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## Smectic phases in rod–coil diblock copolymers

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### Abstract

A fluid of rod–coil diblock copolymers, modelled as wormlike chains, is treated by using self-consistent field theory. The ‘rod’ and ‘coil’ sections of each molecule are distinguished by their degrees of flexibility (or persistence lengths), but are otherwise identical. Interactions between molecules are taken to be of the excluded-volume type, described by the Onsager second-virial approximation. The theory is applied to liquid-crystalline phases which are either uniform (i.e., isotropic and nematic) or exhibit a uniaxial one-dimensional spatial variation (smectic-A). This work extends an earlier study (Düchs and Sullivan 2002 *J. Phys.: Condens. Matter* **14** 12189) to account for the smectic-A phase at arbitrarily large values of the relative rod fraction. The smectic phase is found to have a partial bilayer morphology, exhibiting nearly complete interdigitation of the rod-like sections and little interdigitation of the coil sections.

Fluids of rod–coil diblock copolymers, each consisting of a rigid-rod block bonded to a flexible coil block, exhibit a rich self-assembly and phase behaviour and have attracted extensive experimental [1–5] and theoretical [6–10] interest. Most of the theoretical studies have employed both a rod–rod steric interaction (which induces liquid-crystalline ordering of the rods) and a Flory–Huggins rod–coil interaction which favours segregation of the rod from the coil components. An alternative model was recently introduced [11], which considered only steric (excluded-volume) interactions between all components of the molecules and distinguished the ‘rods’ from ‘coils’ by their differing degrees of flexibility<sup>4</sup>. While this athermal repulsive-interaction model is more directly applicable to lyotropic colloidal systems, such as suspensions of viral particles [14, 15], it can be extended to take account of attractive interactions [13]. When the relative fractions of rod and coil segments are comparable, the

<sup>4</sup> A closely related diblock model has been described by Wessels and Mulder [12] which considers that all components of a molecule (modelled as a freely jointed chain) have the same flexibility while distinguishing the two block components by their lengths and diameters.

theory in [11] was shown to produce lamellar smectic-A phases, somewhat analogous to the occurrence of microphase separation in other models of diblock copolymers [12, 16]. Moreover, the results presented in [11] were in agreement with a density-functional treatment by Holyst [17] of rigid ‘nail-shaped’ molecules, and with Monte Carlo studies by Mazars *et al* [18] of short molecules containing a rigid core and a semiflexible tail.

The study in [11] was based on the wormlike chain model [19] for spatially nonuniform fluids of semiflexible polymers. This is a widely used coarse-grained model for such polymers, neglecting chemical details of the monomers making up a polymer chain and representing a macromolecule by a continuously deformable elastic filament. Following the work of Semenov and Khokhlov [13], excluded-volume interactions between molecules were treated within the Onsager second-virial approximation, while the model was studied by using a well-established self-consistent field theory (SCFT) formalism [16, 20–23]. The SCFT treatment of smectic phases in [11] was limited to systems having comparable fractions of rod and coil segments. This treatment has been recently extended [24] to examine smectic-A formation in a system of homopolymers, each having a uniform degree of rigidity. It was shown that a contribution (omitted in [11]), due to excluded-volume interactions between ‘terminal’ chain segments and interior segments, can also provide a physical mechanism that leads to formation of smectic phases. The aim of the present work is to apply the extended model [24] to rod–coil diblock molecules.

We consider a monodisperse fluid of  $n$  rod–coil diblock copolymers, each of total contour length  $L$  and diameter  $D$ , occupying a total volume  $V$ . The molecular number density  $n/V$  is denoted  $\rho$ . A fraction  $f$  of the total contour length of each copolymer is occupied by relatively rigid (rod) segments, and the remaining fraction by more flexible (coil) segments. In accord with the wormlike chain model for semiflexible chains [16, 19–23, 25, 26], a polymer is treated as a space curve  $\mathbf{r}(t)$  characterized by dimensionless unit tangent vectors  $\mathbf{u}(t)$ , with  $t$  varying between 0 and 1. We will use the (arbitrary) convention that the range  $0 < t < f$  is occupied by rigid segments, and the remainder by flexible segments. Here  $f$  is regarded as a parameter, and later we will present a phase diagram of the system in terms of  $f$ . The rigid and flexible blocks are distinguished solely by their values of the rigidity parameter  $\xi(t)$  depending on the contour variable  $t$ , which equals the persistence length of the corresponding chain section in units of the total contour length  $L$  [16]. This is where the difference between the rigid and flexible blocks of the copolymers enters.

