my of Arts and Sciences and the U. S.-Israel Binational Science Foundation (BSF), Jerusalem, Israel.

---

[1] For an experimental review, see H. Stegemeyer and K. Bergmann, in *Liquid Crystals of One- and Two-Dimensional Order*, edited by W. Helfrich and G. Heppke (Springer-Verlag, Berlin, 1980), p. 161.

[2] S. Meiboom and M. Sammon, Phys. Rev. A 24, 468 (1981).

[3] J. H. Flack and P. P. Crooker, Phys. Lett. 82A, 247 (1981).

[4] M. Marcus, J. Phys. (Paris) 42, 61 (1981).

[5] H. Onussit and H. Stegemeyer, Z. Naturforsch. 36a, 1083 (1981).

[6] J. Her, B. B. Rao, and J. T. Ho, Phys. Rev. A 24, 3272 (1981).

[7] P. H. Keyes, A. J. Nicastro, and E. M. McKinnon, Mol. Cryst. Liq. Cryst. 67, 59 (1981).

[8] R. M. Hornreich and S. Shtrikman, Bull. Israel Phys. Soc. 25, 46 (1979), and J. Phys. (Paris) 41, 335 (1980), and 42, 367(E) (1981), and Phys. Lett. 82A, 345 (1981), and Phys. Rev. A 24, 635 (1981).

[9] S. Alexander, in Proceedings of the Colloquium: Pierre Curie, Paris, 1–5 September 1980 (to be published).

[10] S. Meiboom, J. P. Sethna, P. W. Anderson, and W. F. Brinkman, Phys. Rev. Lett. 46, 1216 (1981).

[11] R. M. Hornreich and S. Shtrikman, Phys. Lett. 84A, 20 (1981). [In Eq. (6) replace $1+\alpha$ by α and multiply the final term by $2k_0$. In Eq. (7), replace $1+\alpha$ by 2α and $1-\alpha$ by $(1-\alpha)/2$. The initial slope is $\omega_p = 1.57/3.37$. All conclusions are unaffected.]

[12] P. G. de Gennes, Mol. Cryst. Liq. Cryst. 12, 193 (1971).

[13] We here parametrize $\hat{n}$ in terms of one degree of freedom rather than two. It can be shown that this form automatically satisfies the third equation of motion which would appear in a complete treatment.

[14] We use the term "soliton" to denote that the solution has a local rather than periodic character; it is *not* a topological soliton.

Freely Suspended Strands of Tilted Columnar Liquid-Crystal Phases: One-Dimensional Nematics with Orientational Jumps

David H. Van Winkle and Noel A. Clark
Department of Physics, University of Colorado, Boulder, Colorado 80309

(Received 12 February 1982)

Observations of stable, freely suspended liquid-crystal strands are reported. Liquid crystals of triphenylene hexa-n-dodecanoate can be stretched into strands of diameter $\gtrsim 1\ \mu\text{m}$, with the disk-shaped molecules arranged into columns along the strand axis. In the $D1$ phase ($T < 110\,^\circ\text{C}$) the molecules are tilted with respect to the strand axis, the tilt orientation behaving as a one-dimensional nematiclike field, interrupted by jumps in orientation between degenerate stable positions relative to the column lattice.

PACS numbers: 61.30.Eb, 61.30.Jf

Certain disk-shaped molecules exhibit nematic[1] and columnar[2] liquid-crystalline phases. The columnar phases are characterized by the partial translational ordering of the molecules into a two-dimensional array of flexible columns, analogous to the one-dimensional layered ordering in smectic phases formed by rod-shaped molecules. It has recently been shown[3] that some liquids with rod-shaped molecules which form smectic phases can be drawn into thin films, freely suspended in air, a discrete number of smectic layers in thickness. In this Letter we report an analogous freely suspended structure for disk-shaped molecules, namely freely suspended strands.

