Effect of chain flexibility on the nematic-smectic transition

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The theory of nematic-smectic phase transition in the system of uniform semiflexible chains with hard-core repulsion is presented. Both the general density-functional formalism and the tube-model calculation show that the flexibility of the chains results in a strong *first-order* transition, in contrast to the common weak-crystallization scenario of the nematic-smectic transition in rigid rods. The calculated spinodal volume fraction of the uniform nematic phase and the period of the modulation instability are consistent with recent experimental results. [S1063-651X(98)15511-3]

I. INTRODUCTION

The nematic-smectic phase transition is among the most interesting phenomena in liquid crystals. This is one of a few examples of a *partial* breaking of translational symmetry: the system in the smectic state has a layered structure, while the translational symmetry along the in-layer directions is preserved. It is believed that normally the physical origin of the transition to the smectic phase is the nonuniform architecture of the constituent particles such that the nematic-smectic transition can be interpreted as a microphase separation of different parts of the molecules[1]. Nevertheless, it is conceptually important to realize that a nontrivial structure of the constituent objects is not a necessary condition for the formation of a smectic state. Both analytical and numerical investigations show that an entropy-driven nematic-to-smectic phase transition occurs even in the system of uniform rigid rods [2–6].

Recent experiments with rodlike viruses have confirmed the predictions of such theories [7,8]. They also showed that a dramatic change in behavior takes place due to the finite flexibility of viruses. In particular, the transition turns out to be of the strong first order rather than of weak-crystallization type typical of most smectics. In addition, the volume fraction at the transition is considerably higher in the case of flexible chains than for rods. The chains are strongly localized within the layers, so that the periodicity of the smectic phase is nearly equal to the length of an individual stretched chain, while in the stiff-rod case it is longer than the length of a rod because of a weaker localization.

In a recent communication [9] we have proposed a theory based on the tube model for the description of the nematic-smectic phase transition in the system of uniform semiflexible chains with hard-core repulsion. This model has been shown to capture all the experimentally observed features of the transition. In this paper we elaborate on our approach by relating the tube-model calculation to a general density-functional formalism. It is shown that the strong first-order character of the transition and the equivalence of the smectic period to the chain length follow from a general form of the density functional of the system.

In Sec. II we review the density-functional approach to the nematic-smectic transition. In Sec. III we derive the general form of the free energy of semiflexible chains expressed as a functional of the density of their midpoints. The breakdown of the stability condition (positivity of the inverse structure factor) yields the limit of stability of the nematic phase and the critical wave vector of the modulation bifurcation. In Sec. III we obtain the parameters of the density functional from the tube model of the nematic state. This allows one to determine the parameters of the transition for various chain lengths. The structure of the theory allows one to understand the difference between the behavior of semiflexible chains and that of rigid rods.

II. DENSITY-FUNCTIONAL APPROACH TO NEMATIC-SMECTIC TRANSITION

A powerful tool for the description of various types of crystallizations and, in particular, of the nematic-smectic phase transition is the density-functional approach. Within such theories the free energy F of the system is parameterized by the one-particle density $\rho(\mathbf{r})$. The thermodynamic stability (or at least metastability) of the spatially uniform (e.g., nematic) phase with respect to density modulation is controlled by the sign of the corresponding second variation of the free energy:

$$G^{-1}(\mathbf{q}) \equiv \frac{1}{kT} \frac{\delta^2 F}{\delta\rho_\mathbf{q}\delta\rho_{-\mathbf{q}}} > 0. \tag{1}$$