In mean field theory, the Helmholtz free energy functional of the system is given by

$$\beta F = \beta F_{\text{int}} + \int D\{\mathbf{r}, \mathbf{u}\} \rho_m(\{\mathbf{r}, \mathbf{u}\}) [\ln(\rho_m(\{\mathbf{r}, \mathbf{u}\})) + \beta U(\{\mathbf{r}, \mathbf{u}\}) - 1]. \quad (1)$$

Here  $\rho_m(\{\mathbf{r}, \mathbf{u}\})$  is the single-molecule probability distribution function, which satisfies the normalization condition,

$$\int D\{\mathbf{r}, \mathbf{u}\} \rho_m(\{\mathbf{r}, \mathbf{u}\}) = n, \quad (2)$$

where the notation  $\{\mathbf{r}, \mathbf{u}\}$  stands for the position  $\mathbf{r}$  and orientation  $\mathbf{u}$  of all segments of a chain molecule [24]. The function  $F_{\text{int}}$  in equation (1) is the contribution of intermolecular interactions to the free energy, while  $U(\{\mathbf{r}, \mathbf{u}\})$  accounts for all ‘one-body’ potentials, including those due to internal bond-bending energies plus any external fields.

As in [11], we assume that the interactions between any type of segment (either rod-like or coil-like) are the same. Following [13], based on the Onsager second-virial approximation for excluded-volume interactions between molecules, the free energy due to these interactions can be derived on representing a wormlike chain by a sequence of  $L/\lambda$  linear segments of length  $\lambda$ , where the latter length is much smaller than the corresponding persistence length.

The interaction free energy is then given by, independent of  $\lambda$  [24]<sup>5</sup>:

$$\begin{aligned} \beta F_{\text{int}} = & \frac{\rho^2}{2} \int d\mathbf{r} \int d\mathbf{u} \int d\mathbf{u}' V(\mathbf{u}, \mathbf{u}') \phi(\mathbf{r}, \mathbf{u}) \phi(\mathbf{r}, \mathbf{u}') \\ & + \rho^2 \int d\mathbf{r} \int d\mathbf{u} \int d\mathbf{u}' V_{\text{ce}}(\mathbf{u}, \mathbf{u}') \phi(\mathbf{r}, \mathbf{u}) \\ & \times [\psi(\mathbf{r}, \mathbf{u}', t = 0) + \psi(\mathbf{r}, \mathbf{u}', t = 1)]. \end{aligned} \quad (3)$$

For any value of  $t$ , the function  $\psi$  represents the dimensionless segment probability density defined by

$$\psi(\mathbf{r}, \mathbf{u}, t) = \frac{1}{\rho} \int D\{\mathbf{r}, \mathbf{u}\} \rho_m(\{\mathbf{r}, \mathbf{u}\}) \delta(\mathbf{r} - \mathbf{r}(t)) \delta(\mathbf{u} - \mathbf{u}(t)), \quad (4)$$

while  $\phi(\mathbf{r}, \mathbf{u})$  is the dimensionless contour-averaged total segment density, related to  $\psi(\mathbf{r}, \mathbf{u}, t)$  by

$$\phi(\mathbf{r}, \mathbf{u}) = \int_0^1 dt \psi(\mathbf{r}, \mathbf{u}, t), \quad (5)$$

which satisfies the normalization condition

$$\int d\mathbf{r} d\mathbf{u} \phi(\mathbf{r}, \mathbf{u}) = V. \quad (6)$$

The first term of equation (3) gives the interaction potential between cylindrical segments in a ‘single-contact’ approximation [12], where  $V(\mathbf{u}, \mathbf{u}')$  is given by (in the Onsager second-virial approximation)  $V(\mathbf{u}, \mathbf{u}') = 2DL^2|\mathbf{u} \times \mathbf{u}'|$ . The second term of equation (3) is the correction introduced in [24], accounting for interactions due to overlap between the ‘cylindrical’ bodies of each molecule (c) with the ‘terminal (or end)’ segments (e) of the other molecules. For capped spherocylinders,  $V_{\text{ce}}$  is given by the constant  $V_{\text{ce}}(\mathbf{u}, \mathbf{u}') = \pi LD^2/2$  [24]. This interaction favours segregation of the polymer terminal segments from the interior cylindrical segments, leading to aggregation of each separate type of segment and hence formation of a smectic phase in a fluid of homogeneous molecules. Its occurrence is analogous to that of separate ‘head group’ and ‘tail segment’ densities in theories of lipid polymorphism [27, 28].