We studied the compound triphenylene hexa-n-dodecanoate, reported by Destrade, Mondon-Bernaud, and Tinh[4] to exhibit three columnar mesophases which they labeled $D0$, $D1$, and $D2$ with transition temperatures, in degrees Celsius, as follows:

$$X \xrightarrow{80} D0 \xrightarrow{93} D1 \xrightarrow{111} D2 \xrightarrow{122} I.$$

To form a strand, a small amount of the compound in its crystalline phase is placed on a cover slide into which a 5-mm-diam hole has been drilled. The temperature of the sample is raised into the $D2$ phase to provide sufficient flow to coat the edges of the hole and the edge of the spreader, another cover slip, with the material. The temperature is then lowered into the $D1$ phase where strands can be drawn by moving the slide relative to the spreader. Initially the sample may spread into a thick film, suspended between the hole boundary and the spreader. The film completely spans the uncovered portion of the hole as long as it is less than ~0.2 mm long. Further spreading leads to an instability characterized by thicker parts of the film thinning at a slower rate than thinner parts. This preferential thinning results in spontaneous formation of pores in the film which expand, leaving thick bridges across the hole. Upon stretching, the diameter of a bridge decreases to form a thin freely suspended strand of more or less constant thickness between two bulky sources of material at its ends [Figs. 1(a)–1(c)]. Freely suspended strands can be formed in the columnar phases for $T < 115\,^\circ\mathrm{C}$, and are more stable at lower temperatures. The $D1$-$D0$ transition is not observed in the strands. Strands thin uniformly as they are stretched until some part of the strand reaches a few microns in diameter. Further stretching results in the continued thinning of only a short length (~20 μm) of strand, leading to rupture when the minimum diameter of this short length decreases to less than 1 μm.

Polarized-light microscopy may be used to study general features of strand structure. These may be summarized as follows:

(1) In the $D2$ strand ($T > 110\,^\circ\mathrm{C}$) observations under crossed polarizers show that light transmitted by the strand is extinguished when Γ, the angle between the strand axis and the polarizer direction (Fig. 2) is zero, mod$\pi/2$. Maximum transmission occurs for $\Gamma = \pi/4$, mod$\pi/2$. Hence, it appears that the $D2$ strand has an optic axis parallel to the strand axis, consistent with the structural identification of the $D2$ phase being a hexagonal two-dimensional column lattice with the molecules perpendicular to the columns.[5]

(2) The $D1$ strands ($T < 110\,^\circ\mathrm{C}$) in general *transmit* light between crossed polarizers for $\Gamma = 0$, but at a given position along the strand, extinction can be achieved by rotating the strand through

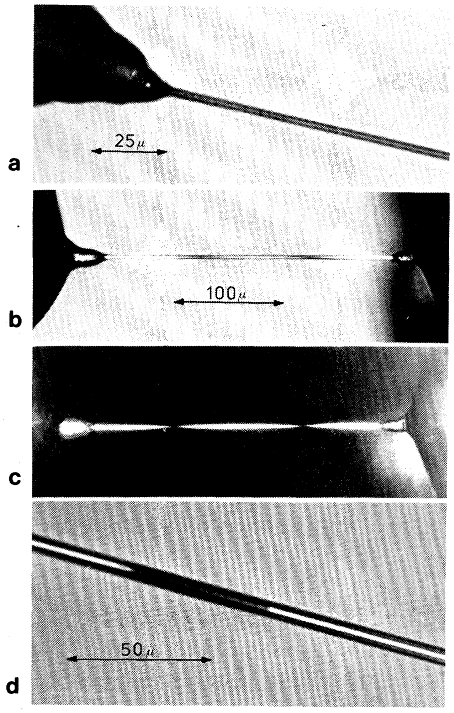

FIG. 1. Transmission photomicrographs of freely suspended strands of triphenylene hexa-n-dodecanoate at 90 °C ($D1$ phase): (a) No analyzer, radius $r = 1\ \mu$m. (b) Strand with a 2π director rotation over its length, $r = 1.5\ \mu$m. (c) Strand in (b) with crossed analyzer and $\Gamma = 0$. (d) Discrete orientational jumps in φ of magnitude $\pi/3$, $r = 3\ \mu$m. The center (dark) portion has φ different from the bright portions by $\Delta\varphi = \pi/3$.

