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Nematic liquid crystal in a tube: The Fréedericksz transition

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We study the configurations of a nematic liquid crystal confined between two concentric cylinders, of radii r_1 and $\rho r_1 > r_1$, with homeotropic anchoring conditions at the walls. For $\rho < \rho_c = \exp[\pi\sqrt{(K_b/K_s)}]$ the director is purely radial, while for $\rho > \rho_c$ the director "escapes into the third dimension" and gains an axial component. This represents a geometrically induced Fréedericksz-like transition. When combined with a radial field and a nematic liquid crystal with a dielectric anisotropy $\epsilon_\perp - \epsilon_\parallel > 0$, the critical voltage of the Fréedericksz transition can be made arbitrarily small. This is of interest for liquid-crystal displays, since in the *planar* geometry the critical voltage is a material constant. A related temperature-induced Fréedericksz-like transition is expected in semiflexible nematic polymers.

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The Fréedericksz transition is a second-order phase transition which occurs in nematic fluids [1]. It reflects a competition between an applied electric or magnetic field, favoring distortion of the fluid, and an antagonistic elastic penalty. The transition has been extensively studied in planar configurations. In the following we present a theoretical analysis of the Fréedericksz transition in a cylindrical geometry involving a nematic fluid between two concentric cylinders. A number of quantitatively novel features appear in this configuration. The most remarkable is the possibility of reducing the critical voltage V_c by controlling the geometry, that is, the two radii. Such an option is of practical interest in the design of liquid-crystalline display devices. It is absent in the planar configuration where V_c is a material constant of order 2 V. Other features of interest are the possibility of triggering a Fréedericksz-like transition in the absence of external fields. This can be attained by control of dimensions and, for polymeric liquid crystals [2], by a change of temperature.

The familiar, planar Fréedericksz transition occurs in thin nematic layers, of width L, confined between two plates. Two ingredients are involved. The first is the boundary conditions. In the simplest configurations the two surfaces impose identical orientation on the adjacent nematic fluid. This surface-induced orientation is known as anchoring. In the following we refer to homogeneous and homeotropic anchoring where the nematic director $\mathbf{n}$ at the interface is respectively parallel and perpendicular to the surface. In the absence of a field $\mathbf{n}$ throughout the sample adopts an identical orientation set by the surfaces. The second ingredient is an external field favoring $\mathbf{n}$ oriented perpendicularly to the direction set by the anchoring. When the field is weak the surface orientation is dominant and $\mathbf{n}$ is not modified by the field. A nematic distortion occurs when the field is stronger than the critical field E_c. The distortion reflects an interplay between the tendency of the bulk nematic to orient with the field and the elastic penalty due to the intrafacial orientation imposed by the anchoring. Roughly speaking the transition occurs when the distortion energy is comparable to the energy of the undistorted nematic in the field. The distortion energy per unit area $(K/L^2)L$ is comparable to the field contribution, $\epsilon E^2 L$ for $E_c \approx (K/\epsilon)^{1/2}/L$. Here E is the electric field strength and $\epsilon = \epsilon_\perp - \epsilon_\parallel$ is the dielectric anisotropy. A more detailed analysis leads to

$$E_c = (\pi/L)(K/\epsilon)^{1/2} . \tag{1}$$

Two features of the planar case should be noted for comparison purposes. (i) The electric field is uniform throughout the layer. (ii) The field-free ground state is undistorted, i.e., $\mathbf{n}$ is identical everywhere. As we shall discuss, the Fréedericksz transition in the cylindrical case differs with respect to these two points. First, the electric field is nonuniform. In particular, the field between two concentric cylinders of radii r_1 and $r_2 = \rho r_1 > r_1$ is $E = V/(r \ln\rho)$, where $V = V(r_1) - V(r_2)$ is the voltage across the cylinders. Second, for an appropriate choice of anchoring conditions, the field-free ground state is already distorted. No such distortion is expected for homogeneous anchoring parallel to the axis of the cylinder, the z axis. Nematic distortions do occur in the presence of homogeneous alignment perpendicular to z and in the case of homeotropic anchoring. In the absence of the inner cylinder, when $r_1 = 0$, these distortions result in "escape into the third dimension" [1,3,4]. Thus, in the case of homeotropic anchoring, the nematic develops an axial component to avoid prohibitive penalties due to splay. By inserting the inner cylinder we gain control over the distortion penalties. It is thus possible to trigger the axial distortion by adjusting r_1. This Fréedericksz-like transition takes place in the absence of an external field. In turn, by making r_1 "subcritical" we can make the critical voltage V_c of the Fréedericksz transition arbitrarily small. The double cylinder geometry, in the absence of a field, was examined earlier in the context of defect structure, both experimentally and theoretically [3–6]. In certain situations the control may be attained