The equilibrium distribution function is obtained by minimizing  $F$  with respect to  $\rho_m(\{\mathbf{r}, \mathbf{u}\})$ , subject to the constraint in equation (2), which as usual can be taken into account by means of a Lagrange multiplier. The functions  $\psi(\mathbf{r}, \mathbf{u}, t)$  and  $\phi(\mathbf{r}, \mathbf{u})$  can be expressed in terms of conditional chain-end distribution functions or propagators  $q(\mathbf{r}, \mathbf{u}, t)$  and  $q^\dagger(\mathbf{r}, \mathbf{u}, t)$  as

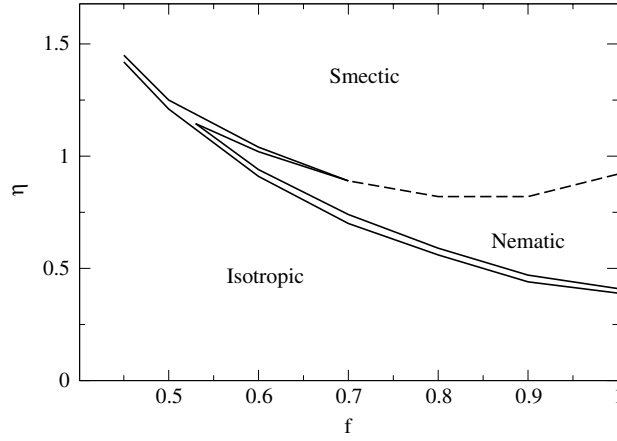
$$\psi(\mathbf{r}, \mathbf{u}, t) = \frac{V}{Q} q(\mathbf{r}, \mathbf{u}, t) q^\dagger(\mathbf{r}, \mathbf{u}, t), \quad (7)$$

where  $Q$  is the single-molecule partition used for satisfying equation (6). As shown in [24], the resulting diffusion-like equations for the propagators  $q(\mathbf{r}, \mathbf{u}, t)$  and  $q^\dagger(\mathbf{r}, \mathbf{u}, t)$  have the same form used in earlier theories [11, 16, 25], namely

$$\frac{\partial}{\partial t} q(\mathbf{r}, \mathbf{u}, t) = \left[ -L\mathbf{u} \cdot \nabla_{\mathbf{r}} + \frac{1}{2\xi(t)} \nabla_{\mathbf{u}}^2 - w(\mathbf{r}, \mathbf{u}) \right] q(\mathbf{r}, \mathbf{u}, t), \quad (8)$$

$$\frac{\partial}{\partial t} q^\dagger(\mathbf{r}, \mathbf{u}, t) = \left[ -L\mathbf{u} \cdot \nabla_{\mathbf{r}} - \frac{1}{2\xi(t)} \nabla_{\mathbf{u}}^2 + w(\mathbf{r}, \mathbf{u}) \right] q^\dagger(\mathbf{r}, \mathbf{u}, t), \quad (9)$$

<sup>5</sup> Since repulsive excluded-volume interactions between molecules are explicitly included in this model, we do not impose an ‘incompressibility’ condition to account for hard-core packing effects.



**Figure 1.** Phase diagram for rod-coil copolymers, for  $L/D = 10$ . Solid lines correspond to first-order transitions, while the second-order part of the nematic-smectic transition is indicated by the dashed line.

where the ‘mean field’  $w(\mathbf{r}, \mathbf{u})$  is given by

$$w(\mathbf{r}, \mathbf{u}) = \rho \int d\mathbf{u}' V(\mathbf{u}, \mathbf{u}') \phi(\mathbf{r}, \mathbf{u}') + \rho \int d\mathbf{u}' V_{ce}(\mathbf{u}, \mathbf{u}') [\psi(\mathbf{r}, \mathbf{u}', 0) + \psi(\mathbf{r}, \mathbf{u}', 1)]. \quad (10)$$

The initial conditions on the propagators  $q(\mathbf{r}, \mathbf{u}, t)$  and  $q^\dagger(\mathbf{r}, \mathbf{u}, t)$  are

$$q(\mathbf{r}, \mathbf{u}, t \rightarrow 0) = q^\dagger(\mathbf{r}, \mathbf{u}, t \rightarrow 1) = e^{-w_q(\mathbf{r}, \mathbf{u})}, \quad (11)$$

where

$$w_q(\mathbf{r}, \mathbf{u}) = \rho \int d\mathbf{u}' V_{ce}(\mathbf{u}, \mathbf{u}') \phi(\mathbf{r}, \mathbf{u}'). \quad (12)$$

Our solution of these self-consistent equations involves expansions of the various densities and fields in spherical harmonics. More details about the calculational procedure, for a uniaxial one-dimensional spatial variation, can be found in [11] and [24].

