I. INTRODUCTION

Recently we investigated the formation of liquid-crystalline mesophases in a fluid of hard spherocylinders, i.e., cylindrical segments of length $L$ and diameter $D$ capped at each end by a hemisphere of the same diameter \cite{1}. More specifically, we analyzed the ordering of the homogeneous and isotropic fluid into a nematic, smectic or solid phase within the framework provided by the one-phase entropy-based criterion originally proposed by Giaquinta and Giunta \cite{2}. This criterion can be implemented through the well known multi-particle correlation expansion of the configurational entropy \cite{2}:

\begin{equation}
  s_{\text{ex}} = \sum_{n=2}^{\infty} s_n .
\end{equation}

In the above formula $s_{\text{ex}}$ is the excess entropy per particle in units of the Boltzmann constant and $s_n$ is the $n$-body entropy that is obtained upon re-summing spatial correlations between up to $n$ particles. In particular, the pair entropy per particle of a homogeneous and isotropic fluid of nonspherical molecules can be written as \cite{2}:

\begin{equation}
  s_2(\rho) = -\frac{1}{2} \frac{\rho}{\Omega} \int \left[ g(r, \omega^2) \ln g(r, \omega^2) - g(r, \omega^2) + 1 \right] \, dr \, d\omega^2 ,
\end{equation}

where $g(r, \omega^2)$ is the pair distribution function (PDF) which depends on the relative separation $r$ between two molecules and on the set of Euler angles $\omega^2 \equiv [\omega_1, \omega_2]$ that specifies their absolute orientations in the laboratory reference frame. The quantity $\Omega$ represents the integral over the Euler angles of one molecule, while $\rho$ is the particle number density.

In order to identify the ordering threshold of the fluid, we monitor the behavior — as a function of the number density — of the so-called residual multiparticle entropy (RMPE). This quantity is defined as the difference

\begin{equation}
  \Delta s \equiv s_{\text{ex}} - s_2 .
\end{equation}

At variance with the pair entropy, the RMPE exhibits a nonmonotonic behavior as a function of $\rho$. In particular, it is negative at low densities, and becomes positive as a more ordered phase is approached. The relevance of the condition $\Delta s = 0$ as a one-phase ordering criterion has been documented for a variety of phase transitions, both in continuous fluids as well as in lattice-gas model systems \cite{3}.

Even for systems composed of non-spherical molecules, such as hard spherocylinders, it turns out that the ordering thresholds detected through the zero-RMPE condition systematically correlate with the corresponding phase-transition points, whatever the nature of the higher-density phase coexisting with the isotropic fluid \cite{1}. Cuetos and coworkers have successfully applied the RMPE criterion to hard spherocylinders with an attractive square well and to spherocylinders with a soft repulsive core \cite{3}.

In this paper we intend to analyze the predictions of the RMPE approach in the case of the nematic-smectic transition undergone by parallel hard spherocylinders with aspect ratio $L/D = 5$. The onset of smectic order out of a nematic phase represents the next step in the process which, upon compression of the isotropic fluid, eventually leads to the formation of the fully crystalline solid. The phase behavior of this model has been investigated with several numerical simulations \cite{3} as well as theoretical studies (see e.g. \cite{10, 11, 12} and references.

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II. THEORY

The formalism developed in [1] for the isotropic fluid needs to be modified in order to describe the nematic and smectic mesophases. Even for uniaxial molecules, the numerical computation of the full pair distribution function $g(r, \omega^2)$ is a formidable task. Costa and coworkers have already shown that, in order to reproduce the phase boundaries of the isotropic fluid, it is enough to take into account the dependence of $g(r, \omega^2)$ on the centers-of-mass separation $r$ and on the angle $\theta$ formed by the molecular axes of two spherocylinders [1]. This angle shows up as the critical parameter which accounts, by itself, for the reduction of orientational states that is ultimately offset by the gain of translational entropy at high densities [13]. On the other hand, it is rather obvious that the angle $\theta$ conveys no useful information on the structural process that may eventually lead to the formation of a smectic phase out of a nematic phase.

