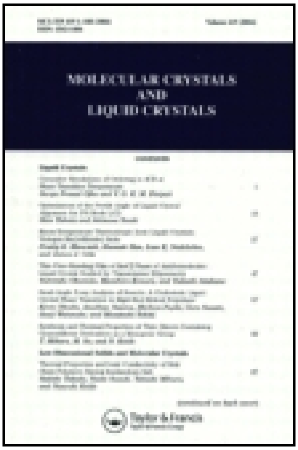

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Liquid Crystals—Porous Glasses Heterogenous Systems as Materials for Investigation of Interfacial Properties and Finite-Size Effects

F. M. Aliev [a] [b]

[a] Liquid Crystal Institute, Kent State University, Kent, OH, 44242, USA

[b] Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, PA, 15260, USA

To cite this article: F. M. Aliev (1994): Liquid Crystals—Porous Glasses Heterogenous Systems as Materials for Investigation of Interfacial Properties and Finite-Size Effects, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 243:1, 91-105

To link to this article: http://dx.doi.org/10.1080/10587259408037763

Mol. Cryst. Liq. Cryst., 1994, Vol. 243, pp. 91–105
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Liquid Crystals—Porous Glasses Heterogenous Systems as Materials for Investigation of Interfacial Properties and Finite-Size Effects

F. M. ALIEV†
Liquid Crystal Institute, Kent State University, Kent, OH 44242, USA

Porous silicate glass can be used as an ideal matrix to study the influence of temperature on the surface effects that occur at the interface between the glass and some other material. Since the structural characteristics of these matrices are nearly independent of the temperature, all observable effects when the temperature is changed can be attributed to the change in the physical properties of the second component (LC). Moreover, the dielectric permittivity of silica porous glass matrix is independent of the temperature and frequency for a wide range of frequencies. This fact and the practically negligible electrical conductivity of the matrix greatly simplify the interpretation of the results and make it possible to avoid a number of difficulties that have been encountered earlier in studies of dielectric properties of heterogeneous systems. It is shown that micro-heterogenous systems which have a liquid crystal as one of the components (the other one is the porous glass) are useful materials for investigations of interfacial and finite-size phenomena in LC. The results on the structure and temperature dependence of the interfacial layer of 5CB at interface between LC and wall of pore as well as dielectric studies of the influence of confinement on dynamics of molecular motion of LC in pores are discussed.

Keywords: dielectric relaxation, interfacial properties, liquid crystal, porous glass

INTRODUCTION

The study of physical properties of condensed matter in confined geometries (pores) is attracting considerable attention from both theoreticians and experimentalists.[1-4] This is due to the fact that this kind of research can provide clear information on interfacial and finite-size effects. Investigations of condensed matter in porous matrices have revealed various new properties and effects not observed in the same substances when they are in the bulk.[2,5-30]

The nontriviality of physical phenomena that occur in pores is manifested, for example, when liquid He[6] was placed in porous material or when phase transition

---

†On leave of absence from Institute of Precision Mechanics and Optics, St. Petersburg 197101, Russia. Present address: Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, PA 15260, USA.

and phase separation was studied in liquid binary mixtures impregnating porous matrices.[7,11-13]

The difference between the surface and bulk properties, as well as finite-size effects, are manifested most strikingly in the case of liquid crystals (LC).[23] This is due to the fact that LC are "soft" systems[31] because the energy responsible for long-range orientational order is fairly small. It follows that the substrates between which a layer of LC is confined can exert their influence on the LC up to distances L which may reach several thousand angstroms.[23] It is clear that investigations of LC in pores of size less than L should, in principle, provide information on the interfacial properties of these LC.

The difference between the surface and volume properties of the substance may be of fundamental character and may be revealed in the appearance of new phases near the surface and transitions between them not found in the bulk.

In spite of considerable progress in the investigation of finite-size effects in the condensed state, the problem advanced by Wilson and Kogut[32] still remains topical: "How far can one reduce the size of a gas, say, without qualitatively changing its properties?" The minimum size one can reach without change is called correlation length. In smectic LC, which have both A and C phases, the correlation length close to SmA-SmC phase transition is about 100 Å, and in this case, it is possible to study the influence of confinement on critical behavior when the correlation length is comparable to the pore size. Until recently it was not clear whether structure formation is possible and what structural features of different smectic-type structures might arise when the characteristic size of the structure and correlation length are comparable to the pore size.

In the case of polar liquid-crystal molecules, the substrate may induce a polar order and give rise to the polarization effects,[33,34] which can also be due to a gradient of the order parameter and inhomogeneity of orientation.[35] Clearly, the bent nature of the pore may induce these effects in porous matrices.

Porous matrices of different types have been effectively used to investigate the finite-size effects in condensed matter. Porous silicate glasses are particularly promising for use as porous matrices, since they are distinguished by their uniformity of chemical composition, purity and mechanical strength. Porous silicate glass can be used as an ideal matrix to study the influence of temperature on the surface effects that occur at the interface between the glass and some other material. Since the structural characteristics of these matrices are nearly independent of the temperature, all observable effects when the temperature is changed can be attributed to the change in the physical properties of the second component (LC). Moreover, the dielectric permittivity of silica porous glass matrix is independent of the temperature and frequency for a wide range of frequencies. This fact and the practically negligible electrical conductivity of the matrix greatly simplify the interpretation of the results and make it possible to avoid a number of difficulties that have been encountered earlier in studies of dielectric properties of heterogeneous systems.[36-38]

In this paper we will show that micro-heterogenous systems which have a liquid crystal as one of the components (the other one is the porous glass) are useful materials for investigations of interfacial and finite-size phenomena in LC. The results on the structure and temperature dependence of the interfacial layer of 5CB at interface between LC and wall of pore as well as dielectric studies of the influence on confinement on dynamics of molecular motion of LC in pores are discussed.

