

Isotropic, nematic, and columnar ordering in systems of persistent flexible hard rods

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We extend previous work on the Khokhlov-Semenov approach to long-range order in solutions of persistent flexible main-chain polymers by including hexagonal columnar ordering. The description of long-range positional order uses a recent model developed for rigid rodlike particles, which is based on the tradeoff of translational entropy between liquidlike and crystal-like dimensions. For moderately flexible polymers, we find an isotropic-nematic-columnar phase sequence with increasing polymer concentration. As the polymers become more flexible, the isotropic-nematic transition recedes to higher concentrations, until finally, near the wormlike chain limit, a direct isotropic-to-columnar transition occurs. We show that the corresponding triple point occurs at longer persistence lengths for polymers of increasing contour length. In addition, we show that the longitudinal packing in the columnar phase becomes much tighter with increasing molecular flexibility to accommodate greater lateral freedom. Finally, we compare our theoretical equation of state with experimental measurements for poly-benzyl-L-glutamate (PBLG).

INTRODUCTION

It is well known that molecular flexibility plays an important role in the statistical thermodynamics of large liquid-crystal polymers. In many lyotropic systems, these polymers seem to be well described by "persistent flexibility," in which the polymers are considered homogeneously bend elastic along their contour. The degree of flexibility is usually described by a single quantity, the persistence length, which is a measure of the distance over which the orientations of two unit vectors tangential to the free polymer contour are correlated. Only if the ratio L/P , where L is the contour length and P is the persistence length, approaches zero, are the polymers well described as being rigid. The statistical mechanics for the rigid limit has been studied thoroughly in the past, starting with seminal work by Onsager [1]. At the other extreme, when L/P approaches infinity, the polymer may be considered a wormlike chain. In this limit, the statistical mechanics are also relatively straightforward because the thermal undulations along the chain are only correlated over distances that are short compared to the contour length (cf. [2] and references therein). However, realistic persistent flexible polymers are characterized by intermediate values of L/P , for which the statistical mechanics is more difficult.

Extending earlier work by Lifshitz [3], Khokhlov and Semenov [4] (KS) were able to calculate the mean-field orientational (or confinement) entropy of a persistent flexible cylindrical fiber for arbitrary L/P . Their result does not depend explicitly on the external potential confining the polymer but is given in terms of the distribution function $f(\mathbf{n}(\tau))$, where $\mathbf{n}(\tau)$ is a tangential unit vector at position τ along the polymer contour. By expanding their expression for the orientational entropy at the two limits $L/P \ll 1$ and $L/P \gg 1$, and by employing a second-order virial approximation of the hard-core interparticle interactions, KS obtained the isotropic-to-nematic coexistence densities, as well as the order parameter at the

transition. In their expansion of the orientational entropy, KS showed that just the two leading terms in each limit are sufficient to obtain quite accurate results for arbitrary L/P via interpolation. Subsequently, a number of authors have applied and extended these investigations to describe, for instance, the equation of state [5]–[7] and the nematic order parameter [8,7] of persistent flexible polymers at higher concentrations, the nematic behavior, induced chain rigidity, splay modulus, and other properties of uncharged and charged flexible polymer liquid crystals [2,9,10], and the effect of flexibility on the isotropic-to-nematic transition for solutions of monodisperse linear aggregates [11]. In general, the agreement of the theoretical results with the experimental data (when available) is quite satisfactory [2,5–8,12–14] and underscores the importance of molecular flexibility in this context.

As formulated, the KS approach does not describe the effects of persistent flexibility on translationally ordered lyotropic liquid-crystalline phases, such as smectic, columnar, or crystalline phases, which may succeed nematic phases as the concentration is increased. Examples of concentration-induced translational ordering are found in solutions of DNA [15–17] and PBLG [16,18]. Translational order is also well known in self-assembling systems, where amphiphilic molecules associate reversibly into elongated, polydisperse aggregates. In fact, in the experimental phase diagrams of such systems, translationally ordered phases usually dominate over purely orientationally ordered phases (e.g., [19] and references therein).

For these reasons, it is interesting to study, at least qualitatively, the effects of flexibility in the context of translational order. Here we take a step in this direction by combining a modification of the KS approach to persistent flexibility with a recent model for positional ordering in systems of rigid particles interacting via hard-core steric exclusion [20]. In many cases, hard-core repulsions seem to provide an adequate approximation of realistic interactions in lyotropic polymer solutions. Further-

more, they are sufficient to induce positional order in systems of rigid asymmetric particles (cf. [21,22] and references therein). For the sake of simplicity, we concentrate on monodisperse systems with the three types of ordering, i.e., isotropic, nematic, and columnar, that have been observed in solutions of PBLG (e.g., [16]) and DNA (e.g., [17]).

