Surface-Dominated Orientational Dynamics and Surface Viscosity in Confined Liquid Crystals

A. Mertelj[1] and M. Čopič[1,2]
[1]J. Stefan Institute, Jamova 39, 1001 Ljubljana, Slovenia
[2]Department of Physics, University of Ljubljana, 1000 Ljubljana, Slovenia

(Received 1 April 1998)

A nematic liquid crystal in cylindrical pores of polycarbonate (Nuclepore) membranes with radii 25–400 nm was studied by dynamic light scattering. The fundamental mode of the orientational fluctuations shows a crossover from bulk behavior, dominated by bulk-elastic constant K, to a surface-dominated one, in which the relaxation rate is determined by the ratio of surface-anchoring strength W and viscosity η. In the smallest pores, the contribution of surface viscosity ζ is also significant. The surface extrapolation length K/W goes approximately as $(T - T_{NI})^{-1}$. The characteristic length for surface viscosity ζ/η is of the order of 10 nm. [S0031-9007(98)08013-2]

PACS numbers: 61.30.Gd, 64.70.Md

Interfaces strongly influence static and dynamic properties of liquid crystalline systems, and are therefore an important area of current research both from the fundamental point of view and for applications. Interfaces become particularly important when liquid crystals are embedded in a solid matrix with small cavities so that the volume to surface ratio approaches some characteristic length of the liquid crystalline phases [1]. The dynamics of liquid crystals at an interface are governed by both elastic interactions (anchoring) and dissipative processes. A considerable amount of knowledge exists about the elastic interactions of the liquid crystals with surfaces [2], but much less is known about the peculiarities of dissipation. A particularly interesting problem is the existence of surface friction [3].

A powerful tool to investigate the dynamic behavior of liquid crystals is photon correlation spectroscopy, and recently several types of confined liquid crystal systems have been studied with this technique. Most investigations have focused on porous glasses and silica aerogels as host matrices [4–6]. Besides the effects of the large surface to volume ratio, the results obtained in these systems are also rather strongly affected by the randomness of the matrix and by multiple scattering, so the interpretation of the data is rather complicated.

In this Letter, we report on dynamic light scattering in nematic liquid crystals embedded in cylindrical pores of polycarbonate (Nuclepore) membranes. These pores have well defined diameters from 50 to 800 nm. Deuterium nuclear magnetic resonance (NMR) measurements were used to determine the director field configurations [7], surface-induced orientational order in the isotropic phase [8], and the surface elastic constant K_{24} [9]. Specific heat studies revealed that the phase transition temperature depends on the pore size due to the director deformations, but the order of the transitions remains unaffected [10]. The well defined geometric static properties of the system allow us to fully analyze the light scattering data and to show that a crossover from bulklike to surface-dominated dynamics of orientational fluctuations occurs when the diameter of the pores becomes comparable to the surface extrapolation length.

Our samples were prepared similarly as described in Ref. [7]. A piece of membrane was wetted with the liquid crystal 4-pentyl-4′-cyanobiphenyl (5CB) that filled the cylindrical pores of the membrane due to the capillary action. The remaining liquid crystal on the surface of the membrane was removed by pressing the membrane between two Whatman filtration papers and then the filled membrane was placed between two glass plates. The configuration of the director field in pores of Nuclepore membranes is known to be either escaped radial with point defects or, for small anchoring strength, planar-polar where the director is in the plane perpendicular to the cylinder and nearly perpendicular to the pore walls except at two opposite points on the perimeter [7,9]. The refractive index of the polycarbonate Nuclepore membranes approximately matches the average refractive index of the 5CB, so multiple scattering in the samples was negligible.

The light source was a He-Ne laser with the wavelength of 632.8 nm. The intensity correlation function was measured using an ALV5000 correlator that enables measurements over a time range of 10^{-8}–10^{3} s. We have measured the normalized intensity correlation function $g^{(2)}(\tau) = \langle I(t)I(t + \tau)\rangle/\langle I(t)\rangle\langle I(t + \tau)\rangle$ of light exiting the sample as a function of scattering angle, the radius of cavities and the temperature. The incoming and scattered directions were chosen so that the scattering vector was perpendicular to the axis of the pores. Following the selection rules, by which the orientational fluctuations are coupled to the off-diagonal elements of the dielectric tensor, we chose orthogonal polarizations of incident and scattered light.