Note that $G^{-1}(\mathbf{q})$ denotes the inverse structure factor in the nematic phase $[G(\mathbf{q}) \equiv \langle \delta\rho_\mathbf{q}\delta\rho_{-\mathbf{q}} \rangle]$. The system becomes unstable with respect to the transition to a spatially modulated (smectic) state, when inequality (1) is violated at a certain finite wave vector $\mathbf{q}_0$. In many cases, the nematic-smectic transition can be successfully described within the weak crystallization theory [10]. In this approach one assumes that near the transition, the local deviations of the density field are dominated by one or by several critical density waves, i.e.,

$$\delta\rho(\mathbf{r}) \simeq \sum_{\alpha=1}^{n} \rho_\alpha(\mathbf{r})\exp(i\mathbf{q}_\alpha\mathbf{r}) + \text{c.c.} \tag{2}$$

Here $\mathbf{q}_\alpha$ are the critical wave vectors. The spatial dependence of the n-component order parameter ρ_α is supposed to be much slower than the critical density modulation itself.

The Landau-type expansion of the free energy in terms of this order parameter is the essence of the weak crystallization approach:

$$F = \int \left(\frac{\epsilon}{2} \delta\rho^2 + \frac{\lambda}{6} \delta\rho^3 + \frac{\gamma}{24} \delta\rho^4 + \frac{g}{2} \sum_{\alpha=1}^{n} |\nabla\rho_\alpha|^2 \right) d\mathbf{r}. \quad (3)$$

The translational symmetry of the free energy demands that any term in the above expansion be a combination of density waves with zero total wave vector. Note that a large third-order term in this expansion would result in a strong first-order transition and thus would violate the requirement of smallness of the order parameter. Therefore, the weak crystallization theory is adequate only for the cases in which the third-order term is zero or small. In particular, its applicability to the nematic-smectic phase transition is normally justified by the broken rotational symmetry of the nematic phase. Indeed, in the rotationally symmetric case, the critical wave vectors would lie on the sphere of radius q_0, and one could choose three critical density waves with zero total wave vector. Therefore, rotational symmetry implies that there is a nonzero cubic term in expansion (3). In the case of the nematic-smectic transition, the degeneracy in the orientation of the critical wave vector is lifted and one cannot construct a third-order combination of the critical density waves. Hence, the weak-crystallization theory can usually be applied to this transition.

As an example, consider the transition to the smectic state in the system of perfectly aligned hard rods. The density-functional theory, developed for this system in Ref. [2], shows that its basic physics can be successfully described even in the second virial approximation:

$$\frac{F^{(\text{rods})}}{kT} = \int d\mathbf{r}\rho(\mathbf{r})\ln\rho(\mathbf{r})$$

$$+ \frac{1}{2} \int \int d\mathbf{r}d\mathbf{r}' \rho(\mathbf{r})v(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}'), \quad (4)$$

which yields the following simple expression for the inverse structure factor:

$$G^{-1}(q) \equiv \left(1 + 8\Phi \frac{\sin qL}{qL} \right). \quad (5)$$

Here we are interested only in the wave vectors parallel to the nematic director, $\mathbf{e}$. The breakdown of the stability condition corresponds to the transition to the spatially modulated smectic phase. Since the instability is dominated by a single density wave (with $\mathbf{q} \simeq \pm 1.5\pi\mathbf{e}/L$), the transition in the hard-rod system is of the *weak-crystallization* type. This means that the smectic modulation of hard rods is weak near the transition point. As a result, the normal-to-layer fluctuations of the rods are of the order of their length L, consistent with the fact that the corresponding period $\lambda^* \simeq 1.3L$ differs considerably from L. Although within the model of freely rotating rods [5,6] the phase transition turns out to be of the first order, it is so weak that the transition can hardly be distinguished experimentally from a second-order one.