In this work, we calculate a phase diagram for hard flexible rodlike polymers in terms of polymer volume fraction v , polymer contour length L , and polymer persistence length P . If for a given L the rods are sufficiently stiff, i.e., P is sufficiently large, then we obtain an isotropic-to-nematic-to-columnar phase sequence with increasing volume fraction. As the rods become more flexible, however, the isotropic-to-nematic phase transition recedes progressively to higher concentrations. Finally, for a small enough P , the nematic phase disappears, and there is a direct transition from the isotropic to the columnar phase. With increasing L , the corresponding triple points shifts to larger values of P . However, as L approaches infinity, the triple-point value of P asymptotically approaches a finite value, so that for persistence lengths beyond this value there is always a stable nematic phase, even for an arbitrarily large contour length. This is consistent with a recent related calculation for infinite wormlike chains [23]. In addition, we find that in the columnar phase flexibility increases the packing density along the director to allow more freedom in the transverse directions. Finally, we compare our theoretical equation of state to experimental osmotic pressure data obtained for PBLG.

ISOTROPIC AND NEMATIC ORDERING OF PERSISTENT FLEXIBLE RODS

There are a variety of different approaches to the isotropic-nematic phase behavior of solutions of hard rigid rodlike particles. Many of these excluded volume theories are based on a dimensionless free energy per particle of the form

$$f = \mu_0 / (k_B T) + \ln c - 1 + \sigma + f_{\text{ex vol}}, \quad (1)$$

$$f_{\text{ex vol}} = A(v, L/D) + B(v, L/D)\rho. \quad (2)$$

Here $\mu_0 / (k_B T)$ is a dimensionless function of temperature, c is the particle number density, and σ is the orientational free energy. The steric particle interactions are incorporated in the excluded volume term, which depends on the volume fraction v , the particle axial ratio L/D , where D is the particle diameter, and the configurational integral

$$\rho = (4/\pi) \int d\mathbf{n} d\mathbf{n}' |\sin(\mathbf{n} - \mathbf{n}')| f(\mathbf{n}) f(\mathbf{n}'),$$

where $f(\mathbf{n})$ is the distribution function of the particle axial unit vector \mathbf{n} . The distinctions between different models (e.g., Onsager's second virial approximation, Alben's free-space model, or various scaled particle theories) are contained entirely in the functions A and B [24].

Khokhlov and Semenov [4] show that to good approximation, Eq. (1) formally also describes long persistent flexible main chain polymers interacting via purely steric

exclusion, if σ includes the orientational free energy due to polymer flexibility. Since their exact expression for σ is too complicated for the purpose of specific calculations, they consider expansions of σ at the stiff-rod and wormlike chain limits, i.e.,

$$\begin{aligned} \sigma &= \sigma_{\text{rigid}}^{(0)} + \frac{L}{P} \sigma_{\text{rigid}}^{(1)} \\ &= \int d\mathbf{n} f(\mathbf{n}) \ln f(\mathbf{n}) \\ &\quad + \frac{L}{12P} \int d\mathbf{n} [\nabla f(\mathbf{n})]^2 / f(\mathbf{n}) \text{ for } L/P \ll 1, \end{aligned} \quad (3)$$

$$\begin{aligned} \sigma &= \frac{L}{P} \sigma_{\text{wormlike}}^{(0)} + \sigma_{\text{wormlike}}^{(1)} \\ &= \frac{L}{8P} \int d\mathbf{n} [\nabla f(\mathbf{n})]^2 / f(\mathbf{n}) \\ &\quad - 2 \ln \int d\mathbf{n} [f(\mathbf{n})]^{1/2} \text{ for } L/P \gg 1, \end{aligned} \quad (4)$$

where ∇ is the gradient with respect to \mathbf{n} . Here $f(\mathbf{n})$ denotes an average along the polymer contour with respect to the orientational distribution of unit vectors \mathbf{n} tangential to the contour [note that $\int d\mathbf{n}$ is defined and $f(\mathbf{n})$ is normalized so that $\int d\mathbf{n} f(\mathbf{n}) = \int d\mathbf{n} = 1$]. Using the second virial approximation in the limit of large L (i.e., $A = 0$ and $B = vL/D$), KS give a detailed account of the coexistence densities and the nematic order parameter at the isotropic-to-nematic transition as functions of L/P [4].