The measured intensity correlation functions showed a well defined relaxation component which is due to the orientational director fluctuations in the pores. The amount of statically scattered light off the sample and pore surfaces was such that the measurements were in the

© 1998 The American Physical Society

heterodyne regime, and the relaxation rate of the intensity correlation function is equal to the relaxation rate of the fluctuations.

In analyzing the data, we first note that in cylindrical pores, similarly as in polymer-dispersed liquid crystals (PDLCs) [11], due to finite size the transverse component of the wave vector of the fluctuations can take on only discrete values given by the eigenvalues of the Helmholtz equation with appropriate boundary conditions. Their exact value also depends on the director configuration in the pores; but in the case of strong anchoring they will be roughly given by $a_N^2 = (A_N/R)^2$ $(N = 1, 2, \ldots)$, where R is the radius of the pore and the constants A_N are determined by the zeros of the eigenfunctions, that is, in cylindrical geometry the zeros of Bessel functions [12]. The relaxation rate of a particular mode (with zero axial component of the wave vector) is given by the expression [13]

$$\frac{1}{\tau_N} = \frac{K a_N^2}{\eta}, \tag{1}$$

where K is an effective Frank elastic constant, and η is an effective bulk viscosity.

At a particular scattering vector, perpendicular to the cylinder axis and with size $q = 2k_0 \sin(\vartheta/2)$, where $k_0 = n\omega/c$, ϑ is the scattering angle, and n is the average index of refraction of the medium, the dominant contribution to light scattering comes from the fluctuation mode with a_N closest to q. When $N \gg 1$, that is, for $R \gg 1/q$, we get from Eq. (1) the usual q^2 dependence of the relaxation rate. When $R \lesssim 1/q$, however, only the fundamental mode contributes and the relaxation rate is independent of q. This effect has been already observed in the case of spherical droplets in PDLCs [11] and in thin planar samples [14]. Figure 1 shows the dependence of the observed relaxation rate on the scattering vector. Clearly, at small scattering vectors, the relaxation rates become independent of q whereas the usual quadratic dependence is obtained for $q \gg 1/R$. So for small pores we observe only the fundamental mode, while for the largest pores we see the fundamental mode for small q and the bulk q^2 dependence for large q. The fact that the curves for different radii in Fig. 1 cross can be explained by noting that the effective viscosity is smaller than the pure orientational viscosity coefficient due to the coupling of the fluid flow and orientation (backflow effect). As the fluid flow is more restricted in the smaller pores, we expect that the effective K/η will be smaller for smaller R. So for small R, $1/\tau$ at small q is larger and the slope for large q is smaller than for large R, producing the observed crossings.

Figure 2 shows the dependence of the relaxation rates on the temperature for different pore radii at $q = 5 \times 10^6$ m^{-1}, so that $1/q = 200$ nm. For $R \gtrsim 200$ nm, we are observing only the fundamental mode, while for $R = 300$ nm and $R = 400$ nm we see a mixture of the fundamental and second eigenmode. Examination of Fig. 2 shows that τ is approximately proportional to R, not to R^2 as one would expect from Eq. (1). This is even more clear in Fig. 3, where τ is shown as a function of R for several temperatures.

In order to explain this behavior, we look at the evolution equation for the fluctuations of the director in the pores and the corresponding boundary conditions. The nature of the fundamental mode strongly depends on the static structure of the director field in the pores.

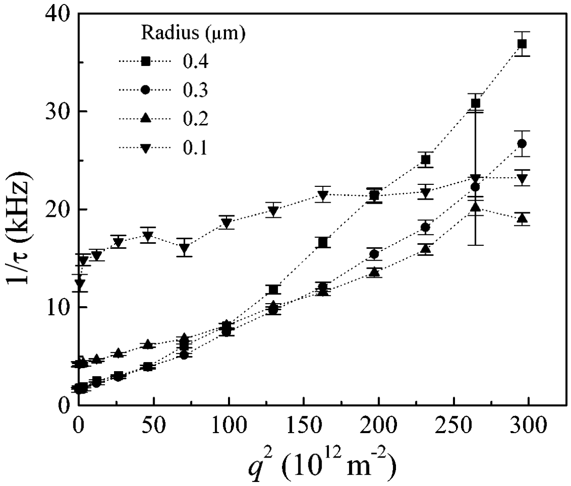

FIG. 1. The relaxation rate of the orientational fluctuations vs the square of the scattering vector. The scattering vector is perpendicular to the axis of the cylindrical pores. Dotted lines are guides to the eye. ($T = 295$ K.)

