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Dielectric investigations of the dynamics of the hexatic-hexatic transition in a chiral liquid crystal

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We report a detailed investigation of the dynamics of the hexatic–smectic-I^* to hexatic–smectic-F^* phase transition in a chiral liquid-crystalline compound. The results show a dramatic softening of the relaxation frequency and an associated divergence of the susceptibility on approaching the transition. The temperature dependence of both these parameters can be described by a power law with an exponent equal to 1, in agreement with the theoretical predictions. [S1063-651X(98)03402-3]

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Smectic-I (I) and smectic-F (F) are tilted hexatic liquid crystals in which the molecules are tilted with respect to the smectic layer normal and exhibit long-range bond orientational (BO) order, but only short-range positional order [1]. In the I phase the molecular tilt direction is towards a nearest neighbor, while in the F phase it is between two nearest neighbors. With the disappearance of the BO order alone, either of these phases can transform into the smectic-C (C) phase. Coupling to the molecular tilt induces long-range BO even in the C phase, albeit of small magnitude.

Since only the magnitude of BO is different, the C and I/F phases have the same point-group symmetry [2]. Consequently, the first-order C-I or C-F phase boundary can terminate at a critical point similar to the gas liquid critical point. Such a critical point has been observed at the termination of the C-I phase transition line [3,4]. Some materials exhibit both the I and F phases with the phase sequence C-I-F on cooling the sample. Several synchrotron x-ray studies on freely suspended films have confirmed the structural characteristics associated with these phases [1,5]. However, not much experimental attention has been given to the dynamics associated with the transition between the phases. This is particularly so in the case of the hexatic-hexatic transition between the I and F phases.

The tilt of the molecules in these phases can be represented by a two-component order parameter $\psi(\Omega,\phi)$, where Ω, the polar angle, is the magnitude of tilt and ϕ, the azimuthal angle, is the angle the in-plane projection of the molecule makes with respect to a reference axis. Similarly, the sixfold BO order can also be represented by a two-component order parameter having a magnitude and a ''bond'' angle, which we shall refer to as θ. In this terminology, θ-ϕ is 0° (mod 60°) in the I phase and 30° (mod 60°) in the F phase. To incorporate a tilted hexatic phase into a theoretical framework, Nelson and Halperin [2] introduced a free-energy expression that essentially had the usual Frank elastic terms and a tilt-bond coupling term. Generalizing this Hamiltonian, Selinger and Nelson [6] wrote the tilt-bond interaction term as $V(\theta-\phi)=-h_6\cos 6(\theta-\phi)-h_{12}\cos 12(\theta-\phi)$. Using this potential, they obtained a phase diagram in the h_6-h_{12} plane exhibiting the I and F phases. In this model for positive values of h_{12}, the I phase exists for $h_6>0$ and the F phase appears for $h_6<0$. At $h_6=0$ there is a first-order transition between the two phases. Selinger and Nelson [6] and later Selinger [7] have worked out the dynamics near this transition. The tilt-bond coupling gives rise to two dynamic modes: a hydrodynamic or acoustic mode corresponding to the in-phase fluctuations of the bond plus the tilt and a nonhydrodynamic or optic mode corresponding to the out-of-phase fluctuation of the bond plus the tilt. The relaxation frequency of the acoustic mode is not expected to vary on passing through the I-F transition. In contrast, the optic mode shows a critical slowing down of the frequency with a concomitant increase in the susceptibility on approaching the transition from either side. This theoretical analysis was motivated by a light-scattering study by Dierker and Pindak [8] in five-layer-thick free-standing films of a chiral material exhibiting an I^* to F^* transition. (The asterisk indicates that the constituent molecules are chiral.) In both these phases the molecules are tilted in the layer and hence they exhibit a spontaneous in-plane ferroelectric polarization, whose direction is coupled to the azimuthal angle of the tilt. This makes it amenable to study by using dielectric spectroscopy especially to probe the dynamics in such systems. In this paper we present results of dielectric investigations on the same compound used by Dierker and Pindak [8], albeit in a bulk sample. Although the transition appears to be first order, strong pretransitional effects are observed just as in the light scattering study [8]. The softening of the relaxation frequency and the enhancement of the associated amplitude are clearly seen on approaching the transition. Further, it is shown that the data can be fit to a power law, the exponent of which turns out to be in agreement with the theoretical prediction.

