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Elasticity-driven texture selection mechanism in mesophase carbon fibers

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In this Brief Report, we identify the parametric conditions and elasticity-driven mechanism that give rise to a characteristic texture commonly found during the fiber melt spinning of carbonaceous mesophase precursors; this mesophase consists of a biphasic isotropic-uniaxial discotic nematic liquid crystal mixture. The essential feature of the characteristic texture consists of a radial zig-zag molecular arrangement on a cross section of the mesophase carbon fiber. Using the Williams elastic-driven mechanism [D.R.M. Williams, Phys. Rev. E **50**, 1686 (1994)] that gives rise to periodic director oscillations in cylindrical geometries, here adapted to discotic nematic fibers subjected to extensional flow, we show that when the bend K_3 constant becomes larger than the splay K_1 constant, the radial trajectories of the molecular planes become unstable in the presence of spatially periodic perturbations, leading to the experimentally observed radial zig-zag texture.

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The industrial fabrication of mesophase carbon fibers [1] typically consists of subjecting a biphasic isotropic-discotic nematic mixture to uniaxial extensional flow, producing a micrometer-sized cylindrical filament whose cross-sectional area displays a wide variety of transverse textures [2]. The selection mechanisms that drive the pattern formation are at present not well understood, but due to strong structure-properties correlations they are essential for product optimization. The transverse texture is defined by the spatial arrangement of the molecular planes formed by the disklike molecules on a cross section of the essentially cylindrical fibers. Figure 1 shows a scanning electron micrograph of the fracture surface of a mesophase carbon fiber displaying a radial zig-zag transverse texture [3]. Although the characteristic amplitude and wavelength of the shown spatially periodic structure is position dependent, the basic feature of interest is the radial zig-zag trajectories of the molecular planes. The objective of this note is to identify the driving force behind the selection of the radial zig-zag pattern, as shown in Fig. 1. The mesophase carbon fiber is approximated by a monodisperse uniaxial discotic nematic liquid crystal [4], and the spinning process is approximated by a steady, isothermal, incompressible, uniaxial extensional flow [5]. To explain the periodic oscillations present in Fig. 1 we must consider (i) the relevant elastic deformations present in a radial zig-zag texture of a uniaxial discotic nematic in a cylindrical fiber, (ii) the stable and steady director orientation of a uniaxial discotic nematic liquid crystal in extensional flow, and (iii) texture selection mechanisms of uniaxial discotic nematics' cylindrical fibers in steady extensional flow.

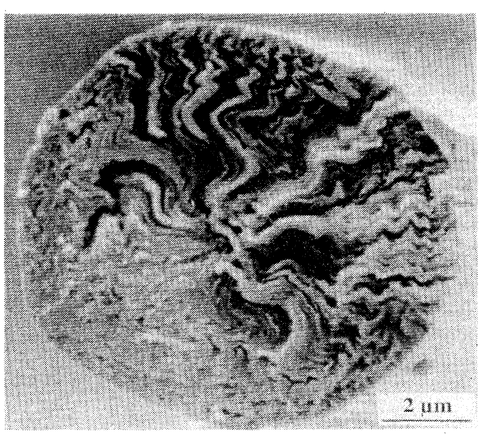

FIG. 1. Scanning electron micrograph of the fracture surface of a mesophase carbon fiber displaying a radial zig-zag transverse texture. [From G. M. Pencock, G. H. Taylor, and J. D. FitzGerald, Carbon **31**, 591 (1993), by kind permission from Elsevier Science Ltd.]

I. ELASTIC DEFORMATIONS

Figure 2 shows the molecular geometry, positional disorder, and uniaxial orientational order of the model uniaxial discotic nematic liquid crystal. The partial orientational ordering of the molecular unit normals **u** is along the average orientation or director **n** ($\mathbf{n}\cdot\mathbf{n}=1$), and differs from that of rodlike molecules in that **u** is along

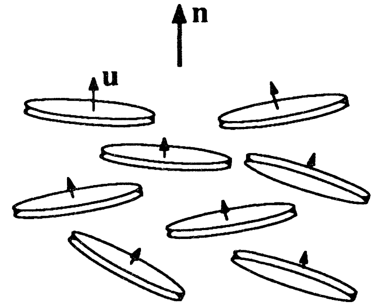

FIG. 2. Orientational ordering in the uniaxial discotic nematic liquid crystal phase. The molecular normals **u** of the randomly positioned disk-like molecules, partially orient along the director **n**.