However, in realistic systems much of the interesting phase behavior occurs at concentrations where the second virial approximation is inapplicable. In Ref. [5], the KS approach was therefore extended to higher concentrations in approximate fashion utilizing Lee's description of excluded volume effects for rigid spherocylinders [25]. Lee's approach is based on a generalization of the Carnahan-Starling description of the hard-sphere fluid via a functional scaling that decouples orientational and translational degrees of freedom for elongated particles. This procedure yields

$$A(v) = 4v \frac{1 - 3v/4}{(1 - v)^2} \quad (5)$$

and

$$B(v, L/D) = \frac{3}{2} v \frac{1 - 3v/4}{(1 - v)^2} \frac{(L/D)^2}{1 + \frac{3}{2} L/D}. \quad (6)$$

The relations (5) and (6) (cf. [5]) are approximately valid for persistent flexible polymers as well, because the steric repulsion governing the excluded volume manifests itself on a scale $O(D)$, on which the polymer is considered as a rigid cylinder. Additionally, in order to obtain results continuously for intermediate L/P , the limiting expressions of KS [(3) and (4)] were interpolated in a simple polynomial ratio of the form

$$\begin{aligned} \sigma &= [\sigma_{\text{rigid}}^{(0)} + (s\sigma_{\text{rigid}}^{(0)} + \sigma_{\text{rigid}}^{(1)})(L/P) \\ &\quad + s\sigma_{\text{wormlike}}^{(0)}(L/P)^2] / [1 + s(L/P)], \end{aligned} \quad (7)$$

where

$$s = (\sigma_{\text{wormlike}}^{(0)} - \sigma_{\text{rigid}}^{(1)}) / (\sigma_{\text{rigid}}^{(0)} - \sigma_{\text{wormlike}}^{(1)}) .$$

Using (5) and (6) in Eq. (2) and substituting (7) for σ in Eq. (1) yields the free energy for persistent flexible polymers. In the limit $L/P \rightarrow 0$, one, of course, recovers Lee's expression for the free energy of hard spherocylinders of length $L + D$.

For the isotropic phase, $f(\mathbf{n})=1$, and σ is trivially zero according to eqs. (3) and (4). For calculations of the nematic behavior it is convenient to employ Onsager's trial distribution function

$$f(\mathbf{n}) = [\alpha / \sinh(\alpha)] \cosh[\alpha \cos(\theta)]$$

[1], where θ is the angle of \mathbf{n} with respect to the director, and α is a parameter determined by minimizing the free energy. By substitution of the trial function into Eq. (7) we obtain the nematic confinement free energy as a function of α :

$$\sigma(\alpha) = \ln(\alpha) - 1 + z(3z + 2r)/(z + r) - q[z/(z + r)]^2 \exp(-\alpha/2) + O(\exp(-\alpha)) , \quad (8)$$

where $z = (L/12P)(\alpha - 1)$, $r = \ln(4) - 1 = 0.386294 \dots$, and $q = 2K(1/2) - 4E(1/2) = -1.694426 \dots$ for the complete elliptic integrals K and E . Note that $\sigma(\alpha)$ is given as an expansion in large α because even though the trial function is rather simple it yields somewhat cumbersome integrations. The exponential corrections of $\sigma(\alpha)$ are usually small, since $1/\alpha$ essentially measures the width of the angular distribution, which decreases quickly with increasing concentration. Nevertheless, some care has to be taken for large L/P because the exponential corrections in α will usually contain terms $O(L/P)$. Using the exact relation $\rho(\alpha) = 2I_2(2\alpha)/\sinh^2(\alpha)$ [1], where I_2 is a modified Bessel function, it is now easy to calculate all thermodynamic quantities of interest within the trial function approach [26].

COLUMNAR ORDERING OF PERSISTENT FLEXIBLE POLYMERS

The above theory applies to lyotropic isotropic and nematic phases of persistent flexible polymers. As the concentration increases, however, new translationally ordered phases, such as smectic columnar, or crystalline phases may occur. In the following, we present a simple argument that combines the above theory of flexibility with a model for translational order in systems of rigid rodlike particles interacting via steric exclusion. Because the underlying assumptions are relatively crude, we focus on flexibility in the context of the columnar phase, for which our line of reasoning is most applicable.

As we have shown in previous work [20,27], translationally ordered phases of orientationally ordered rigid rodlike particles can be well described in terms of the tradeoff of translational entropy between translationally disordered (i.e., liquidlike) dimensions and the translationally ordered (i.e., crystal-like) dimensions. Within the model based on this idea, the contribution to the free energy due to hard-core repulsions in a columnar phase of

aligned rigid rods can to good approximation be written as

$$f_{\text{ex vol}} = f_{\text{fluid}}^{1D}(\Delta) + f_{\text{crystal}}^{2D}(\Delta) , \quad (9)$$

where $f_{\text{fluid}}^{1D}(\Delta)$ denotes the contribution of a one dimensional fluid of hard lines and $f_{\text{crystal}}^{2D}(\Delta)$ denotes the contribution of a two-dimensional crystal of hard disks. The underlying physical picture is that of spherocylindrical tubes of diameter D confined to impenetrable hexagonal tubes of diameter Δ arranged in a close packed hexagonal array. The system is fluid along the tubes and crystalline in the transverse plane. The optimal tube width is determined by minimizing the total free energy with respect to Δ . Using scaled particle theory, we obtain