Nematic-smectic transition of semiflexible chains

Consider a system of wormlike uniform chains of length L with hard-core diameter D. The single-chain Hamiltonian for a given conformation $\mathbf{r}(s)$ $(0 < s < L)$ has the form

$$H^{(0)} = kT \int_0^L \frac{p}{4} \left(\frac{\partial \mathbf{t}_s}{\partial s} \right)^2 ds. \quad (6)$$

Here s is the coordinate along the chain contour and $\mathbf{t}_s = (\partial\mathbf{r}/\partial s)$ is a unit tangent vector. The parameter p is the persistence length of the chain in the isotropic phase. In the nematic phase, however, there are two different scales that play the role of persistence length [11]. One of them is the typical distance between ''hairpins,'' the points at which the tangent vector changes its direction by $180°$. This length becomes exponentially large for high enough nematic order parameter and we assume here that it exceeds the chain length, i.e., the conformations of the chains are straight lines with only weak transverse fluctuations of the tangent vector about the nematic director. The correlations of these transverse fluctuations are determined by another length scale known as the deflection length, $\xi_\perp$. This scale, which is smaller then the bare persistence length p, determines the thermodynamics of the system (the free energy can be estimated as kT per chain segment of length $\xi_\perp$).

We now have to express the free energy as a functional of the density of the chains' centers,

$$\rho(\mathbf{r}) = \sum_{\text{chains}} \delta(\mathbf{r}(L/2) - \mathbf{r}). \quad (7)$$

If the chains were infinite, the conformational free energy averaged over scales larger than $\xi_\perp$ would be a local functional of the volume fraction. For finite chains there is also a translational entropy contribution and a correction due to finite density of chain ends:

$$\frac{F^{(\text{chains})}}{kT} = \int d\mathbf{r}\{\rho(\mathbf{r})\ln\rho(\mathbf{r}) + f^{(\text{con})}(\phi(\mathbf{r}))$$

$$+ \rho_{\text{end}}(\mathbf{r})f^{(\text{end})}(\phi(\mathbf{r}))\}. \quad (8)$$

Because of the low density of chain ends ρ_{end}, their effect is accounted for in the above expression by a term linear in ρ_{end}, coupled to some local function of the volume fraction. Since the chains are strongly stretched along the nematic director, z axis, and do not form hairpins, one can relate the local density of the ends $\rho_{\text{end}}(z)$ and the local volume fraction of chains $\phi(z)$ to the density field $\rho(z)$ (we will not consider any fluctuations of these fields in the plane normal to z):

$$\rho_{\text{end}}(z) = \rho(z+L/2) + \rho(z-L/2), \quad (9)$$

$$\phi(z) = \frac{\pi D^2}{4} \int_{-L/2}^{L/2} \rho(z+s)ds. \quad (10)$$

Due to these nontrivial relationships between the three fields $\rho(\mathbf{r})$, $\phi(\mathbf{r})$, and $\rho_{\text{end}}(\mathbf{r})$, the above local free-energy functional becomes nonlocal when expressed in terms of a single density field, ρ. Such nonlocal properties of the density func-

tional are necessary for the description of the nematic-smectic transition. The semiflexible chains are unique in the sense that this functional has a well defined general form dictated by the property of locality on the mesoscopic scales (below L and above $\xi_\perp$).

In order to study the stability of the nematic state, consider the second variation of the free energy at the fixed average volume fraction Φ (and the corresponding density $\bar{\rho} = \Phi/V_0$, where $V_0 \equiv \pi D^2 L/4$ is the volume of a single chain):

$$\frac{\delta F^{(\text{chains})}}{kT} = \frac{1}{2} \int d\mathbf{r} \left\{ V_0 \frac{\delta\rho(\mathbf{r})\,\delta\rho(\mathbf{r})}{\Phi} \right.$$
$$+ \left. \frac{\partial^2 f^{(\text{con})}}{\partial\phi^2} \right|_\Phi \delta\phi(\mathbf{r})\,\delta\phi(\mathbf{r}) + 2 \left. \frac{\partial f^{(\text{end})}}{\partial\phi} \right|_\Phi$$
$$\left. \times \delta\rho_{\text{end}}(\mathbf{r})\,\delta\phi(\mathbf{r}) \right\}. \tag{11}$$

