

Solution of the Percus-Yevick equation for square well spherocylinders

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The Percus-Yevick equation for square-well spherocylinders has been numerically solved for some selected orientations following a methodology proposed previously for different fluids of elongated molecules. The equation is solved for particles of aspect ratios ranging from $L/\sigma=0.3$ up to $L/\sigma=5.0$, attractive range $\lambda/\sigma=1.5$, and packing fractions within $\eta=0.1-0.3$. The resulting pair correlation functions are checked against isothermal-isobaric Monte Carlo simulations and good agreement is found for the short-range structure, at intermolecular distances within one molecular diameter σ to contact for each of the selected orientations. At larger distances, the integral equation tends to overestimate the pair correlations. The results confirm the prediction of reference-system average Mayer-function perturbation theory for short aspect ratios, reaching the Onsager limit for the greater aspect ratios. Some instabilities of the solution for the longest models and higher densities are tentatively discussed in terms of their possible relation to frustration phenomena found in some polymer and complex systems.

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I. INTRODUCTION

Molecular liquids are relevant for a number of scientific and technological topics [1]. These liquids are often modeled by nonspherical molecules and several more or less popular models, ranging from site-site potentials [2], to more compact molecular core interaction potentials of different symmetry and varying repulsive and attractive contributions [3–7], have been profusely used to give account of the molecular shapes and intermolecular interactions. In order to calculate structural or thermodynamic properties of dense fluids, the model intermolecular potential can be combined with nonlinear integral equation approaches [8], or, alternatively, implemented into a simulation framework to produce ensemble averages [9]. In principle, integral equations have the advantage of their mathematical compactness and offer the possibility of obtaining information of interest about a system even without knowledge of a complete solution. For simple models, a purely theoretical solution is often less expensive in computational terms than a simulation [10]. However, the solution of integral equations becomes quite complicated for nonspherical molecular liquids and it usually requires a greater computational effort [11]. Furthermore, approaches involved in the derivation of integral equations are often physically not well founded and must anyway be checked against simulations. In fact, results reported on integral equations for molecular liquids are relatively scarce, in comparison with the wealth of molecular simulations available in the literature. This situation could be at least partially reversed if rapid and simple algorithms were available for the calculation of relevant magnitudes, such as the pair correlation functions. Indeed, there are important problems waiting for the development of simple and quick applications of integral equations to orientation-depending interactions [12].

In the present work, we have applied a relatively simple integral equation scheme proposed in earlier works to solve the Percus-Yevick (PY) integral equation [13–15], to a fluid of hard-core spherocylinders with an attractive square well (SWSC). This system constitutes an excellent touchstone for recent theories of dense fluids [16,17], but it becomes complicated to simulate under certain high density conditions [18]. On the other hand, the SWSC can be put into relation with more complicated and realistic systems [19] so that the determination of reliable properties for this system with a simple method is particularly valuable. We have solved the PY equation for selected pair orientations in SWSC fluids of different hard-core aspect ratios, while keeping the attractive range and depth of the square-well fixed. Simultaneously, we have performed the Monte Carlo (MC) simulations in the N - P - T , ensemble for the same models and thermodynamic states. In spite of the simplicity of our solution method, the pair correlation functions obtained from theory and simulation are in good agreement for all the molecular elongations investigated, although the range of densities where we are able to solve the PY equation is limited. Such limitation, however, may be related to some interesting phenomena appearing in complex systems, such as geometric frustration [20].

The paper is scheduled as follows: the intermolecular potential and the methods employed to solve the integral equation and to perform the Monte Carlo simulations are presented in Sec. II, whereas the theoretical results for the pair correlation functions are presented and compared to the MC simulations in Sec. III. Section IV closes the paper with a brief concluding discussion and a tentative interpretation of the results.

