Column Buckling Instability in a Discotic Liquid Crystal

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When subjected to a compressive strain along the columns, a tubular discotic liquid crystal must present a buckling instability, where compressive elastic energy is transferred into bend energy of columns. We present the first observation of this column buckling instability in hexa-*n*-octyloxytriphenylene at $T = 75\,°\mathrm{C}$. From the instability threshold, the curvature elastic constant is found to be 6 orders of magnitude larger than in usual liquid crystals, i.e., the correlation length extends on a quasimacroscopic range of 10^3 molecules.

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A number of new liquid crystalline mesophases, consisting of disklike molecules, have been synthesized during recent years.[1] Their structure is now well understood[2]: These phases are formed by a regular packing of parallel and independent columns of molecules and the columns are arranged in a two-dimensional network. Their mechanical properties were predicted from their symmetry[3,4]: For instance, longitudinal compression of the columns is that of a one-dimensional solid, but with a thickness-dependent elastic constant, because of the coupling with the two-dimensional network when the thickness is larger than a critical value.[5]

As in other mesomorphic smectic materials, observation of mechanical instabilities is a way to obtain the elastic properties. A column buckling instability under compression has indeed been predicted[4]: It transforms a part of the compression energy into bend energy and is similar to the undulation of smectic liquid-crystal layers under dilation.[6] In the present work, we present the first observation of this column buckling instability in a discotic liquid crystal. We derive from the deformation threshold the ratio of the bend to compressive elastic moduli of the material.

The sample we use is hexa-*n*-octyloxytriphenylene[7] (HET) which exhibits a columnar discotic mesophase between 67 and 886 °C; the columns are arranged in a hexagonal network and the disklike molecules are "ordered" within each column. The sample is oriented with the columns perpendicular to the surface between two glass plates treated with mellitic acid as a surfactant. Because of the absence of a nematic phase, a good orientation in a large sample is difficult to obtain; the best result is obtained when cooling the sample very slowly (0.02 °C per min) from the isotropic to the discotic phase; we generally obtain a sample with grains, about 1 mm in size, some of them slightly tilted from the perfect homeotropic direction. The glass plates are cemented to piezoelectric ceramics in a holder previously described.[8] The piezoelectric ceramics allow one to create an imposed displacement δ at one of the glass plates and to measure the transmitted force at the other plate through the sample of thickness d. The applied compressive strain $\epsilon = \delta/d$ has a step-function form with a displacement amplitude between 0.4 and 100 Å and a typical duration of 10 sec. The applied voltage on one ceramic and the output voltage due to the transmitted stress on the second ceramic are recorded versus time on a storage oscilloscope. The sample is kept at rest for 10 min for annealing between successive measurements; this annealing is compulsory to ensure reproducibility of the data. The holder is not infinitely rigid; its equivalent stiffness is measured to be 2.3×10^{10} dyn/cm, in series with the sample; we correct strain and stress values to take into account the holder deformation. To detect an eventual tilt of the columns, we also observe the optical birefringence of the sample: A laser beam, parallel to the columns, propagates through the sample placed between two crossed polarizers. The transmitted light intensity is measured with a phototransistor.

In Ref. 4, the buckling instability is predicted to happen above a threshold compressive strain $\epsilon_c = \delta_c/d = -K\pi^2/d^2(\lambda_1 - \lambda_4)$ where the λ_i are compressive elastic constants and K is the column curvature elastic constant. To estimate the strain-stress relationship above threshold, we resume the calculation with a simplified model. The free energy density is written as

$$f = \tfrac{1}{2} b(\partial w/\partial z + \tfrac{1}{2}\theta^2)^2 + \tfrac{1}{2} K(\partial\theta/\partial z)^2,$$

where b is the compressive elastic constant of the columns, oriented along z; w is the column z displacement, shown to be a relevant variable (see Ref. 5); θ is the tilt angle of the columns. The $\theta^2/2$