Performing the Fourier transform of all the fields under consideration (along the z axis, neglecting their variations in other directions) and expressing these fields in terms of the density deviations $\delta\rho$, we obtain the following diagonalized free energy:

$$\frac{\delta F^{(\text{chains})}}{kT} = \frac{V_0}{\Phi} \sum_q \frac{\delta\rho_q \delta\rho_{-q}}{2}$$
$$\times \left[1 + \Lambda(\Phi) \left(\frac{L}{\lambda(\Phi)} \frac{(1-\cos qL)}{(qL)^2} + \frac{\sin qL}{qL} \right) \right]. \tag{12}$$

Here the dimensionless parameter Λ and the length λ are certain functions of the average volume fraction, but not of the chain length or wave vector. Note the universality of the (q,L) dependence of the inverse structure factor for semiflexible chains:

$$G^{-1}(q) \equiv \frac{1}{kT} \frac{\delta^2 F^{(\text{chains})}}{\delta\rho_q \delta\rho_{-q}}$$
$$= \frac{V_0}{\Phi} \left[1 + \Lambda(\Phi) \left(\frac{L}{\lambda(\Phi)} \frac{(1-\cos qL)}{(qL)^2} + \frac{\sin qL}{qL} \right) \right] \tag{13}$$

Before proceeding with the discussion of this general form of G^{-1}, we present a simple model which yields the microscopic expressions for the parameters $\Lambda(\Phi)$ and $\lambda(\Phi)$ appearing in Eq. (13).

III. TUBE-MODEL CALCULATION

The interactions of a chain with its neighbors can be modeled by confining it in an effective tube. If the system is dense enough, it can be viewed as a close-packed array of such tubes. This means that the average tube diameter in the vicinity of some point $\mathbf{r}$ is $D/\sqrt{\phi(\mathbf{r})}$, where $\phi(\mathbf{r})$ is the local volume fraction. Therefore, the allowed amplitude of fluctuations of a chain within the tube is $\Delta = D(1/\sqrt{\phi(\mathbf{r})} - 1)$.
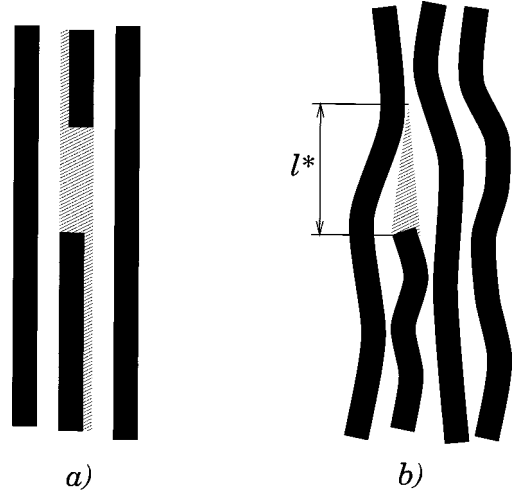

FIG. 1. The shadow region (dashed) in the case of rigid rods (a) and semiflexible chains (b). Note the *screening* of the shadow by neighboring chains in the latter case.

The corresponding conformational free energy of the chain can be evaluated in the Gaussian approximation, with the confinement imposed by a fictitious external field. The resulting value is $(3/16)kT$ per correlation length $\xi_\perp = (2\Delta)^{2/3} p^{1/3}$ [12]. Note that one can obtain this result, up to a numerical coefficient, from simple scaling arguments, since ξ can be identified with a typical contour length between two reflections of the chain from the tube walls. We conclude that the conformational free energy per unit volume is determined by the field $\phi(\mathbf{r})$:

$$f^{(\text{con})}(\mathbf{r}) = \frac{3}{16} \frac{kT}{\xi_\perp(\phi)} \frac{4\phi(\mathbf{r})}{\pi D^2}. \tag{14}$$