II. METHODOLOGY**A. Model fluid**

The system considered here is the so-called square-well spherocylinder fluid. In this model, the molecules interact

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following an intermolecular potential of the spherocylindrical symmetry (cylindrical with hemispherical caps) as defined by

$$u_{12}(\mathbf{r}_{12}, \omega_1, \omega_2) = \begin{cases} \infty, & d_m \leq \sigma \\ -\varepsilon, & \sigma < d_m \leq \lambda \\ 0, & d_m > \lambda, \end{cases} \quad (1)$$

where $d_m \equiv d_m(\mathbf{r}_{12}, \omega_1, \omega_2)$ is the minimum distance between the long axes of the spherocylinders, which is a function of the orientation of the molecules ω_1 and ω_2 and of the distance vector between their centers of mass, \mathbf{r}_{12} (the dependence can be reduced to four independent variables, the distance r_{12} and three angles), as well as of the molecular parameters: diameter σ and elongation L . The attractive square-well interaction is characterized by a depth ε and a range λ , and has the same anisotropy of the hard core. For the present investigation the well range is fixed at $\lambda = 1.5\sigma$.

B. Integral equation approach

The Ornstein-Zernike (OZ) integral equation provides a formal solution to the pair correlation function (PCF):

$$h(\mathbf{r}_{12}, \omega_1, \omega_2) = c(\mathbf{r}_{12}, \omega_1, \omega_2) + (4\pi)^{-1}n \int c(\mathbf{r}_{23}, \omega_2, \omega_3) d\mathbf{r}_3 d\omega_3, \quad (2)$$

where $h = g - 1$ and c are the total correlation function and the direct correlation function, respectively, and n denotes the number density. An additional closure relation between the functions c and h is necessary to solve the OZ equation. We have employed one of the most popular relations, the Percus-Yevick equation which is written as

$$c_{12} = g_{12}[1 - \exp(\beta u_{12})] = g_{12} - y_{12}. \quad (3)$$

Here, g_{12} denotes the pair correlation function and $y_{12} = g_{12} \exp(\beta u_{12}) = (1 + h_{12}) \exp(\beta u_{12})$ with $\beta \equiv 1/(k_B T)$. Traditional methods for solving this equation for linear molecules involve an expansion in a double series of spherical harmonics and an iterative solution using the Fourier transform of Eq. (2). This approach is formally straightforward but the expansion is very poorly convergent for systems composed of molecules of significant aspect ratio so that the computation of a large number of harmonic coefficients becomes necessary. Moreover, the number of iterations for states moderately close to the critical points becomes exceedingly high.

Here, we pursue a more modest aim: to obtain accurate solutions only for specific pair orientations, namely, those known as head-to-tail, parallel, crossed, and T shaped. The numerical solution is based on an interpolation function for the PCF between a definite number of orientations, as described previously for other systems [13]. In particular, we have followed the simplest scheme possible by restricting the number of interpolating orientations just to the selected orientations under the study mentioned above. Denoting the correlation function y_{12} for the head-to-tail, parallel, crossed,

and T-shaped configurations as y_{HT} , y_P , y_C , and y_T , respectively, the interpolation function is given by

$$y_{12}(r_{12}, \alpha, \beta, \theta) = y_{HT}(r_{12}) + [y_P(r_{12}) - y_{HT}(r_{12})] \sin \theta \\ + [y_C(r_{12}) - y_P(r_{12})] \sin \alpha \\ + [y_T(r_{12}) - y_P(r_{12})] \sin \beta, \quad (4)$$

where the angles α , β , and θ are defined in Fig. 1 in the same way as in Ref. [13]. Basically, α and β describe the relative orientation of the molecular directors, whereas θ is the angle described by one of the directors and the vector \mathbf{r}_{12} joining the centers of mass of the pair of molecules.

The PY integral equation has been solved iteratively in real space, taking as first input for the state of lowest density of each aspect ratio, the Boltzmann factor of the intermolecular potential u_{12} [Eq. (1)], $g_{12} = \exp(-\beta u_{12})$. For the subsequent thermodynamic states, the solution of the closest state at lower density is taken as input for the iteration. Further technical details are described in Ref. [13]. We have obtained PY solutions for the PCF of SWSC fluids with seven different aspect ratios ranging $L^* = 0.3 - 5.0$, for packing fractions $\eta = 0.10 - 0.30$ and a fixed reduced temperature $T^* = kT/\varepsilon = 2$. A complete list of the simulated systems appears in Table I.

