## Solution of the Percus-Yevick Equation for Hard Spherocylinders: II. Dependence of the Pair Correlation Function on the Elongation

P. Sevilla[a]; S. Lago[a]; P. Padilla[a]

[a] Dpto. Quimica Fisica, Fac. Ciencias Quimicas, Univ. Complutense, Madrid, Spain

## PLEASE SCROLL DOWN FOR ARTICLE

# SOLUTION OF THE PERCUS–YEVICK EQUATION FOR HARD SPHEROCYLINDERS: II

## Dependence of the pair correlation function on the elongation

P. SEVILLA, S. LAGO*, and P. PADILLA

*Dpto. Quimica Fisica, Fac. Ciencias Quimicas, Univ. Complutense, 28040 Madrid, Spain.*

The Percus–Yevick integral equation has been solved for hard spherocylinders, using an algorithm introduced in a previous paper. The pair correlation function (PCF) and the direct correlation function have been obtained and the dependence of these functions on the elongation as well on the numerical density is presented. Some of the spherical harmonic coefficients corresponding to the PCF are also shown and compared with Monte Carlo simulations. The best agreement is obtained for intermediate elongations, corresponding to molecules such as $Cl_2$ and for the first harmonic coefficient. The variation of the PCF of selected orientations with density is similar to that of hard spheres. Nevertheless, the variation for each orientation with elongation is more complicated trending to the hard sphere limit in different ways.

## 1 INTRODUCTION

In a preceding paper[1], hereafter referred to as I, we have presented an algorithm to solve the Ornstein-Zernike (OZ) equation using the Percus–Yevick closure[2] for systems composed of hard spherocylinders. In these systems, to the difficulty of solving the integral equation, the nontrivial computation of the distance between the surfaces of spherocylinders is added. Fortunately, we have previously proposed an efficient algorithm to overcome this hindrance[3] and we have obtained in I numerical values of the pair correlation function (PCF) and direct correlation function (DCF) of spherocylinders with a ratio cylindrical length/breadth $L^* = 1$. The comparison of our results with previous Monte Carlo simulations for some selected orientations was possible due to the existence of systematic simulations of Nezbeda[4] and Monson and Rigby[5] for this system. Moreover, Perera and Patey[6] have also solved the PY equation for hard spherocylinders using a different algorithm. Unfortunately, a direct

---

* Author to whom correspondence should be addressed.

comparison with our own results is not possible because they have always considered case with $L^* \geq 1$ but their general conclusions seem to be in agreement with ours. However, a lot of interesting relatively simple fluids are composed by linear molecules like $N_2$, $Cl_2$, or $CO_2$ which have $L^* < 1$. Therefore, we feel that it is important to study the behavior of the solution of PY equation for $L^* < 1$ in order to establish a firm basis to use this integral equation for more realistic potentials. Unfortunately, there are only scarce long simulation runs for determined orientations[4] and we have preferred to compare our results for the first spherical harmonic coefficients (SHC) where more simulations are available[5], completing them with our own simulations. In any case, results for the so-called main orientations[1] are also reported in order to complete the study of the dependence of the PCF on the elongation for each orientation.

Thus, this paper is arranged in the following sections: in Section II the equations used in our method are briefly presented and results corresponding to three different elongations for the main orientations are shown. In Section III theoretical results for spherical harmonic coefficients of the PCF are given in comparison with available simulation data. The dependence of the PCF on density for $L^* < 1.0$ is also studied in this Section III, and finally Section IV contains a short discussion of our results.

## 2   DEPENDENCE OF THE CORRELATION FUNCTIONS ON THE ORIENTATIONS

### 2.1   The pair correlation function (PCF)

Our system is formed by hard spherocylinders of axis length $L$ and diameter $\sigma$ interacting with a potential defined by:

$$u(\rho(R_{12}, \omega_1, \omega_2)) = \infty \qquad \text{if } \rho < \sigma \qquad (1a)$$

$$u(\rho(R_{12}, \omega_1, \omega_2)) = 0 \qquad \text{if } \rho > \sigma \qquad (1b)$$

where $\rho$ is the shortest distance between the axes of the cylindrical part of spherocylinders. $L^*$ is defined as $L^* = L/\sigma$. $V$ is the volume of the spherocylinder and the packing fraction $g$ is defined as $\eta = nV$, $n$ being the numerical density of the system. Elongation and reduced density for all the systems considered in this paper are in Table 1.

**Table 1**

| $L^*$ | 1.0 | 0.6 | 0.6 | 0.3 | 0.3 |
|---|---|---|---|---|---|
| $\eta$ | 0.3 | 0.3 | 0.2280 | 0.3 | 0.1740 |

Reduced lengths and densities corresponding to the systems studied.
$L^* = L/\sigma$ and $\eta = nV$, where $V$ is the volume of the spherocylinder.

The solution of the OZ equation with PY equation closure (PY equation) gives the numerical values of the PCF $g$, DCF $c$, and background correlation function $y$, where $y$ and $g$ are related by:

$$g(R_{12}, \omega_1, \omega_2) = y(R_{12}, \omega_1, \omega_2) \exp(-\beta u(R_{12}, \omega_1, \omega_2)) \tag{2}$$

and the Percus–Yevick closure is given by

$$c(R_{12}, \omega_1, \omega_2) = g(R_{12}, \omega_1, \omega_2) - y(R_{12}, \omega_1, \omega_2) \tag{3}$$

where, as usual, $\beta = (kT)^{-1}$, $k$ is the Boltzmann's constant and $T$ is the Kelvin temperature. For hard spherocylinders these formulas take a particular simple expression:

$$y = g \qquad \text{if } \rho > \sigma \tag{4a}$$

$$y = -c \qquad \text{if } \rho < \sigma \tag{4b}$$

where the explicit dependence of functions on positions and orientations through $\rho$ has been suppressed for sake of clarity.