INTERFACIAL PROPERTIES OF 5CB IN PORES

Recently, it was shown theoretically[39] that the confined geometry gives rise to wetting configurations, or microstructures, which have no analog in the planar case. According to this theory, many features observed in experiments on binary liquid mixtures in porous media, which have been interpreted in terms of random-field theory,[40,41] are shown to be consistent with wetting in a confined geometry with no randomness.

The temperature and wave-number dependences of the scattered-light intensity in the isotropic phase of LC in pores (with pore size 1000 Å) were explained[25,26] on the basis of the single assumption that for temperatures above a certain critical value, the LC in pores is a pseudobinary medium with an anisotropic layer at the pore walls formed as a result of orientational wetting.

Effective properties of the micro-heterogeneous system are dependent not only on the properties and volume fraction of the components, but also on the contribution from interfacial regions. This latter contribution increases with decreasing pore size. Such phenomena should be taken into account by assuming that in two-component system there is the third quasi-phase, which exists in the form of an interfacial layer located near the interface in addition to the initial phases.

The temperature dependence of the thickness of this interfacial layer is of fundamental importance. It is not clear whether this dependence is critical and if so, what is associated critical index? If the thickness of the quasi-phase layer is commensurate with the length of a molecule, deviations may occur from the theoretical predictions which hold for the 3D space. To solve this problem, small-angle X-ray scattering was used to study a pentylcyanobiphenyl (5CB) in a quartz-glass matrix.

Porous matrices with through pores were prepared from the original sodium borosilicate glasses by a method described in Reference 42: the sodium borate phase was removed by leaching, and the matrix framework consisted of SiO_2. The characteristics of the matrices were determined by small-angle x-ray scattering (SAXS).[43] The matrix had the following characteristics: volume fractions of the solid phase and pores $\omega_1 = 0.74$ and $\omega_2 = 0.26$, mean radius of the pores $R = 90$ Å, and the density of the matrix framework $d_1 = 2.26$ g/cm^3. The temperatures of phase transitions of 5CB in the free state were $T_{CN} = 295$ K (crystal—liquid crystal) and $T_{NI} = 308$ K (liquid crystal—isotropic phase). The x-ray measurements were carried out using a small-angle Anton Paar chamber in the range of angles from 10′ to 250′. The samples were 0.2 mm-thick porous-glass plates impregnated with 5CB. These plates were placed in a thermally stabilized, flat, 0.23 mm-thick cell which was filled with 5CB. These measures prevented the liquid crystal from leaking out from the pores.

A structural description of such a two-phase system can be found from studies of SAXS with use of Porod's[44] theory. A quantity, called Porod's invariant, is determined experimentally. As a result of slit collimation of the beam, we can describe this invariant as $Q = \int_0^\infty I(h)hdh$, where I is the intensity of scattered radiation, $h = (4\pi/\lambda)\sin(\Theta/2)$, Θ is scattering angle, and $\lambda = 1.54$ Å. If I is given in absolute units, i.e., relative to the intensity of the primary beam, then Q is related to the characteristics of the system under study by the relation:

$$Q = 2\pi\lambda i_e H(\rho_1 - \rho_2)^2\omega_1\omega_2 \tag{1}$$

where ρ_1 and ρ_2 are the electron densities of the solid phase of the matrix and of the liquid crystal, respectively; i_e is the scattering cross section of an electron; and H is the thickness of the scattering layer. Relation (1) is valid if the electron density is constant in each phase and if it varies abruptly at the interface. The temperature dependence of Q in such a two-phase system is determined exclusively by the dependence $\rho_2(T)$, since the density of the matrix framework is nearly constant in the temperature range 0–150°C. Clearly, the density of the liquid crystal decreases with increasing T, that means $\Delta\rho$ increases, and hence Q should also increase. Figure 1 is a plot of the measured $Q(T)$ dependence. We see that this curve cannot be explained only in terms of the temperature dependence of the density of the liquid crystal; therefore, we see the need for including the existence of the interface surface layer to make sense of $Q(T)$.

If an interface layer with a density different from ρ_2 is formed in the liquid crystal at the interface between the phases (see the inset in Figure 1), relation (1) becomes

$$Q = 2\pi\lambda i_e H(\rho_1 - \rho_2)^2(\omega_1\omega_2 - \omega_3) \tag{2}$$

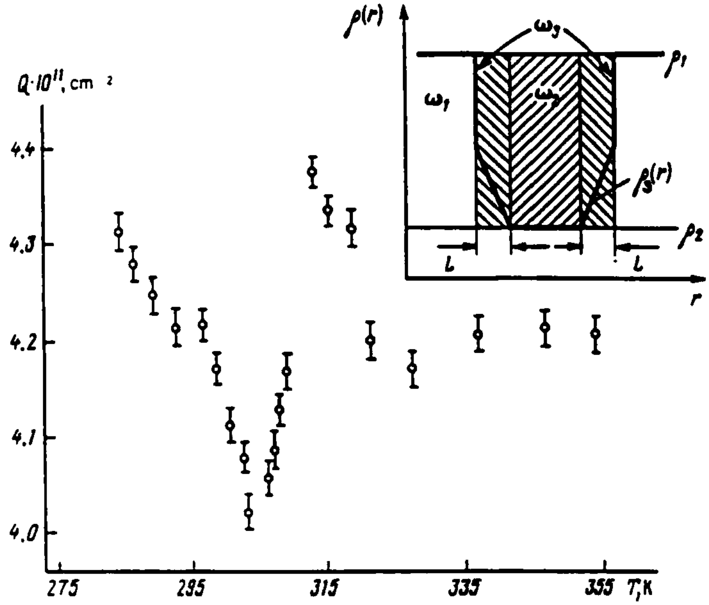

FIGURE 1 Temperature dependence of Porod's invariant Q. The model of a pseudo-two-phase system is shown in the inset.