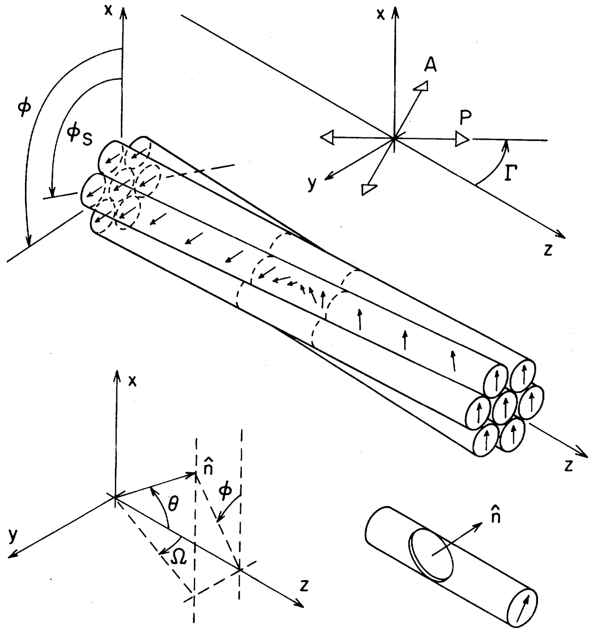

FIG. 2. Schematic of the strand structure according to our observations showing the strand lattice (orientation about z is φ_s) and the director, $\hat{n}$ (orientation about z is φ). Polarized light, incident along x, probes the orientation, Ω, of the director axis projected onto the y-z plane. The two kinds of observed variation of φ with z are shown: (1) Continuous—due to a locally helical strand deformation and rotation of the strand lattice. (2) Jumps—due to switching of the director relative to the strand lattice, from one degenerate orientation to another.

some finite angle. Insertion of a variable wave plate in series with the strand shows that locally the strand behaves as a simple birefringent plate with an optic axis at an angle $\Omega(z)$ with respect to the strand axis.

Polarized-light microscopy reveals several striking features of the dependence of Ω on z in $D1$ strands. We find that Ω may assume any value over a finite range $-\theta < \Omega < \theta$. For fixed z, Ω changes slowly with time, varying continuously over the above range. We interpret this and further observations, cited below, to be a result of rotation of the strand about its axis. That is, in the $D1$ strand, the direction normal to the molecular planes, and therefore the optic axis, is tilted through the angle θ with respect to the strand axis. As the azimuthal optic-axis orientation, φ (Fig. 2), varies, Ω, the orientation of the projection of the optic axis onto the y-z plane, $\Omega = \tan^{-1}(\tan\theta \sin\varphi)$, varies over the range $-\theta < \Omega < \theta$.

The variation of the optic-axis orientation along the length of a strand is characterized by a continuous smooth change of φ with z, interrupted by occasional discrete jumps in φ. A ubiquitous feature of the structure of a strand is the continuous variation of Ω along the strand. Figures 1(b) and 1(c) show a particularly striking example of this feature in which the optic-axis orientation varies nearly linearly along the strand to form a helical structure with a net 2π rotation over the length of the strand. This helix pitch is not an intrinsic property of the strand, but depends on the details of the strand formation history. The helix pitch can vary continuously in time, particularly under conditions of changing temperature or stretching. We interpret this continuous variation of optic-axis orientation as resulting from a continuous rotation of the strand-lattice orientation with z (Fig. 2), since the tilt direction and lattice orientation will in general be coupled. For thin strands ($d < 10$ μm), the observed variation of this orientation field is small over distances comparable to the strand diameter and thus should be describable by a single orientational coordinate $\varphi_s(z,t)$. The energetics and dynamics of φ_s are analogous to the nematic director orientational field [e.g., a distortion free energy per unit length, $F = \frac{1}{2}\kappa(\partial\varphi_s/\partial z)$, where κ is an effective Frank elastic constant]. Thus, in the orientation variations of wavelength larger than the strand diameter, we have a physical realization of a nematic system characterized by a single orientational coordinate varying in one dimension (a one-dimensional nematic).