Details on the algorithm for resolution have been given elsewhere[1] and we shall only remark here that an initial value for $y$ is necessary and an iterative procedure must be used. The closer to the final solution, the faster is the convergence. To speed up this convergence, we choose as initial solution for a given density the final results for a previous lower density if the elongation does not change. To build an initial input function, $y_{IN}$, close to the final solution for a system with $L^* < 1$, we assume that the correlation function for this system should have intermediate values between those of a hard sphere system ($L^* = 0$) and a system of $L^* = 1$ at the same reduced density. The PCF of a hard sphere system is the radial distribution function (RDF) calculated from the PY equation[7]. The PCF for a system with $L^* = 1.0$ and $\eta = 0.3$ has been obtained in the paper I. Then, the PCF of these two systems are combined to obtain a good initial solution for $y$. We have found that a reasonable first input solution could be obtained, assuming that the pair effective potential for $L^* = 0.6$, $\omega_{0.6}$ could be written in the way:

$$\omega_{0.6} = 0.4\omega_0 + 0.6\omega_1 \tag{5}$$

where $\omega_0$ and $\omega_1$ are, respectively, the pair effective potential for $L^* = 0$ and $L^* = 1$. Thus, we could write from the relation between $\omega$ and $g$ the first input function, $y_{IN}^{(1)}$, as:

$$y_{IN, 0.6}^{(1)} = y_0^{0.4} y_1^{0.6} \tag{6}$$

By a similar argument we could write:

$$y_{IN, 0.3}^{(1)} = y_0^{0.7} y_1^{0.3} \tag{7}$$

for $L^* = 0.3$.

In any case, the direct iteration does not converge and a linear combination between the input and output function of a cycle must be taken as input function
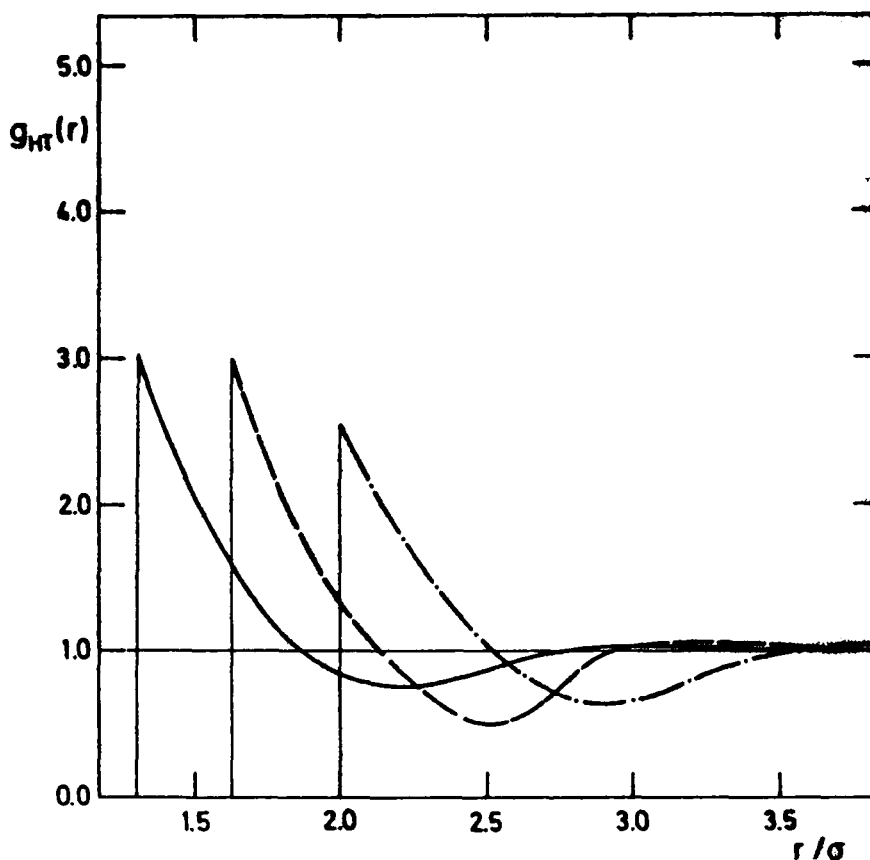
**Figure 1**   Pair correlation function for head-to-tail orientation at $\eta = 0.3$, $-\cdot-$ $L^* = 1.0$, $--$ $L^* = 0.6$, $\underline{\qquad}$ $L^* = 0.3$.

for the next cycle:

$$y_{IN}^{(n+1)} = \alpha y_{OUT}^{(n)} + (1 - \alpha)y_{IN}^{(n)} \qquad (8)$$

where $\alpha \simeq 0.2$.

The numerical PCF results for the three considered elongations at the same reduced density $\eta = 0.3$ are shown in Figures 1 to 4 for the four main orientations. The values of the PCF at the contact for the main orientations are displayed in Table 2.

First, we compare the functions obtained with the RDF of a hard sphere system at $\eta = 0.3$ calculated from the PY equation. The contact value for hard spheres for this density is $g(O) = 2.2557$ and this value is smaller than anyone in the Table 2. The first minimum for hard spheres is located at $r/\sigma \simeq 1.7$ and the corresponding RDF is $g_{min} = 0.860$. For the three lengths and all the main orientations considered in this paper the first minimum appears at larger $r/\sigma$ and the PCF are always deeper than for a hard sphere system.
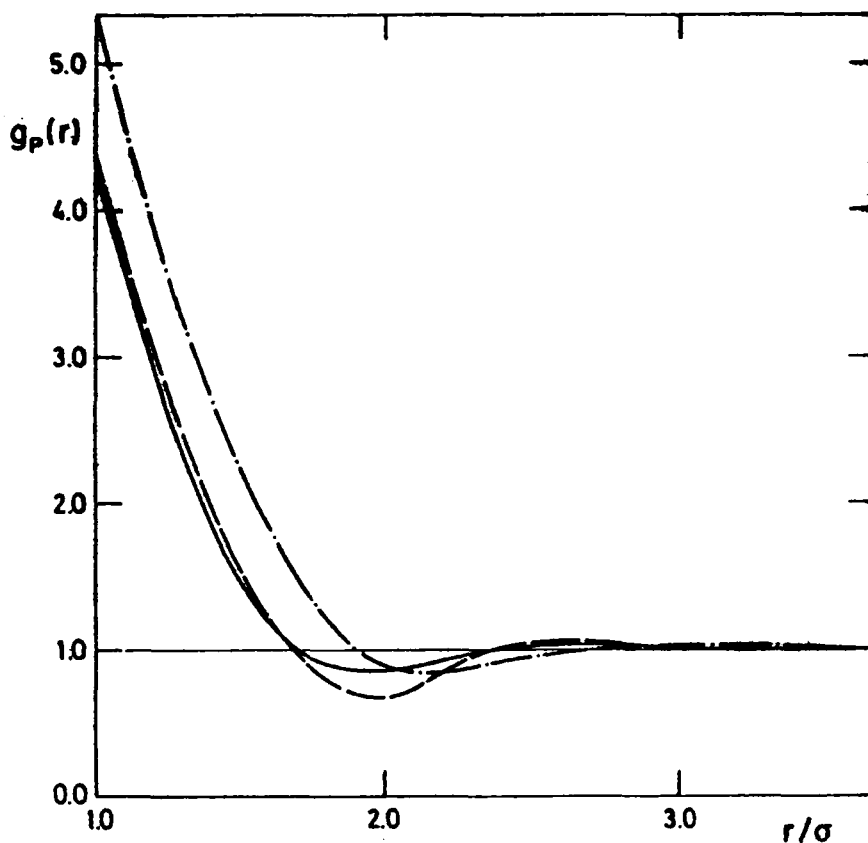
**Figure 2**   Pair correlation function for parallel orientation at $\eta = 0.3$, $-\cdot-$ $L^* = 1.0$, $--$ $L^* = 0.6$, $\underline{\hspace{1cm}}$ $L^* = 0.3$.