It is important to stress that *a priori* one cannot necessarily expect reliable results for any orientation by simply using Eq. (4). The fact that such a simple interpolation is found to work reasonably well under the integral symbol is probably due to a fortuitous cancellation of errors when the PY equation is used. This may also be the reason for the fact that the PY equation gives acceptable results in the context of the present work, while it is usually considered worse than the hypernetted chain (HNC) equation since the classical work by Henderson *et al.* [21,22] for the square-well fluid with $L^* = 0$. Application of the HNC formalism to nonspherical system is, however, not straightforward. For instance, trouble arising from the calculation of the logarithmic term in the HNC equation for nonspherical systems has been reported by some authors [23–25], and it is not clear whether the HNC approach should work better than the PY one for fluids of elongated molecules. Equation (4) could be refined with the classical procedure of expanding the PCF in a double spherical harmonic or rotation matrices series [26–29] to obtain intermediate orientations, the price now being the poor convergence of the series as pointed out above.

C. Monte Carlo simulations

In order to assess the accuracy of the integral equation approach described in the preceding section, the same SWSC fluids and thermodynamical states have been investigated by means of MC simulations in the N - P - T ensemble. In the simulations, a system of $N_p = 768$ particles was allowed to equilibrate for up to 5×10^5 cycles, and a similar number of cycles was employed for the averages. Each cycle involves N_p attempts for random displacements and/or reorientation of a randomly chosen particle, plus an attempt to change the system volume. The procedure is described in

TABLE I. Contact values of the pair correlation function (PCF) as obtained from the PY equation for the square-well spherocylinder systems considered in this work. The PCFs for the head-to-tail, parallel, crossed, and T-shaped configurations are denoted by g_{HT} , g_P , g_C , and g_T , respectively. The values in italics for the hard spherocylinder (HSC) fluid (Ref. [13]) are included for comparison. The PY calculation for $L^*=0.6$, $\eta=0.3$ with an increased system temperature $T^*=10$ is meant to show how the behavior of the SWSC fluid approaches that of the HSC fluid in the high-temperature limit.

L^*	T^*	η	$g_{HT}(\mathbf{r}_{12}=\rho_c)$	$g_T(\mathbf{r}_{12}=\rho_c)$	$g_P(r_{12}=\rho_c)$	$g_C(\mathbf{r}_{12}=\rho_c)$
0.3	2	0.1	1.69	1.68	1.80	1.77
0.3	2	0.15	1.71	1.72	1.93	1.87
0.3	2.0	0.3	1.74	1.92	2.62	2.46
<i>0.3¹</i>		<i>0.3</i>	<i>3.04</i>	<i>3.20</i>	<i>4.25</i>	<i>3.97</i>
0.6	2	0.3	1.77	2.10	3.62	3.22
0.6	10	0.3	2.58	2.75	4.23	3.87
<i>0.6¹</i>		<i>0.3</i>	<i>2.97</i>	<i>2.91</i>	<i>4.33</i>	<i>4.14</i>
1.0	2	0.3	1.75	2.15	4.83	4.08
<i>1.0¹</i>		<i>0.3</i>	<i>2.54</i>	<i>2.61</i>	<i>5.34</i>	<i>4.42</i>
1.2	2.0	0.1	1.68	1.72	2.15	2.03
1.2	2	0.15	1.69	1.78	2.57	2.34
1.2	2	0.3	1.68	2.16	5.41	4.46
2.0	2.0	0.1	1.66	1.73	2.42	2.21
2.0	2.0	0.15	1.63	1.78	3.07	2.67
3.0	2.0	0.1	1.63	1.73	2.80	2.37
3.0	2.0	0.15	1.49	1.74	3.82	2.88
5.0	2.0	0.1	1.28	1.65	3.56	2.46

¹Hard spherocylinder fluid from Ref. [13].

detail elsewhere [30]. Such long simulation runs, similar to previous simulations for hard spherocylinders [31] and relatively expensive in computational time (several days for each state in a PC nowadays), are needed primarily due to the extensive averaging required to compute the PCF for specific orientations. A tolerance of 5° was employed to calculate each pair orientation; i.e., in the averaging process, a pair configuration was included as head to tail if $\alpha, \beta, \theta = 0^\circ - 5^\circ$, as parallel if $\alpha, \beta = 0^\circ - 5^\circ$, $\theta = 85^\circ - 90^\circ$, as crossed if $\beta = 0^\circ - 5^\circ$, $\theta, \alpha = 85^\circ - 90^\circ$, and, finally, as T shaped if $\alpha = 0^\circ - 5^\circ$, $\theta, \beta = 85^\circ - 90^\circ$, where the angle definitions are given in Fig. 1.