In order to resolve ordering effects associated with the orientational degrees of freedom on one side, and with the modulation of the density along the nematic director on the other side, we shall restrict our analysis to a system composed of parallel spherocylinders. Assuming that the molecules are perfectly aligned does not significantly alter the main aspects of the phenomenology that we want to investigate. As emphasized above, different mechanisms drive the phase transformation of an isotropic or of a nematic fluid into a more ordered phase. Moreover, at the nematic-smectic transition threshold the nematic fluid is typically characterized by a very high degree of relative alignment of the molecules. For example, the nematic order parameter is about 0.85-0.89 for spherocylinders with aspect ratio $L/D = 5$ [14]. The constraint on the relative orientation of the particles hugely simplifies the expression of the PDF. In fact, in order to specify the spatial configuration of a given spherocylinder relative to that fixed at the origin one just needs two parameters: the distance $r$ and the angle $\theta$ formed by $r$ and by the nematic director. The other polar angle $\phi$ is actually averaged out on account of the macroscopic cylindrical symmetry of the model. We emphasize that in this case, at variance with the freely rotating model already investigated in [1], no approximation is needed in order to compute the PDF of the system. Correspondingly, the pair entropy of the fluid can be written as:

$$s_2(\rho) = -\pi \rho \int_0^\infty r^2 dr \int_0^\pi \sin \theta d\theta \{ g(r, \theta) \ln[g(r, \theta)] - g(r, \theta) + 1 \}. \quad (4)$$

Using a formalism analogous to that introduced in [1], we can extract from Eq. (4) the excluded-volume contribution to the pair entropy of the fluid. This contribution arises from the space integration carried out over the regions where $g(r, \theta) = 0$:

$$s_2 = -B_2 \rho + s_2'. \quad (5)$$

In Eq. (5) $B_2$ is the second virial coefficient of hard parallel spherocylinders that is just four times the volume, $V_{hsc}$, of a spherocylinder:

$$B_2 = 4[(\pi/4)D^2L + (\pi/6)D^3]. \quad (6)$$

The residual contribution, $s_2'$, explicitly accounts for the decrease of the pair entropy associated with the onset of interparticle correlations at short and medium-range distances. For parallel spherocylinders, a further separation of this term into a translational and an orientational contribution as done in [1] does not make much sense.

The total excess entropy of the nematic fluid can be evaluated upon integrating the equation of state (EoS):

$$s_{ex}(\rho) = s_{ex}(\bar{\rho}) - \int_\bar{\rho}^\rho \left[ \frac{\beta P}{\rho'} - 1 \right] \frac{d\rho'}{\rho'}. \quad (7)$$

In Eq. (7) $P$ is the pressure, $\beta$ is the inverse temperature in units of the Boltzmann constant, and $\bar{\rho}$ is the density of a suitably chosen reference state. The EoS of the fluid was obtained through a Monte Carlo sampling of the system at different pressures, while the quantity $s_{ex}(\bar{\rho})$ was calculated using the Widom test-particle insertion method [12, 14] in order to calculate the excess chemical potential, $\mu_{ex}$, at low enough densities. The excess entropy can then be obtained through the thermodynamic equation:

$$s_{ex} = -\beta \mu_{ex} + \frac{\beta P}{\rho} - 1. \quad (8)$$

III. SIMULATION

We investigated the phase diagram of a system of parallel hard spherocylinders with elongation $L/D = 5$, spanning a density range which goes from a rather dilute nematic state up to the smectic transition threshold. We carried out Monte Carlo (MC) simulations at constant pressure as is usual for systems of non-spherical hard-core particles where it may be difficult to calculate the equation of state in a constant-volume simulation through the contact values of the distribution functions [16].

The typical sample was composed of $N = 1500$ particles, aligned along the $z$ axis and enclosed in an orthorhombic box with edges $L_x = L_y = 1/3L_z$. In order
to quantify the influence of the size of the system as well as of the shape of the simulation box, we also investigated the behavior of a system composed of 500 particles aligned along the main diagonal of a cubic box and of a fluid of 768 particles enclosed in an orthorhombic cell with the same relative dimensions used for the main sample.

All thermodynamic states at constant pressure were sequentially generated from a translationally disordered low-density configuration upon gradually compressing the nematic fluid. The equilibration period was typically $10^5$ MC cycles, a cycle consisting of an attempt to change sequentially the center-of-mass coordinates of each molecule followed by an attempt to modify the volume of the sample. Simulation data were obtained by generating chains consisting of $5 \times 10^5 - 20 \times 10^5$ MC cycles, depending on the pressure. Equilibrium averages and standard deviations were computed by dividing chains into independent blocks. During the production runs, we cumulated different histograms of the PDF. In particular, $g(r, \vartheta)$ was sampled at intervals $\Delta r$ and $\Delta \vartheta$ of 0.05$D$ and $1^\circ$, respectively. Different choices of $\Delta r$ and $\Delta \vartheta$ were investigated for $P^* = 1.0$ and $P^* = 2.0$. As for the Widom insertion method, 100 trial insertions per MC cycle turned out to be sufficient to insure a stable statistics for the excess chemical potential of the fluid.