where ω_3 is the volume fraction of this layer. It is natural to assume that the layer in all pores is formed under the same conditions. We can then introduce a thickness of the interface layer L (see inset in Figure 1). Taking into account the fact that the electron and mass densities (d) are related by relation $\rho = N_e N_A d/M$, where N_e is the number of electrons per molecule, M is molecular mass, N_A is Avogadro's number, and the ratio N_e/M is approximately equal to 0.5 mole/g, the following formula is valid for such a pseudo-two-phase system[45]:

$$Q = 2\pi\lambda i_e H(N_e^2 N_A^2/M^2)(d_1 - d_2)^2(\omega_1\omega_2 - LS/6V) \tag{3}$$

The dependence $L(T)$ calculated from Equation (3) is a critical dependence (see Figure 2). A layer of thickness no less than the length of a molecule $L_0 \approx 18$ Å, can always be assumed to exist, and L can be represented as a sum of L_0 and the singular part. Figure 3 is a plot of $\log(L - L_0)$ versus $\log \tau$, where $\tau = (T_c - T)/T_c$ for $T < T_c$ and $\tau = (T - T_c)/T_c$ for $T > T_c$. The fit (the straight line in Figure 3) corresponds to $T_c = 304.5$ K and to the critical index 0.25 ± 0.03. Note that the solid lines in Figure 2 were drawn based on the data in Figure 3: $L = L_0 + A\tau^{-0.25}$, where $A = 3.2 \pm 0.2$ Å.

There are two ways in which $L(T)$ can be described theoretically: by using scaling theory and by using theory of capillary waves. These methods give sharply differing results in the 2D case (see Reference 46 and the literature cited therein) but are in agreement for $D \geq 3$. According to scaling approach, $L \sim (T_c - T)^{-\nu}$, where ν is the critical index of the correlation radius for any dimensionality of space, and $\nu = 1$ in 2D. On the other hand, it follows from the theory of capillary waves in 2D,[46] that

$$L \sim (T_c - T)^{(\mu+\beta)/4} \tag{4}$$

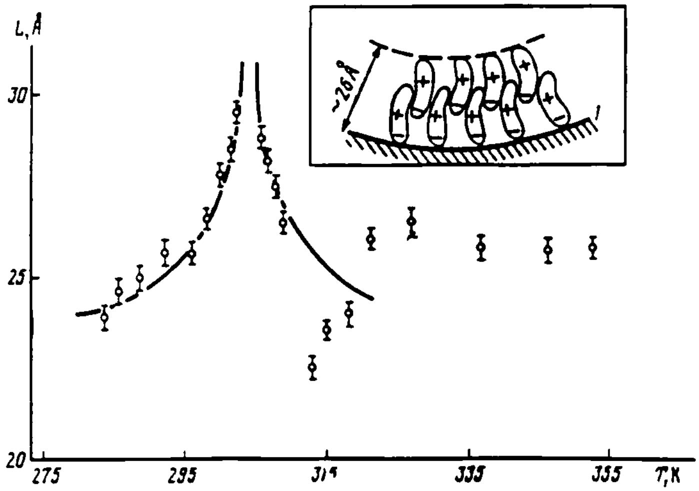

FIGURE 2 Temperature dependence of the thickness of the interface layer. The model of a polar bilayer is shown in the inset. 1—the liquid crystal-glass interface.

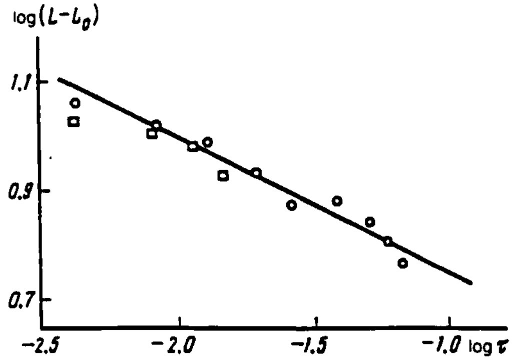

FIGURE 3 Singular part of the surface layer versus the reduced temperature on the log-log scale. ○: $T < T_c$; □: $T > T_c$.

where μ and β are the critical indices of the surface tension and the order parameter. In 2D the exact values of μ and β are 1 and $\frac{1}{8}$ (the two-dimensional Ising model) and the critical index in Equation (4) is $\frac{9}{32}$. In the system under study, the liquid crystal layer enclosed in the pore is of limited size, is not flat, and is not two-dimensional. At best it may be regarded as a quasi-two-dimensional layer because of inappreciable thickness of the transition layer. The experimental value of critical index is nonetheless approximately equal to the value predicted by the theory of capillary waves in a 2D space. At temperatures $T > 312$ K, the experimental points in Figure 2 diverge sharply from the theoretical curve because of the onset of a broad (with respect to the temperature) transition to the isotropic phase. An interface layer of thickness ≃26 Å, which does not depend on the temperature, forms at the wall at temperatures bigger than 332 K (see the inset of Figure 2). The key factors responsible for the formation of such a polar bilayer are the dipole structure of the 5CB molecules, the properties of the adsorbing surface, and the spatial restrictions imposed by the rigid substrate. The coupling responsible for the liquid-crystal order facilitates the establishment of the surface order.

DIELECTRIC PROPERTIES OF NEMATIC LIQUID CRYSTALS IN PORES

The influence of the substrate on the orientational mobility of the liquid crystal molecules and the distance from the substrate at which this influence is important are questions which have yet to be addressed. Information on the dynamics of molecular motion in surface layers may be obtained directly from the study of liquid crystals in porous matrices.[28] We investigated this topic by the method of dielectric spectroscopy. Nematic liquid crystalsl 5CB and cyanophenyl ester of heptylbenzoic acid, i.e., cyanophenyl heptylbenzoate (CPHB), and ferroelectric liquid crystal SCE 12 were studied. The dipole moment μ of the 5CB molecule is 5D, and it is parallel to the longitudinal axis of the molecule (β = 0, where β is the angle between the dipole and the long axis of a molecule); and for CPHB μ = 6.1D and β = 16°. For dielectric measurements, two types of matrices with characteristics R_1 = 65 Å, ω_1 = 0.27 (microporous matrices) and R_2 = 1000 Å,