We emphasize at this point the distinction between the lattice orientation φ_s and the optic-axis orientation φ. In a tilted columnar structure of the sort observed, there will be coupling between the molecular orientation and translational position. Two possible sets of six degenerate orientations for the tilt direction relative to the lattice are allowed [either tilt in any of the six (1, 0) or in the six (1, 1) directions]. Thus φ and φ_s are not uniquely related. Furthermore, as Prost has noted,[6] the possibility exists that two or more degenerate orientations could exist in different regions of a given sample, meeting in solitonlike steps of the optic-axis orientation field. We have observed such structures: They result in the discrete jumps in the optic-axis orientation noted above. Figure (1d) shows a 6-μm-diam strand with a pair of discrete orientational jumps. These orientational step structures can be mobile, moving along the strands at velocities ~ 50 μm/sec.

Arguments concerning the stability of circular cylindrical liquid jets against diameter fluctuations, first presented by Rayleigh,[7] suggest there should be some minimum stable diameter for a freely suspended strand. Consider a fluid circular cylinder coaxial with the z axis, having a radius $r(z)$ and a small fluctuation in radius of amplitude α, which is periodic in z with wave number k, i.e., $r = r_c + \alpha \cos kz$. For a fluid cylinder there is only a surface contribution to the potential energy due to this type of distortion, exactly that discussed by Rayleigh: $V_s = (\nu\pi\alpha^2/2r)(k^2r^2 - 1)$, where ν is the surface tension and V_s is the excess surface potential energy per unit length. Note that at sufficiently long wavelength ($k^{-1} > r$) V_s is negative, and the jet is unstable. In a columnar liquid-crystal structure there is an additional bulk energy contribution arising from the compression of the columnar structure.[8] This compressional energy is $2\pi\alpha^2 C$, where C is the compressional modulus associated with a change in the column density in a plane normal to the strands. The net potential energy is of the form $V = B\pi\alpha^2/2r$, and the strand is unstable against all fluctuations for which $B < 0$. The stability limit is

$$B = k^2\nu r^2 + 4Cr - \nu > 0.$$

In the limit of small k, instability occurs for strand radius smaller than $r_c = \nu/4C$ and $k < k_c = 1/r[r_c/(r_c - r)]^{1/2}$. Thus, strands of subcritical radius are stable only if they are short enough to suppress these long-wavelength fluctuations ($L < 1/k_c$). This situation is essentially different from that of freely suspended planar smectic films which are stable against all long-wavelength thickness fluctuations since bulk and surface energies are always positive. Sufficiently thin planar films are unstable against short-wavelength fluctuations (spontaneous pore formation[9]).

Our strands consistently rupture when their radius approaches 5000 Å, which is significantly larger than the largest reasonable estimate for r, ~750 Å, obtained with $\nu = 30$ erg/cm^2 and $C = 10^6$ erg/cm^3. However, even the above rather low estimate of C may be too large, since the stretching of the strands must be accompanied by the breaking of columns resulting in a reduced compressional elasticity (plastic flow). The portion of the strand attaining a minimum diameter will thus be subjected to the largest stress normal to the columns, reaching the yield stress for plastic flow, first. The result is thinning and rupture in this region of minimum diameter, a behavior commonly exhibited by solid rods experiencing plastic flow due to extensive stress.[10]

In conclusion, we have made stable, freely suspended strands of columnar-phase liquid crystals formed by disk-shaped molecules. Our smallest strands are about 400 molecular diameters wide, which is large compared with the minimum achievable thickness of planar smectic films (1 or 2 smectic layers). This difference may be accounted for in part by the different surface energetics associated with the shape of these freely suspended structures. Freely suspended strands of tilted columnar phases, such as the $D0$ and $D1$ of triphenylene hexa-n-dodecanoate, should be useful as model one-dimensional nematic systems, and should be amenable to study by techniques developed for nematics. For example, reorientation of the optic axis by a transverse electric field ought to prove useful in static and dynamic studies. We anticipate that such freely suspended strands will also be useful in x-ray scattering studies of liquid crystals formed by disk-shaped molecules, as they represent preparations with exceptionally well-ordered columns. Finally we note that it may be possible to spread planar films of disk-shaped liquid crystals in the nematic phase,[1] which may be fluid enough for the instability leading to strand formation, described above, to relax away.