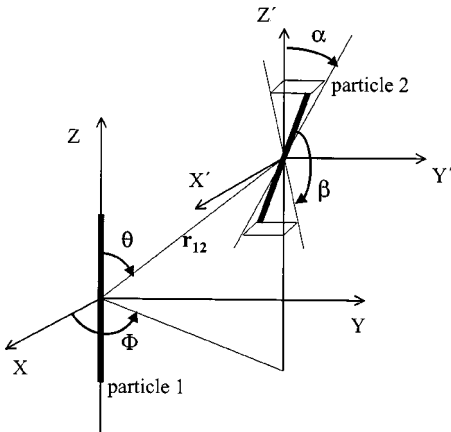


FIG. 1. The system of coordinates used in the work showing the angles appearing in Eq. (4).

III. RESULTS

A. Percus-Yevick pair correlation functions

A selection of the PCFs obtained by the Percus-Yevick integration for different SWSC fluids are shown in Figs. 2–5. As expected, each of the PCFs becomes nonzero only at

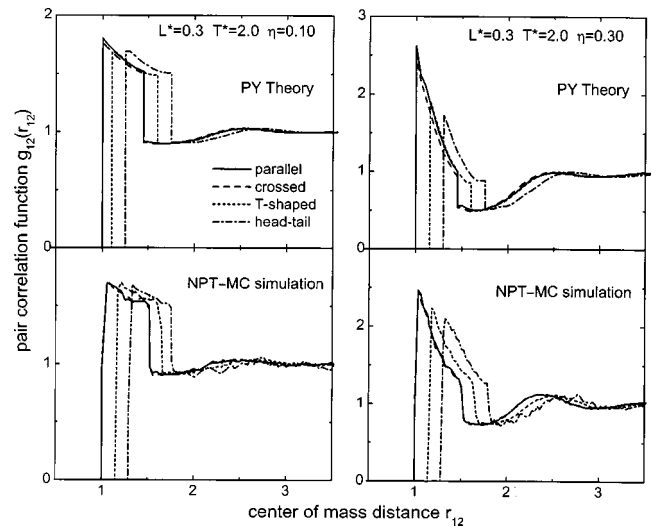


FIG. 2. The pair correlation function of the square-well spherocylinder system for selected relative pair orientations (parallel, crossed, T-shaped and head-to-tail). Results for $L^*=0.3$, $T^*=2$, $\eta=0.10$ (left panels), and $\eta=0.30$ (right panels) are shown. The upper panels correspond to the Percus-Yevick equation solution and the lower panels show the corresponding Monte Carlo simulations.

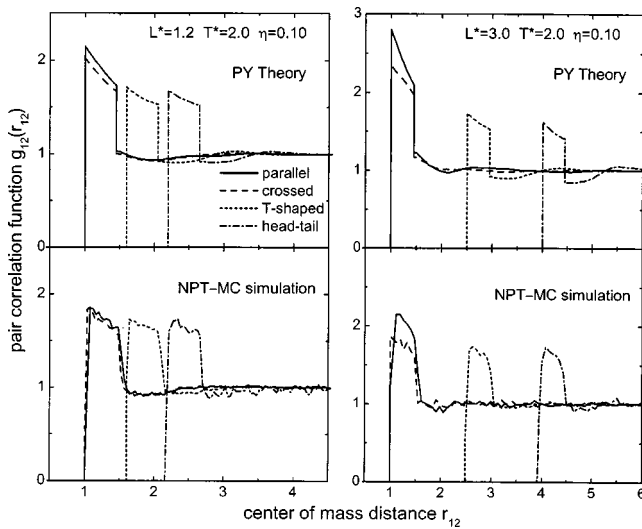


FIG. 3. Same as Fig. 2 for the SWSC fluids with $L^*=1.2$, $T^*=2$, $\eta=0.10$ (left panels) and $L^*=3.0$, $T^*=2$, $\eta=0.10$ (right panels).