$\omega = 0.38$ were used. The samples were porous glass plates, of dimension 2 × 2 × 0.1 cm; they were heated to 150°C and pumped out; and this was followed by impregnation with the liquid crystals from an isotropic melt. The quantities measured directly were the permittivities $\varepsilon'_{\text{syst}}$ and the dielectric loss factors $\varepsilon''_{\text{syst}}$ of the two-phase heterogeneous systems comprised of a matrix and a liquid crystal. The permittivity of the disperse phase (liquid crystal) calls for a theory allowing for anisotropy and local inhomogeneity of liquid crystal dispersed in a matrix and valid at high concentrations of liquid crystal. Such a theory is not known to us, so that we had to calculate the permittivity of the second phase (liquid crystal) using Bottcher's theory[36]

$$\varepsilon = \varepsilon_1 + 3\omega\varepsilon \frac{\varepsilon_2 - \varepsilon_1}{2\varepsilon + \varepsilon_2} \tag{5}$$

where ε, ε_1, ε_2 are measured dielectric constant of system, matrix material and liquid crystal; ω is volume fraction of pores. We shall use $\langle\varepsilon\rangle$ to denote the volume averaged real part of the permittivity of a liquid crystal in the pores, calculated from Equation (5). A satisfactory theory may first of all alter the absolute values of $\langle\varepsilon\rangle$, but it should have less effect on the nature of the temperature and frequency dependences which are discussed below.

The dependence of $\langle\varepsilon\rangle$ on the frequency of the external electric field is shown in Figure 4 for 5CB in micropores (curve 1) and in macropores (curve 2) and for CPHB in micropores (curve 3). It is evident that all curves of $\langle\varepsilon\rangle$ are relaxational in character and exhibit three regions of the permittivity dispersion. The low-

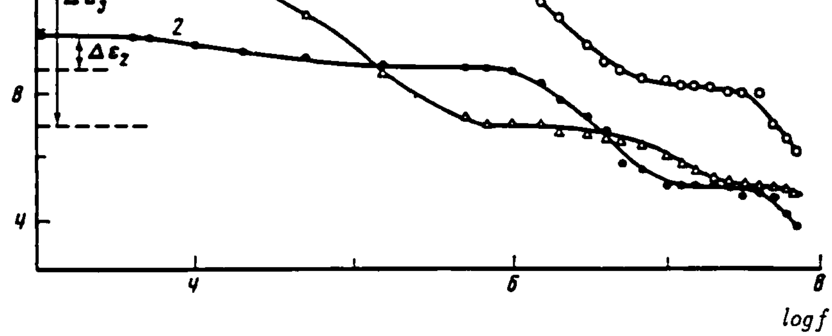

FIGURE 4 Frequency dependence of $\langle\varepsilon\rangle$ at $T = 290$ K: 1) 5CB in micropores; 2) 5CB in macropores; 3) CPHB in micropores. The dashed horizontal lines are the values of $\langle\varepsilon_s\rangle$ for the second dispersion region.

frequency (first) region of the dispersion is not present in nematic liquid crystals in the free state. Plotting ε'' as a function of ε' (the Cole-Cole diagrams) (Figure 5) enables us to separate the dispersion regions and to determine the values of the permittivities which in the second dispersion region were static and at the same time corresponded to the "high-frequency" plateau for the first dispersion region. These values, are identified by dashed lines in Figure 4. The Cole-Cole diagrams indicate that for LC in pores the parameters α, which represent empirically the spectrum of the relaxation times, vary from 0.2 to 0.35. For the free state of the nematic phase, the Cole-Cole parameter is $\alpha = 0$. For LC inside the pores, α is not equal to zero, and then there is a spectrum of relaxation times. This is due to the fact that the properties of the surface layers begin to vary at distances of the order of molecular dimensions, and depending on the distance from the surface of a pore, the various layers of LC can have different relaxation times. This procedure was performed for all the samples and permits the use of the Debye equation for complex permittivity ε^*, modified by Cole and Cole, to describe frequency dependences of $\langle\varepsilon\rangle$:

$$\varepsilon^* = \varepsilon_\infty + \sum_{j=1} (\varepsilon_{js} - \varepsilon_\infty)/(1 + i4\pi f\tau_j)^{1-\alpha_j} \qquad (6)$$

where ε_∞ is the high-frequency limit of the permittivity, ε_{js} the low-frequency limit, and τ_j the mean relaxation time. A graphical fitting enables us to determine ε_{js} and τ_j. The relaxation times for the second dispersion region are plotted in Figure 6 as a function of reciprocal temperature. The dashed lines in Figure 6 represent the

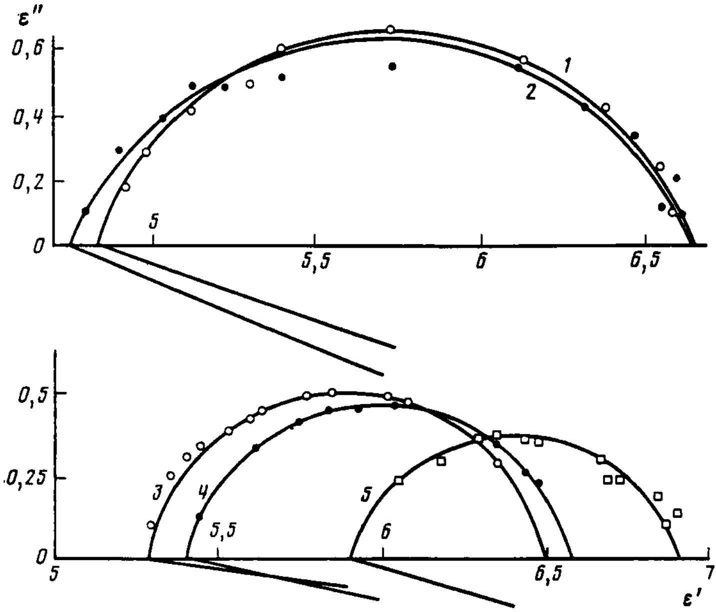

FIGURE 5 Cole-Cole diagrams: 1), 2) 5CB in macropores at 293 and 301 K respectively; 3), 4), 5) CPHB in micropores at 318.5, 343, and 383 K, respectively.