This research was supported by National Science Foundation Grant No. DMR 79-20169 and U. S. Army Research Office Grant No. DAAG 29-79-C-0174. We are greatly indebted to C. Destrade and the Bordeaux group for providing the discotic sample studied.

---

[1] Nguyen Huu Tinh, C. Destrade, and H. Gasparoux, Phys. Lett. 72A, 251 (1979).

[2] S. Chandrasekhar, B. K. Sadashiva, and K. A. Suresh, Pramana 9, 471 (1977).

[3] C. Y. Young, R. Pindak, N. A. Clark, and R. B. Meyer, Phys. Rev. Lett. 40, 773 (1978).

[4] C. Destrade, M. C. Mondon-Bernaud, and Nguyen Huu Tinh, Mol. Cryst. Liq. Cryst. 49, 169 (1979).

[5] G. Sigaud, M. F. Achard, C. Destrade, and Nguyen Huu Tinh, *Liquid Crystals of One- and Two-Dimensional Order*, edited by W. Helfrich and G. Heppke (Springer-Verlag, New York, 1980), p. 403.

[6] J. Prost, in Proceedings of the Colloquium: Pierre Curie, Paris, 1–5 September 1980 (to be published).

[7] J. W. Strutt and Lord Rayleigh, Proc. London Math. Soc. x, 4 (1879).

[8] J. Prost and N. A. Clark, in *Proceedings of the International Conference on Liquid Crystals*, edited by S. Chandrasekhar (Heyden, Philadelphia, 1980), p. 53.

[9] A. J. de Vries, Recl. Trav. Chim. Pays-Bays 77, 383 (1958).

[10] T. Y. Thomas, *Plastic Flow and Fracture in Solids* (Academic, New York, 1961), p. 214.

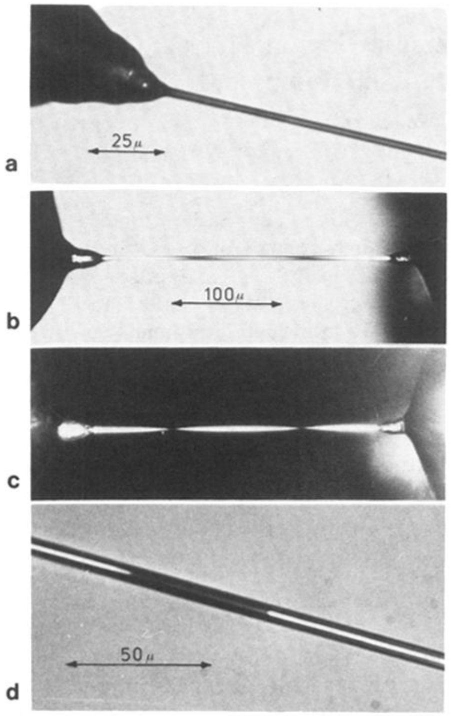

FIG. 1. Transmission photomicrographs of freely suspended strands of triphenylene hexa-n-dodecanoate at 90 °C ($D1$ phase): (a) No analyzer, radius $r = 1\ \mu$m. (b) Strand with a 2π director rotation over its length, $r = 1.5\ \mu$m. (c) Strand in (b) with crossed analyzer and $\Gamma = 0$. (d) Discrete orientational jumps in φ of magnitude $\pi/3$, $r = 3\ \mu$m. The center (dark) portion has φ different from the bright portions by $\Delta\varphi = \pi/3$.