The compound studied is the chiral material 4-(2′-methylbutyl)phenyl 4-(n-octyl) biphenyl-4-carboxylate, showing the phase sequence isotropic–blue phase–cholesteric–smectic A–smectic C^*–smectic I^*–smectic F^*–crystal J^* [9]. The samples were taken between two indium tin oxide (ITO) coated glass plates treated with polyimide solution and unidirectionally rubbed. Mylar spacers were used to define the cell thickness (~4 μm). To get a uniform planar orientation of the molecules, the sample was cooled slowly (6 K/h) from the isotropic phase through the cholesteric phase

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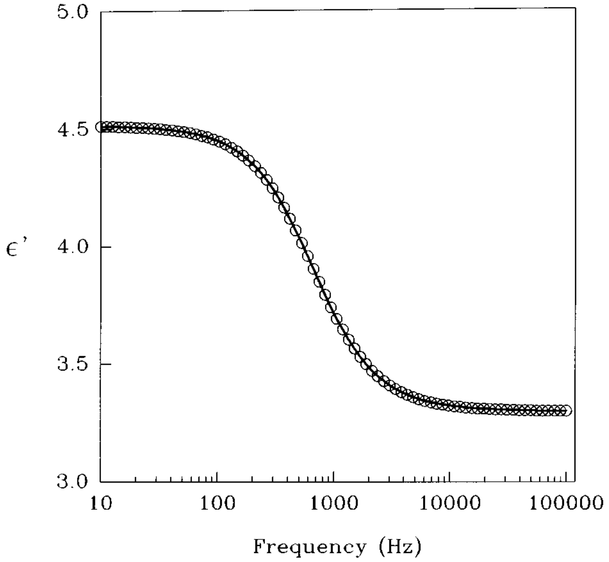

FIG. 1. Representative plot of the frequency dependence of the dielectric constant ϵ'. The circles are from the experiment and the line through the circles indicates the fitting done to the standard Cole-Cole expression (1) for extracting the relaxation frequency f_R and the dielectric strength $\Delta\epsilon$.

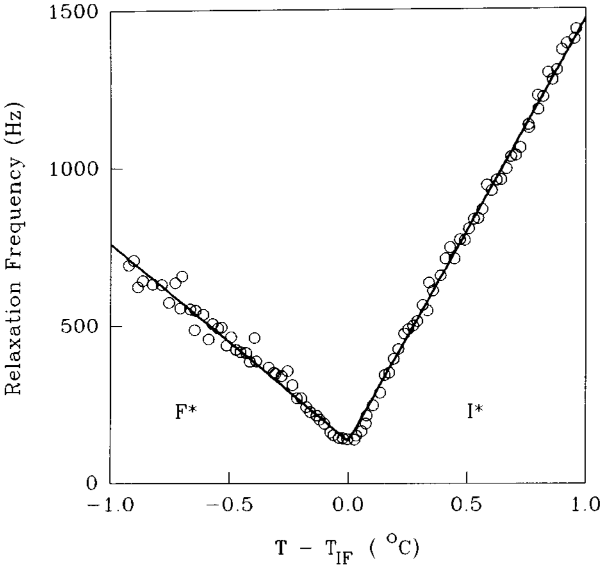

FIG. 2. Temperature dependence of the relaxation frequency f_R showing a strong softening on approaching the I^*-F^* transition. The fitting done to Eq. (4) is shown as a solid line through the circles and yields an exponent $z=1$.

into the smectic-*A* phase. The sample alignment was monitored during the measurements using an optical polarizing microscope.