As a second aspect, we study the dependence on elongation for each particular orientation. There are two remarkable different behaviors: for parallel (P) and crossed (C) orientations, the contact PCF decreases as elongation does it. However, for head to tail (HT) and $T$ orientations, the contact PCF increases as the elongation decreases. This behavior does not agree with that shown in the simulations by Nezbeda and Smith[8] but it does with the results from the zero and first order RAM perturbation theory which they present[8]. The RAM theory also implies that $y(R_{12}, \omega_1, \omega_2)$ is independent of the polar angle, $\phi_{12}$, namely the predicted PCF for parallel and crossed orientations are the same. Nevertheless, this approximation is not considered in the solution of the integral equation and, in fact, we obtain different contact values for different orientations for every $L^* > 0$. Table 2 also shows that when elongation decreases the value of the contact PCF tends to be independent of the orientation as one could intuitively expect.

Finally, we would like to comment that angular dependence of the PCF at the same density has the same features for $L^* < 1$ as those pointed out in I for $L^* = 1$.
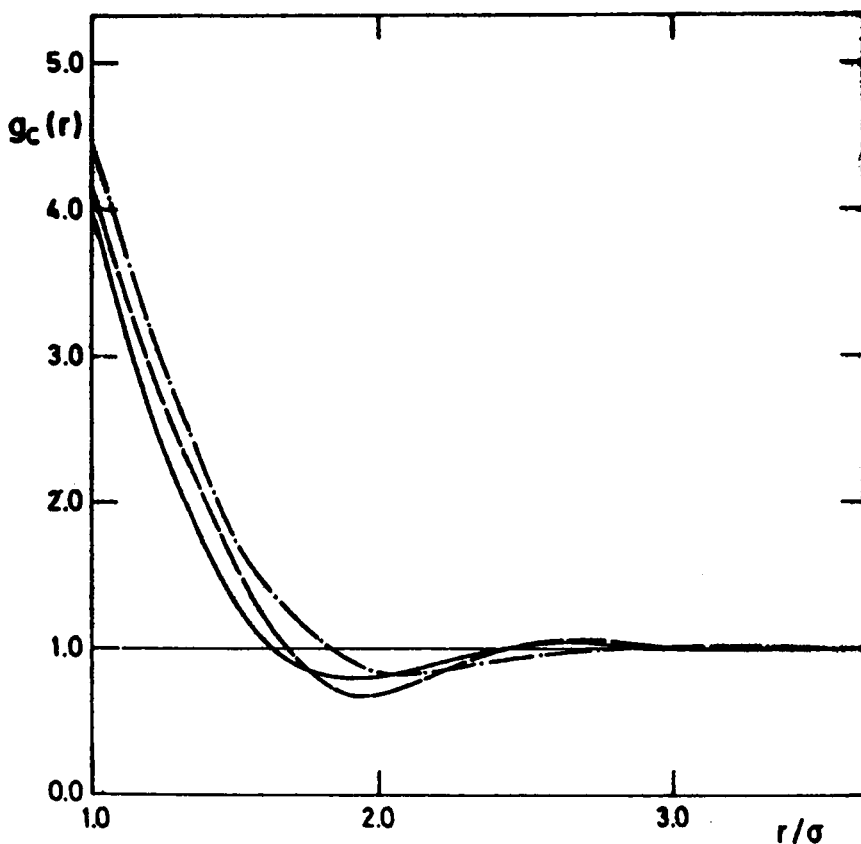
**Figure 3**   Pair correlation function for crossed orientation at $\eta = 0.3$, $-\cdot-$ $L^* = 1.0$, $--$ $L^* = 0.6$, ——
$L^* = 0.3$.

The contact values for parallel and crossed orientations are systematically larger than those for $T$ and head to tail orientations, and these two latter have similar values for the complete distance range. Therefore, we can conclude that even for small elongations the preferred orientation of a linear molecule is parallel if strong multipolar forces are not present[9]. This fact is well-known for molecules as $N_2$ with $L^* \simeq 0.3$.

## 2.2   The direct correlation function (DCF)

The behavior of the DCF for parallel and crossed orientations is shown in Figures 5 and 6, respectively. Concerning the dependence on elongation for head to tail and parallel orientations, it is observed that the DCF values at $r = 0$ are nearly the same. The values of the DCF for the crossed and $T$ orientations at $r = 0$ are clearly different and decrease as the elongation decreases. All the DCF increase monotonically with $r$ and no plateau is noticeable for $T$ orientation and small elongations. Several crosses between the DCFs appear in Figure 6 and this fact and the different contact distance
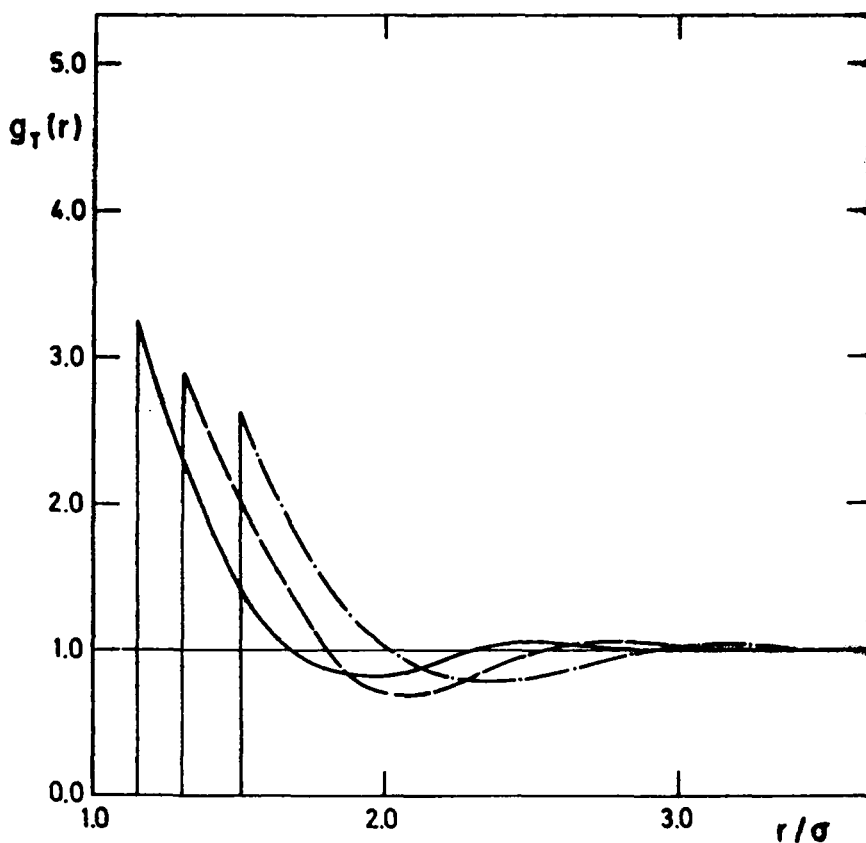
**Figure 4**   Pair correlation function for $T$ orientation at $\eta = 0.3$, $-\cdot-L^* = 1.0$, $--L^* = 0.6$, $\underline{\hspace{1cm}} L^* = 0.3$.