$$f_{\text{fluid}}^{1D}(\Delta) = -\ln[1 - v_1(\Delta/D)] , \quad (10)$$

where v_1 is the volume fraction in the one-dimensional fluid

$$v_1(\Delta/D) = (2\sqrt{3}/\pi)v(\Delta/D)^2 \frac{L/D + 1}{L/D + 2/3} \quad (11)$$

and, using a simple cell model, we obtain

$$f_{\text{crystal}}^{2D}(\Delta) = -\ln[V_2^{\text{free}}(\Delta, D)/V_2^{\text{cell}}(\Delta)] = -2\ln(1 - D/\Delta) , \quad (12)$$

where $V_2^{\text{free}}(\Delta, D)$ is the two-dimensional free volume of a disk of diameter D confined to a hexagonal cell of two-dimensional volume $V_2^{\text{cell}}(\Delta)$ [20,27].

If the rodlike particle is not rigid but persistent flexible, it is subject to thermal bending fluctuations along its contour, and the corresponding confinement entropy has to be taken into consideration. The thermal bending fluctuations are constrained in the lateral direction by the walls of the tube, where Δ is not much larger than D . This means that for flexible rods, the "nematic confinement," which is characterized by the width of the distribution function as measured by $1/\alpha$, is replaced by the hard walls of the tube at a distance Δ . Therefore, there ought to be a relation $\alpha = \alpha(\Delta)$, which yields $\sigma(\alpha)$ approximately as a function of Δ for the case of columnar ordering. This relation can be obtained via a simple scaling argument [8], which we summarize here for the sake of completeness.

Because the columnar phase is already highly ordered (i.e., $1/\alpha$ is small), the distribution function $f(\theta)$ is approximately Gaussian, and one can write $\langle \theta(\alpha)^2 \rangle \approx 2/\alpha$, which is a measure of the angular deflection limited by the columnar confinement. On the other hand, from the definition of the persistence length, one has the correlation function $\langle \mathbf{n}(0)\mathbf{n}(\tau) \rangle = \langle \cos[\theta(\tau)] \rangle = \exp(-\tau/P)$ for an unconfined polymer, where τ is the distance between the two tangential unit vectors. Thus, $\langle \theta(\tau)^2 \rangle / 2 \approx \tau/P$ for small τ . The effect of confinement is seen for $\tau \gtrsim \lambda$, where λ is the mean deflection length imposed by interaction of the polymer with its tube of neighbors (cf. Fig. 1). Therefore, $\langle \theta(\lambda)^2 \rangle \approx \langle \theta(\alpha)^2 \rangle$, which defines $\lambda \approx P/\alpha$. Finally, λ can be approximately related to Δ via

$$(\Delta - D)/2 \approx \int_0^\lambda [\langle \theta(\tau)^2 \rangle]^{1/2} d\tau \approx (\lambda^3/P)^{1/2} ,$$

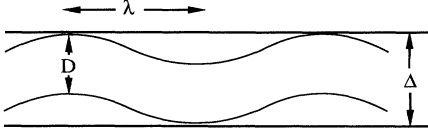


FIG. 1. Schematic illustration of a persistent flexible polymer of width D confined to a tube of diameter Δ . λ is the deflection length, the mean distance over which the polymer contour interacts with the walls of the tube.

where $(\Delta - D)/2$ is the average unconstrained lateral displacement. Note that an analogous relation tying the tube width to the deflection length has been used by Odijk in the context of entangled polymers [28]. Writing α in terms of P/D and Δ/D we finally obtain

$$\alpha = \kappa [(P/D)/(\Delta/D - 1)]^{2/3}, \quad (13)$$

where $\kappa = O(1)$ is an as yet undetermined proportionality constant. In order to avoid end effects, it is assumed that $L \gg \lambda$ (i.e., $\alpha L/P \gg 1$).

Using Eq. (13), we can now express σ in terms of Δ . Furthermore, if we assume that the excluded volume of the persistent flexible fibers within a narrow tube are reasonably approximated by the excluded volume of similarly confined stiff spherocylinders, we can utilize the above expressions for $f_{\text{fluid}}^{1D}(\Delta)$ and $f_{\text{crystal}}^{2D}(\Delta)$. With these assumptions, the free energy of a well-ordered columnar phase is again given by Eq. (1), where $f_{\text{ex vol}}$ is now given by Eqs. (9), (10), (11), and (12), and $\sigma(\alpha)$ can be expressed in terms of Δ via (13). As mentioned above, the optimal Δ is obtained using the condition $0 = df/d\Delta$, which can be written as

$$0 = \frac{ck_B T}{\Pi} \left[\frac{1}{2} \left[1 - \frac{\Delta}{D} \right] \Delta \frac{\partial}{\partial \Delta} \sigma(\alpha(\Delta)) + \frac{\Delta}{D} \right] + 1 - \Delta/D, \quad (14)$$

where

$$\Pi/(k_B T) = c/[1 - v_1(\Delta/D)]$$

is the pressure in the columnar phase (cf. Table I of [27]). We can now compare the calculated columnar free energy with the free energy describing isotropic and nematic ordering, to determine the stable phase corresponding to the lowest free energy for a given set of variables v , P/D , L/D , and κ .