Dielectric measurements were done in the range of 10 Hz–100 kHz using a capacitance divider network and a lock-in amplifier (EG&G Instruments Model 7260) as a phase-sensitive detector [10]. The samples were kept in a hot stage, which was controlled by an INSTEC temperature controller. The constancy of temperature during any frequency scan was better than 10 mK.

Figure 1 is a typical plot of the real part of the dielectric constant (ϵ') versus the probing frequency (f) showing the existence of a single relaxation mode. It is a standard practice to express the frequency dependence of the dielectric constant using a ''Cole-Cole'' equation [11]

$$\epsilon' = \frac{\Delta\epsilon}{1+(f/f_R)^{1-h}} + \epsilon_\infty , \tag{1}$$

where ϵ_∞ represents the sum of the dielectric strengths of all high-frequency modes other than the one under consideration and h is the distribution parameter of the mode and is a measure of the deviation from a simple Debye type of expression. Two parameters that are characteristic of the mode and are important for the purpose of this paper are the relaxation frequency f_R and the dielectric strength $\Delta\epsilon$. Notice that $\Delta\epsilon$ is nothing but the difference in the dielectric constant at frequencies well below and well above f_R. To extract all these parameters, we fitted the ϵ' versus f data at each temperature to Eq. (1). Such a fit is also shown in Fig. 1 as a solid line and is seen to describe the frequency dependence excellently.

Figure 2 shows the temperature dependence of the relaxation frequency f_R. We do indeed find that the I^*-F^* transition is accompanied by a strong softening of the mode as reflected in the appreciable decrease in the relaxation frequency near the transition. This result qualitatively agrees with the data of Dierker and Pindak [8] and confirms that the tilt-bond coupling (represented by the coefficient h_6) does reduce significantly on approaching the transition, as is expected from the theory. Notice that f_R has a nonzero value at the transition. This is supposed to indicate that the transition is first order [7]. However, it should be mentioned that differential scanning calorimetric (Perkin Elmer DSC7 with DDSC attachment) scans, run in both the usual dc temperature ramping method (DSC) and ac temperature superposition method (Dynamic DSC), failed to show the I^*-F^* transition. In contrast, even the hexatic-crystal (F^*-J^*) transition, which is known to be weak, was clearly observed. If the I^*-F^* transition is in fact first order, we can place an upper limit of 10 J/mol on its enthalpy. It may be mentioned that a similar case of a transition with immeasurably small latent heat displaying the first-order transition character in a dynamic measurement has been reported by Cladis *et al.* [12].

Generally, the critical slowing down of cooperative ordering can be explained [13] by a power-law expression with a functional form given by

$$f_R \propto t^z, \tag{2}$$

where t is the reduced temperature. In the more specific theory of Selinger and Nelson [6], the relaxation frequency is proportional to the tilt-bond coupling coefficient h_6. Close to the I-F transition, h_6 is expected to be proportional to the reduced temperature. Thus one can write

$$f_R \propto |T-T_{IF}| + \text{const.} \tag{3}$$

Here T_{IF} is the I^*-F^* transition temperature. Comparing Eqs. (1) and (2), we see that the exponent $z=1$. This value is the same in both the mean-field and renormalization-group analyses [7].

To extract the actual value of the exponent, we rewrite Eq. (2) as

$$f_R = F^{\pm}|T-T_{IF}|^z + F_0, \tag{4}$$

where F_0 is a temperature-independent constant and F^+ and F^- are the amplitudes above and below T_{IF}. In terms of the dimensionless temperature $(T-T_{IF})/T_{IF}$, the available fitting range is (6.5×10^{-5})–(3.8×10^{-3}) above T_{IF} and (-6.8×10^{-5})–(-3.3×10^{-3}) below T_{IF}. A least-squares fit done with Eq. (3) by floating all four parameters describes the data very well. This is shown as a solid line in Fig. 2 and yields $T_{IF}=337.70$ K and an exponent $z=0.99\pm0.02$. Within the error limits, the exponent value is exactly as predicted by the theory, thus proving that even in bulk systems the frequency of the relaxation mode is simply proportional to the tilt-bond coupling coefficient h_6. Noninclusion of the data in the rounding region (very close to the transition) did not alter the results much.