We assume that the dominant effect responsible for the smectic ordering is that the *internal parts of the chains cannot occupy a ''shadow'' region in the vicinity of a free end.* This is a particular realization of the *correlation hole effect* [13]. In the extreme case of perfectly aligned rigid rods, the space behind the edge of one rod can be filled only by the complementary end part of another one [see Fig. 1(a)]. However, in the system of semiflexible chains, the size of the shadow region can be reduced by appropriate readjustments of the conformations of the neighboring chains, as shown in Fig. 1(b). The screening of the shadow region can be described by a *screening length* l_s. The conformational free-energy penalty for the creation of the free space near the edge of every chain is given by the product of the local transverse pressure $\Pi_\perp = \phi \partial f^{(\text{con})}/\partial\phi - f^{(\text{con})}$ and the typical volume of the shadow region $\gamma\pi l_s D^2/4$. Here γ is a geometrical factor of order of unity. Approximating the shape of a typical shadow region with a cone, one obtains $\gamma = 1/3$. The typical bending energy associated with the distortion of chain contour needed for the screening of the shadow region is $kTD^2 p/l_s^3$ per chain involved. The screening length and the energy of the end defect is determined by the balance between the osmotic energy penalty and the bending energy, i.e., they can be obtained by minimization of the following free energy:

$$f^{(end)}(l_s) = D^2 \left(\frac{\gamma \pi l_s}{4} \Pi_\perp + \frac{Zp}{l_s^3} kT \right). \qquad (15)$$

Here Z is the effective number of distorted chains (fortunately, the final result is nearly insensitive to the choice of this parameter). The minimal value of the above free energy is given by

$$f^{(end)} \simeq \frac{\pi \gamma D^2}{2} \Pi_\perp^{3/4} (kTp)^{1/4} \simeq \frac{\gamma kT}{8} (1/\sqrt{\phi(z)} - 1)^{-5/4}. \qquad (16)$$

The correspondong optimal screening length is

$$l_s = 2(2D)^{2/3} p^{1/3} (1/\sqrt{\phi(z)} - 1)^{5/12} \equiv 2l^* (1/\sqrt{\phi(z)} - 1)^{5/12}. \qquad (17)$$

Here $l^* \equiv (2D)^{2/3} p^{1/3}$ is the fundamental length scale of the problem. Up to a ϕ-dependent factor, it determines both the screening length and the correlation length $\xi_\perp$ discussed earlier. For practical purposes, the screening length can be taken roughly equal to l^*. Note that our estimate of the energy of the end defect is somewhat different from the one described in Ref. [14], which is based on elasticity theory. The elastic approach neglects the energy penalty associated with the nonzero osmotic pressure $\Pi_\perp$, which in our case turns out to be considerably stronger than next-order elastic corrections. Nevertheless, the very notion of the effective attraction between chain ends discussed in the present paper is conceptually close to the one in Ref. [14].

Depending on the total chain length, one can distinguish between two qualitatively different limiting regimes. If $L \ll l^*$, the screening effect is not significant and the chains can be considered as rigid rods. Here, we consider the opposite limit, $L \gg l^*$, when the total volume fraction of the shadow regions is low and one can neglect their overlap in the spatially uniform nematic phase.

Summarizing the above calculation, one can write the total free energy of the system as

$$F^{(chains)} = \frac{kT}{V_0} \int d\mathbf{r} \left\{ V_0 \rho(z) \ln \rho(z) + \frac{3}{16} \frac{L}{l^*} \right.$$

$$\left. \times \frac{\phi(z)}{(1/\sqrt{\phi(z)} - 1)^{2/3}} + \frac{\gamma}{8} \frac{V_0 \rho_{ends}(z)}{(1/\sqrt{\phi(z)} - 1)^{5/4}} \right\}. \qquad (18)$$