RESULTS

Using the above equations, we obtain the isotropic-nematic-columnar phase diagram for persistent flexible hard rods as a function of polymer volume fraction v and polymer persistence length P divided by the polymer hard-core diameter D . Figure 2 shows the phase diagram for various values of the polymer axial ratio L/D and the columnar deflection parameter κ . Note that the range of validity of our model corresponds roughly to $1 < P/D \ll \alpha L/D$ [cf. Eq. (13)]. Within this range, for a

given contour length and sufficiently stiff polymers, we find an isotropic-to-nematic transition at low-volume fractions followed by a nematic-to-columnar transition at high-volume fractions. With decreasing stiffness, i.e., decreasing P/D , the isotropic-nematic transition progressively shifts to higher volume fractions, until finally it disappears and a direct isotropic-to-columnar transition occurs. As P/D is decreased further, the isotropic-to-columnar transition shifts to higher packing fractions.

Whereas the overall topology of the phase diagram is independent of L and κ within the range of validity of our model, the actual positions of the phase boundaries depend significantly on these quantities. Increasing L/D shifts all phase boundaries to lower volume fractions, as one might expect in analogy to stiff polymers. Increasing the parameter κ , on the other hand, as illustrated by the different line types in Fig. 2, diminishes the stability of the columnar phase in comparison to isotropic and

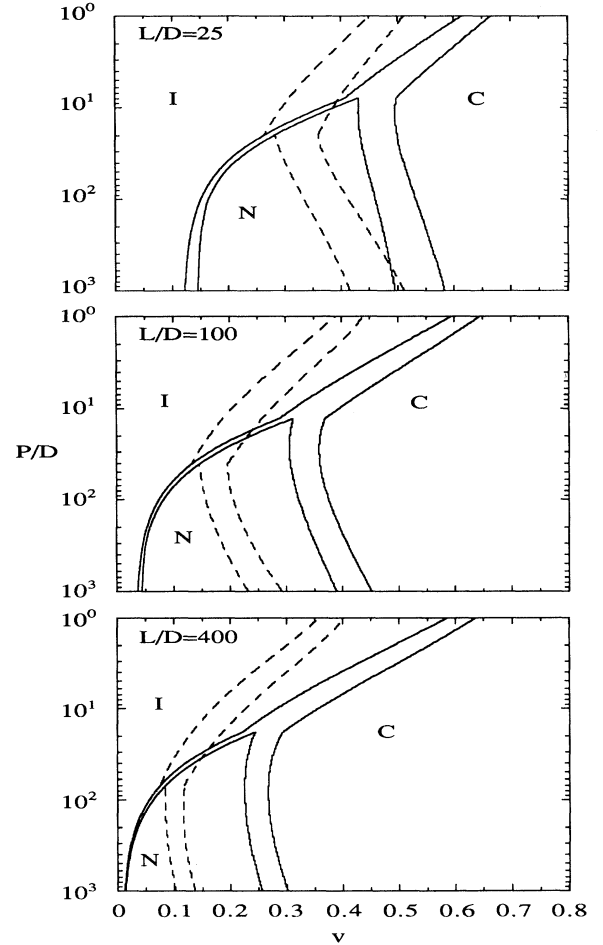


FIG. 2. Phase diagram for persistent flexible rods of axial ratio $L/D=25$, 100, and 400 as a function of volume fraction v and persistence length P divided by the polymer width D . I, N, and C indicate isotropic, nematic, and columnar phases, respectively. Solid lines and dashed lines outline the phase coexistence regions for $\kappa=3.5$ and 2.5, respectively.

nematic ordering. This is because, for a given tube width, a larger value for κ implies greater constraint on the polymer, as manifest in increased α and therefore increased columnar free energy. Note again that we cannot determine the value of κ *a priori*, due to the scaling-type arguments on which Eq. (13) is based. The two values for κ used throughout Fig. 2, however, roughly bracket the range of κ values, which are consistent with the experimental equation of state for PBLG in dimethylformamide (DMF), discussed below. It is also worth mentioning that the stringent positional constraints imposed by the above cell model for positional ordering force the transitions into the columnar phase to be discontinuous (see also [20] and [27]). However, a recent related continuum elastic treatment of infinite wormlike polymers also finds analogous isotropic-nematic-columnar phase behavior, where the transitions into the columnar phase are first order [23].