for each orientation causes the complex dependence of the PCF at contact ($= -$DCF at contact) discussed above. The same systematic differences between head to tail and parallel orientations, and between $T$ and crossed orientations, reported in I are observed and as we pointed out[1] this difference can be considered as an estimation of the error in our algorithm.

## 3   NUMERICAL RESULTS FOR THE SPHERICAL HARMONIC COEFFICIENTS OF THE PCF

The PCF for a linear molecule can be written as[10]:

$$g(R_{12}, \omega_1, \omega_2) = 4\pi \sum_{l,l',m} g_{l,l',m}(R_{12})Y_{l,m}(\omega_1)Y_{l',-m}(\omega_2) \tag{9}$$

**Table 2**

|  | $L^* = 1.0$ | $L^* = 0.6$ | $L^* = 0.3$ |
|---|---|---|---|
| $g_{HT}(r)$ | 2.5419 | 2.9709 | 3.0405 |
| $g_P(r)$ | 5.3374 | 4.3260 | 4.2490 |
| $g_C(r)$ | 4.4202 | 4.1369 | 3.9683 |
| $g_T(r)$ | 2.6110 | 2.9068 | 3.2003 |

Values of the contact PCF for the main orientations and different elongations. All systems correspond to $\eta = 0.3$.

where $\omega_i = (\theta_i, \phi_i)$ denote the polar angles determining the orientation of the molecular axis of the molecule $i$. $g_{l,l',m}(R_{12})$ are the well-known spherical harmonic coefficients (SHC) of the PCF and $Y_{l,m}(\omega_i)$ are the spherical harmonics.

Equation (9) can be inverted to give the SHC in terms of the PCF as:

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

$$\times \, d\cos(\theta_1) d\cos(\theta_2) d\phi_{12} \tag{10}$$

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

Equation (10) allows the computation of the SHC using the PCF previously calculated by the integration of the PY. The angular coordinates in Eq. (10) are related with those defined in I by:

$$\theta_1 = \theta_{12} \tag{11}$$

$$\phi_{12} = \beta_{12} \tag{12}$$

$$\cos \theta_2 = \cos \beta_{12} \cos(\theta_{12} + \alpha_{12}) \tag{13}$$

where the angles $\alpha$, $\beta$ and $\theta$ in the right hand side have been previously defined in the Figure 2 of paper I.

SHC in the Eq. (10) are numerically evaluated using the Conroy's method[11] for multiple integration. In this method the integral is approximated by a sum of the integrand function computed in $M$ selected points. We have used 6044 integration points. The functions in these points have to be obtained by interpolation because we only have numerical tables of PCF. As we reported in I, linear interpolation on $R$ is enough to give good results. For the angular variables, we use the same interpolation formula that in I, namely:

$$y(R, \alpha, \beta, \theta) = y_{HT}(R) + (y_P(R) - y_{HT}(R)) \sin \theta + (y_T(R) - y_P(R)) \sin \alpha$$
$$+ (y_C(R) - y_P(R)) \sin \beta \tag{14}$$

Since we have only a few orientations, mostly 18, the error coming from this interpolation may be important for some SHC but we were not able to find an alternative satisfactory way.
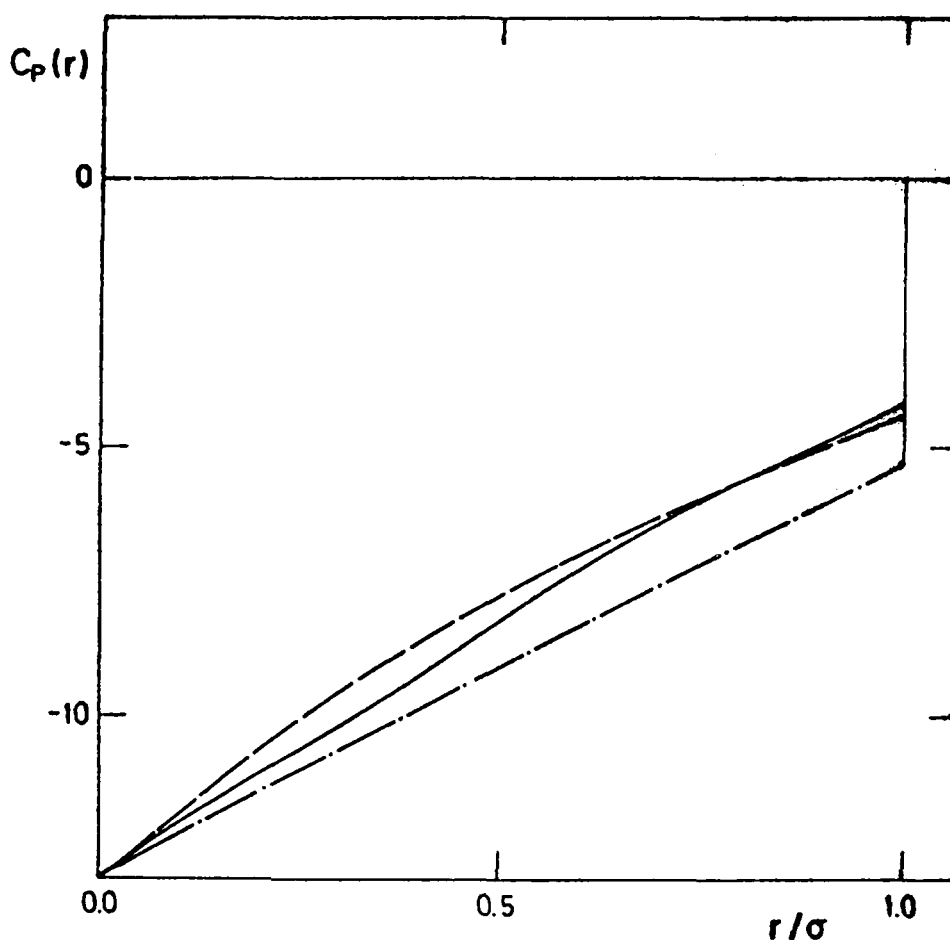
**Figure 5**  Direct correlation function for parallel orientation at $\eta = 0.3$, $-\cdot-$ $L^* = 1.0$, $--$ $L^* = 0.6$, $\underline{\qquad}$ $L^* = 0.3$.