In addition to the slowing down of f_R, the theory also expects the static susceptibility to grow at a rate that is inversely proportional to h_6 on approaching T_{IF}. In other words, near the transition the dielectric strength, which is the susceptibility in our case, should become enhanced as

$$\Delta\epsilon \propto |T-T_{IF}|^{-z} \quad \text{with } z=1.$$

For the convenience of representing the power-law fit mentioned below, we have plotted in Fig. 3 the inverse dielectric strength as a function of reduced temperature. Since $1/\Delta\epsilon$ has a nonzero value at the transition, again, perhaps due to its first-order nature, we have fitted the data to a functional form similar to Eq. (3), viz.,

$$\frac{1}{\Delta\epsilon} = A^{\pm}|T-T_{IF}|^z + \text{const.} \tag{5}$$

This fitting was not straightforward. If we include all the data that were considered for the f_R fitting, it results in high values of χ^2 (which is a measure of the goodness of fit) and yields $z=0.86$. However, limiting the data on the I^* side to $T_{IF}+0.5$ °C, but retaining all the data on the F^* side gives an excellent fit with $z=0.98\pm0.04$, which is again in agreement with the theoretical prediction. The departure from linearity for the data above $T_{IF}+0.5$ °C is possibly due to the proximity of the C^*-I^* transition, which is only 3 °C above the I^*-F^* transition.

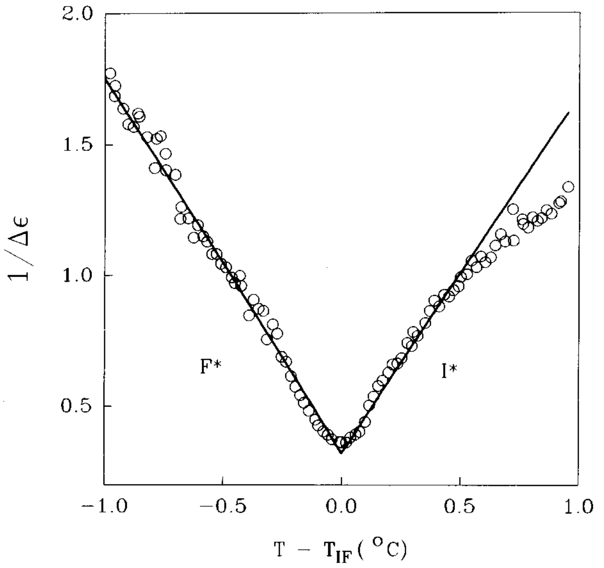

FIG. 3. Thermal variation of the inverse dielectric strength (or inverse susceptibility) in the vicinity of the I^*-F^* transition. The solid line is a fit to a modified power law [Eq. (5)] with an exponent = 1. The nonzero value at the transition and a slight rounding seen in the vicinity of it are indicative of the transition being first order. The departure from linearity observed above T_{IF} + 0.5 °C is perhaps due to the proximity of the C^*-I^* transition.

In summary, we have carried out a detailed investigation of the dynamics near the hexatic-hexatic transition in a chiral liquid crystal. The features observed, viz., the critical slowing down of the relaxation frequency and the associated increase in the dielectric strength, both of them varying linearly with reduced temperature, are in agreement with the theoretical prediction. There are indications that strong pretransitional effects are seen, although the transition could be first order, even if weakly so. Further studies on a suitable binary system or as a function of pressure could perhaps lead to the observation of a tricritical point on the hexatic-hexatic boundary.

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