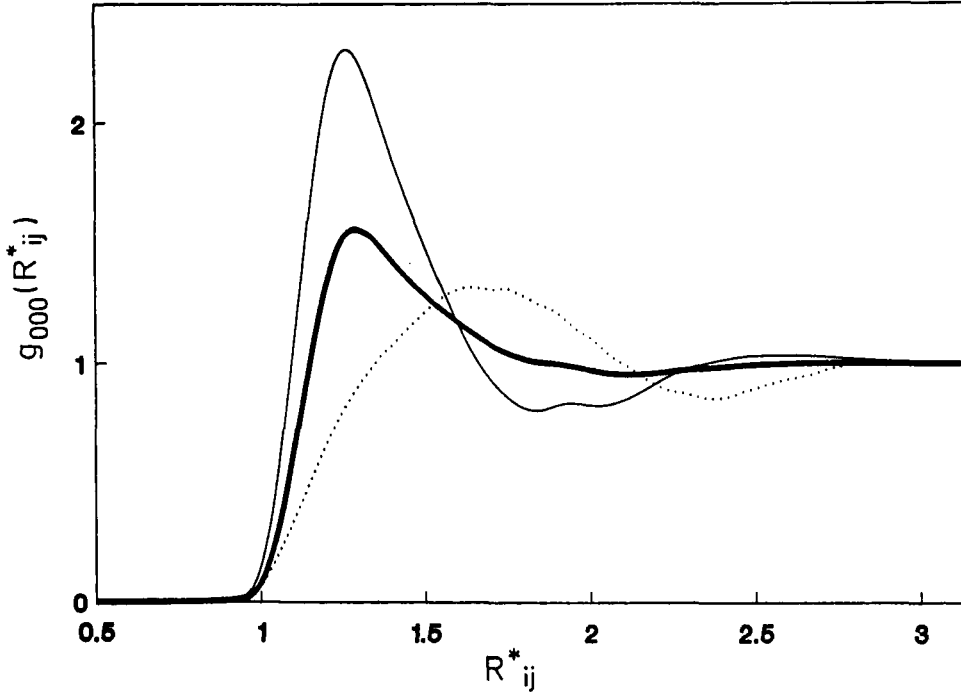
Figure 7   Values of $g_{000}(r)$ for systems interacting with a soft repulsive potential. Solid line $T^* = 1.35$, $L^* = 0.2899, \eta = 0.3$. Gross line $T^* = 1.35, L^* = 0.2899, \eta = 0.2$. Dotted line $T^* = 1.35, L^* = 1.0, \eta = 0.3$.

V   THERMODYNAMIC PROPERTIES

Once the PCF is obtained the equation of state (EOS) and the internal energy are straightforwardly obtained for soft spherocylinders from the well-known formulae[21]:

$$P = (NkT/V) - n^2/(6kTV\Omega^2) \int R_{12}(R_{12}, \omega_1, \omega_2)(\delta u(R_{12}, \omega_1, \omega_2)/\delta R_{12})$$

$$\times \ g(R_{12}, \omega_1, \omega_2)dR_{12}d\omega_1 d\omega_2 \tag{11}$$

and

$$(U - U^{id})/N = (n/2\Omega^2) \int u(R_{12}, \omega_1, \omega_2)g(R_{12}, \omega_1, \omega_2)dR_{12}d\omega_1 d\omega_2 \tag{12}$$

The integration algorithm in the Eqs. (11) and (12) has been that of Conroy as in the PY equation, using 6044 grid points. Integrals were truncated in 4σ taking the PCF as 1 beyond this limit for the same reason we explained before. The interpolation formulae for the PCF has been the same used in (4) for solving the PY equation.

