Dynamics of Collective and Molecular Modes of a Ferroelectric Liquid Crystal in Confined Geometry Using Dielectric Spectroscopy

H. Xu and J. K. Vij*

School of Engineering, University of Dublin, Trinity College, Dublin 2, Ireland

A. Rappaport and N. A. Clark

Condensed Matter Laboratory, University of Colorado, Department of Physics, Boulder, Colorado 80309
(Received 19 September 1996)

Two aerogel systems containing a ferroelectric liquid crystal (FLC) with smectic phases over a wider temperature range are investigated using dielectric spectroscopy. The second order transition from Sm-A to Sm-C^* is considerably broadened and the collective modes are detected for the FLC confined in aerogel pores. An additional relaxation process (AP) seen in these confined systems arises from the interface layer, the relaxation strength of AP decreasing and of the Goldstone mode gradually increasing as temperature is lowered. [S0031-9007(97)03484-4]

During the last several years, the study of liquids [1] and liquid crystals [2–4] in confined geometry has been an active area of research in condensed matter and statistical physics. Understanding of the layer structure, phase transitions, order parameter fluctuations, liquid-solid interface, dynamics of collective modes, and molecular motions will be advanced if results on samples restricted to confined geometries are used compared with those of the bulk. The experimental results are to test theoretical models. The most extensively employed confining substrate for the study of a variety of physical systems is porous Vycor glass with rough pore surfaces; the pores are elongated and independent of each other [5]. Work on ferroelectric liquid crystals (FLCs) in confined geometry [6], however, has only scantily been carried out. The study of FLCs confined in nm size pores allows a determination of the dominant effects of the surfaces on the collective processes originating from the director fluctuations. This type of confined geometry is extremely important due to the difficulty of making cells thinner than 1 μm. The mechanisms of molecular director orientations constrained by the surfaces of superfine pores is probed using dielectric spectroscopy. Furthermore randomness of pores and their extreme internal roughness may hinder the growth of the smectic layers and/or the collective modes. For 8CB (cyanobiphenyl) with nematic and smectic phases, confined in aerogel (a highly porous and interconnecting solid [7] with pore length to diameter aspect ratio of almost unity compared to 4 for Vycor glass), the phase transitions and the smectic ordering were investigated using specific heat, x-ray, and quasielastic light scattering [2,3]. In some cases, calorimetry and NMR studies of 8CB made in Vycor glass [5] contrasted with those in the aerogel.

In this Letter, we focus on the effects of the confined geometry on the collective modes of an FLC with Sm-C^* and Sm-A phases and investigating this second order phase transition. The measurements of complex permittivity $\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ are carried out in the frequency range 1 Hz to 13 MHz both for the bulk FLC and under aerogel confinement with two dimensions of pores. The ferroelectric liquid crystal used is W314 [8], having phase transition temperatures in °C: Sm-X, 31.2; Sm-C^*, 89.9; Sm-A, 124.6. The W314 is filled into two aerogel systems having large surface to volume ratio and almost unity pore volume fraction. Aerogels [7] with densities of 0.17 g/cm^3 (pore chord, 430 $\pm$ 65 Å); volume to surface ratio 137 Å; pore volume fraction 0.90) and of 0.08 g/cm^3 (pore chord, 700 $\pm$ 100 Å; volume to surface ratio, 159 Å; pore volume fraction, 0.95) are filled with the FLC sample in the isotropic phase under vacuum. This method of filling ensures elimination of absorbed water, air bubbles, and other impurities that give rise to spurious ε'' up to the MHz range. The 50 μm thick FLC-aerogel samples were sandwiched between the two indium-tin-oxide (ITO) coated glass plates. Mylar spacers were also inserted between the electrodes so as not to crack the aerogel structure due to strain during temperature cycling. In order to determine the effect on measured $\varepsilon(\omega)$ of the liquid crystal (LC) material on the electrodes or from leakage during temperature cycling, we made a set of two experiments. In one case we did not treat surfaces of the cell, and in the second we treated these for a homeotropic LC alignment. Homeotropic alignment does not give rise to observable collective director reorientations in the dielectric experiment since the FLC polarization is normal to the applied field and its rotation axis is along the field. Measurements were always made on the sample during cooling with conditions similar to those for the transition sequence. Furthermore any LC material that may have leaked during the first heating cycle is drawn back into the pores during cooling. Measurements were repeated several time, and results so obtained were reproducible within experimental errors, as were the main features of the results for the two sets of experiments (with and without surface alignment). For comparing the results