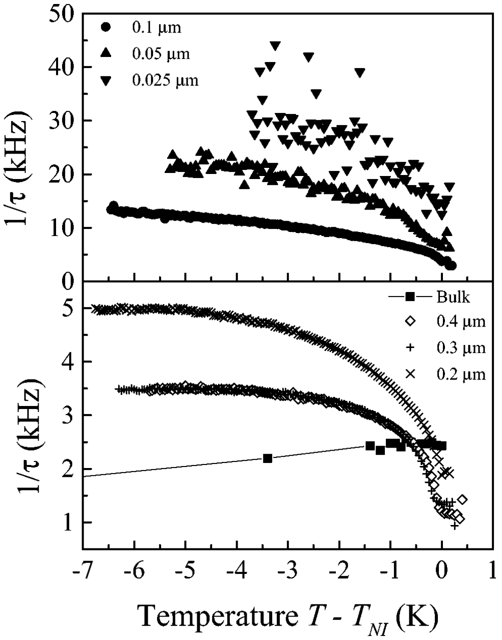

FIG. 2. Temperature dependence of the relaxation rate of the orientational fluctuations in cylindrical pores and in bulk 5CB ($q = 5 \times 10^6$ m^{-1}). T_{NI} is the nematic-isotropic transition temperature.

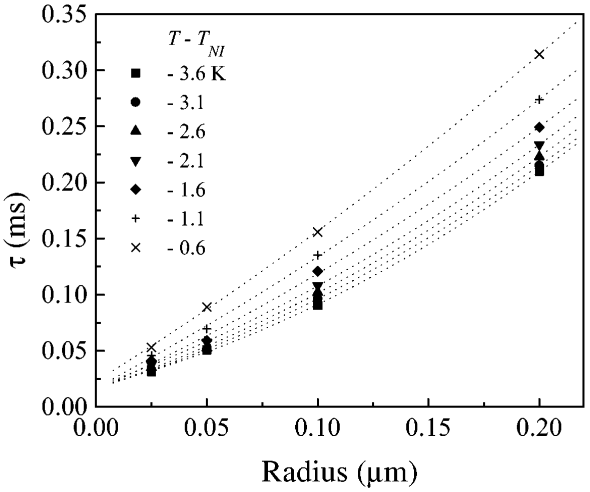

FIG. 3. Dependence of the relaxation rate of the fundamental mode on the cylinder radius at different temperatures. The dotted lines are second order polynomial fits.

Because of cylindrical symmetry and the properties of the vector wave equation, for the escaped radial configuration the amplitude of all modes, including the fundamental mode, must be zero at the center, so the eigenvalue for the fundamental mode must be proportional to $(1/R)^2$ for any anchoring strength. In fact, for zero anchoring strength it will be by about a factor of 4 smaller than for very strong anchoring. This observation is also borne out by detailed calculation. According to Eq. (1) the relaxation rate can then only be proportional to $(1/R)^2$.

This leaves us with the planar structure, where there are no symmetry constraints on the fluctuations of the director at the center of the cylinder. In the one elastic constant approximation, its analytic form is known [9]. From this solution, we deduced the linearized equation of the fluctuations in the axial direction of the static structure in the following form:

$$\nabla^2 u + \frac{4\gamma^2 r^2}{R^4 + \gamma^2 r^4 - 2\gamma^2 R^2 r^2 \cos 2\varphi}\, u = -a^2 u\,, \tag{2}$$

where φ is the polar coordinate, and $\gamma = \sqrt{4\lambda^2 + R^2} - 2\lambda/R$. The extrapolation length is given by $\lambda = K/W$, where W is the surface anchoring strength. The boundary condition for u reads

$$\left[2(\gamma + \gamma^2 + \gamma^3 \cos 2\varphi)u + r\,\frac{\partial u}{\partial r}\right]_{r=R} = 0\,. \tag{3}$$