distances larger than the contact distance, ρ_C , for the corresponding pair orientation ($\rho_C=1$ for parallel and crossed orientations, $\rho_C=1+L^*/2$ for the T-shaped orientation, and $\rho_C=1+L^*$ for the head-to-tail orientation, always in units of the molecular diameter σ). In addition, each of the PCF features a steplike structure within the location of the square well for each orientation, $\mathbf{r}_{12}=[\rho_C, \rho_C+\lambda^*]$. Within this interval, the PCF decreases slowly with \mathbf{r}_{12} for the fluids with small aspect ratios at low densities, whereas it does so more rapidly at higher densities and for the fluids of more elongated molecules. A sudden fall of the PCF takes place immediately beyond the well, at $\mathbf{r}_{12}=\rho_C+\lambda^*$, which is followed by a shallow minimum and by a secondary maximum at larger distances.

Some preliminary conclusions can be advanced from a more detailed inspection of the PY PCFs in relation to simple

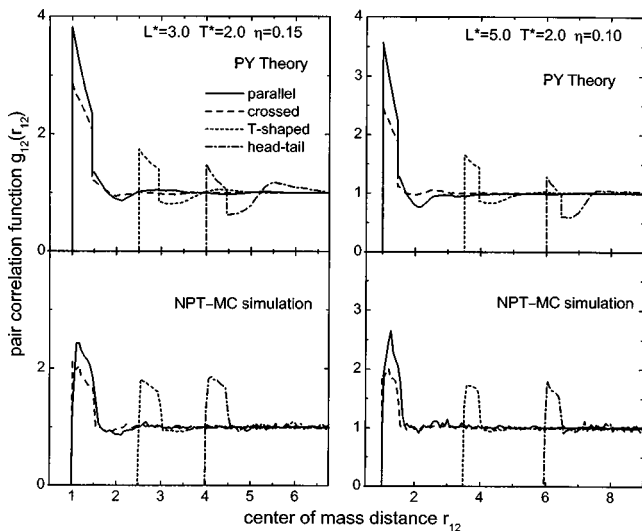


FIG. 4. Same as Fig. 2 for the SWSC fluids with $L^*=3.0$, $T^*=2$, $\eta=0.15$ (left panels) and $L^*=5.0$, $T^*=2$, $\eta=0.10$ (right panels).