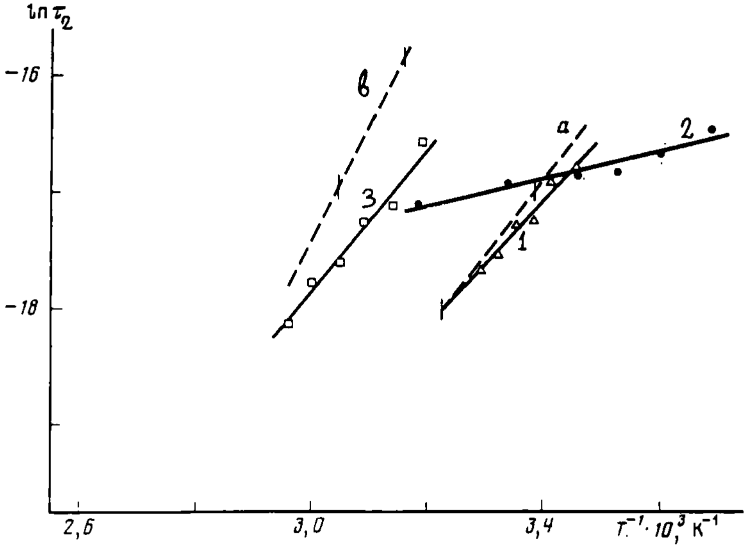

FIGURE 6 Dependence of ln τ_2 on the reciprocal temperature: a) 5CB; b) CPHB; 1) 5CB in micropores; 2) 5CB in macropores, 3) CPHB in micropores.

relaxation times for 5CB and CPHB in the free state, corresponding to the rotation of molecules around the short (5CB) and long (CPHB) axes.

The main difference between the behavior of the permittivity of liquid crystals in pores and the behavior in the free state is the existence of a low-frequency dispersion region, absent in the free state and characterized by relaxation times $\tau \sim 10^{-6}$ s, which could not be attributed to the orientational motion of the molecules, but represents some collective process. The relaxation times τ_2 for the second region were close to τ for the free state, but the temperature dependence of τ_2 was weaker in both micropores and macropores. The values of τ_2 and their temperature dependences in macropores were closer to the bulk behavior than the behavior observed in micropores, in agreement with expectations.

All these properties and the temperature hysteresis of $\langle\varepsilon\rangle$ measured at a frequency of 1 kHz (Figure 7) can be explained using the assumption that the wall induces polar order of smectic type. In fact, it is known that the $\varepsilon'(T)$ dependence for bulk liquid crystals in the smectic A and smectic C phases exhibits a hysteresis,[47] and the temperature dependence of the relaxation times governing the rotational mobility of molecules around the short axis becomes weaker[48] than in the nematic phase.

It is evident from Figure 6 that the dependence of ln τ_2 on T^{-1} is linear and may be described by the relation $\tau = \tau_0 \exp(U/kT)$, where U is the activation energy. This activation energy is equal, in barrier theories, to the difference in potential energy of the stable orientations $\theta = 0$ or π and the highest potential energy of intermediate orientation ($\theta = \pi/2$) (where θ is the angle between the director and the dipole). There is no polar ordering in the free state; and therefore, the orientations $\theta = 0$ and $\theta = \pi$ are equally probable (see Figure 8, curve a). The values of the activation energies of the investigated nematic liquid crystals in

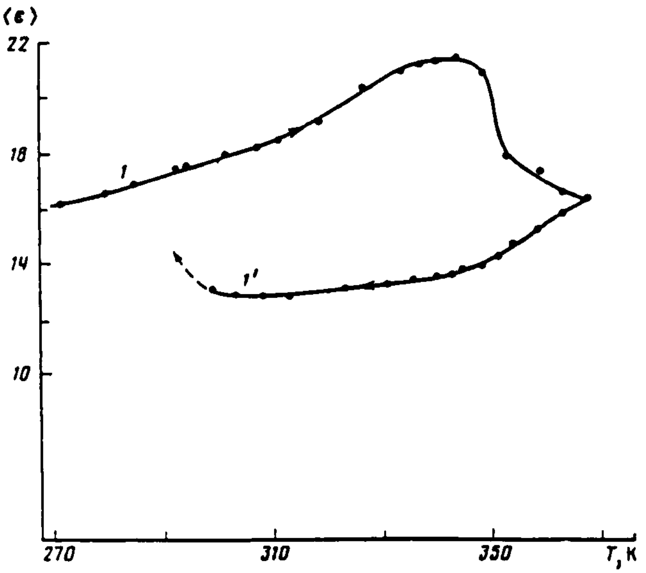

FIGURE 7 Temperature dependence of ⟨ε⟩ of 5CB in micropores (1 kHz).

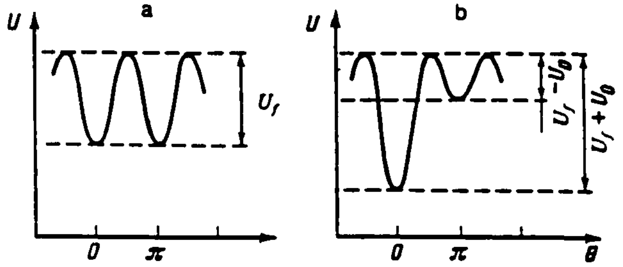

FIGURE 8 Dependence of the potential on the angle θ: a) nematic liquid crystal in the free sate; b) in pores.

the free state were found to be $U_{1f} = 8.8 \times 10^{-13}$ erg for 5CB and $U_{2f} = 14 \times 10^{-13}$ erg for CPHB.