For $\lambda \gg R$, that is, for small anchoring strength, $\gamma = R/4\lambda$, so we may seek an approximate solution to (2) and (3) correct to linear terms in γ. This gives us just the standard Helmholtz equation with mixed boundary conditions, so the eigenvalues are given as the solution of the transcendental equation:

$$a_N \lambda = \frac{J_0(a_N R)}{J_1(a_N R)}\,, \tag{4}$$

where $J_0(a_N R)$ and $J_1(a_N R)$ are Bessel functions of the first kind. As $\lambda > R$, to calculate the fundamental eigenvalue, we can expand the right-hand side of Eq. (4) in power series and calculate a_1 to the second order in $1/R$. Using Eq. (1), we then get the following expression for the relaxation time of the fundamental mode of the planar structure with weak anchoring:

$$\tau_1 \approx \frac{R\eta}{2W} + \frac{\eta R^2}{8K}\,. \tag{5}$$

The corrections to the relaxation time due to the second term in Eq. (2), which can be obtained by perturbation theory, are proportional to γ^2, so they do not influence the leading terms in Eqs. (5) and (7). Also, numerical examination of the solutions to Eqs. (2) and (3) shows that this approximation holds reasonably well even when $\lambda \lesssim R$. The first term in Eq. (5) dominates when $\lambda \gtrsim R$, so the observed approximately linear dependence of τ vs R (Fig. 3) shows that the orientational fluctuations in the pores for $R \lesssim 200$ nm are governed by surface anchoring and not by bulk orientational elasticity.

According to Eq. (5), for $R = 0$ we should have $\tau = 0$. The measurements at all temperatures, however, consistently extrapolate to a positive value for $R = 0$. We can explain this by the contribution of orientational surface friction to the dissipation. The existence of a surface specific dissipation coefficient has been a matter of some debate [3,15]. It can be due to dissipation coming from surface processes like adsorption-desorption or molecular slipping on the surface. Its existence could also influence the performance of thin liquid crystalline displays. With surface friction, the boundary condition at the pore surface correct to linear terms in γ is

$$K\,\frac{\partial u}{\partial r} + Wu = \zeta\,\frac{\partial u}{\partial t}\bigg|_{r=R}\,, \tag{6}$$

where ζ is the surface viscosity. The right-hand side of Eq. (6) only modifies W to $W + \zeta/\tau$, and the relaxation time of the fundamental mode obtained in the same approximation as Eq. (5) is

$$\tau_1 \approx \frac{\eta R}{2W} + \frac{\eta R^2}{8K} + \frac{\zeta}{W}\,. \tag{7}$$

Figure 3 shows the fits of measured τ vs R to Eq. (7). The coefficient of the linear term, together with the bulk values of K/η, gives the extrapolation length λ, plotted vs T in Fig. 4. The constant term can be used to get the ratio ζ/η which has the dimension of length, and is shown in Fig. 5. The quadratic coefficient, giving the bulk orientational diffusivity K/η, can be obtained only for $T_{NI} - T > 0.5$ K and then is quite scattered, but the average value is of the order of 10^{-10} m^2/s, which is close to the known bulk values for 5CB if we assume that backflow does not contribute to the effective viscosity (inset of Fig. 4). The correct value for the quadratic coefficient gives a strong support to our analysis.

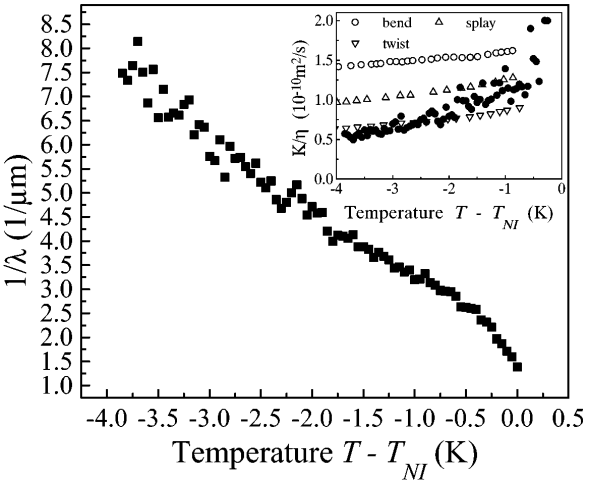

FIG. 4. Temperature dependence of the inverse penetration depth. Inset: comparison of measured diffusivity (full circles) with the diffusivities of pure modes where the backflow is not considered.

The dependence of λ^{-1} on T in Fig. 4 is nearly linear, so that $\lambda^{-1} \propto S^2$, where S is the scalar order parameter. As $K \propto S^2$ [13], and $\lambda = K/W$, $W \propto S^4$. That λ increases as T approaches T_{NI} has also been observed by other authors [16].

Using the known values for K, we find that the surface anchoring strength is 3×10^{-6} J/m^2, close to T_{NI}, and 5×10^{-5} J/m^2, 4 K below T_{NI}. At these anchoring strengths the deuterium NMR experiments have shown that the configuration of the director is planar-polar [9].