In order to complete our comparisons, we have also simulated a few SHC for the systems of the Table 1 with $\eta = 0.3$. SHC have been evaluated as averages over a large number of configurations of 108 hard spherocylinders generated by a Monte Carlo method[12]. As usual, we set up the initial spatial configuration corresponding to a face centered cubic lattice. Initial orientations were partially disordered to speed up the equilibration[13] and periodic boundary conditions were used. Each new configuration in a MC run was formed by simultaneous random shifts in the position and the orientation of a single particle. Translational and orientational parameters[14] were monitored through the complete MC runs to ensure sampling over equilibrium
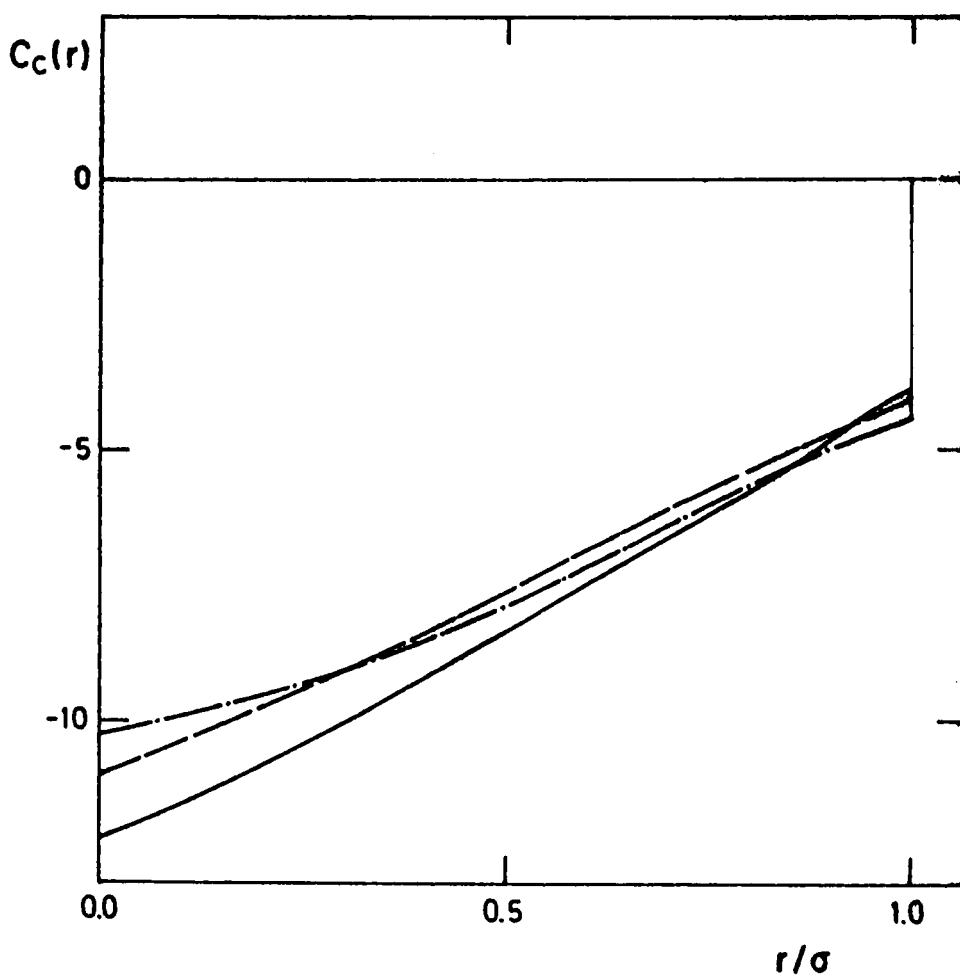
**Figure 6**   Direct correlation function for crossed orientation at $\eta = 0.3$, $-\cdot-$ $L^* = 1.0$, $--$ $L^* = 0.6$, $\underline{\qquad}$ $L^* = 0.3$.

configurations. The system typically reached equilibrium after $5.10^6$ moves and about the same number of moves were necessary to get the averages sampling every 20 trial moves per particle. About half of the moves were rejected in every run.