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by varying the temperature T, rather than the geometry. In the homeotropic anchoring case the axial distortion relieves the splay at the price of a bend distortion. It is thus possible to trigger an escape into the third dimension by changing the relative values of K_s and K_b, the splay and bend elastic constants. This strategy may be realized for semiflexible, thermotropic liquid-crystalline polymers (LCP's) [2]. The K_s of such LCP's exhibits an exponential T dependence, while K_b is only a weak function of T. The strong T dependence of K_s is traceable to the presence of thermally activated hairpin defects [7–10]. At high temperatures, there are many hairpins, and K_s is small. On the other hand, K_s becomes very large at low temperatures when the hairpins are annealed out of the chains, which become rodlike. Accordingly, it is possible to trigger a temperature-induced Fréedericksz-like transition by lowering T, thus increasing K_s.

We now present a more quantitative analysis of these effects, focusing, for brevity, on the case of homeotropic anchoring. In this case we require that the dielectric constants perpendicular and parallel to $\mathbf{n}$ satisfy $\epsilon=\epsilon_\perp-\epsilon_\parallel>0$. Thus an applied field favors perpendicular alignment of $\mathbf{n}$ and $\mathbf{E}$. The free energy per unit length of the cylinder is [1]

$$F=\tfrac{1}{2}\int_{r_1}^{r_2} dr\, 2\pi r[K_s(\nabla\cdot\mathbf{n})^2+K_b|\mathbf{n}\times(\nabla\times\mathbf{n})|^2 -\epsilon(\mathbf{n}\cdot\mathbf{E}(r))^2-\mathbf{P}\cdot\mathbf{E}] \ . \tag{2}$$

The integrand is $f 2\pi r\, dr$, where $f/2$ is the free-energy density of the nematic, allowing for four contributions. The first two reflect the distortion penalties due to splay and bend. The third term allows for the dielectric contribution due to the induced dipole $\epsilon(\mathbf{E}\cdot\mathbf{n})\mathbf{n}$. Finally, the last term accounts for flexoelectricity, that is, the bulk electric polarization induced by the nematic distortion $\mathbf{P}=k_\parallel\mathbf{n}\cdot\nabla\mathbf{n}+k_\perp(\nabla\times\mathbf{n})\times\mathbf{n}$, where $k_\perp$ and $k_\parallel$ are the flexoelectric coefficients. The detailed effect of the last term is beyond the scope of this Rapid Communication. Suffice it to say that it does not modify the functional form of the resulting F, but may affect the numerical constants involved and the resulting phase behavior. A detailed discussion of this issue will be presented elsewhere. We use the following parametrization for the director in cylindrical coordinates $\mathbf{n}\equiv(n_r,n_\phi,n_z)\equiv(\cos\alpha,0,\sin\alpha)$. The boundary conditions at the walls are those of homeotropic, perpendicular anchoring, $\alpha=0$ at $r=r_1,r_2$. In a purely radial configuration we have $\alpha=0$ throughout the sample and a state of pure splay. This state we refer to as the ground state. When α becomes nonzero a bend distortion occurs, which relieves some of the splay. By symmetry there is no variation in the z or ϕ directions in the distorted state of lowest free energy. To detect the onset of the phase transition, knowing it is of second order [1], it is sufficient to consider small deformations about pure splay, $\alpha(r)=0$. Thus $f=K_s r^{-2}(dr\cos\alpha/dr)^2+K_b(d\sin\alpha/dr)^2-\epsilon E^2\cos^2\alpha$ reduces, upon expansion to second order in α and deletion of terms independent of α to $f\approx -K_s r^{-2}d(r\alpha^2)/dr+K_b(d\alpha/dr)^2-\epsilon E^2\alpha^2$. Integration, allowing for $\alpha=0$ at the boundaries and knowing that $E=V/r\ln\rho$, yields