In the presentation of the results, we shall refer to the reduced density $\rho^* = \rho/\rho_{cp}$, where $\rho_{cp} = 2/(\sqrt{2} + (L/D)\sqrt{3})$ is the maximum density attained by parallel spherocylinders at close packing, and to the reduced pressure $P^* = \beta PV_{hs}$. The current MC results for the EoS of the model are presented in Fig. 1. The comparison between the data collected for 1500 particles (in an orthorhombic box) and those for 500 particles (in a cubic box) shows that the EoS of the fluid is rather weakly affected by the size of the sample only at high densities. The results for 768 particles in an orthorhombic box were not reported in the graph since they can be hardly resolved from those pertaining to the largest size investigated. The present EoS is in good agreement with that computed by other authors over the whole density range explored, apart from a modest deviation, at high densities, from the molecular dynamics results obtained by Veerman and Frenkel. Both these authors as well as Stroobants and coworkers noted a weak change of slope in the EoS at $P^* \approx 2.47$. Fully developed arrangements of several well-separated smectic layers distributed along the $z$ direction are clearly visible for $P^* = 2.50$ and $\rho^* \approx 0.49$. Instead, the transversal arrangements of the spherocylinders along the $x$-$y$ plane look disordered in all states investigated (compare left and right panels in Fig. 2).

We show in Fig. 3 the excess entropy of the fluid plotted as a function of the reduced density. The data were obtained using both the thermodynamic integration of Eq. 7 as well as Widom’s ghost-particle method implemented at moderately low densities. We also show the datum recently reported by Koda and Ikeda which was obtained using a multistage Widom test, based on the gradual insertion of a ghost particle with a variable shape. The modest discrepancy between this finding and the present results is likely due to the multistage method, that is known to work better at high densities. On the other hand, our results for the excess entropy are closely interpolated by the expression obtained upon integrating the five-term virial fit of the EoS reported in 7.

The PDF of the fluid, $g(r, \vartheta)$, was plotted in Fig. 1 as a function of $\vartheta$ for a set of interparticle distances at increasing pressures across the transition point ($P^* \approx 2.2$). We note, for separations $r < L + D$, the existence of a forbidden range around $\vartheta = 0$ and $\pi$ that is due to the overlap of two spherocylinders. This correlation gap decreases with increasing intermolecular separations. The maximum attained by $g(r, \vartheta)$ corresponds to the hard-core contact between spherocylinders and its height consistently decreases with increasing interparticle distances. For $r \geq L + D$, the entire angular range between $0$ and $\pi$ can be sampled by a second spherocylinder. Of course, there is a blow up of the contact value of the PDF for $\vartheta = 0, \pi$, which progressively decreases for increasing distances. An increase of the pressure enhances the overall structure of the PDF; however, no specific signature of the nematic-smectic transition can be detected in the resulting modification of the PDF.

Upon plugging the PDF into Eq. 4, we obtained the pair entropy that was plotted together with the excess entropy in Fig. 4 as a function of the density. The RMPE exhibits a change of sign from negative to positive values for $\rho^* \approx 0.453$. This threshold practically coincides with the currently accepted nematic-smectic transition density.
The simulations carried out for 500 particles enclosed in a cubic box show a similar behavior of the RMPE whose morphology is not substantially modified with respect to that of 1500 spherocylinders in an orthorhombic box. This finding is noteworthy in that it demonstrates the high sensitivity of the RMPE to the structural changes occurring in the fluid, irrespectively of the difficulty to accommodate a well resolved smectic layering in a relatively small cubic box.

Figure 6 shows the quantity that, upon integration, yields the pair entropy in Eq. (4). For very short interparticle distances the $\vartheta$ range which can be sampled by two neighboring particles is rather limited. As a result, angular correlations are strong and give rise to the deep well in the integrand function. A steady modulated increase follows up to $r = L + D$ where a negative jump witnesses the onset of new strong correlations between spherocylinders lying on top or below the central reference particle. This effect is the integrated counterpart of the behavior that was already discussed for $g(r, \vartheta)$ in Fig. 4.