Figures 7 to 10 show the four first SHC comparing them with simulations for the three elongations considered. At a given constant elongation the agreement is qualitatively good for all coefficients except for $g_{220}(r)$. Qualitatively means here that the positions of the first maximum or first minimum in Figures 7, 8 and 10 are well predicted but not the corresponding SHC values. The discrepancies are smaller for
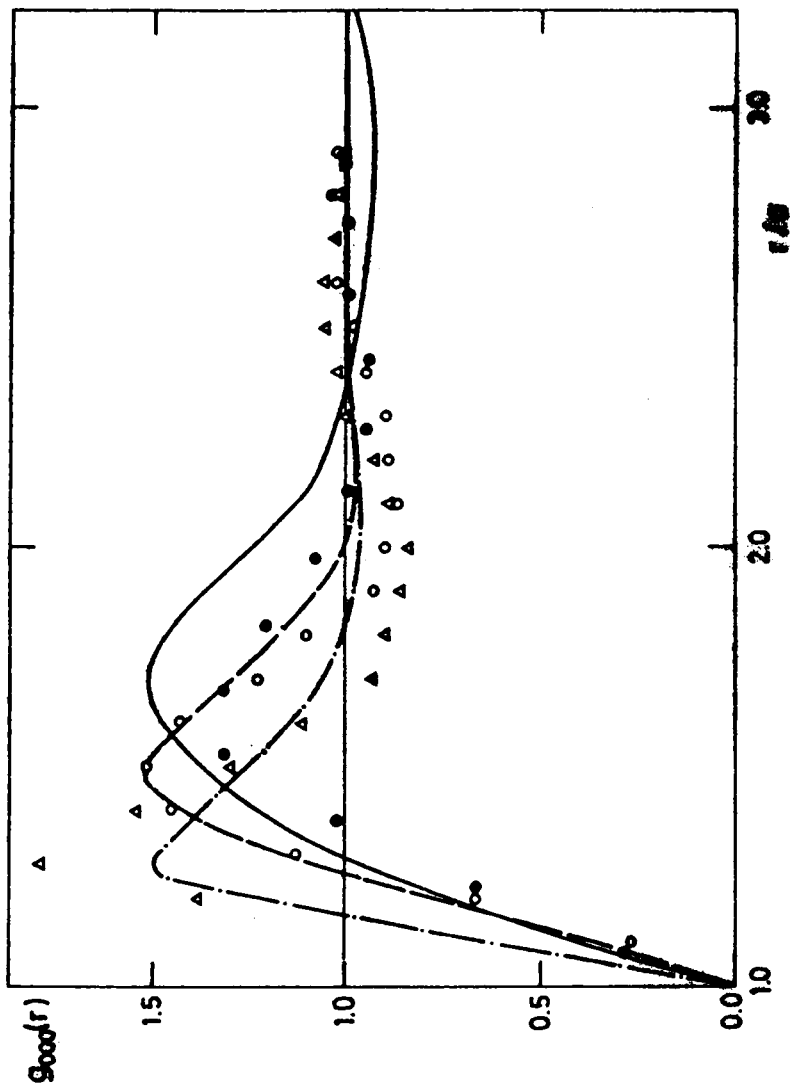
**Figure 7** Comparison of $g_{000}(r)$ with simulation of $\eta = 0.3$, ● $L^* = 1.0$, ○ $L^* = 0.6$, △ $L^* = 0.3$, points are simulation —— $L^* = 1.0$, - - $L^* = 0.6$, - · -
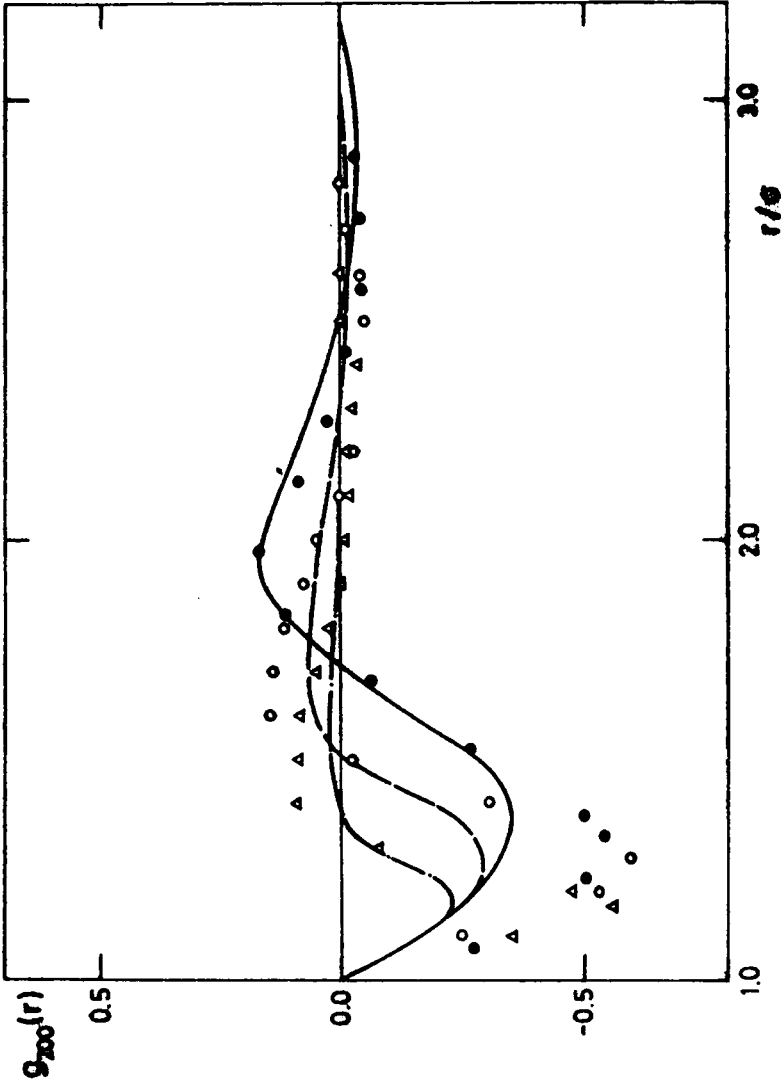$L^* = 0.3$.

228



**Figure 8** Comparison of $g_{200}(r)$ with simulation at $\eta = 0.3$, ● $L^* = 1.0$, ○ $L^* = 0.6$, △ $L^* = 0.3$, points are simulation —— $L^* = 1.0$, —·— $L^* = 0.6$, —··— $L^* = 0.3$.

**Figure 9** Comparison of $g_{220}(r)$ with simulation at $\eta = 0.3$, ● $L^* = 1.0$, ○ $L^* = 0.6$, △ $L^* = 0.3$, points are simulation —— $L^* = 1.0$, -- $L^* = 0.6$, -·- $L^* = 0.3$.

