PHYSICAL REVIEW E

STATISTICAL PHYSICS, PLASMAS, FLUIDS, AND RELATED INTERDISCIPLINARY TOPICS

THIRD SERIES, VOLUME 55, NUMBER 6 PART B **JUNE 1997**

ARTICLES

Fracture in columnar phases

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(Received 24 September 1996)

Columnar phases are composed of a regular array of columns characterized by either short-range, long-range, or quasi-long-range internal positional order. We discuss the Griffith problem of such systems where a thin cavity parallel or perpendicular to the columnar axis is extended by a tensile stress $\sigma_{\alpha\beta}$. The shape of the cavity is characteristic of the type of order present inside the columns. This simple test could be used to clarify the nature of the still ambiguous H phase of hexa(hexylthio)triphenylene. This fracture mode would be observable in polymerized samples. [S1063-651X(97)12405-9]

PACS number(s): 61.30.Cz, 46.30.Nz, 62.20.Mk, 61.30.Jf

I. INTRODUCTION

Since the discovery by Chandrasekhar *et al.* [1] of mesophases formed by discotic molecules, an important number of such compounds have been synthesized (for a recent review, see [2]). As a result, a large variety of phases have been reported to be stabilized. Of that group, the phases that are characterized by the formation of columns showing two-dimensional positional long-range order are called columnar phases. Except for tilted structures, the notation used traditionally is based on the symmetry of the two-dimensional array of columns and on the type of positional order present inside the columns [3]. For example, the structure of the D_{ro} phase (where D stands for discotic) is a rectangular array of ordered columns, while that of the D_{hd} phase is a hexagonal (triangular) array of disordered columns. Note that, strictly speaking, the ordered columnar phases are not liquid crystals: they are true three-dimensional solids [4].

However, a series of experiments has challenged this classification. Let us review them and recall the possible existence of positional quasi-long-range order inside the columns to explain those results. High-resolution x-ray measurements on well-oriented strands of hexa(hexylthio)triphenylene (HHTT) [5,6] have shown the existence of two columnar phases as a function of temperature. For 70 °C$<T<$93 °C (D_{hd} phase), the intracolumnar correlations are short ranged and the columns are liquidlike. For 62 °C$<T<$70 °C, the HHTT compound is in an *ordered* phase. In this case, the diffraction pattern shows (a) intracolumnar orientational helical order, (b) intercolumnar off-axis correlations (resolution limited), and (c) a single resolution limited (001) peak [5]. The orientational degrees of freedom here describe the internal rotation of the disklike molecules around its axis of symmetry. These results first lead these authors to classify this phase as a D_{ho} phase [5]. Careful analysis of the data revealed that the (001) peak could not be associated with positional long-range order. Fluctuations in the positions of the molecules inside the columns were of the order of 1 Å, large compared with the intermolecular average distance of 3.64 Å [5,6]. The authors of this study renamed this phase an H phase (H for helical) to distinguish it from a D_{ho} phase.

It is not yet established that the conclusion reached for the HHTT compound can be extended to other materials. However, the quality of the study makes it a prototype for columnar phases showing an ambiguous nature [4]. It would be challenging to reanalyze data from other compounds showing an ordered columnar phase (D_{ho} phase) allowing for the existence of quasi-long-range order inside the columns. This suggestion is the main conclusion of the study of a structural model for the H phase of HHTT [7].