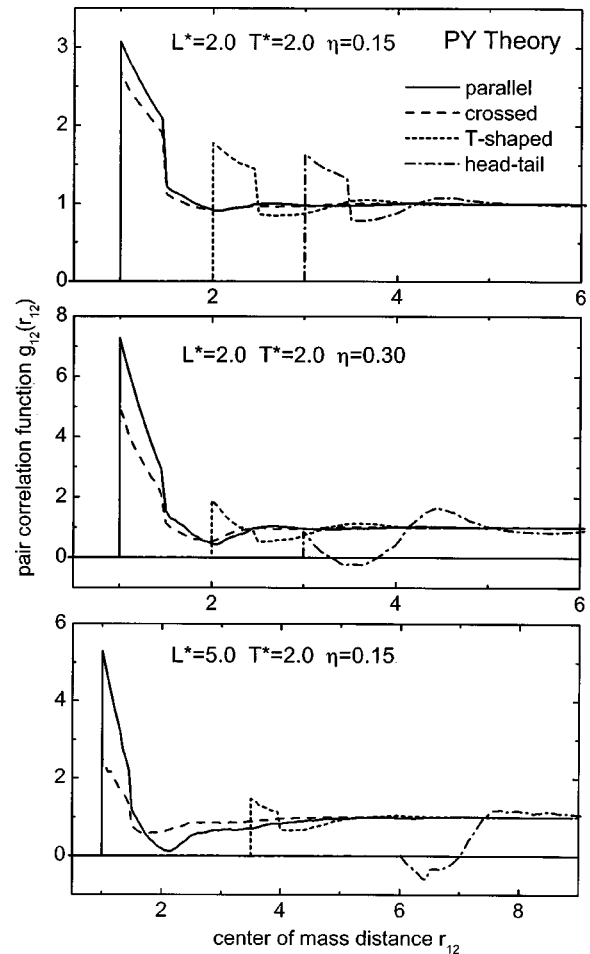


FIG. 5. Percus-Yevick pair correlation function for SWSC fluids with the indicated aspect ratios, temperatures, and packing fractions. The PY distributions shown in the upper panel ($L^*=2.0$, $\eta=0.15$) are physically consistent and resemble the typical behavior of the SWSC fluid in the isotropic phase. The nonphysical negative values for the head-to-tail distribution obtained in the PY solutions at high L^* and η are illustrated by the middle ($L^*=2.0$, $\eta=0.3$) and lower panels ($L^*=5.0$, $\eta=0.15$).

perturbation theories. First of all, it can be appreciated that the common zero-order assumption of the constancy of the PCF for any orientation, when scaled with the distance between the repulsive cores [32], is only acceptable for the less anisotropic systems at low density ($L^*=0.3, \eta \leq 0.1$). Indeed, for instance, the value of the PCF within the square well is larger for the parallel and crossed configurations. Interestingly, the prediction of reference-system average Mayer-function (RAM) perturbation theories [33] of an identical PCF for the parallel and crossed orientations is approximately corroborated for the shortest aspect ratios studied $L^*=0.3$. However, the parallel orientation is clearly favored for longer molecules, which can be rationalized from geometrical considerations and it is in consonance with the expected behavior in the Onsager limit ($L^* \rightarrow \infty$) [34]. When the aspect ratio L^* increases, the accessible volume within the square well and around the cylindrical body of the molecule, $V_C = \pi(\lambda^* - 1)^2 L^* \sigma^3 / 4$, grows, whereas the volume of the square-well region around the spherical ends of the

molecule, $V_S = \pi(\lambda^* - 1)^3 \sigma^3 / 6$, remains constant. Thus, molecules tend to move from the spherical to the cylindrical part of the interaction and this induces a notable increase in the PCF of the crossed orientation and, more remarkably, of the parallel orientation with respect to *T*-shaped and head-to-tail orientations. In our case study, with $\lambda^* = 1.5$, the volume of the square well around the cylindrical core becomes dominant ($V_C/V_S > 1$) when $L^* > 1/3$. In fact, it is apparent from Figs. 2–5 and Table I that only for the shortest elongation, $L^* = 0.3$ is the value of the PCF at short distances comparable for the parallel and crossed configurations, whereas the former orientation dominates in the calculations at larger L^* .

We found no physical solution to our Percus-Yevick approximation for the fluids with the higher aspect ratios at sufficiently high density, e.g., for $L^* = 2$, $\eta > 0.2$, or $L^* = 5$, $\eta > 0.1$. In particular, in such cases the PCF of the head-to-tail orientation became negative at short distances within or in the vicinity of the square well. Figure 5 illustrates this effect for the PY calculations for $L^* = 2$, $\eta = 0.3$ and $L^* = 5$, $\eta = 0.15$, which may be compared to the physically consistent solutions for $L^* = 2$, $\eta = 0.15$ (also included in Fig. 5), and for $L^* = 5$, $\eta = 0.1$ (see Fig. 4). This limitation is not surprising, given the approximations involved in our treatment and the growing internal order expected in the fluid at increasing densities. We will return to these latter considerations in Sec. IV. In any case, the range of densities for which our method provides stable results goes far beyond those of the virial series approaches, typically valid at packing fractions significantly smaller than the critical packing fraction, which for the systems presently under study ranges [19] $\eta_c = 0.16$ – 0.18 .