The disappearance of the nematic phase for sufficiently flexible polymers is illustrated in a different fashion in Fig. 3. The value of P/D at the isotropic-nematic-columnar triple point is shown to increase asymptotically to a finite value as L/D approaches infinity. Qualitatively this suggests that for a chain polymer with a suitably small persistence length ($P/D \approx 10-20$), the two regimes separated by the triple point may be experimentally accessible by simply using different molecular weight preparations. This is useful because the molecular weight, i.e., L/D , can usually be varied more easily over a wide range than the persistence length.

The case of hard flexible rods confined to hard tubes can also be used to illustrate another consequence of molecular flexibility in the context of translationally ordered phases. Figure 4 shows the packing fraction in the fluid dimension v_1 as function of the total volume fraction for various L/D and P/D . In the limit of very long, very flexible polymers (curve f), the fluid dimension is virtually close packed ($v_1 \approx 1$). This means that the particles are packed essentially end-to-end in the columnar phase. As the polymers become less flexible (either by increasing P/D or by decreasing L/D), v_1 is gradually re-

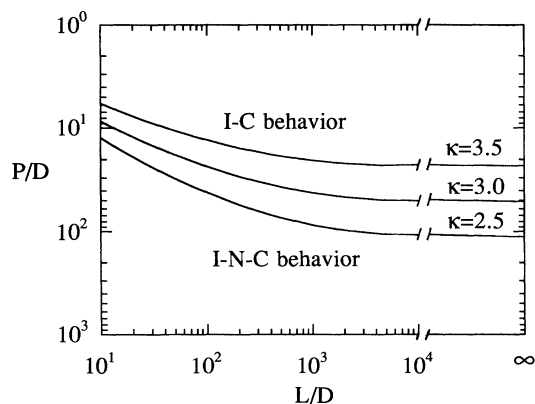


FIG. 3. Location of the isotropic-nematic-columnar triple point as a function of persistence length P and contour length L for $\kappa=2.5, 3.0$, and 3.5 .

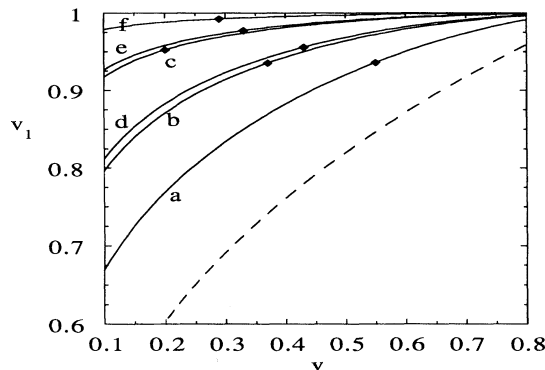


FIG. 4. 1D-fluid volume fraction v_1 along the columnar tube vs total volume fraction v . (a) $L/D=25$, $P/D=1000$; (b) $L/D=100$, $P/D=1000$; (c) $L/D=400$, $P/D=1000$; (d) $L/D=25$, $P/D=10$; (e) $L/D=100$, $P/D=10$; (f) $L/D=400$, $P/D=10$. Curves a-f are for $\kappa=3$. The dashed line illustrates the corresponding result for rigid hard cylinders, for which $v_1=[(2\sqrt{3}/\pi)v]^{1/3}$ [27]. The symbols indicate the lowest volume fractions at which the columnar phase is globally stable.

duced. Note, however, that the condition $\alpha L/P \gg 1$, which is necessary for the validity of Eq. (13), only allows limited polymer stiffness within our model. Therefore, as a reference, Fig. 4 also shows the considerably lower v_1 obtained previously for the case of completely rigid rods [27].

The flexibility-induced tightening of the longitudinal packing may also be characterized by the quantity $-\partial \ln(\Delta)/\partial \ln(v)$, which in the wormlike chain limit approaches $\frac{1}{2}$ for all v , whereas in the case of aligned rigid rods we obtain the value $\frac{1}{3}$. Physically, this again means that for very flexible particles the packing is essentially end-to-end, and compression only occurs in the lateral directions as v increases. In the case of rigid rods, on the other hand, the volume around each particle decreases

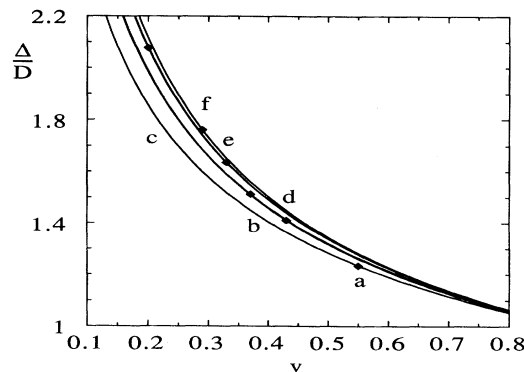


FIG. 5. Width Δ of the columnar tube divided by the polymer width D vs volume fraction v . All parameters and symbols are as in Fig. 4. The letter coding is aligned vertically with corresponding symbol for each curve. Note that lines b and d and lines c and e are virtually superimposed.

uniformly in all three directions. Note that the tight end-to-end packing of the molecules has been taken as an *a priori* assumption in various studies on hexagonal phases of flexible polymers (e.g., [23,29]). The present result provides a theoretical basis for this assumption and indicates where it would fail.