$$F=\pi K_b\int_{r_1}^{r_2} dr\, r\left[\left(\frac{d\alpha}{dr}\right)^2-\left(\frac{\epsilon}{K_b}\frac{V^2}{\ln^2\rho}+\frac{K_s}{K_b}\right)\frac{\alpha^2}{r^2}\right] . \tag{3}$$

Extremization of (3) with respect to the unknown function $\alpha(r)$, yields

$$\frac{d}{dr}\left(r\frac{d\alpha}{dr}\right)=-\left(g^2+\frac{K_s}{K_b}\right)\frac{\alpha}{r} , \tag{4}$$

where $g=\pi(V/V_p)/\ln\rho$ and $V_p\equiv\pi\sqrt{K_b/\epsilon}$ is the critical voltage for the Fréedericksz transition in the *planar* geometry. This has the trivial, pure splay solution $\alpha=0$. Nontrivial solutions can be found by using the guess $\alpha(r)=r^w$, with an undetermined w, or by the substitution $x=\ln(r/r_1)$. Either way, the nontrivial solutions are $\alpha(r)=A\sin[\sqrt{(K_s/K_b)+g^2}\ln(r/r_1)+\theta]$, where A and θ are constants. The anchoring conditions at the walls imply $\sqrt{(K_s/K_b)+g^2}\ln\rho=m\pi$, with m an integer. The nontrivial solution of lowest energy corresponds to $m=1$. This first occurs for a critical voltage (Fig. 1)

$$V_c=V_p[1-(K_s/K_b)(\ln\rho/\pi)^2]^{1/2} , \tag{5}$$

where we have used our definition of g. Accordingly, for $\rho>\rho_c$ given by

$$\rho_c=\exp(\pi\sqrt{K_b/K_s}) , \tag{6}$$

the critical voltage is zero, i.e., a Fréedericksz-like transition occurs in the absence of an applied field. For $\rho<\rho_c$ an external field is necessary for the transition to occur. However, the characteristic V_c is reduced. Furthermore, for ρ close to ρ_c, V_c approaches zero as

$$V_c=V_p(2/\ln\rho_c)^{1/2}(1-\rho/\rho_c)^{1/2} . \tag{7}$$

The critical voltage (5) can be understood simply as follows. Using the new coordinate $x=\ln(r/r_1)$, the free energy (3) has the form $\int_0^\rho dx[(d\alpha/dx)^2-(g^2+K_b/K_s)\alpha^2]$. The derivative term in this expression is the

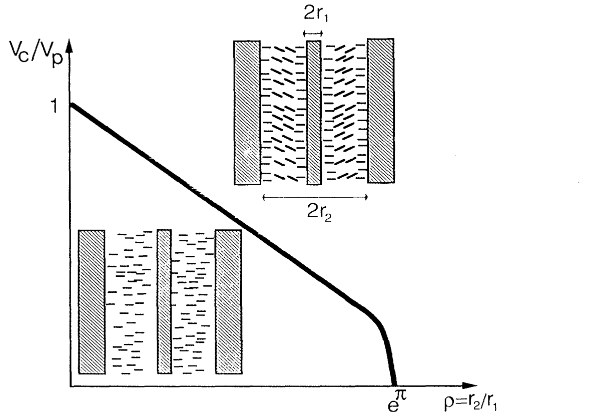

FIG. 1. The critical voltage V_c/V_p for the Fréedericksz transition in the cylindrical geometry as a function of the radius ratio of the two cylinders $\rho=r_2/r_1$, for the case where $K_s=K_b$. The insets present side views of the system in the (a) pure splay and (b) "escaped" splay-bend configurations.

bend penalty, and is approximately $\ln\rho(A/\ln\rho)^2 = A^2/\ln\rho$. The second term is the decrease in splay and electric energy and is roughly $(g^2+K_b/K_s)A^2$. At the transition we expect these two to be equal. Equating them gives an approximation to (5). Physically the pure splay state is one of high energy, and is forced upon the system by geometry and anchoring. For extreme geometries $\rho>\rho_c$ the system escapes into the third dimension, and relieves splay at the expense of bend. When $\rho<\rho_c$, the effect does not occur in the absence of a field. However, the necessary field is weaker.