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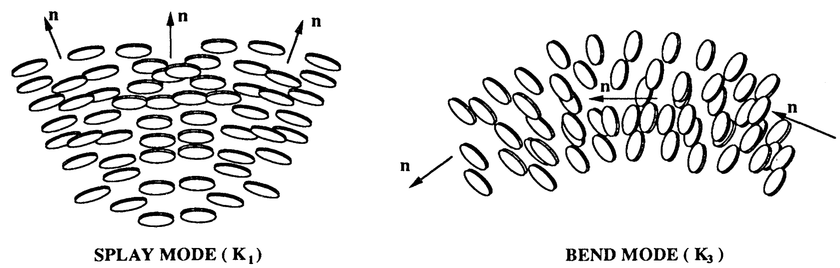

FIG. 3. Schematics of the elastic splay deformation (left) and bend deformation (right) for uniaxial discotic nematics. Note that the splay (bend) mode involves bending (splaying) of the disk's trajectories, in contrast to the case of uniaxial rodlike nematics. A disk trajectory is a curve locally orthogonal to the director.

the shortest molecular dimension. This geometric difference is the source of the reversal in the ordering of viscoelastic [6,7] as well as other properties [2] that arise when comparing disklike and rodlike uniaxial nematics. Figure 3 shows the splay mode of modulus K_1 and the bend mode of modulus K_3. Note that in contrast to rodlike nematics, for disk-like nematics the bending disc's trajectories give rise to a splay deformation (left figure), and the splaying disk's trajectories give rise to a bend deformation (right figure); by disk trajectory we mean the curve locally orthogonal to the director. Using a circular cylindrical coordinate system (r,φ,z), the z coordinate is along the fiber axis, and the transverse plane is spanned by the azimuthal direction (φ) and the radial (r) direction; here $0 \le \varphi \le 2\pi$ and $r_c \le r \le r_0$, where r_c is the core radius of molecular dimensions, and r_0 is the outer radius which for typical mesophase carbon fibers is in the micrometer-size zero range. In this cylindrical geometry, the stationary radially dependent director field of Fig. 1. can be parametrized as $\mathbf{n}\,(r)=(n_r,n_\varphi,n_z)=(\cos\theta,\sin\theta,0)$; here $n_z=0$ means planar orientation. Figure 4 shows schematics of a radial transverse texture (left) and a radial zig-zag texture (right). The full lines indicate the disk's trajectories, which are locally orthogonal to the director trajectories. Based on our discussion, it follows that the radial texture of a uniaxial discotic nematic, defined by $n_\varphi(r)=1$ and $r_c \le r \le r_0$, contains a pure bend mode. On the other hand, a radial zig-zag texture consists of a mixed splay-bend deformation mode, and in addition $n_\varphi(r_0)\neq 1$. Figure 1 can then be approximated by a planar radial zig-zag texture containing splay-bend deformations. A comparison of the two schematics of Fig. 4 indicates that if the radial zig-zag texture is selected over the pure radial texture because of the director orientation at the outer boundary, then the trade-off of bend by splay in an oscillatory pattern must be energetically favorable, as quantitatively shown below.

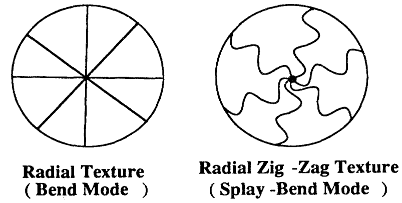

FIG. 4. Schematics of a planar radial transverse fiber texture (bend mode) and the planar radial zig-zag fiber texture (splay-bend mode). If the bend mode is energetically unfavorable when compared to the splay mode, director oscillations reduce the free energy per unit fiber length.