This model assumes, based on reported HHTT experimental results, (a) long-range helical orientational order, (b) a lowest order coupling between orientation and position of the molecules, and (c) a vanishing effective C_5 shear elastic constant (see [8] for the definition of the continuum elastic free energy for columnar phases). The authors concluded to

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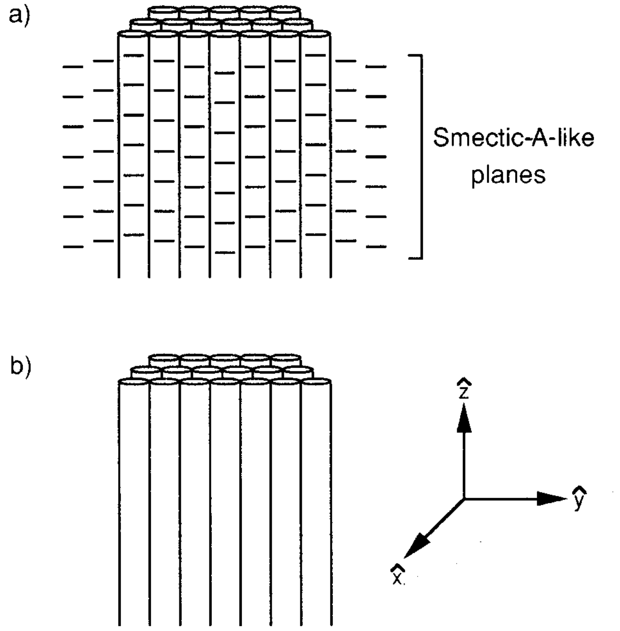

FIG. 1. (a) Tentative structural model for the HHTT compound. (b) Definition of the reference frame. The displacements from equilibrium position is $\vec{u}=(u_x,u_y,u_z)$.

the existence of quasi-long-range order in the positions of the molecules inside the columns. This is consistent with the large fluctuations reported experimentally. The effective C_5 constant set to zero would turn the (001) and off-axis (hkl) Bragg peaks into Bragg maxima [9]. Another consequence of the quasi-long-range order is the appearance of a curvature term in the elastic free energy [7]. This term is identical to the curvature term of a plane in smectic-*A* compounds [8], thus we can imagine the structure of the HHTT as a regular array of columns in which the molecules show quasi-long-range positional order in the form of smectic-*A*-like planes that add a curvature term to the elastic free energy [Fig. 1(a)]. To be consistent with established notations, the name D_{hq} could be used to identify a columnar phase with positional quasi-long-range order inside the columns.

The main aim of this paper is to study, using scaling arguments based on the continuum elastic free energy, the shape of fractures in columnar phases showing short-range, quasi-long-range, and long-range positional order inside the columns. The secondary, but still important, issue is to propose a simple experiment to support the existence of quasi-long-range order in the HHTT compound and maybe other ordered columnar phases.

As in the case of smectic-*A* compounds [9], the experimental verification of quasi-long-range order requires a detailed x-ray Bragg maxima profile analysis. In view of the difficulty of x-ray measurements on well-oriented samples needed to distinguish between the various types of order possible, we propose a simple experiment that would hint on the nature of the order present in the *H* phase of HHTT. A thin cavity (fracture) perpendicular to the columnar axis is extended by a tensile stress $\sigma_{\alpha\beta}$. See Fig. 1(b) for the definition of the reference frame with respect to the columnar axis. Depending on the type of order present in the columns the crack tip profile will be different. We think, however, that such an experiment can provide only a *strong hint* on the nature of the *H* phase; mechanical instability and Bragg maxima profile analysis will be needed for definite conclusions.

The rest of this paper is organized as follows. The various forms of the continuum elastic free energy (including curvature terms) implicated in our treatment are recalled in Sec. II. Particular attention is given to the range over which a spatial perturbation is felt. The scaling fracture tip profiles are derived in Sec. III for columnar phases with short-range, quasi-long-range, and long-range order. In the Conclusion (Sec. IV), we suggest a simple experiment to support the existence of quasi-long-range order in the HHTT compound.