The first term accounts for the translational entropy of the chains, the second one represents the bulk conformational free energy of infinitely long chains, and the last term is due to the end anomalies. One can easily verify that our model free energy has the general form obtained in the preceding section, Eq. (8). There is a one-to-one correspondence between the three discussed contributions to the free energy and the three terms in the following expression for the inverse structure factor in the uniform nematic phase, as a function of the average volume fraction Φ:

$$G^{-1}(q) \equiv \frac{1}{kT} \frac{\delta^2 F}{\delta \rho_q \delta \rho_{-q}}$$

$$= \frac{V_0}{\Phi} \left(1 + \frac{5}{16} \frac{1}{\Phi(1/\sqrt{\Phi} - 1)^{9/4}} \right.$$

$$\left. \times \left[\frac{2L}{3l_s(\Phi)} \frac{(1 - \cos qL)}{(qL)^2} + \gamma \sqrt{\Phi} \frac{\sin qL}{qL} \right] \right) \qquad (19)$$

This expression has exactly the same general structure as was derived in the preceding section. The uniform nematic is stable (or at least metastable) with respect to the transition to the spatially modulated (smectic) state as long as the calculated inverse structure factor is positive. The end effect contribution is the only term in expression (19) that may be negative [due to the sign-changing factor $\sin(qL)/qL$]. For most wave vectors, however, this term cannot change the overall sign of the structure factor because of the dominant positive conformational contribution, which contains the large factor L/l_s. This is related to the fact that the shadow regions are *screened* in the many-chain system, and the corresponding end effect is just a small correction to the conformational free energy. This correction is important only in the vicinity of the zeros of the expression $(1 - \cos qL)/(qL)^2$, which determines the q dependence of the bulk conformational contribution to the inverse structure factor.

We conclude that the modulation instability in the system is expected only for nearly L-periodic density waves, which are the zero modes of the conformational term. One can expand the inverse structure factor in the vicinity of such wave vectors, $2\pi n/L$ $(n = \pm 1, \pm 2, \dots)$:

$$G^{-1}(\delta q)|_{\delta q = q - 2\pi n/L}$$

$$= \frac{V_0}{\Phi} \left(1 + \frac{5}{16} \frac{1}{\Phi(1/\sqrt{\Phi} - 1)^{9/4}} \right.$$

$$\left. \times \left[\frac{L}{3l_s} \left(\frac{\delta q L}{2\pi n} \right)^2 + \gamma \sqrt{\Phi} \left(\frac{\delta q L}{2\pi n} \right) \right] \right).$$

Its minima are the candidates for the critical wave vector of the modulation instability:

$$q_n^* = \frac{2\pi n}{L} \left(1 - 3\sqrt{\Phi} \gamma \frac{l_s(\Phi)}{L} \right), \quad n = \pm 1, \pm 2, \dots. \qquad (20)$$

The control parameter Φ at which $G^{-1}(q_n^*) = 0$ turns out to be independent of n (up to a cutoff $n_{max} \sim L/l^*$, where the small-δq expansion becomes inadequate):

$$\Phi^* = \left[1 + \left(\frac{15\gamma^2 l^*}{16L} \right)^{6/11} \right]^{-2} \simeq \left(1 + \gamma \sqrt{\frac{l^*}{L}} \right)^{-2}. \qquad (21)$$

The existence of the family of critical wave vectors (20) that differ only by integer multiplier is the signature of *the first-order phase transition* to the smectic state. Indeed, unlike the case of a *single* dominating density wave typical of
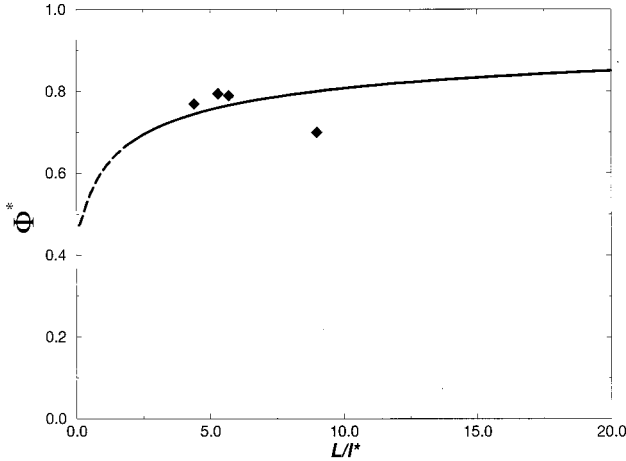
FIG. 2. Spinodal volume fraction of uniform nematic Φ^* as a function of reduced chain length L/l^*. The solid line corresponds to the theoretical result obtained for semiflexible chains ($L/l^* \gg 1$) and the dashed line is an interpolation of the crossover to the rigid-rod limit ($L/l^* \ll 1$). The geometrical factor γ is taken to be 1/3, as suggested in the text. Experimental points (diamonds) are taken from Ref. [5].