The pair entropy was finally resolved into an excluded-volume and a correlation term in Fig. 7 (see Eq. 5). It is clear that the second-order virial term cannot account by itself for the crossover between $s_{\text{ex}}$ and $s_2$ that is indicative of the smectic ordering of the nematic fluid.

As for the numerical reliability of the current results, we note that the statistics cumulated on $g(r, \vartheta)$ was such that a smooth integration over the sampled points yielded stable values for $s_2$, the dispersion being always lower than a percent of the average value. However, we observed a moderate sensitivity of the angle-dependent quantities in Eq. (4) on the resolution of the angular width $\Delta \vartheta$. In order to gain a better insight into the numerical accuracy of the calculations, we performed a series of test runs for two different pressures ($P^* = 1.0$ and 2.0) with several $r$ and $\vartheta$ grid meshes. The tests were reported in Fig. 8 where the higher sensitivity of $s_2$ on the angular grid size — as compared with the radial one — is quite manifest. We estimated, in the limit of $\Delta r, \Delta \vartheta \rightarrow 0$, an asymptotic shift of $s_2$ toward lower values not larger than 2%. As a result, we expect a comparable shift of the transition threshold signalled by the RMPE to lower densities.

V. CONCLUDING REMARKS

In this paper we have analyzed the residual multiparticle entropy (RMPE) of parallel hard spherocylinders with aspect ratio $L/D = 5$ across the nematic-smectic transition. The correspondence between the intrinsic ordering threshold detected through the vanishing of the RMPE ($\rho^* \approx 0.453$) and the independently ascertained phase-transition density ($\rho^* = 0.46$) is quantitative. It also turned out that the indication of the zero-RMPE criterion is not significantly affected by the size and shape of the simulation box, even when the smectic layering of the fluid cannot be easily accommodated in the sample as is the case of a small cubic box. This finding further corroborates the sensitivity of the RMPE to the ordering of the fluid on a local scale.

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FIG. 1: Equation of state of parallel hard spherocylinders with aspect ratio $L/D = 5$. Line with solid circles and crosses: this work for $N = 1500$ and $N = 500$ molecules, respectively. Triangles, squares and diamond: simulations by Veerman and Frenkel [8], Stroobants and coworkers [7], and Koda and Ikeda [9], respectively. The error bars are systematically smaller than the size of the markers.
FIG. 2: Snapshots of equilibrated configurations for (from top to bottom) $P^* = 2.50 \ ((\rho^* = 0.23))$, $P^* = 2.30 \ ((\rho^* = 0.44))$, $P^* = 2.00 \ ((\rho^* = 0.47))$, and $P^* = 0.50 \ ((\rho^* = 0.49))$. Left panels: projections of the centers of mass of the spherocylinders onto the $x-y$ plane. Right panels: configurations along the $z$ axis.
FIG. 3: Excess entropy plotted as a function of the reduced density. Line with solid circles: this work with $N = 1500$; diamonds: Widom insertion-method estimates. Square: multistage Widom test [9]. Dashed line: excess entropy evaluated by integration of the five-term virial fit of the simulation data of Ref. [7]. The vertical line indicates the nematic-smectic transition threshold according to Ref. [7] and [8].
FIG. 4: Pair distribution function $g(r, \theta)$ plotted as a function of $\theta$ for different distances $r/D$ and for increasing pressures.
FIG. 5: Residual multiparticle entropy (circles) resolved into the excess (squares) and pair (solid diamonds) contributions. Lines are smooth interpolations of the simulation data.

FIG. 6: Integrand function appearing in Eq. (4), after integration over $\vartheta$, plotted for several pressures.
FIG. 7: Pair entropy (diamonds) resolved into the excluded-volume (circles) and correlation (squares) contributions (see Eq. (5)). Lines are smooth interpolations of the simulation data.

FIG. 8: The pair entropy $s_2$ plotted as a function of the grid mesh parameter $\Delta \theta$ and for several choices of $\Delta r$, for $P^* = 1.00$ (solid symbols) and $P^* = 2.00$ (open symbols). Triangles, $\Delta r = 0.10D$; circles, $\Delta r = 0.05D$; squares $\Delta r = 0.02D$. 