Here we present results for a fluid of copolymers with  $\xi_{\text{rigid}} \equiv \xi(0 < t < f) = 10$  and  $\xi_{\text{flex}} \equiv \xi(f < t < 1) = 0.1$ . In our calculations, we hold the value of the aspect ratio fixed at  $L/D = 10$ , while varying the rod fraction  $f$  from  $f = 0.45$  to 1.0. The overall number density is expressed in terms of the volume fraction  $\eta$  defined by [29]

$$\eta = \frac{\pi \rho L D^2}{4} \left( 1 + \frac{2D}{3L} \right). \quad (13)$$

The phase boundaries of this model are shown in figure 1 in terms of the volume fraction  $\eta$  and the parameter  $f$ . These phase boundaries are reflected by changes in the equilibrium structure indicated by the probability density  $\psi$ . The coexistence regions of first-order transitions have been obtained by applying double-tangent constructions to curves of the free energy per volume  $\beta F/V$  versus  $\eta$  [24]. On the other hand, for large  $L/D$  when  $f = 1$  (see [24]) and over a wide range of  $f < 1$  in the present case of  $L/D = 10$ , the nematic-smectic (N–A) transition is found to be second order. In these cases, the location of the N–A transition line  $\eta_c$  versus  $f$  was determined from the behaviour of the smectic order parameter  $O_{\text{sm}}$  defined in [11], by fitting this with a power law in the vicinity of  $\eta_c$  [24]

$$O_{\text{sm}} \sim (\eta - \eta_c)^{\frac{1}{2}}. \quad (14)$$

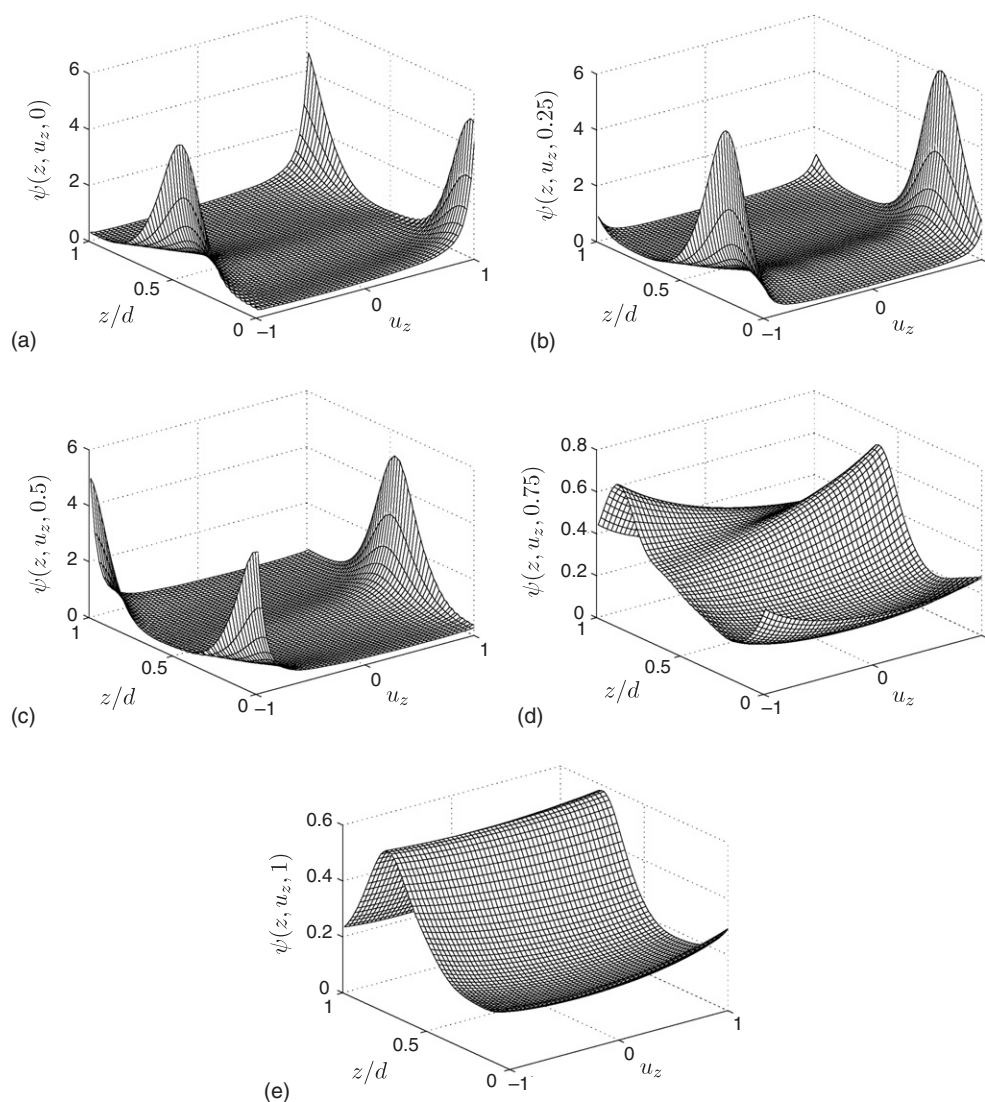
In the smectic phase, the densities  $\psi(\mathbf{r}, \mathbf{u}, t)$  and  $\phi(\mathbf{r}, \mathbf{u})$  are periodic functions of  $z$  with period denoted  $d$ . For this phase, all phase-boundary calculations employed the equilibrium value of the period, i.e., the value of  $d$  which minimizes the free energy per volume.