The interaction of nematic LC molecules with the surface (characterized by the interaction energy U_0) is equivalent to the interaction with an external field producing a polar order close to the surface, stabilizing one orientation ($\theta = 0$) and correspondingly changing U_f to $U_f + U_0$. For $\theta = \pi$ the potential becomes to $U = U_f - U_0$ and corresponds to the activation energy (see Figure 8, curve b).[48]

The activation energies U_i, corresponding to the dependences $\tau_2(T)$ in micropores are: $U_1 = 1.7 \times 10^{-13}$ erg (5CB) and $U_2 = 8.5 \times 10^{-13}$ erg (CPEH). A comparison of U_f and U_{0i} gave the energy of the interaction of molecules with the surfaces of the pores $U_{0i} = U_f - U_i$, and these values were $U_{01} = 7.1 \times 10^{-13}$ erg (5CB) and $U_{02} = 5.5 \times 10^{-13}$ erg (CPHB). These estimates are only qualitative; it would be reasonable to assume that $U_0 \approx 5 \times 10^{-13}$ erg. Bearing in the mind that the number of molecules per cm^2 is $n_s \approx (2\text{–}3) \times 10^{14}$ cm^{-2}, we found that the surface energy of the nematic liquid crystal $F_s = U_0 n_s$, should be $F_s \sim 10^2$ erg/cm^2.

Another argument in support of existence of polar ordering at the wall is the low-frequency dispersion. It is natural to assume that the ratio of low-frequency increments $\Delta\varepsilon_2'$ and $\Delta\varepsilon_1'$ corresponding to curves 2 and 1 in Figure 4 is proportional to the volume fraction g of the polar ordered surface layer (thickness l) in the macropores, if all the molecules in the micropores belong to this layer. Then, if the macropore is modeled by a cylinder of radius R

$$\Delta\varepsilon_2/\Delta\varepsilon_1 \approx 1 - (R - l)^2/R^2 \qquad (7)$$

Using the experimental values $\Delta\varepsilon_1 = 3.5$ and $\Delta\varepsilon_2 = 1$ determined at the same temperature, we find that $l = 150$ Å. It therefore follows that the thickness of the polar-ordered layer is $\sim 10^2$ Å.

Of special interest is the first dispersion region $\langle\varepsilon\rangle$ of CPHB in micropores. Figure 9 shows that the dispersion curves corresponding to the first region, which is associated with the surface polar order, are shifted toward lower frequencies when T increases. The vertical arrows identify the frequencies corresponding to τ_1. The dependence of τ_1 on T is presented in Figure 10, and the experimental points show the dependence $\tau_1(T)$, which is typical of the critical slowing down of relaxation corresponding to the soft mode in ferroelectric liquid crystals (FLC). As is known[49,50] in FLC, the soft mode corresponds to synphase fluctuations in the amplitude of the molecules' tilt angle (between the axis of a molecule and the normal to the smectic layer) and of polarization, which are order parameters. In the case of CPHB in the pores, the nature of the polar order is different from bulk FLC in principle, but the angle θ between the dipole and normal to the pore surface may be chosen as one of the order parameters.

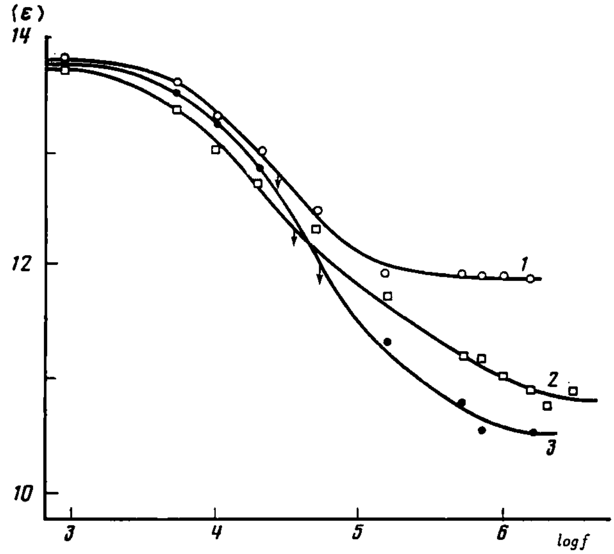

FIGURE 9 Frequency dependence of $\langle\varepsilon\rangle$ of CPHB in the first dispersion region at different temperatures: 1) T = 363 K; 2) T = 343 K; 3) 318.5 K. The vertical arrows identify the frequencies corresponding to τ_1.

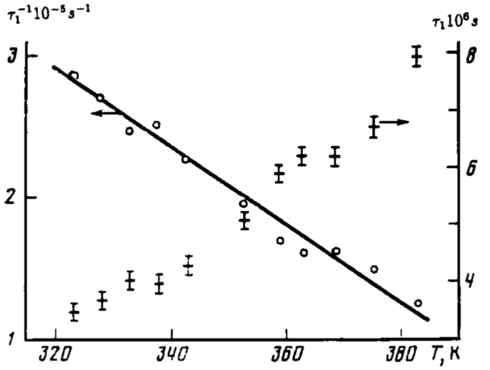

FIGURE 10 Temperature dependence of τ_1 and its reciprocal for CPHB in micropores.

The molecules of CPHB have a large dipole moment. This means that the dimensionless parameter $n\mu^2/kT$ (where n is the number of molecules per cm^3) characterizing the ratio of the energy of dipole-dipole interaction to the energy of thermal motion is 1.4. The electrostatic interactions of the dipole molecules in the nematic LC are insufficient to overcome the disordering effect of the thermal motion and the creation of a polar order is thus impossible. However, near the solid surface of the pores, the polarized state arises as a result of at least two factors: a very strong dipole-dipole (static) interaction and the interaction with the pore wall, which stabilizes the orientational order and suppresses the thermal fluctuations. The curvature of the surface of a pore may be another important factor in the establishment of a polar order. Thus, if we select the order parameter in the form of the angle θ, we can use the expression for τ, which describes a soft mode due to relaxation of the molecular tilt angle[49]:

$$\tau = \gamma_1/4a'(T_c - T),\ T < T_c \tag{8}$$

where, for pores, γ_1 is the effective viscosity and a' is the coefficient of the quadratic term in the expansion of the free energy in powers of the order parameter. The critical index in Equation (8) is one (mean-field theory). As is evident from Figure 10, the dependence of the inverse relaxation time τ^{-1} on T is linear, and the corresponding critical index is 1 ± 0.15 and $a'/\gamma_1 = 800\ s^{-1}\ K^{-1}$. Assuming[49] that $a' \approx 10^3$ erg $cm^{-3}\ K^{-1}$, we estimate γ_1 to have a value $\gamma_1 \approx 1.25P$, which is a reasonable value for the viscosity.

