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Simulating polymer liquid crystals

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Abstract. A model suitable for simulating lyotropic polymer liquid crystals (PLCs) is described. By varying the persistence length between infinity and 25, the effect of increasing flexibility on the nematic–smectic transition of a PLC with a length-to-width ratio $L/D = 6$ is investigated. It is found that increasing flexibility shifts the formation of a smectic phase to higher densities. Comparison is made with a recent theory of the nematic–smectic transition of slightly flexible rods.

1. The model

In the 1940s, Onsager [1] showed that thin hard rods (with length-to-width ratio $L/D \rightarrow \infty$) can form a nematic phase at high enough densities. Subsequently, theories and computer simulation of a variety of hard-body models of liquid crystals showed that excluded volume effects could account not only for the stability of nematics but also for the existence of smectic and columnar liquid crystalline phases [2–5]. However, in reality, liquid-crystal-forming particles invariably exhibit some degree of flexibility. The effect of flexibility on the isotropic–nematic transition of rod-like particles has been investigated both theoretically [6–9] and by computer simulation [10–13]. The mesogen is modelled as a smooth semiflexible chain with a bending energy, which gives rise to a characteristic length P , the persistence length, over which the chain loses memory of its orientation. When $L \gg P$, the chain is properly a polymer liquid crystal (PLC), with a shape that is dramatically dependent on the state of order; when $L \ll P$, the chain can be considered a slightly flexible rod. Even when the degree of flexibility is slight, the properties of the system deviate significantly from those of the idealized rod model. The location of the isotropic–nematic phase transition moves to higher concentrations, and the phase gap decreases with increasing flexibility [13].

The effect of flexibility on the nematic–smectic transition is, as yet, unclear. Recent theoretical work [14] valid for the limit $P \gg L \gg D$ (i.e. flexible rods) indicates that the smectic phase occurs at a higher density with increasing flexibility, and that the layer spacing decreases with increasing flexibility. It was also tentatively speculated that the smectic phase may become unstable for chains more than several deflection lengths long. More highly ordered mesophases may be formed in preference to the smectic phase, i.e. a columnar phase. Suspensions of tobacco mosaic virus ($L/P < 0.1$) and fd virus ($L/D \simeq 0.4$) have a smectic phase [15], whereas DNA fragments ($L/P \simeq 1$) form a columnar phase at high densities [16].

The aim of this work is to use computer simulation to investigate the effect of flexibility on the nematic–smectic transition of lyotropic semiflexible rods. Essentially, we adopt the model studied by Dijkstra and Frenkel [13]. A chain is modelled as N spherocylinders of length $l = L/N$, width D and orientation \mathbf{u}_i , joined end over end to form a chain of fixed length. A bending force acts on each of the $N - 1$ joints in the chain to give the chain rigidity. The energy of joint i is given by

$$E_i = \frac{C}{l} (1 - \mathbf{u}_i \cdot \mathbf{u}_{i+1}). \quad (1)$$

C is the bending energy which, for an isolated chain, is related to the persistence length via $P = C/k_B T$. In the limit of small angles, (1) reduces to the more familiar $E_i = \frac{1}{2} C \theta_{i,i+1}^2 / l$ used by Dijkstra and Frenkel, where $\theta_{i,i+1}$ is the angle between the two spherocylinders. The model has the advantage that the persistence length is easily controlled (in contrast with the model of [12]), and in the limit $P \rightarrow \infty$ the chain behaves as a rigid smooth rod, providing contact with existing simulation and theoretical results. Dijkstra and Frenkel used configurational bias Monte Carlo techniques to move the chains, an efficient scheme for densities in the region of the isotropic–nematic transition. At higher densities this scheme becomes unworkable; the system is just too dense to allow any Monte Carlo move to be accepted. In order to use time-stepped molecular dynamics, which is much more efficient than any Monte Carlo technique at high densities, we ‘soften’ the hard spherocylinder. Our soft spherocylinders are described using a Kihara [17] potential. Particles interact via a pair potential that depends on the distance c of closest approach of two convex bodies. When the convex body is a line segment and the pair potential is

$$U(c) = \begin{cases} \infty & \text{for } c < D \\ 0 & \text{for } c > D \end{cases}$$

the Kihara potential describes hard spherocylinders of width D . We choose

$$U(c) = \begin{cases} 4\varepsilon \left[\left(\frac{D}{c}\right)^{12} - \left(\frac{D}{c}\right)^6 + \frac{1}{4} \right] & \text{for } c/D < 2^{1/6} \\ 0 & \text{for } c/D > 2^{1/6} \end{cases}$$

i.e. the WCA potential, where D is our unit of length. The forces and torques at the closest approach distance are then derived from this potential. Tests showed that equations of state for spherocylinders interacting via this potential (with $k_B T/\varepsilon = 1$) is extremely close to those of hard spherocylinders [5].