term describes the z dilation equivalent to a tilt of the columns, for $\partial w/\partial z=0$. The equilibrium equations are written as $\partial w/\partial z+\frac{1}{2}\theta^2=\alpha$, and

$$b(\partial w/\partial z+\tfrac{1}{2}\theta^2)\theta-K\,\partial^2\theta/\partial z^2=0,$$

which results in $\alpha b\theta-K\,\partial^2\theta/\partial z^2=0$. To accept the solution $\theta=\theta_0\sin(\pi z/d)$, one must have

$$\alpha b+\pi^2/d^2=0.$$

At threshold, θ_0 and $\alpha=-\delta_c/d$, which gives

$$\epsilon_c=\delta_c/d=-(K/b)\pi^2/d^2.$$

Above threshold, one finds $\theta_0^2=-4(\delta-\delta_c)/d$, which results in a *constant* stress $b\delta_c/d$. One can introduce a coherence length $m=(K/b)^{1/2}$. We call L the lateral extension of the sample on the plates. As shown in Ref. 5, the clamping of the columns on the glass plates prevents the two-dimensional (2D) array of columns from being distorted for thin samples $[d<2(mL)^{1/2}]$ and b is just the column compressional elastic constant. For thick samples $[d>2(mL)^{1/2}]$ the 2D array of columns can be distorted under compression and the resulting b is lower. In usual liquid crystals, m is of the order of a molecular length.

We first observe the time dependence of the transmitted stress along the columns. This signal is composed of an instantaneous elastic response, followed by an exponential relaxation; this latter part corresponds to the dissipative part of the viscoelastic response observed under low-frequency sinusoidal strain.[9] On the other hand, very soon (5 ms) after the applied step-function strain, the measured stress σ_e is characteristic of the high-frequency elastic response of the material. In what follows, we have measured σ_e vs ϵ.

For $d=90$ μm, the measured relationship $\sigma_e(\epsilon)$ is shown in Fig. 1. We observe that for low strain, σ_e is proportional to ϵ; for large compressive strain, above a threshold ϵ_c we obtain a lower slope for the curve, with a smaller compression modulus; nothing appears for dilative strain. Figure 1 shows also the intensity of the transmitted light, measured at 5 ms versus ϵ: The stress-induced birefringence is zero below ϵ_c. It increases with ϵ above ϵ_c indicating a tilt of the columns from the initial homeotropic orientation. This transient birefringence signal depends critically on the focusing of the light beam and seems to originate from well defined parts of the sample. We identify ϵ_c as the buckling-instability threshold.

We must now compare our data quantitatively with the predictions of our simple model. We do observe an abrupt change of the slope in the strain-stress relationship, correlated with an optically detected tilt of the columns above ϵ_c, as expected. However, the prediction of a constant stress above ϵ_c is not fulfilled. This can be explained by the inhomogeneity of the sample. The buckling must appear in the best homeotropically oriented domains, for which b is the largest. In consequence, superimposed on the constant $\sigma(\epsilon)$ curve above threshold, one must see a linear response from tilted domains, with a smaller apparent b. This inhomogeneity also explains the observed localization of the transient birefringence.

To check the thickness dependence of the threshold, we measure ϵ_c vs d with $L\sim 2$–5 mm. Our results are shown in Fig. 2, which presents the observed variation of $|\delta_c|$ vs $1/d$. In the limit of large thickness ($d>80$ μm) we do observe a linear dependence as expected. For thin samples ($\delta<40$ μm) we also find a linear dependence, with a smaller slope. We can interpret these data with the model of Ref. 5. In all cases δ_c is given by

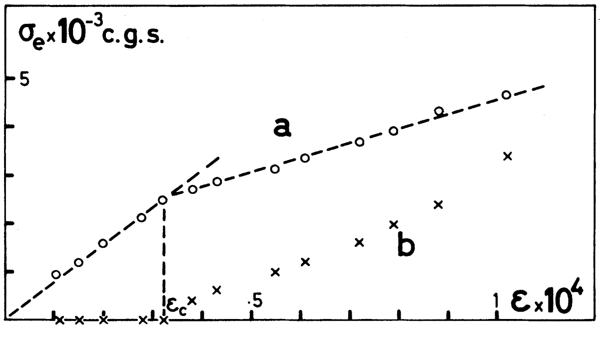

FIG. 1. Curve a, elastic stress σ_e vs strain ϵ for HET at $T=75\,°$C, $d=90$ μm. ϵ_c is the buckling threshold. Curve b, strain dependence of the birefringence signal (in arbitrary units).