Thus, results of the dielectric investigation of NLC in pores show that the difference in the dynamics of orientational motion of NLC molecules in pores as compared to the free state arises at distances of 10^2 Å. In addition, we quantitatively determined the total energy of interaction of the molecules with pore surface. For NLC whose molecules have a large dipole moment a soft mode associated with the polar is observed in pores. Hence it is interesting to study ferroelectric liquid crystal in pores.

FERROELECTRIC LIQUID CRYSTAL IN MACROPORES

Dielectric spectroscopy, DSC and X-ray scattering were used to study dynamics, phase transitions and the structure of ferroelectric liquid crystal (FLC) confined in silica porous glass with average pore size 800 Å and volume fraction of pores 40%. The FLC we used was SCE 12 synthesized by BDH Ltd. through E. M. Industries. This FLC has been investigated thoroughly in the free state (see for example References 51 and 52). The main purpose of these investigations was to answer the following questions:

- Does smectic ordering exist in restricted geometries?
- What is the effect of temperature on smectic structure in pores?
- What is the influence of confinement on Sm C^*-Sm A phase transition?
- What are the dynamics of Goldstone and the soft modes in pores?
- And what is the temperature dependence of the rotational viscosities in pores?

It is expected that due to boundary conditions the helical structure, which is characteristic of bulk FLC will not form in pores.

As a result of experimental studies, the central results are that:

- Smectic C and smectic A phases are formed in 800 Å pores.
- The smectic C–smectic A phase transition temperature is reduced in pores by about 10 degrees.
- Even if the helical structure which is characteristic of bulk FLC does not form in pores due to the boundary conditions, the Goldstone mode is still found in pores because spontaneous polarization can arise in a system composed of chiral molecules which form a layered structure with the molecules tilting out of layer planes.
- The rotational viscosities associated with the Goldstone and soft modes are about 10 times higher in the pores than in the bulk, and temperature dependences of these viscosities are described by the Arrhenius equation.
- In order to describe the experimental temperature dependences of the dielectric permittivities and relaxation times of the Goldstone and soft modes by equations based on the Landau expansion of the free-energy density F, the additional term taking into account the liquid crystal—pore wall interaction surface energy F_s should be included in F. There is good agreement between theory and experiment if $F_s \approx 50$ erg/cm^2.

Detailed arguments for these conclusions will be published separately.

The investigation of physical properties of LC in porous silicate matrices with pores of different sizes makes it possible to study new phenomena and to determine characteristics of these LC. The use of porous matrices with invariable structure characteristics is an experimental procedure permitting successful investigation of interfacial and finite-size effects.

Acknowledgment

I wish to express thanks to J. Kelly, K. S. Pozjivilko and M. N. Breganov for useful collaboration and discussions. The work on ferroelectric LC was performed in collaboration with J. Kelly and was supported by NSF Science and Technology Center ALCOM. The work on interfacial properties of 5CB and dielectric properties of NLC was performed with assistance from K. S. Pozjivilko and M. N. Breganov. I would also like to thank T. Blum for discussions and assistance in completing the paper.