230



**Figure 10** Comparison of $g_{221}(r)$ with simulation at $\eta = 0.3$, ● $L^* = 1.0$, ○ $L^* = 0.6$, △ $L^* = 0.3$, points are simulation —— $L^* = 1.0$, -- $L^* = 0.6$, --- $L^* = 0.3$.
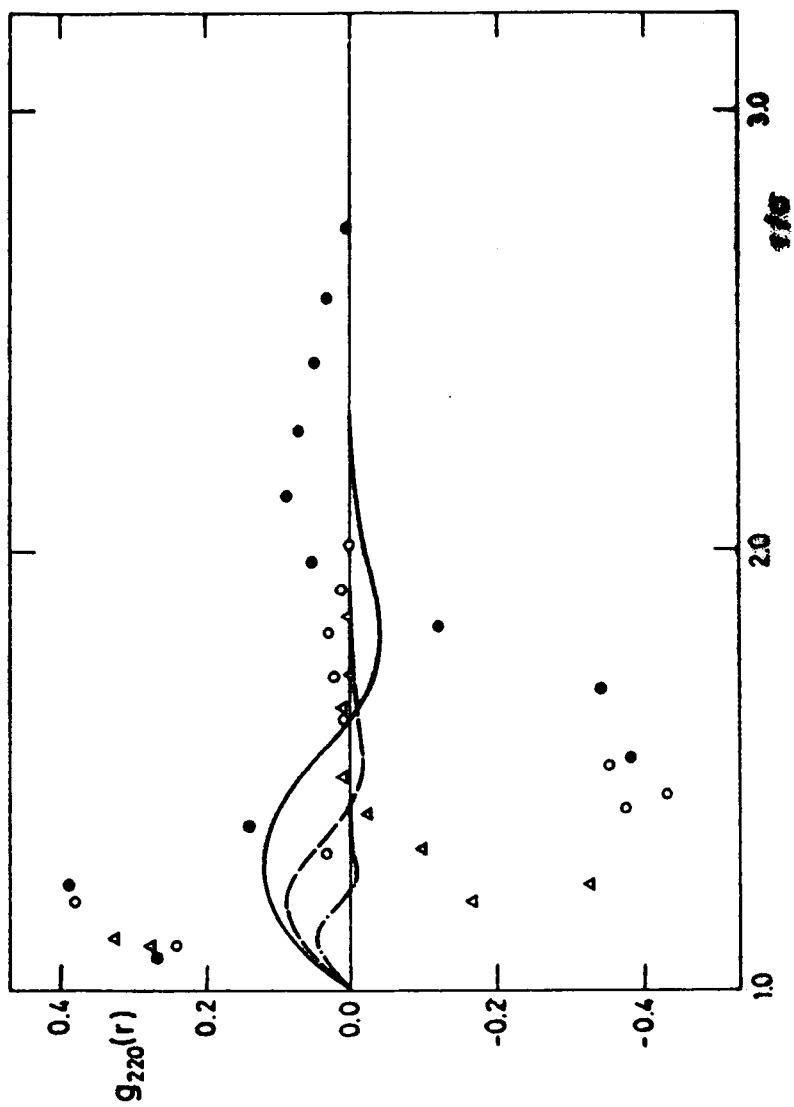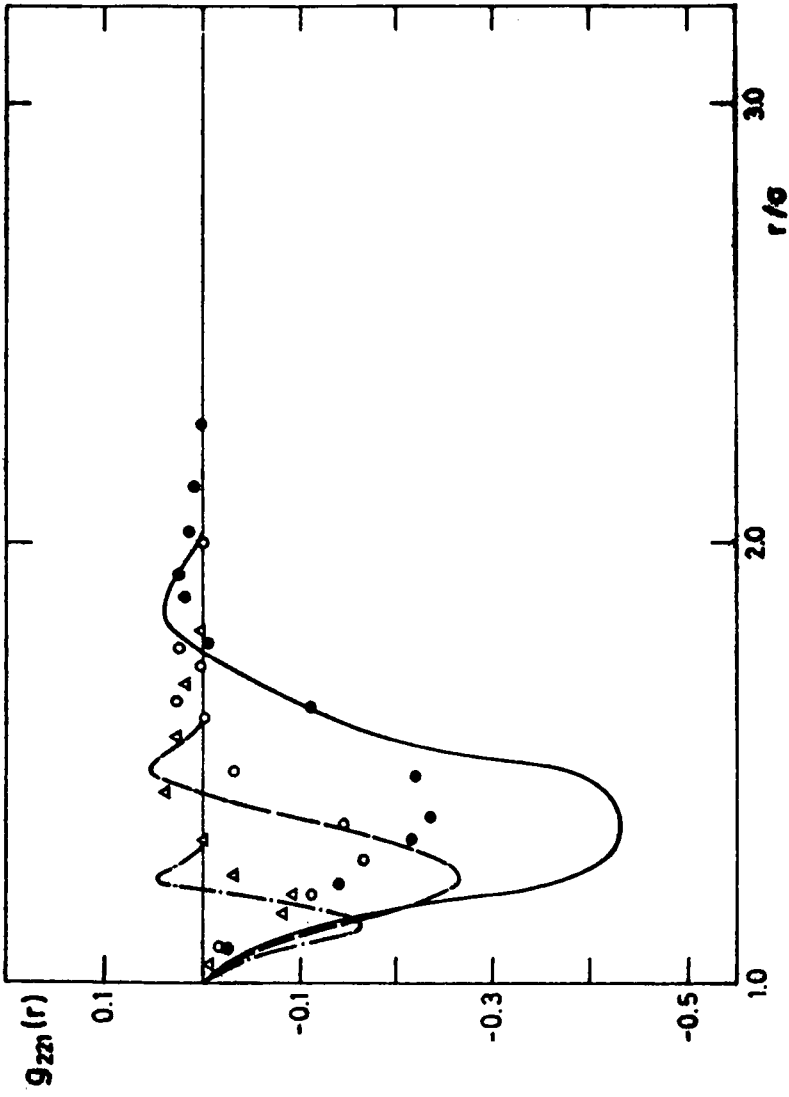
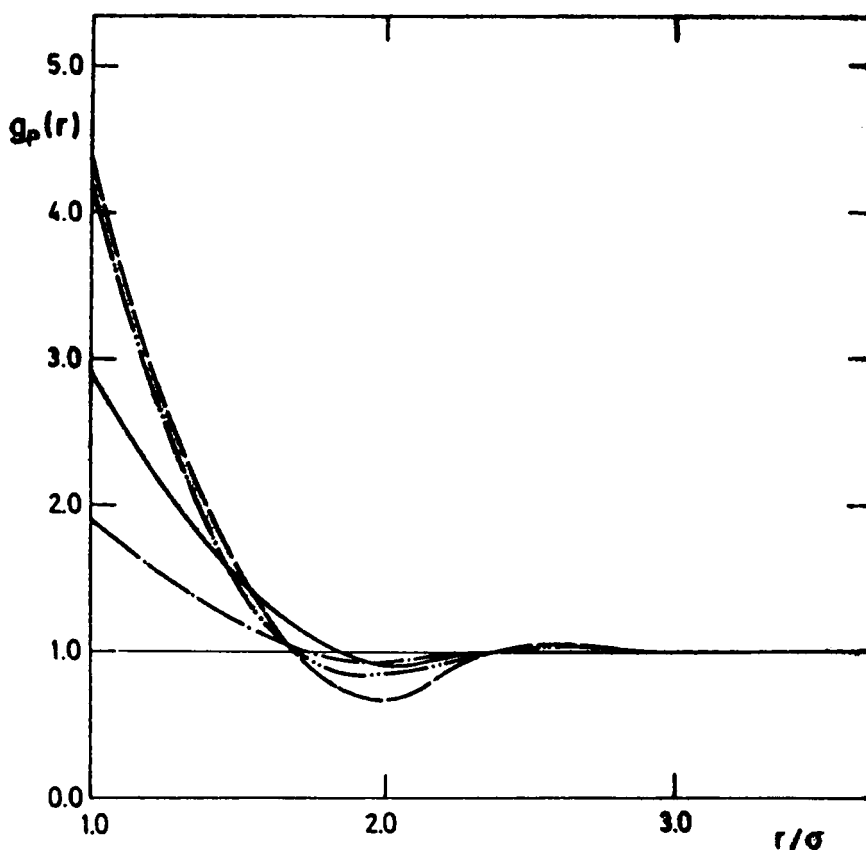**Figure 11**   Pair correlation function for parallel orientation $--$ $L^* = 0.6$ and $\eta = 0.3$, $\rule{1cm}{0.4pt}$ $L^* = 0.6$ and $\eta = 0.2280$, $-\cdots-$ $L^* = 0.3$ and $\eta = 0.3$, $-\cdot-$ $L^* = 0.3$ and $\eta = 0.1740$.