II. CURVATURE TERMS (REF. [8])

Before considering the problem of fracture in columnar phases, let us recall basic properties of the elastic free energy with curvature terms. It will be helpful to define notations. The main interest, for the present scaling analysis, is the range over which a perturbation is felt. Consider the elastic free energy for liquid columns [D_{hd} phase, one-dimensional (1D) objects in a 3D space]:

$$\mathcal{F}_{\rm col}=\int d^3r\left\{\frac{B_\perp}{2}\left(\frac{\partial u_x}{\partial x}+\frac{\partial u_y}{\partial y}\right)^2+\frac{K_{33}}{2}\left[\left(\frac{\partial^2 u_x}{\partial z^2}\right)^2+\left(\frac{\partial^2 u_y}{\partial z^2}\right)^2\right]\right\}. \tag{1}$$

The two terms in Eq. (1) represent the compression and bending of columns. A spatial perturbation of length $\delta_\parallel$ along the columns will decrease exponentially in the perpendicular directions with the characteristic length $l_\perp=\delta_\parallel^2/\lambda_1$, with $\lambda_1=\sqrt{K_{33}/B_\perp}$ a microscopic length. In the case of liquid planes (smectic-*A* planes, 2D objects in a 3D space), the free energy is

$$\mathcal{F}_{\rm plane}=\int d^3r\left[\frac{B_\parallel}{2}\left(\frac{\partial u_z}{\partial z}\right)^2+\frac{K}{2}\left(\frac{\partial^2 u_z}{\partial x^2}+\frac{\partial^2 u_z}{\partial y^2}\right)^2\right], \tag{2}$$

where the terms are, respectively, the compression and curvature of planes. This time, a perturbation in the $\hat{x}$-$\hat{y}$ plane of length $\delta_\perp$ will have an exponential decay in the $\hat{z}$ direction with characteristic length $l_\parallel=\delta_\perp^2/\lambda_2$ ($\lambda_2=\sqrt{K/B_\parallel}$, a microscopic length). Based on known values of $B_\perp$, $B_\parallel$, K_{33}, and K [7,8], we find $\lambda_1\approx\lambda_2$. For simplicity, we set $\lambda_1=\lambda_2=\lambda$ (that is, $B_\perp=B_\parallel=B$ and $K_{33}=K$). It is to be noted that within a thickness $l_\perp$ [or $l_\parallel$], the two terms (1) [or (2)] are comparable [8] and we need only to consider one of them in this simple analysis.

III. FRACTURE IN COLUMNAR PHASES

We will use the arguments exposed earlier to calculate the scaling fracture tip profile. The strategy is the following. We simply minimize a scaling free energy composed of three terms: interfacial (γ_0), elastic [see Eqs. (1) and (2)], and applied stress ($\sigma_{\alpha\beta}$). In determining the typical deformation ($\partial u_\alpha/\partial x_\beta$) and volume of integration (volume over which the deformation exists), we use R, $l_\parallel$, or $l_\perp$, depending on the context. For each type of intracolumnar order, two cases

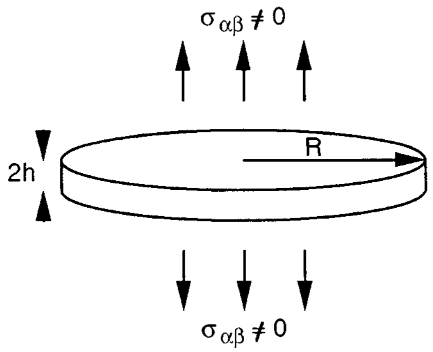

FIG. 2. Fracture shape considered (mode I). The typical size of the crack parallel (perpendicular) to the direction of the stress $\sigma_{\alpha\beta}$ is h (R). The particular shape of the edges of the crack depends on the order present inside the columns and on the direction of the applied tensile stress $\sigma_{\alpha\beta}$.

are studied: applied stress parallel or perpendicular to the columnar axis.

A. With short-range order

In the D_{hd} phase, the material is composed of a regular array of liquid columns. When the tensile stress is applied in the direction of the liquid columns ($\sigma_{zz} \neq 0$), the resulting fracture mode is characteristic of viscous fluids, controlled by tensions at the surface of the specimen.