most smectics (e.g., for rigid rods), this *degeneracy* enables one to compose the third-order combinations of the critical modes $[\psi(q_n^*)\psi(q_m^*)\psi(q_l^*), \ n+m+l=0]$, which contribute to the term $[\delta\psi(z)]^3$ in the density-deviation expansion of the free energy, Eq. (3). The nonzero cubic term in the Landau expansion is known to result in a first-order transition.

The common period of all the critical modes is

$$\lambda^* = L + 3\sqrt{\Phi^*} \gamma l^s(\Phi^*) . \tag{22}$$

In a general case this critical period can differ from that of the equilibrium-modulated phase. Nevertheless, the above result suggests that the period of the smectic λ nearly coincides with the chain length L, and that the small correction $\lambda - L$ is of the order of $l_s \simeq l^*$. This correction determines both the typical gap between well formed smectic layers and the typical longitudinal fluctuations of the chains in these layers. This is consistent with the observations reported in Ref. [7], for which the calculated length $l^* \simeq 100$ nm is of the order of the measured correction to the period $\lambda - L \simeq 50$ nm. The effective hard-core diameter in the experiments can be estimated as the interchain separation at which the electrostatic repulsion becomes of the order of kT. This length depends on the ionic strength, so it was possible to change it independently of the particle density. Since $l^* \equiv (2D)^{2/3}p^{1/3}$ depends on the hard-core diameter D, the measured points on the phase diagram (concentration-ionic strength) can be transformed to the coordinates of our theory ($\Phi - L/l^*$). The calculated spinodal volume fraction, Eq.(21), is in agreement with the experimental value, which is about 0.75 for L/l^* in the range of 4–10. Note that the chain-length dependence of the critical volume fraction is rather weak, as shown in Fig. 2.
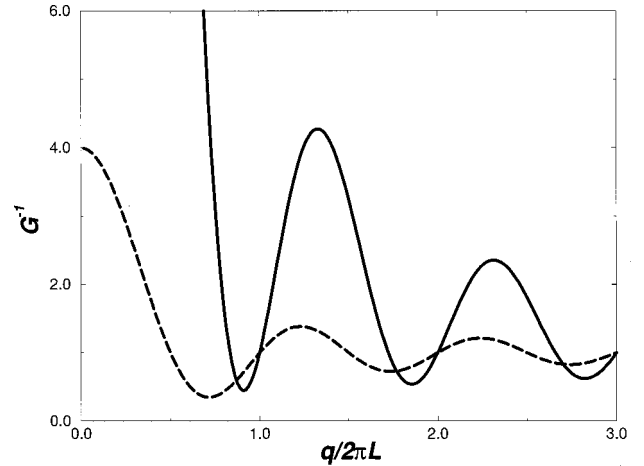

FIG. 3. Typical inverse structure factors (in arb. units) of the nematic phase for rigid rods (dashed line) and semiflexible chains (solid line).