II. FLOW-INDUCED ORIENTATION

We next discuss the effect of an external extensional flow in the z direction on the texture formation in the φ-r plane. The nonzero components of the rate of deformation tensor A_{ij} for such a flow are [5] $A_{zz}=-A_n=\dot{\varepsilon}$, where $\dot{\epsilon}$ is the extension rate, and the vorticity tensor of this irrotational flow is $\mathbf{W}=0$. At steady state, the viscous torques Γ^v acting on the director are $\Gamma^v=-\mathbf{n}\times(\gamma_2\mathbf{A}\cdot\mathbf{n})$, where γ_2 is a torque coefficient [8]. As is well known [9], in this flow the stable director orientation is normal to the extension direction (i.e., transverse φ-r plane), and therefore $\Gamma^v=0$. Thus the net effect of the extensional flow on the texture formation is to keep the director in the φ-r transverse plane. Therefore, we may conclude that, given sufficient long process times as compared to reorientation times, the transverse radial zig-zag pattern is selected by the minimization of the splay-bend elastic free energy per unit fiber length.

III. TEXTURE SELECTION MECHANISM

Since there is no twist deformations in a planar orientation, the Frank elastic energy per unit volume is just [8]

$$F_d=K_1(\nabla\cdot\mathbf{n})^2+K_3|\mathbf{n}\times(\nabla\times\mathbf{n})|^2\ . \tag{1}$$

If for a uniaxial discotic nematic $K_3>K_1$, the most cost effective way to replace bend by splay within an annular region and subjected to the outer boundary orientation constraint is through director oscillations. This pattern selection mechanism was identified by Williams [10] for planar radial textures of rodlike nematics confined to cylindrical cavities. For rodlike nematics the radial texture is a pure splay mode with $n_r(r_0)=1$, and Williams has shown [10] that when $K_1>K_3$ and $n_r(r_0)\neq 1$, the radial zig-zag is the lowest energy mode, a case expected to be found for polymeric rodlike nematics. For low molar mass discotic nematics, theory [6] and experiment [11] show that $K_1>K_3$. An increase in the molecular weight of disklike nematics, just as for rodlike nematics [12], can be expected to reverse the ordering of the elastic constants, so that for higher molecular weight discotic nematics, like carbonaceous mesophases, we can expect that $K_3>K_1$. Thus, just as polymeric rods avoid the splay of the radial texture by introducing director oscillations, polymeric disks avoid the bend of the radial texture by a zig-zagging director field.

Assuming radial dependence, the minimization of the free energy per unit length of the discotic nematic in an annular region $(0\le\varphi\le 2\pi, r_c\le r\le r_0)$ can be shown to lead to the following dimensionless nonlinear differential

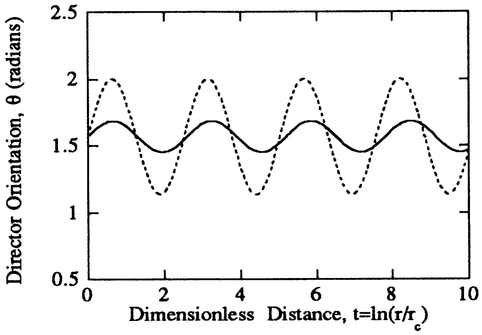

FIG. 5. Director orientation θ as a function of dimensionless distance (t), predicted by the linear (dashed line) and nonlinear theory (full line), for $\kappa=K_1/K_3-1=-6.2$, $t_0=10$, and $\theta(t_0)=\pi/2-0.1$ rad. Nonlinearities decrease the amplitude of the director oscillations. The amplitude and wavelength are functions of $|\kappa|$. If $\kappa>0$, the director profiles are monotonic and nonoscillatory.

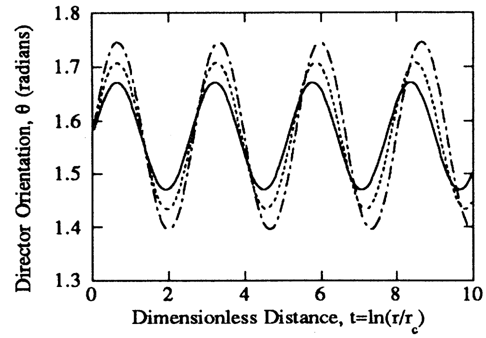

FIG. 6. Director orientation θ as a function of dimensionless distance (t) predicted the nonlinear theory [Eq. (2)], for $\kappa=-6.2$, $t_0=10$, and three boundary conditions $\theta(t=t_0)$: 1.497 (full line), 1.44 (dashed line), and 1.396 (dashed-dotted line) rad. Increasing the boundary perturbation for a given κ increases the amplitude of the director oscillation.