In the case where $\sigma_{xx} \neq 0$ (see Fig. 2), we follow the Griffith approach [10], which was reformulated using scaling arguments by de Gennes for the case of smectic-A compounds [11]. We consider a disk-shaped fracture [Fig. 2, typical size R^2 in the $\hat{y}$-$\hat{z}$ plane ($\delta_\parallel = R$) and h in the $\hat{x}$ direction] extended by a tensile stress σ_{xx}. The scaling elastic free energy (omitting all numerical factors) is

$$f \simeq \gamma_0 R^2 + B\left(\frac{h}{l_\perp}\right)^2 R l_\perp^2 - \sigma_{xx}\left(\frac{h}{l_\perp}\right) R l_\perp^2, \tag{3}$$

since the disturbance in the $\hat{z}$ direction extends at distances $l_\perp = R^2/\lambda \gg R$ (because $\lambda \ll R$) in the perpendicular directions. The first term in Eq. (3) is the interfacial energy of the crack. The other terms are elastic [$(\partial u_x/\partial x) \propto h/l_\perp$ is the typical deformation localized in a volume $R l_\perp^2$]. We consider only the B term (column compression) since the two terms in Eq. (1) are supposed to be comparable within the volume $R l_\perp^2$. Minimizing Eq. (3) with respect to h gives

$$\sigma_{xx} \simeq \frac{h^\star \lambda B}{R^2} \tag{4}$$

and the free energy becomes (ignoring again all numerical prefactors)

$$f \simeq \gamma_0 R^2 - \frac{\sigma_{xx}^2 R^5}{\lambda^2 B}. \tag{5}$$

It has a maximum at

$$R^\star \simeq \frac{(\gamma_0 B \lambda^2)^{1/3}}{\sigma_{xx}^{2/3}}. \tag{6}$$

If the crack has a radius $R < R^\star$, it contracts and vanishes; on the contrary, if $R > R^\star$ it expands indefinitely. Equations (4) and (6) also give the scaling profile of the crack tip [$\zeta(z) \propto |z|^{1/2}$] and the scaling of the stress distribution ($\sigma_{xx} \propto z^{-3/2}$).

B. With quasi-long-range order

We are now considering fractures in phases composed of a regular array of columns having quasi-long-range order in the positions of the molecules inside the columns. As pointed out earlier, the elastic free energy will have two curvature contributions: bending of the columns and curvature of the smectic-A-like planes.

When the short axis of the crack is oriented parallel to the columnar axis ($\sigma_{zz} \neq 0$, see Fig. 2), the range of spatial perturbations will be $l_\parallel = R^2/\lambda \gg R$ and $l_\perp = h^2/\lambda \ll R$ (bending of the columns does not contribute here). Then the scaling elastic free energy is

$$f \simeq \gamma_0 R^2 + B\left(\frac{h}{l_\parallel}\right)^2 R^2 l_\parallel - \sigma_{zz}\left(\frac{h}{l_\parallel}\right) R^2 l_\parallel. \tag{7}$$

The typical deformation ($\partial u_z/\partial z$) is $h/l_\parallel$ and the volume over which it is felt is $R^2 l_\parallel$ since $l_\perp \ll R$ in this case. We are exactly in the situation of fracture in a smectic-A compound [11]. The crack is formed by two spherical caps intersecting at a finite angle $2\theta_0$ characteristic of the material:

$$\theta_0 \simeq \frac{h^\star}{R^\star} \simeq \left(\frac{\gamma_0}{B\lambda}\right)^{1/2} \ll 1 \quad \text{(by assumption)}. \tag{8}$$

This means that the scaling profile of the crack tip is

$$\zeta(x) \propto |x|, \tag{9}$$

and that the stress distribution at the crack tip will be given by (from [11])

$$\sigma_{zz}(x) \propto x^{-1}. \tag{10}$$

These results can be interpreted from renormalization, by curvature terms, of the interfacial energies [11].