IV. DISCUSSION AND CONCLUSIONS

We now compare the results obtained for semiflexible chains with those for perfectly aligned rigid rods. Consider the inverse structure factor of perfectly aligned rigid rods, Eq. (5):

$$G^{-1}(q) \sim \left(1 + 8\Phi \frac{\sin qL}{qL} \right) .$$

The first term here is due to translational entropy and the second one is the excluded-volume contribution, which is essentially the shadow-region end effect. Naturally, the rigid-rod structure factor does not contain the conformational contribution, which dominates the similar expression for semiflexible chains. Hence, the shadow-region effect, which drives the nematic-to-smectic transition, is no longer a small correction. As a result, the transition in the system of rods takes place at a lower volume fraction, which is $\Phi^* \simeq 0.57$ within the second virial approximation, Eq. (5). Taking the higher virial terms into account changes this value to 0.36. If the rods are freely rotating, the critical volume fraction depends on the length-to-diameter ratio. For long enough chains ($L/D \gg 10$) the transition volume fraction reaches a "universal" value $\Phi \simeq 0.46$ [5,6]. In the case of considerable flexibility of the "molecules," the critical (spinodal) volume fraction given by expression (21) is not constant even for a high length-to-diameter ratio, since the relevant parameter here is L/l^*, rather than L/D (see Fig. 2).

The typical behavior of the inverse structure factors for rigid rods, Eq. (5), and semiflexible chains, Eq. (19), are depicted in Fig. 3. Unlike the case of semiflexible chains ($L \gg l^*$), in which the q^* degeneracy of the bifurcation point results in a strong first-order transition, the deepest minimum of the rigid-rod inverse structure factor determines a *single* critical wave vector of the modulation instability. This explains why the nematic-smectic transition for rigid rods is much softer than for semiflexible chains.

Another important implication of the theory is the effect of polydispersity. Since the inverse structure factor describes the effective two-body interactions, expressions (19) and (5) can be extended to the polydisperse case by replacing a

single parameter L with the mean length of two interacting particles $(L_1+L_2)/2$, and averaging over the distribution of lengths. The polydispersity acts against the modulation instability, because it reduces the depth of minima of the inverse structure factor. Hence, the critical volume fraction is expected to increase with polydispersity for both chains and rods. However, while the smectic phase can form in systems of rods with quite broad distribution of lengths [15], the typical deviation of the chain length, which completely suppresses the transition in systems of chains, is of the order of l^*. Thus, in order to observe the smectic phase in the system of chains, the distribution of lengths has to be very narrow.

It should be noted that although we have shown that the above behavior follows from a very general form of the density functional for semiflexible chains, our formalism cannot be directly applied to the case of long-range (hexagonal) in-layer structure. In that case, a chain end becomes a real topological defect, and there is no reason to expect that the corresponding energy penalty is finite, i.e., that the corresponding contribution to the total free energy, Eq. (8), is linear in the chain-end density.

In summary, the theory of nematic-smectic phase transition for uniform semiflexible chains with hard-core repulsion has been developed. Similarly to the case of rigid rods, the transition is driven by the shadow region end effect. The difference is that due to the finite flexibility of the chains this effect is screened and the size of the empty space near a free end is limited by the screening length $l_s \simeq l^* \ll L$. The presence of shadow regions yields just a small correction to the conformational free energy that stabilizes the spatially uniform nematic state. As a result, the spinodal volume fraction for flexible chains is much higher than for rigid rods. This trend is consistent with the experiments as well as with the recent theory of weakly flexible rods [16]. The modulation instability of the nematic state can appear only for nearly L-periodic density waves, which are the soft modes of the bulk conformational free energy. Therefore, unlike the rigid-rod case, the period of the smectic phase near the transition point almost coincides with the chain length L. Another important difference is that in the case of semiflexible chains, the point of modulation instability is highly degenerate in the critical wave vector resulting in a strong first-order phase transition. The theory also implies that the flexibility of the chains results in higher sensitivity of the transition to polydispersity. The agreement of the theory with existing experimental data confirms that it captures the basic physics of the phenomenon.

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