The values of the comprehensibility factor and internal energy obtained for the different systems are shown in Table 1 for soft repulsive potentials and in Table 2
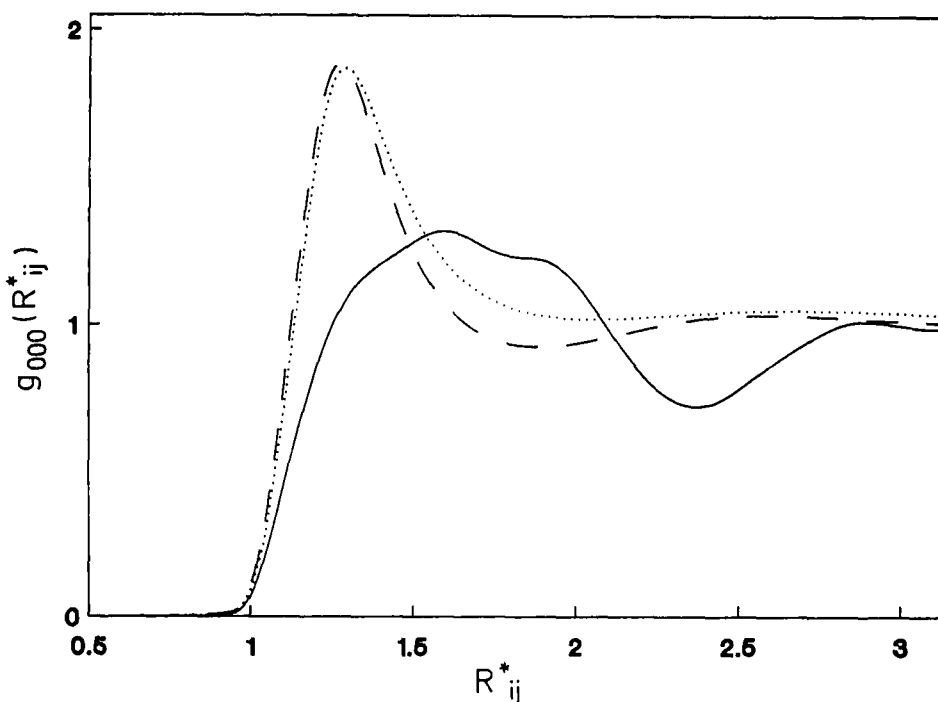
Figure 8   Values of $g_{000}(r)$ for systems interacting with a realistic potential. Solid line $T^* = 1.0$, $L^* = 1.0$, $\eta = 0.3351$. Dashed line $T^* = 1.35$, $L^* = 0.2899$, $\eta = 0.2$. Dotted line $T^* = 1.35$, $L^* = 0.2899$, $\eta = 0.1$.

for realistic ones. Some values are compared with those obtained by simulation. The internal energy is coincident in all cases except in one. For the EOS the theory gives values that differ from the simulation with bigger errors. Results are good, and this make think that the possible errors coming from the inexact values of the PCF cancelled themselves and become less important in calculating Eqs. (11) and (12).

VI   DISCUSSION OF RESULTS

We have obtained numerical values for the PCF for a reference WCA and a Kihara potential; from the PCF the few first SHC and thermodynamical properties: equation of state and internal energy have also been calculated. Similarly to atomic liquids[17], for all the orientations, at low densities the repulsive potential gives lower values of the PCF than for the realistic system, and evidence that repulsive forces do not determine totally the structure of molecular liquids at low densities. For apolar linear systems in all the studied thermodynamic conditions the most favourite position is the parallel. At the density and length used difference with temperature has the order of magnitude of the error of the algorithm. The concordance of the SHC with the simulation is excellent for $g_{000}(r)$ regardless of the elongation but it is only qualitative

for $g_{200}(r)$ and $g_{220}(r)$. These results were found previously for hard spherocylinders[12] and indicate that also for these systems the orientational structure is not very well represented in the PY equation. One factor could be due to the fact that we use a simple interpolation formula, but we have to remark that this is not the only cause of error, because the same interpolation has been good enough to obtain concordant values for $g_{000}(r)$. These errors can compensate when used below the integral sign and the internal energy of the systems can be predicted more accurately for short molecules and low and intermediate packing fractions as occurs with the case of perturbation theories[19,7]. The equation of the state of systems is worse than predicted and the discrepancies bigger in the case of the soft repulsive potential. Finally, we present here a way to solve the PY equation for systems interacting through soft potentials and obtain theoretically, and using only small approximations, structural and thermodynamic properties of realistic systems like N_2. The algorithm can also be applied for studied reference systems, which can be used in a perturbation scheme. To improve these results we propose either the use of different closure equations or of better interpolation formulae.

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