References

1. Physics and Chemistry of Porous Media, AIP Conf. Proc. **107**, (ed. by D. L. Jonson and P. N. Sen) AIP, NY (1984).
2. Molecular Dynamics in Restricted Geometries, (ed. by J. Klafter and J. M. Drake) Wiley, NY (1989).
3. Finite Size Scaling and Numerical Simulation of Statistical Systems, (ed. by V. Privman) Wold Scientific, Singapore (1990).
4. Statistical Models for the Fracture of Disorder Media, (ed. by H. J. Herrmann and S. Roux) Norf-Holland, Amsterdam (1990).
5. F. M. Aliev, *Sov. Phys. JETP Lett.*, **41**, 310 (1985).
6. Y. Kondo, Y. Kodama, Y. Hirayoshi, T. Mizusaki, A. Hirai and K. Eguchi, *Phys. Lett.*, **A123**, 471 (1987).
7. M. C. Goh, W. I. Goldburg and Ch. M. Knobler, *Phys. Rev. Lett.*, **58**, 1008 (1987).
8. D. D. Awschalom and J. Warnock, *Phys. Rev.*, **B35**, 6779 (1987).
9. M. B. Ritter, D. D. Awschalom and M. W. Shafer, *Phys. Rev. Lett.*, **61**, 966 (1988).
10. J. H. Erdmann, S. Zumer and J. W. Doane, *Phys. Rev. Lett.*, **64**, 1907 (1990).
11. S. B. Dierker and P. Wiltzius, *Phys. Rev. Lett.*, **66**, 1185 (1991).
12. B. J. Frisken and D. S. Cannell, *Phys. Rev. Lett.*, **69**, 632 (1992).
13. F. Simoni, G. Gipparrone, D. Duca and I. C. Khoo, *Optics Lett.*, **16**, 360 (1991).
14. F. Simoni, G. Gipparrone and C. Umeton, *Appl. Phys. Lett.*, **57**, 1949 (1990).
15. H-I. Wu, W. I. Goldburg, M. X. Lin and J. Z. Xue, *Phys. Rev. Lett.*, **69**, 470 (1992).
16. T. Bellini, N. A. Clark, Ch. D. Muzny, L. Wu, C. W. Garland, D. W. Schaefer and B. J. Oliver, *Phys. Rev. Lett.*, **69**, 788 (1992).
17. G. P. Crawford, D. W. Allender and J. W. Doane, *Phys. Rev.*, **A45**, 8693 (1992).
18. F. M. Aliev, K. S. Pojivilko and V. N. Zgonnik, *Eur. Polym. J.*, **26**, 101 (1990).
19. F. M. Aliev and V. N. Zgonnik, *Eur. Polym. J.*, **27**, 969 (1991).
20. D. Armitage and F. P. Price, *Chem. Phys. Lett.*, **44**, 305 (1976); *Mol. Cryst. Liq. Cryst.*, **44**, 33 (1978).
21. M. Kuzma and M. M. Labes, *Mol. Cryst. Liq. Cryst.*, **44**, 100 (1983).
22. G. S. Iannacchione and D. Finotello, *Phys. Rev. Lett.*, **69**, 2094 (1992); M. Kuzma and M. M. Labes, *Mol. Cryst. Liq. Cryst.*, **44**, 100 (1983).
23. M. M. Telo da Gama, *Molec. Phys.*, **52**, 585 (1984); A. Poniewierski and T. J. Sluckin, *Liq. Cryst.*, **2**, 281 (1987); H. Yokoyama, *J. Chem. Soc.*, *Faraday Trans.*, **2**, 84, 1023 (1988); P. Sheng, *Phys. Rev. Lett.*, **37**, 1059 (1976); *Phys. Rev.*, **A26**, 1610 (1982); K. Miano, *Phys. Rev. Lett.*, **43**, 51 (1976); K. Miano, *Phys. Rev. Lett.*, **43**, 51 (1976); H. Yokoyama, S. Kobayashi and H. Kamei, *Appl. Phys. Lett.*, **41**, 438 (1982); Y. Iimura, H. Mada and S. Kobayashy, *Phys. Lett.*, **A103**, 342 (1984); P. Sheng, B-Z. Li and M. Zhou, *Phys. Rev.*, **A46**, 946 (1992); B. Jerome, *Rep. Prog. Phys.*, **54**, 391 (1991).
24. G. P. Montgomery and N. A. Vaz, *Phys. Rev.*, **A40**, 6580 (1989).
25. F. M. Aliev, *Mol. Cryst. Liq. Cryst.*, **222**, 147 (1992).
26. F. M. Aliev, G. Yu. Vershovskaya and L. A. Zubkov, *Sov. Phys. JETP*, **72**, 846 (1991).
27. F. M. Aliev and K. S. Pozhivilko, *Sov. Phys. JETP Lett.*, **49**, 308 (1989).
28. F. M. Aliev and M. N. Breganov, *Sov. Phys. JETP*, **68**, 70 (1989).
29. G. P. Crawford, G. S. Innnaccione, J. W. Doane and D. Finotello, *Mol. Cryst. Liq. Cryst.*, **222**, 205 (1992).
30. F. M. Aliev, *Sov. Phys. Crytallogr.*, **33**, 573 (1988).
31. P. G. de Gennes, *Rev. Mod. Phys.*, **64**, 645 (1982).
32. K. G. Wilson and J. Kogut, *Phys. Report.*, **12C**, 75 (1974).
33. P. Guyot-Sionnest, H. Hsiung and Y. R. Shen, *Phys. Rev. Lett.*, **57**, 2963 (1986).
34. S. Tripathi, M.-X. Lu, E. M. Terentjev, R. G. Petschek and Ch. Rosenblatt, *Phys. Rev. Lett.*, **67**, 3400 (1991).
35. G. Barbero, I. Dozov, J. F. Palierne and G. Durand, *Phys. Rev. Lett.*, **56**, 2056 (1986).
36. L. K. H. Van Beek, *Progress in Dielectrics*, **7**, 69–114 (J. B. Birks, ed.) Haywood, London (1967).
37. R. A. M. Hikmet and B. H. Zwerver, *Liq. Cryst.*, **10**, 835 (1991).

38. D. K. Rout and S. C. Jain, *Mol. Cryst. Liq. Cryst.*, **210**, 75 (1992).
39. A. J. Liu, D. J. Durian, E. Herbolzheimer and S. A. Safran, *Phys. Rev. Lett.*, **65**, 1897 (1990).
40. Y. Imry and S.-k. Ma, *Phys. Rev. Lett.*, **35**, 1399 (1975).
41. G. de Gennes, *J. Phys. Chem.*, **88**, 6469 (1985).
42. S. P. Zdanov, *Physics and Chemistry of Silicates* (ed. by M. M. Shul'ts and G. L. Grebenshchikov), Nauka, Moscow, p. 175 (1987).
43. F. M. Aliev and K. S. Pozhivilko, *Sov. Phys. Solid State*, **30**, 1351 (1988).
44. G. Porod, *Z. Kolloid*, **124**, 83 (1951).
45. C. G. Vonk, *J. Appl. Cryst.*, **6**, 81 (1973).
46. M. Robert, *Phys. Rev.*, **A30**, 2785 (1984).
47. M. Massalska-Arodz, J. K. Moscicki and W. Wrobel, *Acta Phys. Pol.*, **A58**, 443 (1980).
48. C. Druon and M. Wacrenier, *Mol. Cryst. Liq. Cryst.*, **88**, 99 (1982).
49. L. M. Blinov and L. A. Beresnev, *Sov. Phys. Usp.*, **27**, 492 (1984).
50. F. Gouda, K. Skarp and S. T. Lagerwall, *Ferroelectrics*, **113**, 165 (1991).
51. Z. Li, G. A. Di Lisi, R. G. Petschek and Ch. Rosenblatt, *Phys. Rev. A.*, **41**, 1997 (1990).
52. Z. Li, R. Ambigapathy, R. G. Petschek and Ch. Rosenblatt, *Phys. Rev. A.*, **43**, 7109 (1991).