2. Results

Results are presented for a system consisting of 832 polymers of four segments, with $L/D = 6$, at a fixed temperature $k_B T/\varepsilon = 1$. P was varied between infinity and $25D$. A constant chain length was maintained by constraint dynamics, and the temperature maintained using Nosé–Hoover thermostats [18]. In order to ensure that the pressure tensor was isotropic, the box shape was varied using a standard Metropolis Monte Carlo procedure. Henceforth we shall adopt $D = 1$ as our unit of length and define the reduced density $\rho = n/n_{cp}$ where n is the number density, and $n_{cp} = 2/(\sqrt{2} + (L/D)\sqrt{3})$ is the density of regular close packing of hard spherocylinders.

The equation of state in the vicinity of the nematic–smectic transition was calculated for a system of rods (i.e. $P = \infty$), by slowly compressing a low-density isotropic phase,

and by slowly expanding a high density HCP solid of four layers of 208 particles. The nematic–smectic transition appears very weakly first order, indicated by a slight hysteresis in the equation of state. The transition occurs between $\rho = 0.50$ and $\rho = 0.52$, in broad agreement with the results of Bolhuis and Frenkel [5] for hard spherocylinders. Configurations generated by expansion contained four smectic layers aligned along the z direction. An analysis of the layer structure shows liquid-like order: the smectic is a smectic A phase.

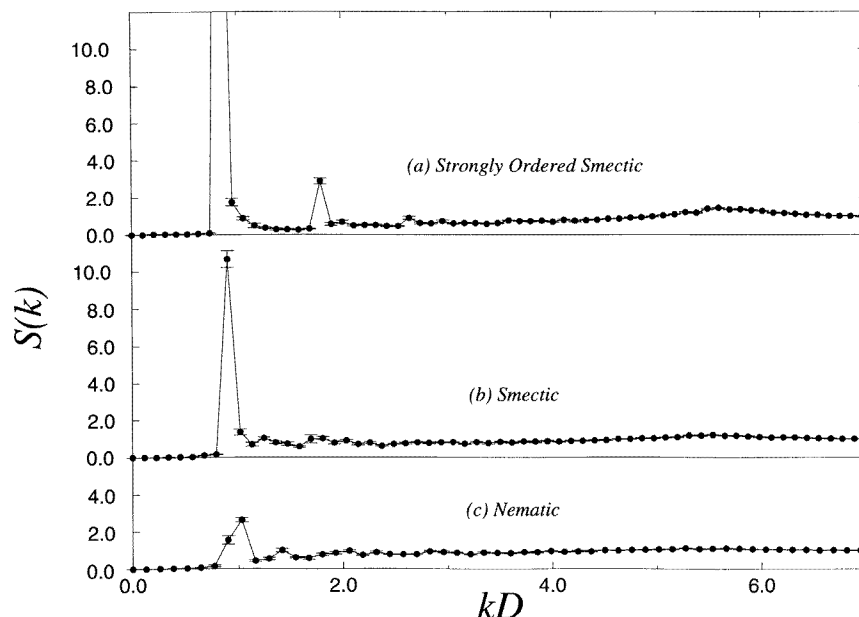


Figure 1. The radially averaged structure factor $S(k)$ versus kD for a system with $L/D = 6$, $P = 100$ at three different densities. (a) $\rho = 0.56$ is a strongly ordered smectic. The large peak at $kD = 0.844$ corresponds to a well established smectic layering in the z direction with spacing $7.44D$. The broad peak at $kD \simeq 6$ is indicative of local ordering within the layers. (b) $\rho = 0.54$ is a smectic phase with less established layering. (c) $\rho = 0.52$ is a nematic phase with strong smectic fluctuations.

Eight configurations from the expansion branch of the equation of state were used as starting configurations for the polymer simulations, at reduced densities 0.49–0.56. Four different persistence lengths, $L = 200, 100, 50$ and 25 , were simulated. It was found that, in general, increasing the flexibility of the polymer moves the nematic–smectic transition to higher densities with a consequent decrease in the layer spacing of the smectic. The classification of the phases as nematic and smectic presents some difficulties. Owing to the small number of state points simulated, it was impossible to decide from the equations of state whether a given state point was nematic or smectic. In high-density nematic phases, long-lived smectic fluctuations develop and grow in amplitude with increasing density, giving rise eventually to a well defined smectic state. This is seen in a plot of the radially averaged structure factor $S(k)$. Figure 1 shows $S(k)$ versus kD for $P = 100$, at densities of 0.56, 0.54 and 0.52. At $\rho = 0.56$, the system is clearly smectic. There is a strong peak at $kD = 0.844$, indicating layers with a spacing of $d = 2\pi/k = 7.44D$. Two subsequent harmonics are also visible: the layering is well established. There is also a broad peak at