the coefficient $g_{000}(r)$ which represents the distribution function of the geometrical centers. Moreover, available simulation data exhibit an increase for the first maximum in $g_{000}(r)$ as the elongation decreases but the corresponding theoretical values are practically independent of elongation. The coefficients $g_{200}(r)$ and $g_{221}(r)$ show a similar behavior for simulated and theoretical values but the extreme intensities agree poorly. Simulation and theoretical results for the coefficient $g_{220}(r)$ are considerably different. This coefficient is usually worst predicted by the different approximate theories[8,15]. One can conclude from the dependence of the coefficients on $L^*$ and their comparison with simulation data that our theoretical results are better, in general, for intermediate elongation and this is specially true for the coefficient $g_{000}(r)$. Integrals containing PCF or its coefficient $g_{000}(r)$ are used to calculate thermodynamic functions[16] and some errors are probably cancelled up to $L^* < 0.6$ where the differences between simulations and theory can be compensated each other. However, this is not the case for $L^* = 1$ where the integral equation systematically overestimates the value of $g_{000}(r)$ for a long range of $r$. Similar results were found

using accurate perturbation theories[15] and also using a different algorithm of solving the OZ equation with the PY closure[6].

Finally, we can use the results of four systems of Table 1 to analyze the dependence of the correlation functions of density at constant orientation when $L^* < 1.0$. We have found that this dependence is essentially the same as in the case $L^* = 1$ studied in paper I for every orientation. Figure 11 shows the PCF for parallel orientations and these four systems. For every orientation the contact PCF increases as density does. Moreover, the first minimum becomes deeper and move towards smaller $r/\sigma$ values at larger densities for every orientation. The second maximum is nearly irrelevant and does not change with density and the contact values for parallel and crossed orientations are larger than those of $T$ and head-to-tail orientations for every density.

## 4   CONCLUSIONS

Taking into account the results of this paper and those of the paper I, we think that we can sketch some definitive conclusions about the solution of the PY equation for hard spherocylinders:

a) The results of the PCF obtained up-to-now show that the structure in the fluid increases monotonically with density and in a more complicated way with the elongation.

b) From our results is predicted that nonpolar linear molecules tend to adopt parallel configurations.

c) As the elongation decreases all the orientations tend to be equally probable and the values of PCF tend towards the RDF of a system of hard spheres at the same reduced density.

d) The approximations of Fischer[15] and Lombardero and Lago[17], and RAM[8] theories that assume the same value for parallel and crossed orientations are only expected to be reasonably good for small elongations. Similar results have been obtained by Perera and Patey[6] for systems with $L^* > 1$.

e) The comparison of the theoretical spherical harmonic coefficients with simulation data is better for $g_{000}(r)$ which mainly accounts for the spatial, not the orientational structure. The agreement is poorer for the other coefficients, specially for $g_{220}(r)$, which include the angular structure. It can be thought that the PY closure used to solve the OZ integral equation for hard spherocylinders provides a better description for the radial than for the orientational part of the PCF. Because our method is not restricted to this closure, we are presently working in other alternatives.

Finally, the best agreement of $g_{000}(r)$ for intermediate elongations ($L^* \simeq 0.6$) explains why the usual perturbation theories give good results up to about this elongation. Integrals containing PCF for smaller elongations must approximately vanish, but for larger elongations these errors are not compensated. However, we should tell

that a recent perturbation theory[18,19] seems to give good results at least up to $L^* \simeq 0.8$ and we were not able to find any explanation for this fact.

*References*

1. S. Lago and P. Sevilla, *J. Chem. Phys.*, **89**, 4349, (1988).
2. J. K. Percus and G. J. Yevick, *Phys. Rev.*, **110**, 1, (1958).
3. P. Sevilla and S. Lago, *Comput. Chem.*, **9**, 39, (1985).
4. I. Nezbeda, Czech. *J. Phys.*, **B30**, 601, (1980).
5. P. A. Monson and M. Rigby, *Mol. Phys.*, **38**, 1699, (1979).
6. A. Perera and G. N. Patey, *J. Chem. Phys.*, **89**, 5861, (1988).
7. D. A. McQuarrie, Statistical Mechanics, chap. 13, Harper & Row Pub., New York, 1976.
8. W. R. Smith and I. Nezbeda, *Mol. Phys.*, **44**, 347, (1981).
9. T. Kihara and A. Koide, *Adv. Chem. Phys.*, **33**, 51, (1975).
10. W. A. Steele, *J. Chem. Phys.*, **39**, 3197, (1963).
11. H. Conroy, *J. Chem. Phys.*, **17**, 5307, (1967).
12. N. Metropolis, M. N. Rosenbluth, A. W. Rosenbluth, A. H. Teller and E. Teller, *J. Chem. Phys.*, **60**, 1087, (1953).
13. P. A. Monson and M. Rigby, *Chem. Phys. Lett.*, **58**, 1, (1978).
14. J. Vieillard-Baron, *J. Chem. Phys.*, **56**, 4729, (1972).
15. J. Fischer, *J. Chem. Phys.*, **72**, 5371, (1980).
16. S. Lago and C. Vega, *Comput. Chem.*, **12**, 343, (1988).
17. M. Lombardero and S. Lago, *Phys. Chem. Liq.*, **11**, 141, (1981).
18. P. Padilla and S. Lago, *Fluid Phase Equil.*, **48**, 53, (1989).
19. S. Lago and P. Padilla (to be published).