equation for the director orientation q:

$$\frac{\kappa}{2}\sin(2\theta)\left[1+\left[\frac{d\theta}{dt}\right]^2\right] +[1+\kappa\sin^2(\theta)]\frac{d^2\theta}{dt^2}=0;\quad 0<t<t_0\ , \qquad (2)$$

where

$$\kappa=\frac{K_1}{K_3}-1;\quad t=\ln(r/r_c);\quad t_0=\ln(r_0/r_c)\ . \qquad (3)$$

To capture the radial zig-zag texture the relevant boundary conditions are $\theta(0)=\pi/2$, $\theta(t_0)=\pi/2-\beta$, where $t_0=\ln(r_0/r_c)$. As discussed above, we assume that for a high molecular weight discotic nematic $\kappa<0$. Following Williams [10], linearizing (2) around $\theta=\pi/2$, and using the substitution $\theta=\pi/2-\psi$, we obtain

$$\frac{d^2\psi}{dt^2}=-|\kappa|\psi,\quad 0<t<t_0;\quad \psi(0)=0;\quad \psi(t_0)=\beta \qquad (4)$$

whose spatially oscillatory solution is

$$\psi(t)=\beta\sin(\sqrt{|\kappa|}t)/\sin(\sqrt{|\kappa|}t_0)\ .$$

Note that both the amplitude and wavelength are $|\kappa|$ dependent. The linear analysis then establishes that the mechanism of radial zig-zag planar texture selection is due to the elastic anisotropy $\kappa=K_1/K_3-1<0$, expected from relatively high molecular weight uniaxial discotic nematics; a typical molecular weight for the polydisperse carbonaceous mesophases is 2×10^3 [1]. It should be emphasized that if $\kappa>0$ oscillations are not present then the director profiles are monotonic and nonoscillatory. The range of validity of the linear analysis is drastically restricted by $\beta/\sin(\sqrt{|\kappa|}t_0)\ll1$. We have performed a numerical analysis (3) using Galerkin finite elements [13], with 200 linear elements. Figure 5 shows the director orientation, as predicted by the linear theory (dashed line) and the numerical solution to (2), for $\kappa=-6.2$, $t_0=10$, and $\theta(t_0)=\pi/2-0.1$. These representative solutions clearly show the predicted constant amplitude director oscillations. For this particular case the number of oscillations is $n=\sqrt{|\kappa|}t_0/2\pi=3.96$, and the shown amplitude differences between the two curves is due to nonlinearities. As expected we found that nonlinearities quench the unbounded growth of the oscillation amplitude as $\sqrt{|\kappa|}t_0\rightarrow m\pi$, where m is an integer. Figure 6 shows the director orientation profiles $\theta(t)$ predicted by (2), for several boundary orientations and $\kappa=-6.2$. As predicted by linear theory, increasing the magnitude of the outer surface director orientation from $\pi/2$ increases the amplitude of the director wave; the numerical solution also show a slight effect on the selected wavelength.

In summary, we have presented an idealized and greatly simplified analysis to a complex process that is able to qualitatively explain, using well-established liquid crystal physics concepts and equations, a characteristic transverse fiber texture found in the industrial melt spinning of carbonaceous mesophases. In particular, the radial zigzag texture selection is found to be driven by the elastic anisotropy between bend and splay, expected to be found in higher molecular weight uniaxial discotic nematic liquid crystals.

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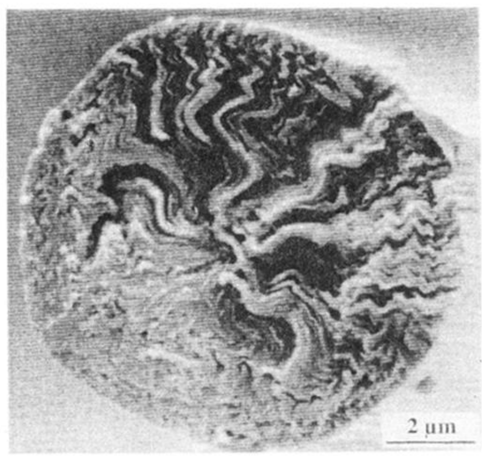

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