of FLC aerogels with the bulk, we made test cells with 10 μm spacers containing the FLC (the "bulk" sample). For such cells, a uniform planar alignment was achieved using surface treatment and/or applied field across the cell. For dielectric measurements, a test cell was mounted onto a hot stage, the temperature of which was controlled automatically. For the dielectric measurement a 0.1 V ac voltage was applied across the cell, on which a dc bias voltage up to 40 V could be superimposed. The complex permittivity $\varepsilon(\omega)$ of the cells was measured in the direction normal to the ITO plates, parallel to the smectic layers in the planar (bookshelf) bulk samples, which is connected to the dipole moment directed normal to the tilt plane. $\varepsilon(\omega)$ was fitted to Havriliak-Negami (HN) equation [9]. The relaxation strength $\Delta\varepsilon_i$ and the relaxation frequency ($f_{mi} = 1/2\pi\tau_i$) of the relaxation processes are obtained by fitting the data to the HN equation.

For the bulk sample, Fig. 1(a) presents a 3D plot of log ε'' vs frequency and temperature. Figure 1(b) shows typical plots of $\Delta\varepsilon$ and f_m varying with temperature for the collective mode features of $\varepsilon(\omega)$. In the
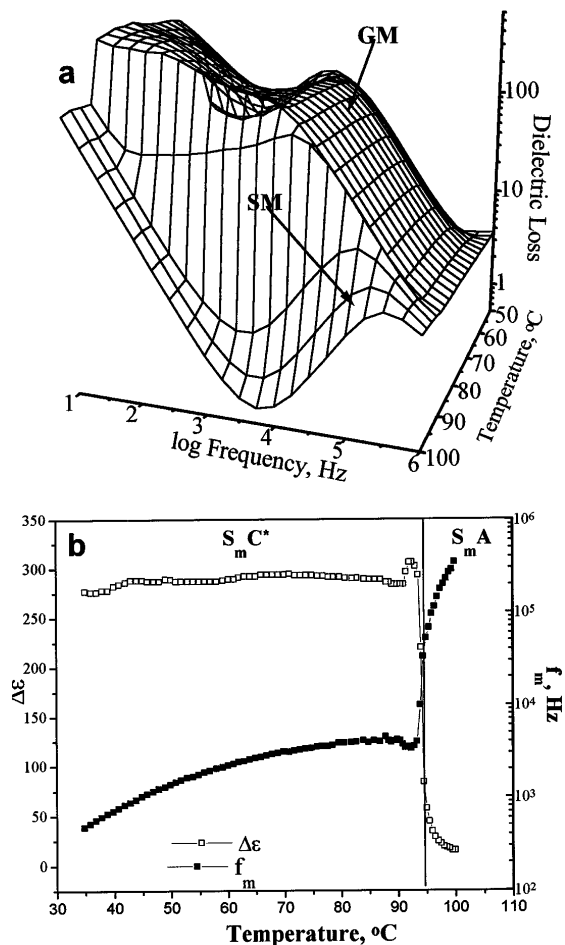

FIG. 1. (a) 3D plots of log ε'' vs frequency and temperature. (b) Temperature dependence of $\Delta\varepsilon$ and frequency f_m for bulk W314 sample.

Sm-A phase, $\Delta\varepsilon$ refers to the dielectric strength of soft mode (SM), close to the transition it refers to the combined strengths of Goldstone (GM) and SM modes, and away from the transition it refers to the GM alone as the strength of SM is significantly reduced. The plot of f_m similarly refers to the SM in Sm-A phase and GM in Sm-C^* phase. These data are typical of bulk FLCs [10] and are shown here for comparison with spectra obtained under aerogels confinement. The soft and Goldstone modes refer to the fluctuations of the amplitude of molecular tilt and its azimuthal orientation, respectively. The loss peak at 100 Hz is probably caused by the smectic layer deformation. It does not appear under aerogel confinement and is therefore ignored in analysis of the data. Figure 2(a) shows ε'' in the FLC confined to the 0.08 g/cm^3 geometry. The increase in $\varepsilon'' \sim 5$ MHz is caused by the ITO; a fitting procedure was used to eliminate it from the data. Figure 2(b) is constructed from measurements with a dc bias voltage of 1.5 V, where the soft mode is also observed and the GM is slightly suppressed. Figures 2(a) and 2(b) show an additional high-frequency relaxation process, AP, in the Sm-C^* phase under confinement. The frequency of this mode is almost temperature independent, and its $\Delta\varepsilon$ decreases somewhat with a reduction in temperature below the Sm-A to Sm-C^* transition temperature. In the Sm-A phase, a process labeled as molecular process, MP, is also observed. This process is Arrhenius with activation energy of 184 kJ/mole and may arise from the rotation of the molecules, around their short axes, lying in pores whose long axes are normal to the plane of the electrodes. An unusually large activation energy arises from hindrance to such rotations by the aerogel structure.