In the next case considered, we have set $\sigma_{xx} \neq 0$ (see Fig. 2). Assuming that bending of the columns and curvature of the smectic-A-like planes contribute to the free energy, thus extending the range of the deformations, we find that $l_\parallel = R^2/\lambda \gg R$ and $l_\perp = R^2/\lambda \gg R$. The scaling elastic free energy reads

$$f \simeq \gamma_0 R^2 + B\left(\frac{h}{l_\perp}\right)^2 l_\perp^2 l_\parallel - \sigma_{xx}\left(\frac{h}{l_\perp}\right) l_\perp^2 l_\parallel, \tag{11}$$

where $h/l_\perp$ is the typical deformation and $l_\perp^2 l_\parallel$ is the volume over which it is felt. Minimization with respect to h and R gives (see Sec. III A)

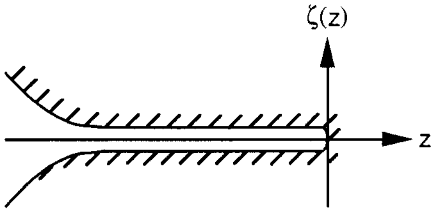

FIG. 3. Tentative representation of a fracture showing a constant tip profile.

$$\sigma_{xx} \simeq \frac{h^\star \lambda B}{R^2} \tag{12}$$

and

$$R^\star \simeq \frac{(\gamma_0 B \lambda^3)^{1/4}}{\sigma_{xx}^{1/2}}. \tag{13}$$

The equations (12) and (13) also give the scaling profile $[\zeta(z) \simeq \sqrt{(\gamma_0 \lambda)/B} = cte]$ and the stress distribution $[\sigma_{xx}(z) \propto z^{-2}]$ at the crack tip.

The preceding result $[\zeta(z) = cte]$ is quite surprising. It is an example of a fracture of typical size R for which the deformation is felt inside a volume much larger than R^3: in fact $l_\perp^2 l_\parallel = R^6/\lambda^3 \gg R^3$. A tentative fracture profile is given in Fig. 3. Note that this result requires that bending of the columns and curvature of the smectic-A-like planes contribute to the free energy. From the geometry of the crack (Fig. 2), one can be tempted to rule out the contribution from the curvature of the plane, but it is to be remembered that a perturbation of characteristic length R is present in the direction perpendicular to the columnar axis. This question still remains open.

C. With long-range order

When the columnar phase exhibits long-range positional order inside the columns, it is a true three-dimensional solid (D_{ho} phase). To first order, the curvature terms are no longer relevant and the scaling of the fracture tip profile should be independent of the direction of the applied stress. For the purpose of comparison, we recall the main results of the Griffith problem (fracture in a simple solid [10]) reformulated using scaling arguments by de Gennes [11]: $R^\star \propto \sigma_{zz}^{-2}$ and $\zeta(z) \propto |z|^{1/2}$.

IV. DISCUSSION

We have calculated with scaling arguments the characteristic crack tip profiles (ζ) and the stress distribution ($\sigma_{\alpha\beta}$) at the edge of disk-shaped fractures in columnar phases for various geometries. Although based on the HHTT compound, the arguments used should be valid for other columnar liquid crystals.