B. Pair correlation function at the potential discontinuities

The thermodynamics of the SWSC fluid is depending only on the values of the PCF at the discontinuities of the square-well potential. The contact PCFs, i.e., the value of the PCF for each model fluid at the closest distance, $r_{12} = \rho_C$, are presented in Table I for our case studies. The tabulated values show that the contact values are systematically larger for the parallel and crossed orientations than for the *T*-shaped and head-to-tail ones. In addition, the contact PCFs at a fixed density present a dissimilar variation with the aspect ratio for each type of pair orientation. Figure 6 illustrates the evolution of the contact PCF with L^* arising from our calculations with a packing fraction $\eta = 0.10$. As can be seen in the figure, the contact PCF increases rapidly with increasing L^* for the relatively more important orientations (i.e., the crossed and, even more so, the parallel orientations), whereas it remains roughly constant for the *T*-shaped and the head-to-tail orientations. This kind of behavior, which is further reinforced with growing packing fractions, was also found for the hard spherocylinder fluid (HSC) [13], as can be appreciated from the values quoted in Table I. On the other hand, the introduction of the square-well attractive forces in the SWSC fluid reveals new elements with respect to the HSC system, especially at distances close to contact. Whereas, in the HSC system the PCF decreases rapidly at distances larger than contact [13], in the SWSC fluid the PCF varies more slowly

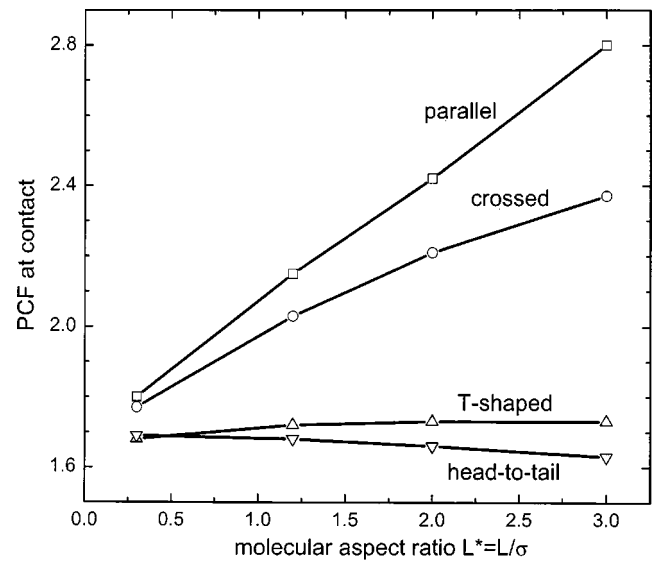


FIG. 6. Percus-Yevick values of the pair correlation function at the contact distance of each of the pair orientations considered in this work, for SWSC fluids of growing aspect ratio, while the packing fraction is kept fixed at $\eta = 0.10$.

within the range of the square well, especially at low density. While confined by the attractive interaction, the molecular pairs can move relatively free within the square well without change of energy, hence increasing the entropy of the system and lowering its free energy. As a consequence, in comparison to the HSC fluid, the molecules are not as much concentrated at the contact distance in the SWSC fluid and the corresponding contact PCF values are systematically smaller, a feature that becomes, particularly, visible at the lower aspect ratios (see Table I). The calculation for $L^* = 0.6$, $\eta = 0.3$ with an increased system temperature $T^* = 10$ included in Table I is meant to show how the behavior of the SWSC fluid approaches that of the HSC fluid in the high-temperature limit.

C. Comparison to Monte Carlo simulations

The PCFs obtained from the MC simulations for the same cases selected to illustrate our solution of the PY equation, are shown in the lower panels of Figs. 2–4. Within the statistical noise of simulations, the MC PCFs display a good overall agreement with the PY ones. The simulations reproduce well the form and behavior of the step in the PCF within the square well observed in the PY solution, and also resemble well the greater probability of the parallel configuration at high density or large aspect ratios. Note that the discontinuities of the PCF associated with the square well are slightly smoothed out in the MC simulations, as a consequence of the 5° tolerance employed to average each of the pair orientations (see Sec. II C). As expected, the closest agreement between both types of calculations are observed for the shorter elongations, up to $L^* \approx 1.2$. For the more elongated models, the agreement is more qualitative.

There are also some remarkable differences between the PY and the MC distributions. In general, but especially for high L^* , the results from the PY equation overestimate the

value of PCF for every orientation at short distances. In particular, such overestimation is apparent at distances close to contact, which should have a quantitative effect on the thermodynamics of the system, but would not alter the qualitative considerations developed in the preceding section. We also remark that no attempt has been made within the scope of the present work to obtain accurate contact values of the PCF from the MC simulations.