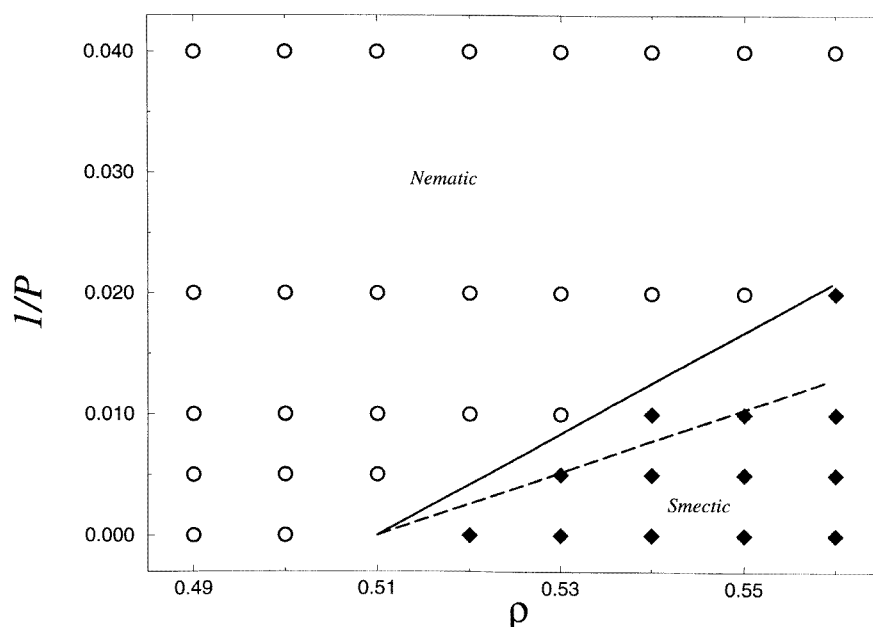


Figure 2. The phase diagram. The inverse persistence length $1/P$ is plotted against reduced density ρ . Nematic points are denoted by open circles, and smectic points by full diamonds. The lines are two theoretical estimates of the nematic–smectic spinodal instability, the full curve for a value of $\beta = 0.0236$, and the broken curve for $\beta = 0.0381$; see text.

below $kD \simeq 6$, indicative of local ordering within the layers. Visual inspection confirms that this is a strongly ordered smectic phase. At $\rho = 0.54$, the layering is still pronounced, and again a visual inspection confirms this to be a smectic phase. For $\rho = 0.52$, the situation is less clear; the peak in $S(k)$ is much smaller and visual inspection shows something that might be a nematic phase with strong smectic fluctuations. A plot of the density as a function of the z coordinate (i.e. along the axis of the smectic) confirms that $\rho = 0.52$ is probably a nematic phase. On the basis of visual inspection, the projected density and the radially averaged $S(k)$, it was decided (arbitrarily) that state points with a maximum value of $S(k) = S_{max}(k) > 5$ would be deemed smectic. This classification gives the phase diagram (figure 2). Smectic state points are indicated by full diamonds, and nematic points by open circles. The lines are two estimates for the phase boundary determined from the work of van der Schoot [14]. The nematic–smectic spinodal line is given by

$$\rho = \rho_0 \left(1 + \beta \frac{L\alpha_0}{P} \right)$$

where β is a constant; ρ_0 is the corresponding spinodal for the rigid rod system and α_0 is related to the deflection length in the rod limit [8]. Setting $\rho_0 = 0.51$, and measuring $\alpha_0 = 33$ from the orientational distribution function for rods at $\rho = 0.51$, we obtain the two lines in figure 2; the full curve with $\beta = 0.0236$ is obtained from analysis of the free energy, and the broken curve with $\beta = 0.0381$ is obtained from $S(k)$. The agreement (probably fortuitous) is surprisingly good for $\beta = 0.0236$.

In conclusion we have observed that increasing the flexibility of liquid crystalline molecules increases the density at which a smectic phase is formed and decreases the

smectic layer spacing, in agreement with [14]. It may be that for sufficiently flexible chains the smectic phase is completely suppressed and other, more highly ordered phases such as the columnar phase appear. To date, however, we have no evidence that this occurs. At much higher densities, $\rho = 0.7$, for all the values of P studied here, the smectic phase is always mechanically stable with respect to the columnar. States prepared in a columnar phase relax to a smectic in a relatively short time (several tens of thousands of molecular dynamics time steps). Simulations of longer chains $L/P \simeq 1$ are currently in progress.

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