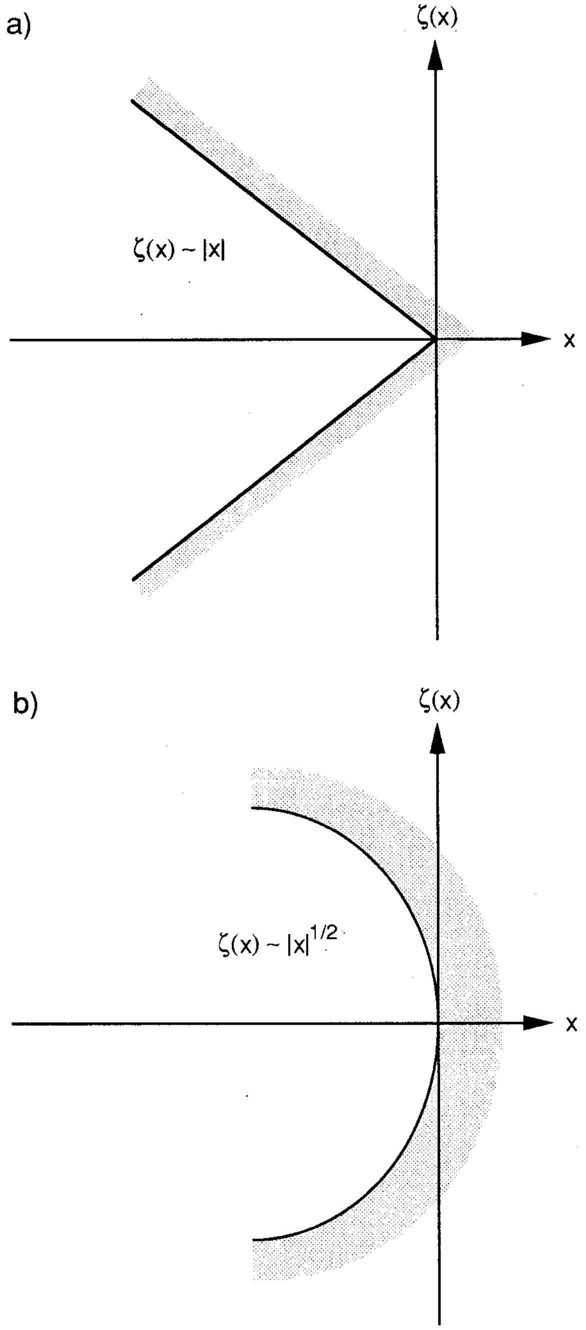

FIG. 4. Fracture tip profile characteristic of (a) quasi-long-range and (b) long-range order in the positions of the molecules inside the columns.

When gathered together with results for smectic-A compounds [11] $[R^\star \propto \sigma_0^{-1}$ and $\zeta(z) \propto |z|]$, certain conclusions can be drawn.

(1) Since the applied stress is small, we can deduce that columnar phases are more fragile than smectic-A compounds and solids. This is readily seen by inspection of the threshold radius in the different cases (σ_0 is a common notation for tensile stresses):

$$R^{\star}\propto\begin{cases}\sigma_0^{-1/2} & \text{for the } H \text{ phase of HHTT } (\text{with } \sigma_{xx}\neq 0)\\ \sigma_0^{-2/3} & \text{for the } D_{hd} \text{ phase of columnar phases}\\ & \quad (\text{with } \sigma_{xx}\neq 0)\\ \sigma_0^{-1} & \text{for a smectic-}A \text{ compound}\\ \sigma_0^{-2} & \text{for a solid.}\end{cases}$$

The tendency of columnar phases to fracture easily is a known fact, but the failure mechanism is best described by a flow process where columns slide over each other [12].

(2) We are in a position to propose a simple experiment to hint at the nature of the H phase of HHTT and, maybe, to revisit the D_{ho} phase of other compounds. When a tensile stress is applied along the columnar axis, the fracture tip will exhibit a characteristic profile depending on the nature of the phase: $\zeta(x)\propto|x|$ for a columnar phase with quasi-long-range positional order inside the columns or $\zeta(x)\propto|x|^{1/2}$ for a simple solid (Fig. 4). As mentioned earlier, this simple experiment based on scaling arguments can only give us a *strong hint* on the nature of the order present inside the columns; detailed Bragg maxima profile analysis would be required to draw definite conclusions.