Our measured values for the ratio ζ/η, shown in Fig. 5, are in the range of molecular size. This is similar to those obtained for the translational surface friction in ordinary liquids [17]. ζ has also been obtained in rather different conditions in Ref. [15]. There, the obtained ratio ζ/η is of the order of extrapolation length, a macroscopic length having nothing to do with dissipation and nearly 2 orders of magnitude larger than our value.

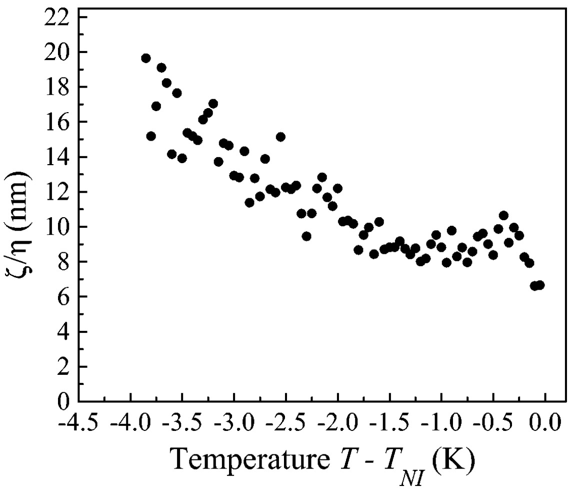

FIG. 5. Temperature dependence of surface to bulk viscosity ζ/η.

In conclusion, in dynamic light scattering we observed that the orientational fluctuations in small pores are dominated by surface properties. From the measurements, we deduce the temperature behavior of the surface extrapolation length and surface anchoring strength W. We can obtain a consistent fit to our data only by assuming the existence of orientational surface friction. Its ratio to the bulk viscosity is in the range of molecular lengths.

This work was supported by Ministry of Science and Technology of Slovenia (Grant No. J1-7474) and European Union (Grant No. IC15-CT96-0744).

[1] *Liquid Crystals in Complex Geometries Formed by Polymer and Porous Networks,* edited by G. P. Crawford and S. Žumer (Taylor and Francis, London, 1996).
[2] For a recent review, see G. Barbero and G. Durand, *Liquid Crystals in Complex Geometries Formed by Polymer and Porous Networks* (Ref. [1]), p. 21
[3] M. Nobili, R. Barberi, and G. Durand, J. Phys. II (France) **5**, 531 (1995).
[4] X. I. Wu, W. I. Goldburg, M. X. Liu, and J. Z. Xue, Phys. Rev. Lett. **69**, 470 (1992).
[5] T. Bellini, N. A. Clark, and D. W. Schaefer, Phys. Rev. Lett. **72**, 2740 (1995).
[6] W. I. Goldburg, F. Aliev, and X.-I. Wu, Physica (Amsterdam) **213A**, 61 (1995).
[7] G. P. Crawford, D. W. Allender, J. W. Doane, M. Vilfan, and I. Vilfan, Phys. Rev. A **44**, 2570 (1991).
[8] G. P. Crawford, R. Stannarius, and J. W. Doane, Phys. Rev. A **44**, 2558 (1991).
[9] D. W. Allender, G. P. Crawford, and J. W. Doane, Phys. Rev. Lett. **67**, 1442 (1991).
[10] G. S. Iannacchione and D. Finotello, Phys. Rev. Lett. **69**, 2094 (1992).
[11] A. Mertelj, L. Spindler, and M. Čopič, Phys. Rev. E **56**, 549 (1997).
[12] P. Ziherl and S. Žumer, Phys. Rev. E **54**, 1592 (1996).
[13] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1993).
[14] M. M. Wittebrood, Th. Rasing, S. Stallinga, and I. Muševič, Phys. Rev. Lett. **80**, 1232 (1998).
[15] A. G. Petrov, A. Th. Ionescu, C. Versace, and N. Scaramuzza, Liq. Cryst. **19**, 169 (1995).
[16] Dai-Shik Seo, Yasufumi Limura, and Shunsuke Kobayashi, Appl. Phys. Lett. **61**, 234 (1992); Takashi Sugiyama, Seiyu Kuniyasu, and Shunsuke Kobayashi, Mol. Cryst. Liq. Cryst. **238**, 1 (1994).
[17] L. Bocquet and J.-L. Barrat, Phys. Rev. Lett. **70**, 2726 (1993).