For the same parameters as in Fig. 4, Fig. 5 illustrates the rapidly decreasing tube width Δ , or, equivalently, the interaxial spacing between polymers, as a function of the volume fraction. The value of Δ/D , calculated using Eq. (14), provides a consistency check, in that it should not exceed 2, if the assumption of 1D-fluid behavior along the tubes is to be a good one.

We have previously compared the isotropic-nematic equation of state derived using Eqs. (1), (2), (5), (6), and (8) [5] with experimental osmotic pressure measurements obtained for PBLG-DMF system by Kubo and Ogino [24,30]. For volume fractions $v \lesssim 0.4$, there is excellent agreement for various polymer weights. However, at higher volume fractions the theory progressively overestimates the experimental pressure. It is, therefore, interesting to compare the experimental pressure data to the theory when columnar ordering is included. Because Kubo and Ogino do not discuss the possibility of positional order on the basis of their measurements, our comparison is necessarily somewhat speculative in nature. The result is shown in Figs. 6 and 7 for two PBLG preparations corresponding to $L/D=26$ and 63. The best overall agreement is found for $P=2000 \text{ \AA}$ and $\kappa \approx 3$. Note that the comparison is not extended beyond $v \approx 0.75$, because the hard-core approximation for the particle interaction eventually loses its validity, and, in

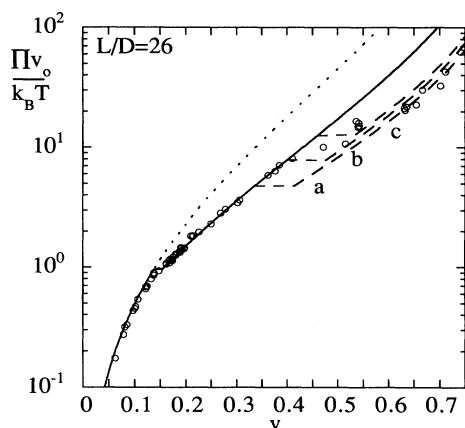


FIG. 6. Comparison of the theoretical reduced pressure $\Pi v_0 / (k_B T)$, where v_0 is the volume of the polymer molecule, with the osmotic pressure data (symbols) for PBLG in DMF of Kubo and Ogino [24,30]. The solid line is the theoretical result for the isotropic-nematic equation of state ($P=2000 \text{ \AA}$, $D=16 \text{ \AA}$, and $L/D=26$) reported previously [5,8]; the dotted line is the theoretical result for the metastable isotropic state; dashed lines indicate the pressure in the globally stable columnar phase for $\kappa=2.5$ (a), 3.0 (b), and 3.5 (c). The theoretical values for Δ/D at the B point of the nematic-to-columnar transition are $\Delta/D=1.40$ (a), 1.33 (b), and 1.27 (c).

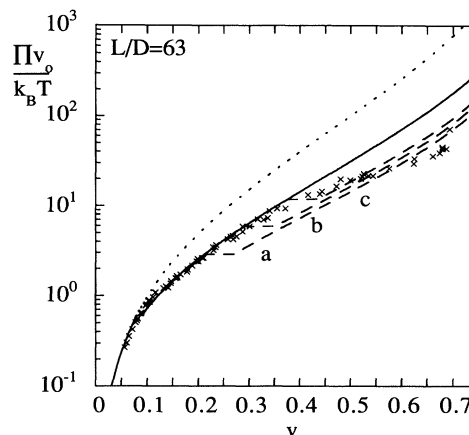


FIG. 7. The same as Fig. 6, but for a different weight polymer preparation corresponding to $L/D=63$. Here the theoretical values for Δ/D at the B point of the nematic-to-columnar transition are $\Delta/D=1.74$ (a), 1.55 (b), and 1.41 (c).

fact, side chain mixing dominates at these high volume fractions [30].