In the confined geometry [Figs. 2(a) and 2(b)], a single relaxation process seen in the Sm-A phase (SM excluding the MP mode) is found to split in three processes at Sm-A to Sm-C^* phase transition temperature. This observation is made for both pore sizes but shown here for the larger pore size aerogels. The relaxation process with the lowest frequency is assigned to the GM. The reason for this assignment is given later. The process with the highest frequency is the SM since it is observed under bias field and its $\Delta\varepsilon$ follows Curie-Weiss law close to the transition temperature. The relaxation process in the middle frequency range 10 to 100 kHz is the AP. In order to clarify the origin of the AP, we consider three possibilities: (a) a soft mode; (b) a molecular rotation around the short axis, for molecules confined in pores whose lengths are normal to the cell electrodes; (c) rotation around long axes of molecules within pores, long axes parallel to the cell electrodes. We further measure ε'' for the FLC-aerogel system, average pore chord of 700 Å as a function of dc bias voltages up to 40 V within Sm-A and Sm-C^* phases. The relaxation process in the Sm-A phase at 91 °C shows a decrease in $\Delta\varepsilon$ and an increase in f_m caused by an increase in bias voltage. This is a typical feature of soft mode in the
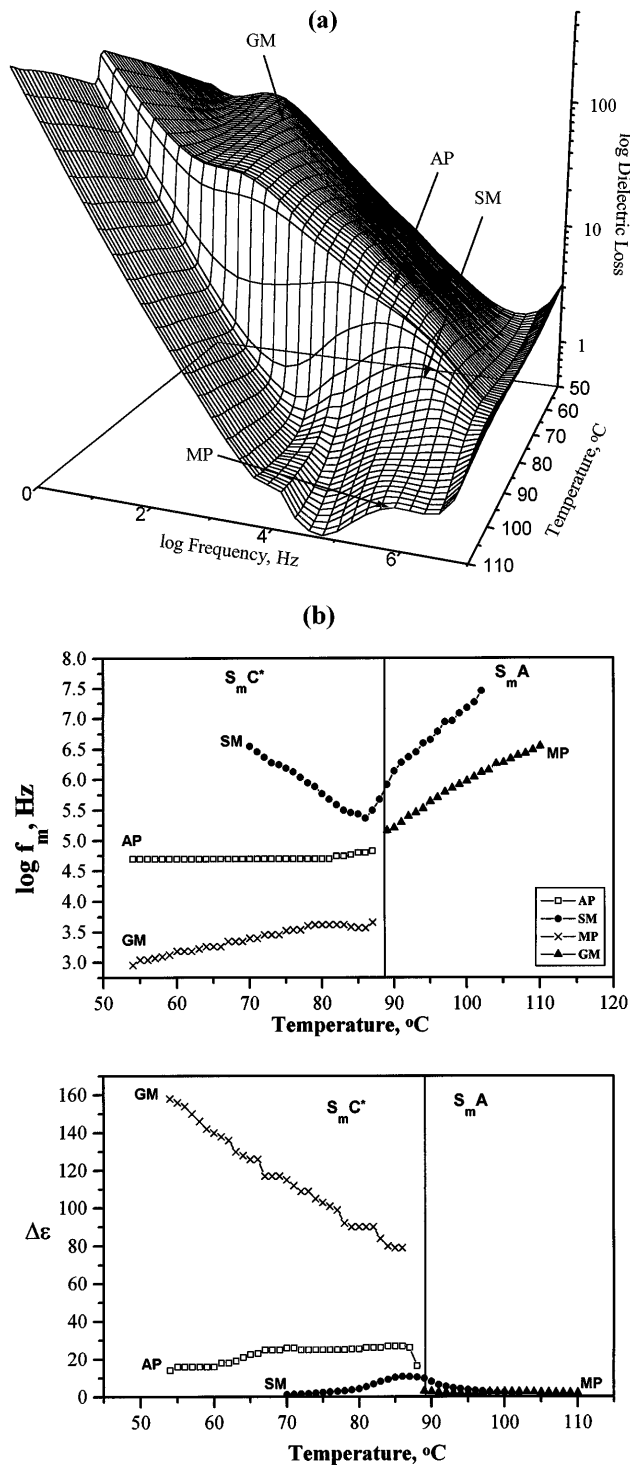
FIG. 2. (a) $\log \varepsilon''$ vs frequency and temperature. (b) Temperature dependence of $\Delta\varepsilon$ (lower part) and f_m (upper part) for bulk W314-aerogel (0.08 g/cm^3) sample.