The PCF from the MC simulations also shows systematically less structure than the PY solution at long distances. In particular, the MC simulations show weaker second maxima in the PCF, especially for the longer elongations here considered $L^*=3,5$ (Figs. 2 and 3). Furthermore, the minimum present systematically in the PY PCF after the square well, while satisfactorily reproduced in the MC simulations for $L^*=0.3$ (Fig. 2), is only appreciable for the greater aspect ratios in the MC PCF of the parallel orientation at the higher computed densities. Hence, even though these considerations might be somewhat obscured by the poorer simulation statistics at the longer intermolecular distances in comparison with the shortest ones, especially for the head-to-tail configuration, we can draw the conclusion that the integral equation solutions overestimate the mutual orientation correlations beyond the potential attractive range.

IV. CONCLUSIONS

The results presented in this paper appeal for a reevaluation of the utility of integral equations to obtain the structure and thermodynamic properties of complex fluids. The advantage of the integral equation methodology employed here for the treatment of the angular dependence of the PCF relies on its less expensive computational cost (roughly one order of magnitude) with respect to the MC simulation. While keeping in mind the exceptions discussed in the preceding section, on qualitative grounds the overall agreement between the Percus-Yevick and the Monte Carlo pair correlation function and its dependence on the molecular aspect ratio and fluid density can be regarded as quite satisfactory for the cases considered in this work. Thus, the main aim of the work, namely, to provide information about the structure of the SWSC fluid through the accurate solution for specific pair orientations, has been fulfilled.

On the other hand, our PY integral equation approach only provides consistent solutions at moderate aspect ratios and densities where the SWSC fluid displays the typical features of an isotropic fluid. For sufficiently high densities and aspect ratios, the PY solution shows a lesser degree of agreement with the MC simulations and eventually becomes physically unstable, yielding negative values for the PCF of the head-to-tail orientation in the region of the attractive square well. Following some of the argumentations outlined in Sec. III A, the negative PCF of this particular pair orientation for large aspect ratios and high densities may be linked to a drastic reduction of the volume accessible around the

spherical ends of the molecules with respect to the predominant interaction around the cylindrical part of the molecular cores. Note that a negative value of the PCF corresponds to a complex value of the effective pair potential defined as

$$w(\mathbf{r}_{12}, \omega_1, \omega_2) = -k_B T \ln g(\mathbf{r}_{12}, \omega_1, \omega_2) \quad (5)$$

and the subsequent restriction of the available phase space in the language of the energy landscape theory [36]. In fact, the behavior observed in the PY PCF recalls what is known as frustration [20] in some polymer and biological systems [35]. The phenomenon of frustration is well characterized for hard spheres where a recent paper by Debenedetti and Truskett [37] has revived the older ideas from Speedy [38]. For non-spherical particles, the case is less documented but some spectacular examples in living systems are known [39]. For these latter systems frustration arises when, at sufficiently high density, hard bodies, typically with small attractive forces, tend to remain parallel, whereas contact along the major axes (e.g., of the head-to-tail type) becomes severely unfavorable.

The appearance of these nonphysical solutions cannot be related to a transition to the formation of a liquid crystal phase, which for the SWSC system are known to take place at even higher densities [30], but it seems to be closer to a metastable glassy state [40,41]. Although this comment is meant to be purely tentative, the fact that integral equations sometimes converge to a solution for a metastable state instead of a true equilibrium state has been previously reported [42,43]. Furthermore, according to previous works [30], the flat attractive well imposed in the SWSC interaction apparently favors the propensity of this model fluid to enter metastable phases (such as a frustrated state). For instance, a more significant degree of hysteresis was found in NPT MC simulations of the SWSC fluid in the vicinity of the isotropic-nematic and nematic-smectic phase transitions [30], in comparison to the same simulations for a soft interaction model, namely, a soft repulsive Kihara potential [44]. Compression on the SWSC system may eventually not alter the intermolecular energy and, therefore, not vary the total energy; but the entropy will be diminished, exactly as in a frustrated state [40]. In principle, this particularity of the square-well potential would not be a disturbance in the solution of integral equation for soft continuous potentials. Although some results from integral equations are long time known for these latter kind of systems [15], a more systematic investigation is currently in progress in our group.

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