DISCUSSION

In obtaining the above result, we have made a number of assumptions. For the case of purely nematic behavior, the trial function approach and the interpolated confinement free energy [Eqs. (7) and (8)], as well as the approximate expressions for the excluded volume contribution to the free energy, are discussed in detail in Ref. [5]. In approximating the excluded volume contribution to the free energy in terms of expressions for rigid particles, we follow a reasoning similar to that of Khokhlov

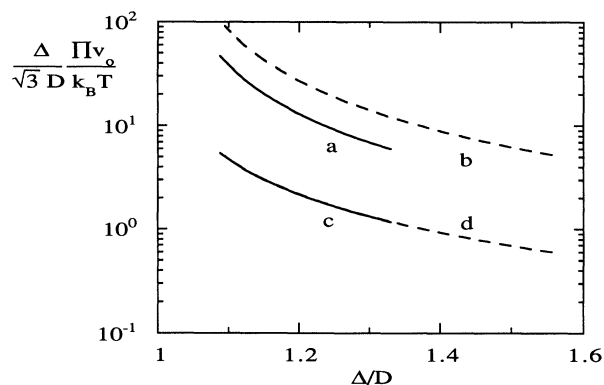


FIG. 8. Theoretical reduced pressure $\Pi v_0 / (k_B T)$ times $\Delta / (\sqrt{3} D)$ vs the mean interaxial separation Δ divided by the polymer diameter D . Curves (a) and (b) correspond to the theory for the columnar phase of PBLG shown in Figs. 6 and 7 for $\kappa=3$ and $L/D=26$ (a), 63 (b). Curves (c) and (d) illustrate the corresponding results for completely rigid rods again with $L/D=26$ (c) and 63 (d) using the theoretical reduced pressure given in Ref. [27].

and Semenov [4], which is based on the locality of the steric repulsions compared to the much larger scale on which flexibility is manifest (cf. above). This approach does not apply to freely flexible systems, where the particles interact as globular coils rather than as persistent flexible rods.

Our approach to columnar ordering is discussed in Refs. [20] and [27] for the case of rigid rods, and much of this discussion also applies in the present case. In this work, we do not address other types of positional order, such as smectic-*A* or crystalline phases. It is known from both experimental work (e.g., [31]) and theoretical work (e.g., [22]) that monodisperse stiff rodlike particles exhibit a transition from nematic into a smectic-*A* phase. However, to what extent a stable smectic phase can persist in the presence of molecular flexibility is an open question.

Another point, which has not been addressed, is soft interparticle interactions. Recently, osmotic pressure data for biopolymers in the columnar phase have been used to characterize intermolecular interactions [32-34]. The osmotic pressure multiplied by $1/\sqrt{3}$ times the center-to-center distance between polymers is taken as a measure of the force between neighbors per unit length, and the decay of this force with increasing center-to-center distance is taken as a measure of the range of the force. The corresponding plot [using our dimensionless reduced osmotic pressure $\Pi v_0/(k_B T)$ and our dimensionless reduced center-to-center distance Δ/D] for our columnar phase of hard particles is shown in Fig. 8. Clearly, the osmotic "force" (ordinate) increases with increasing polymer flexibility (i.e., reduced persistence length and/or increased contour length). On the other hand, the decay distance of the osmotic "force" (the inverse slope of the curve) is not sensitive to polymer flexibility. Furthermore, the decay distance is several tenths of D , and approximately doubles with increasing center-to-center distance in the columnar phase, even though the interactions between the particles are strictly hard core (i.e., have a decay length of zero). These results suggest that the decay distance of the osmotic "force" does not strongly reflect details of the interparticle interactions and that the magnitude of the osmotic "force" should be more informative (see, e.g., [29]).

The present theory does not apply when the polymer interactions cannot be well described in terms of hard core repulsions. This is because in deriving Eq. (13), we

assume free polymer statistics over distances that are shorter than a certain deflection length. For relatively long-range polymer interactions (e.g., Coulomb repulsions), this concept may not be applicable at the densities where the columnar phase becomes stable. This is illustrated in recent osmotic pressure measurements for polyelectrolytes by Podgornik, Rau, and Parsegian [33]. Reasonable agreement with their experiments was obtained by considering infinite wormlike polymers, where the undulations are constrained by a harmonic potential [29] rather than by an infinite square well.

Interestingly, isotropic-nematic-columnar phase behavior very similar to that obtained here is also found in theoretical and experimental studies on a number of reversibly assembling systems, in which disklike amphiphilic molecules stack to form labile rodlike aggregates (cf. [19] and references therein). For a strong aggregation, i.e., for sufficiently large aggregation numbers, a nematic phase intervenes between a low-density isotropic phase and a high-density columnar phase. As aggregation becomes weaker, e.g., as a function of temperature, the nematic phase is gradually abbreviated and finally abolished. Note in this context that the entropic effect of a small aggregation number is similar to that of a small persistence length in that it shifts the isotropic-to-nematic transition to higher concentrations, where finally the columnar phase becomes stable before the nematic phase.

In conclusion, even though our model employs a number of crude approximations, it provides a series of interesting results concerning the liquid-crystalline behavior of hard persistent flexible polymers. We hope that the ideas outlined above can be extended to self-assembling systems, where the elongated aggregates formed by association of amphiphilic molecules often exhibit considerable flexibility.

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