Finally, can we witness this fracture phenomena before the undulation instability when the tensile stress σ_0 is applied [8]? For a sample of thickness D (in the direction of the applied stress), the undulation threshold is $\sigma_u\simeq B\lambda/D$. If we consider the case where the positions of the molecules inside the columns show quasi-long-range order (from [11])

$$\frac{\sigma_0}{\sigma_u}\simeq\left(\frac{\gamma_0}{B\lambda}\right)^{1/2}\frac{D}{R}. \tag{14}$$

Moreover, since we assumed that $D>l_{\parallel}=R^2/\lambda$, the following inequalities hold:

$$\left(\frac{\gamma_0 D}{B}\right)^{1/2}\frac{1}{\lambda}<\frac{\sigma_0}{\sigma_u}<1 \tag{15}$$

provided that the fracture occurs before undulation instabilities. This requires that $K/\gamma_0>D$. In general, K/γ_0 scales like d (where d is the distance between columns or between smectic-A-like planes). The inequalities (15) can never be verified since $d\ll D$. However, columnar mesophases of discotic main chain polymers have been reported [13]: basically, the different molecules have their aliphatic tails linked together by flexible polymeric spacers. The ratio K/γ_0 should now scale like d', where d' is the average length of the discotic main chain polymer along the direction of the applied stress. At the percolation threshold (gelation point), $K/\gamma_0\propto D$ and the inequalities (15) could be verified. Note finally that the presence of flexible polymer spacers between molecules would prevent the fracture mechanism to be characterized by the flow of columns over each other and is not supposed to disturb the order inside the columns. To obtain a highly ordered phase of this material would most likely require *in situ* polymerization of an already formed liquid crystalline or crystalline columnar phase.

ACKNOWLEDGMENTS

We would like to thank P. A. Heiney, A. Caillé, E. Raphaël, and P.-G. de Gennes for useful discussions. The support of the Natural Sciences and Engineering Research Council of Canada (NSERC) is acknowledged.

[1] S. Chandrasekhar, B.K. Sadashiva, and K.A. Suresh, Pramana **7**, 471 (1977).
[2] S. Chandrasekhar, Liq. Cryst. **14**, 1 (1993).
[3] S. Chandrasekhar, *Liquid Crystals* (Cambridge University Press, Cambridge, England, 1992).
[4] H.R. Brand and H. Pleiner, Phys. Rev. Lett. **69**, 987 (1992); G. Durand, *ibid.* **69**, 988 (1992).
[5] E. Fontes, P.A. Heiney, and W.H. de Jeu, Phys. Rev. Lett. **61**, 1202 (1988); P.A. Heiney, E. Fontes, W.H. de Jeu, A. Reira, P. Carroll, and A.B. Smith III, J. Phys. (Paris) **50**, 461 (1989).
[6] E. Fontes, Doctoral Dissertation, University of Pennsylvania, 1989.
[7] A. Caillé and M. Hébert, Phys. Rev. E **54**, R4544 (1996).
[8] P.-G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, 2nd ed. (Oxford University Press, Oxford, 1993).
[9] A. Caillé, C. R. Acad. Sci. Paris **274**, 891 (1972); J. Als-Nielsen, J.D. Litster, R.J. Birgeneau, M. Kaplan, C.R. Safinya, A. Lindegaard-Andersen, and S. Mathiesen, Phys. Rev. B **22**, 312 (1980).
[10] A.A. Griffith, Philos. Trans. R. Soc. London Ser. A **221**, 163 (1921).
[11] P.-G. de Gennes, Europhys. Lett. **13**, 709 (1990).
[12] P.A. Heiney (private communication).
[13] O. Herrmann-Schönherr, J.H. Wendorff, W. Kreuder, and H. Ringsdorf, Makromol. Chem., Rapid Commun. **7**, 97 (1986); N. Boden, R.J. Bushby, and A.N. Cammidge, J. Am. Chem. Soc. **107**, 924 (1995).