As seen from (6), ρ_c depends exponentially on the ratio K_b/K_s. For monomeric nematics, $K_b \approx K_s$ [1] and ρ_c is fairly close to $e^{\pi}\approx 23$ and is weakly temperature dependent. A radically different situation appears in main chain LCP's. For rigid mesogens, chain ends are necessary to accommodate splay. However, for rigid polymers, the concentration of free ends is small and splay is difficult. In the case of perfectly rigid rods of length l_r the splay constant, as calculated by Meyer [9], is $K_s \approx kTa^{-2}l_r$, where a is a monomer size. Splay is somewhat easier for semiflexible LCP's. These are fully extended only at low temperatures. At higher temperatures such LCP's support hairpin defects [7–9]. These are abrupt reversals in the trajectory of the chain which store an energy of U_h. The hairpins are thermal excitations and their average number n in a chain of length L exhibits a Boltzmann T dependence with $n=(L/l)\exp(-U_h/kT)$. Here l is a microscopic length associated with the localization of a single hairpin. By treating each chain segment between hairpins as an effective rod we can estimate the splay constant for a semiflexible chain $K_s \approx kTa^{-2}l\exp(U_h/kT)$. This has the Boltzmann T dependence that is typical of all properties that depend on hairpins. For specificity we use the bend-splay ratio as obtained by Petschek and Terentjev [11–18] $K_s/K_b \sim f(T)e^{U_h/kT}$, with $f(T) = (a/l_p)^2(U_h/kT)^{7/4}$, where l_p is the bare persistance length of the chain. In these terms the temperature dependence of ρ_c of an LCP is

$$\rho_c=\exp\{\pi f^{-1/2}\exp[-U_h/(2kT)]\}\ . \tag{8}$$

ρ_c exhibits a very strong temperature dependence, an exponential of an exponential, and for $kT<0.1U_h$, ρ_c is very close to 1. This implies that a Fréedericksz-like transition is favored even for very weakly bent plates, i.e., $(r_2-r_1)/r_1=\rho-1\approx 0$. In marked contrast, $\rho-1\sim 20$ for monomeric nematics. Thus the behavior of polymeric nematics in the cylindrical geometry is expected to be quantitatively different from their monomeric counterparts.

Our discussion of nematic fluids between concentric cylinders leads to two main conclusions. First, for a proper choice of anchoring conditions it is possible to have a Fréedericksz-like transition in the absence of an external field. The transition can be triggered by control of the ratio of the two radii or, in the case of LCP's, by a change of temperature. Second, by combining the first effect with the familiar Fréedericksz transition it is possible to make the critical voltage arbitrarily small. For LCP's it is possible to combine all the ingredients. The degree of curvature of the plates can be measured by $\kappa=\rho-1=(r_2-r_1)/r_1$. The critical value κ_c is much less than unity since $K_s \gg K_b$. When $\rho<\rho_c$ and $\rho\approx\rho_c$ the critical voltage is

$$V_c=V_p 2^{1/2}(1-\kappa/\kappa_c)^{1/2}\ . \tag{9}$$

Since κ_c is very small V_c can be made very small even for weakly curved plates.

The effects considered above are due, essentially, to the combination of geometry and anchoring conditions. Similar scenarios may be obtained by using a variety of constrained LCP's rather than geometry. One example involves a Fréedericksz-like transition driven by the confinement of free LCP's in a slit imposing homeotropic anchoring [19,20]. The second combines the Fréedericksz transition with an anchoring transition due to tethered LCP's grafted onto a surface imposing homogeneous anchoring [21,22]. It is possible to make V_c arbitrarily small in both cases. In these systems the deformation free energy of the LCP's plays the role of the splay energy in our problem.

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