Sm-A phase [11]. In the Sm-C^* phase at 80 °C (Fig. 3), the low-frequency relaxation process is gradually suppressed and frequency increased slightly with bias field. Finally, this process vanishes for bias of $\sim$10 V (see the inset of Fig. 3). This behavior is reminiscent of the splay in the director orientations of molecules within pores being minimized (X mode) [12] such that a small alternating voltage

for the dielectric experiment can no longer induce the polarization. This observation also confirms the assignment of the lowest frequency process [Figs. 2(a) and 2(b)] to be the GM. However, an increase of bias field gives rise to a small reduction in ε'' for the AP mode which is found to saturate for bias voltages in excess of $\sim$30 V [shown up to 10 V, also inset in Fig. 3], and its frequency is found not to shift with the bias field. Such an observed behavior excludes the possibility of the AP mode being SM or GM. Next we may suppose that this mode is connected with rotation around the short axis, i.e., *case b*, mentioned above. Such a rotation should exhibit Arrhenius temperature dependence. However, the plot of $\ln f_m$ vs $1/T$ (not shown) for AP mode shows no temperature dependence except close to the transition temperature. Furthermore, the frequency of this mode is too low to correspond to such a rotation and the process is only observed in the Sm-C^* phase. For the same reason *possibility c* given above is also ruled out. The interesting observation from Fig. 2(b) is that $\Delta\varepsilon$ of the GM gradually increases, whereas that of AP slightly decreases with a reduction in temperature. It seems reasonable to conclude that molecules within the pores are of two types: those belonging to the smectic layers and behaving similar to those in the bulk and the others contained in a FLC-aerogel interface. In glass forming liquids, too, an interface layer distinct from the bulk is observed [13]. This result is thus interpreted in terms of a continual growth of bulk-like smectic regions, as T is lowered, at the expense of liquid crystalline order affected by the aerogel pore walls. This explains an increase in $\Delta\varepsilon$ for the GM and a decrease for the AP with a reduction in temperature. The frequency of AP is higher than for the bulk switching because dynamics of the molecules within this interface layer is not collective. We note AP is found to be independent of the cell-surface treatment: confirming that the interface layer which gives rise to the AP process lies within the pores. W314 as bulk subjected to dc bias voltage was
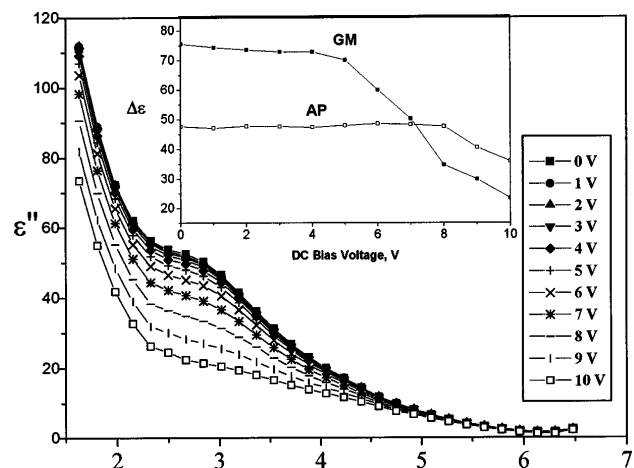

FIG. 3. dc bias dependence of $\log \varepsilon''$ vs frequency at 80 °C in Sm-C^*, for W314-aerogel (0.08 g/cm^3); $\Delta\varepsilon$ vs dc bias voltage for GM and AP modes shown in the inset.

studied at 85 °C (Sm-C^* phase). These studies did not show AP in the bulk as seen in the confined geometry; the mode is that environment specific to the aerogel confined geometry only.