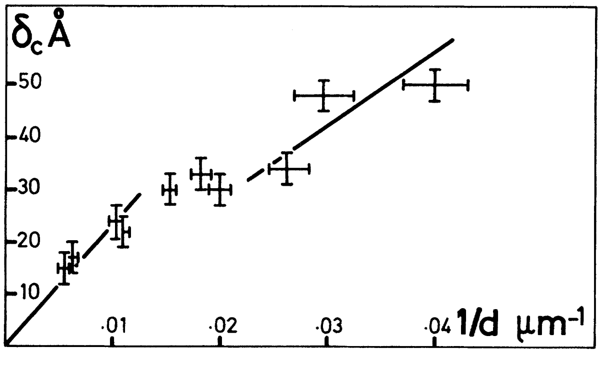

FIG. 2. Displacement threshold δ_c vs $1/d$. The transition thickness d_t is of the order of 50 μm.

$|\delta_c| = (K/b)(\pi^2/d)$. Thin samples present a larger $b = b_1$ than thick ones ($b = b_2$), as already explained. From our data, $b_1/b_2 = 1.6$. In addition, we can estimate the transition thickness $d_t \sim 50$ μm $\sim 2(Lm)^{1/2}$, which results in $m = 0.2$ μm, very large compared to a molecular length. We can derive directly the ratio K/b from threshold data: For $d = 100$ μm, $\delta_c = 24$ Å, which results in $K/b = 2.4 \times 10^{-10}$ cm^2, i.e., $m = (K/b)^{1/2} = 0.15$ μm, comparable to the previous estimate. From our low-strain regime, we derive $b \sim (4 \pm 2) \times 10^8$ cgs units for thick samples. This value is certainly underestimated because of the inhomogeneity problem. A realistic value must be $\sim 1 \times 10^9$ cgs units, which results in $K = 0.24$ cgs units. We must emphasize that this value of K is 6 orders of magnitude larger than in usual liquid crystals. This is obviously related to the large coherence length $m = 0.15$ μm $\sim 10^3$ times a molecular dimension. m is 2 orders of magnitude larger than the correlation length along the columns measured by x-ray diffraction[2] for this "ordered" discotic phase. m does not change significantly with temperature, i.e., its large value cannot be attributed to a pretransitional effect. One explanation for this large m, as suggested by Levelut,[10] could be the entangling of the lateral paraffinic chains between columns. Dynamical experiments would be useful to check this point. Our result also explains previously unexplained observations by Bouligand[11] and Oswald and Kleman.[12] Close to the core of a disclination, the columns tend to break into radiating walls rather than to bend; the core radius of developable domains is found to be anomalously large, in the micrometer range. From elasticity arguments, this radius must be $\sim m$, which is anomalously large in discotic tubular materials. Finally, this result is also consistent with the large value of the high-frequency shear elastic constant C_{44}, measured[9] by application of a sinusoidal shear strain in a direction perpendicular to the columns. In this case the shear modulus, of the order of k/d^2, comes essentially from the column curvature and becomes anomalously large with K.

To conclude, we have observed the buckling instability of columns in a discotic liquid crystal under compression. The thickness dependence of the instability threshold confirms the existence of two distortion regimes related to the clamping of the columns on the boundary plates; the coherence length relating curvature constant to compression modulus is anomalously large (in the range of 10^3 times molecular size), resulting in a curvature constant 6 orders of magnitude larger than in usual liquid crystals. This result explains the anomalously large core radius of developable domains and the large shear modulus observed in this kind of material.

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