In the phase diagram of figure 1, we note that all values of  $f > 0.45$  are accessed, in contrast with [11]. At low volume fraction  $\eta$ , the weakness of the orientational interactions favours a disordered isotropic phase. A first-order isotropic–smectic transition is found for molecules which are predominantly flexible ( $f < 0.53$ ). This splits into separate isotropic–nematic and nematic–smectic branches for  $f > 0.53$ . The nematic to smectic phase transition occurs at higher values of  $\eta$ . For smaller values of  $f$ , this transition is first order, while it becomes second order following a tricritical point at  $f \approx 0.7$ . The solid and dashed lines in figure 1 define the first-order and second-order regions of this transition, respectively. In all cases, the optimal smectic periods are in the interval  $1.04 < d/L < 1.24$ . On increasing  $\eta$  at fixed  $f$  in the smectic phase, the equilibrium value of the period undergoes little change, while it notably increases on going from relatively flexible molecules ( $f = 0.45$ ;  $d/L = 1.04$ ) to rigid ones ( $f = 1$ ;  $d/L = 1.24$ ).

The occurrence of the isotropic phase at low volume fraction in figure 1 contrasts with an assumption used in many previous theoretical studies [6, 8, 10] (exceptions are [7, 9]), where an oriented nematic state is the reference uniform phase. For small rod fraction  $f$ , we find only a direct isotropic–smectic-A transition. Experimentally, this is a region where smectic-C and related ordered morphologies not considered in this work, as well as disordered micellar structures, have been found [2–4]. Figure 1 shows that there is a weak minimum in the nematic–smectic-A phase boundary of  $\eta$  versus  $f$ , as found earlier [11]. This is analogous to a general trend found in thermotropic rigid–flexible liquid crystals, as summarized in [30], as well as in rod–coil copolymers [9]. As  $f \rightarrow 1$ , the nematic–smectic phase boundary approaches that for homogeneous semiflexible polymers obtained in [24].

In the remainder of this paper, we focus on the structure of the smectic phase, as revealed by the probability distribution function  $\psi(z, u_z, t)$ , where  $u_z \equiv \cos(\theta)$  and  $\theta$  is the angle between a segment axis and the  $z$  axis. The distribution function is plotted versus  $z$  (over one period) and  $u_z$  at several values of  $t$  in figures 2(a)–(e), indicating the density of segments at the point  $t$  along a chain in terms of the segment position  $z$  and orientation  $u_z$ . These figures describe the case  $f = 0.5$  and volume fraction  $\eta = 1.4$ , well into the smectic region of the model, with corresponding equilibrium period  $d = 1.08L$ . Qualitatively similar behaviour is found at all other values of  $f$  and  $\eta$ . We see that, for the rigid sections of the molecule ( $t < f$ ) (figures 2(a)–(c)), the segment orientations are very strongly peaked parallel or antiparallel to the  $z$ -axis (i.e., values of  $u_z = \pm 1$  are favoured). A much weaker orientational anisotropy is indicated for the flexible segments (figures 2(d) and (e)).