Figure 4 shows a comparison between $\Delta\varepsilon$ as a function of temperature for the bulk and two aerogel systems with different pore sizes indicating that (i) the second order Sm-A to Sm-C^* phase transition is broadened by confinement; (ii) $\Delta\varepsilon$ of the aerogel systems is reduced by a factor varying from 2 to 3 depending on the temperature; the reduction, however, is not found to be proportional to the pore chord diameter but to the mean distance between the surfaces which is 954 and 822 Å for 0.08 and 0.17 g/cm^3 aerogels, respectively; (iii) a step-like increase in $\Delta\varepsilon$ is found with decreasing T for both confined systems, with the jump in $\Delta\varepsilon$ found in bulk replaced by a gradual increase under aerogel confinement. This implies a gradual buildup of the smectic C order with molecules continuing to tilt within the layers, i.e., a gradual increase in the correlation length for molecular tilt in the smectic layers; (iv) a wider distribution of the relaxation times of the collective modes (not shown in a figure) caused by confinement through randomness of interactions between the director and surfaces of the pores has been observed; (v) the frequency of the GM close to the transition temperature in the confined geometry is ~650 Hz as opposed to 4 kHz for the bulk. Aliev [6] recently reported a much lower frequency ~50 Hz for SCE12 (a E. Merck FLC) in a pore size of 1000 Å, than observed in our systems. The frequency depends on the type of mode: helical [14] or X mode [12]. For a helical mode, $f = 2\pi K_\varphi/\gamma_\varphi p^2$, whereas for the X mode, where the directors are splayed along the direction of the electric field (X axis), $f = 4.8K/\pi\gamma d^2$; p is the pitch of the helix and d is the pore size, K_φ and K are the elastic constants, and γ_φ and γ are the viscosities for the two cases. For $d = 0.0954$ μm and $p \approx 2.0$ μm, f of GM in the confined case is higher by a factor of 108 (on the assumption $\gamma_\varphi/K_\varphi \approx \gamma/K$), rather f is found *lower* by a factor of 6. If this dynamic model for the bulk is to be applica-

ble to the confined case, we must have $\gamma/K \gg \gamma_\varphi/K_\varphi$. This is plausible for FLC molecules within the confined system if the viscosity for the collective modes were to be much greater than prevalent in the bulk. Extremely large viscosity for molecular orientations is found for nematic and smectic phases of 8CB in silica aerogel systems [2,15] through an observation of a low-frequency mode in light scattering experiments. The $\Delta\varepsilon$ for the aerogels is $\sim\frac{1}{3}(\Delta\varepsilon)_{max}$ for the bulk at the transition temperature. $(\Delta\varepsilon)_{max}$ is the maximum strength for an undisturbed helical structure. However, it tends to rise to almost $\frac{1}{2}(\Delta\varepsilon)_{max}$ with a decrease in T. On the basis of simple arguments, one finds that $\Delta\varepsilon_\delta$ for the layers tilted at an average angle of δ is given by $\Delta\varepsilon_\delta = (\Delta\varepsilon)_{max}\langle\cos^2\delta\rangle$; δ is the angle with which the layer is tilted with respect to the normal to the electrodes, usually $\delta < \theta$ (tilt angle); for a complete 3D randomization $\langle\cos^2\delta\rangle = \frac{1}{3}$ or for 2D $= \frac{1}{2}$. The comparison is only tentative since the molecular arrangement within the pores is different than in the bulk, i.e., helix within the pores is significantly distorted. Furthermore for $\delta < \theta$, $\Delta\varepsilon$ also depends on φ_0 (the azimuthal pretilt angle) which in turn depends on δ [12]. Hence a comparison between $\Delta\varepsilon$ for the bulk and the pores requires further experimentation and analysis. Nevertheless the results do provide evidence for the smectic layer structure to be randomized within pores.

*Author to whom correspondence should be sent.

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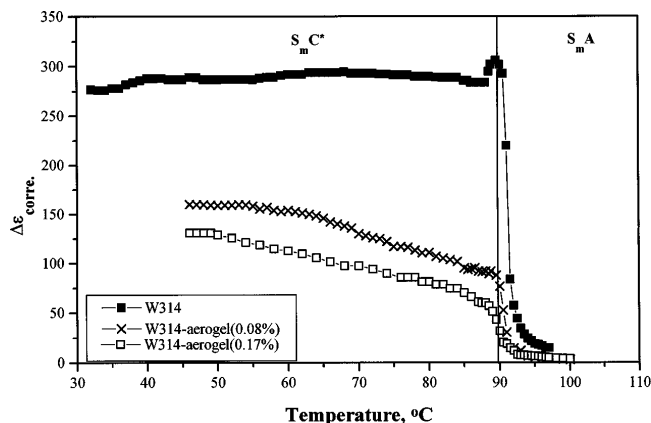[15] T. Bellini, N. A. Clark, and D. W. Schaefer, Phys. Rev. Lett. **74**, 2740 (1995).

FIG. 4. (a) Comparison of temperature dependence of $\Delta\varepsilon$ for bulk and two W314-aerogel (0.08 and 0.17 g/cm^3) samples.