Several features of figure 2 indicate that the smectic-A phase has the morphology of a partial bilayer structure. First, figure 2(a) shows that the maxima in the distributions  $\psi(z, u_z, t = 0)$  (i.e., at the rigid terminals) in opposite orientations  $u_z = \pm 1$  are separated by slightly less than half a period  $d$  (more precisely, by an amount  $0.42d = 0.45L$ , which is slightly smaller than  $L/2$ , the length of the rigid part of each molecule), indicating almost complete interdigitation of the rigid cores in opposite orientations. This conclusion is reinforced by figure 2(b) for  $t = 0.25$ , i.e., at the mid-points of the rigid parts, whose maxima in opposite orientations are at nearly equal values of  $z$ , that for  $u_z = 1$  being at slightly larger  $z$  than that for  $u_z = -1$ , by about  $0.02d$ . In figure 2(c), at the junction points  $t = 0.5$  between rigid and flexible parts, there again is a wide separation ( $0.48d = 0.52L$ ) between maxima in opposite orientations, slightly *larger* than the length of the rigid part. We also see that the maximum in the distribution of junction points ( $t = 0.5$ , figure 2(c)) in one orientation is near the maximum in the distribution of the  $t = 0$  points in the opposite orientation, consistent with

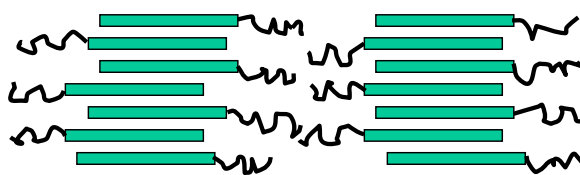


**Figure 2.** The distribution function  $\psi(z, u_z, t)$  of a smectic configuration with  $f = 0.5$ , for segments at different values of  $t$ , corresponding to a packing fraction  $\eta = 1.4$ , where the equilibrium period  $d = 1.08L$ .

nearly complete interdigitation of the rigid molecular cores in opposite orientations. This is shown schematically in figure 3, where perfect alignment of the rigid cores is assumed for simplicity, and agrees with computer simulation snapshots of the configurations of short rigid-flexible molecules with purely hard-core interactions [31].

On the other hand, the flexible tails show negligible interdigitation, in contrast with the earlier interpretation of [11]. This is first shown by the distribution  $\psi(z, u_z, t = 1)$  of the flexible terminals (see figure 2(e)), which is nearly symmetrical with respect to the orientation  $u_z$ , having maxima at almost identical (within numerical resolution) values of  $z$  for all values of  $u_z$ . Next, unlike the behaviour of the distribution of the midpoints of the rigid segments, the maxima of the midpoints of the flexible segments at  $t = 0.75$  (figure 2(d)) in opposite





**Figure 3.** Schematic diagram of the conformation of a partial bilayer deduced in this work. For simplicity, the rigid parts of the molecules are assumed to be perfectly aligned.

(This figure is in colour only in the electronic version)

orientations have a significant separation, which we find to be  $0.24d = 0.26L$  (now with the maximum for  $u_z = -1$  being at larger  $z$ ). We find that the overall end-to-end distance (between  $t = 0.5$  and 1) of the flexible parts of any single chain in its most favourable orientation is slightly greater than this,  $0.263d = 0.284L$ . The fact that this distance is considerably smaller than the contour length  $L/2$  of the flexible tails implies that the tails are significantly contracted due to bending fluctuations, rather than being interdigitated, as sketched in figure 3.

The finding that the smectic-A phase has a partial bilayer structure is consistent with that of [11], although the present results (interdigitation of the rod domains and a bilayer structure of the coil domains) are stronger than those deduced in [11]. We attribute this difference to the additional excluded-volume interactions contained in the present model. Such partial bilayer structures are not considered in earlier theories [6, 8], but are consistent with some of the structures observed experimentally in [2].

The main limitation of this work is its basis in the second-virial treatment of excluded-volume interactions, as noted previously [11, 24]. For example, this yields values of the volume fraction  $\eta$  at the smectic phase boundaries in figure 1 which are beyond those expected at physical close packing. High-density corrections beyond the second virial will be examined in future, as well as alternative numerical treatments, as the present treatment limits the study to small aspect ratios  $L/D \leq 10$ . In addition, it will be interesting to apply this model to liquid-crystalline phase transitions in confined geometries, as we have done recently in the case of homopolymers [32], a topic which is relevant to DNA packaging in viral capsids [33].

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