

## Slow Dynamics of Isotropic-Nematic Phase Transition in Silica Gels

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We report a quasielastic light scattering measurement of the isotropic-nematic phase transition of a liquid crystal in silica gel. The normalized intensity autocorrelation function,  $G_2(t)$ , which samples the order-parameter fluctuations, is consistent with the form  $G_2(x) \sim 1/(1+x^2)$ , where  $x = \ln t / \ln \tau$ . The relaxation time,  $\tau$ , diverges near a temperature  $T^*$  and can be quantitatively described by the Vogel-Fulcher law,  $\tau = \tau_0 \exp[\text{const}/(T - T^*)]$ . The measurements suggest that the silica gel imposes a weak random anisotropy on the system, with the bulk nematic phase being replaced by a "glassy" state. However, hysteresis, normally associated with random-"field" behavior, is absent.

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Liquid-crystalline ordering in a confined geometry has been the subject of considerable recent research. Previous work has concentrated on well-characterized confining geometries such as planar, spherical, and cylindrical cavities [1-4]. Those studies established that cavity size and wall-liquid interaction have a profound influence on the liquid-crystalline ordering. In this Letter we are concerned with the confinement of a liquid crystal in a porous medium having a disordered geometric structure. The experiment addresses the effect of this disordered host on the isotropic-nematic phase transition. In our dynamic light scattering study of a liquid crystal that saturates a porous medium (silica gel), we observe that the fluctuations of the orientation order parameter relax at a much slower rate than in the bulk liquid crystal. In a certain temperature range the decay time of the fluctuations is more than 10 orders of magnitude slower than in the bulk. Many of our observations are consistent with glassy behavior produced by a random field.

Theoretically the effect of a random field was investigated by Imry and Ma [5]. Their argument, when applied to systems with continuous symmetry, predicts that the usual phase transition is suppressed to  $T = 0$  in three dimensions (3D). Our situation is somewhat different since the director of the liquid crystal is a "headless" vector. It has been suggested by Goldschmidt that a more appropriate model that may describe our system is that of random uniaxial anisotropy [6]. In this model, the random anisotropy vector  $\vec{a}$  couples to the order parameter  $\vec{S}$  in the form of  $(\vec{a} \cdot \vec{S})^2$  instead of  $\vec{a} \cdot \vec{S}$  as in the conventional random-field case. This model predicts a phase transition from a disordered state to a spin-glass state at a finite temperature in 3D. For a liquid crystal imbedded in the gel, the random anisotropy or "field" is due to the percolating gel structure, which provides local but random preferential orientation for the nematic order. If the gel structure produces barriers much larger than  $k_B T$ , the fluctuations may very well be statistically rare

events. Our experiment is consistent with this picture.

Dynamically, order-parameter fluctuations in liquid crystals are interesting in that they are not restricted by local conservation. The nematic fluctuations in the isotropic phase of the bulk material have a decay rate which is given by  $\Gamma \simeq \Gamma_0(1 + \xi^2 q^2)$ , where  $\Gamma_0$  is a transport coefficient and  $\xi$  is the correlation length of the order parameter [7]. Note that  $\Gamma$  does not vanish, even for long-wavelength fluctuations,  $q \rightarrow 0$ . This is in sharp contrast with the behavior of systems having a conserved order parameter, for which  $\Gamma \sim q^2$  and approaches zero in the long-wavelength limit. Therefore, liquid-crystal order-parameter fluctuations in the isotropic phase are intrinsically faster compared with the fluctuation rate in conservative systems such as liquid-gas or binary liquid mixture systems. We expect this to be true even when the liquid crystal is imbedded in a porous material.

The liquid crystal used in this experiment is 4'-n-octyl-4-cyanobiphenyl (8CB) purchased from BDH Co. It was filtered through a 0.2- $\mu\text{m}$  filter to remove dust particles. Static light scattering and visual observation indicated that a bulk liquid-crystal sample has a well-defined isotropic-nematic transition temperature  $T_{IN} \simeq 40.5^\circ\text{C}$ . The correlation length  $\xi$  diverges as  $\xi = \xi_0(\frac{T}{T_C} - 1)^{-\nu}$ , with  $\xi_0 = 7 \text{ \AA}$  and  $\nu = 1/2$  [8]. Since the nematic-isotropic phase transition is weakly first order [9], the correlation length at the transition  $T_{NI} (> T_C)$  is finite, with  $\xi \sim 200 \text{ \AA}$ . However, near a solid surface it is possible that the correlation length will be different from the above bulk value [8].

The liquid crystal saturated a silica gel sample, which has a pore size of  $200 \pm 30 \text{ \AA}$  and a porosity of 30% - 35% volume fraction [10]. Before the gel samples were filled, they were boiled in hydrogen peroxide and vacuum baked at  $\sim 100^\circ\text{C}$ . The liquid crystal was introduced into the gel in vacuum and at a temperature several degrees above the bulk isotropic-nematic transition temperature. The procedure effectively eliminates all air bubbles inside the

gel. The saturated sample, of size  $2 \times 3 \times 4 \text{ mm}^3$ , was wiped clean of excess liquid crystal and sealed in an ampule. The ampule was placed in a water bath which has a thermal stability of a few mK over several days. The light scattering source was a HeNe laser. The intensity correlation function was measured using an ALV5000 correlator, which has a dynamic range of  $10^{-8} - 10^3 \text{ sec}$ .

For polarized incident light, nematic fluctuations are known to produce almost equal intensities of polarized ( $I_{\parallel}$ ) and depolarized ( $I_{\perp}$ ) light scattering, with  $I_{\parallel}/I_{\perp} = 4/3$  [11]. Observation of the depolarized component of the scattering intensity is of great convenience for this experiment, because it effectively blocks out the scattering from the fixed gel structure and permits detection of the nematic fluctuations alone. Figure 1 shows the temperature dependence of the static light scattering intensity  $I_{\perp}$  of pure 8CB and 8CB+gel at  $90^\circ$  scattering angle. In the pure 8CB sample (solid line),  $I_{\perp}$  increases continuously as the sample is cooled from  $50$  to  $40.5^\circ\text{C}$  with a cooling rate  $\dot{T} \simeq -2 \text{ mK/sec}$ . The sharp jump in  $I_{\perp}$  at  $\sim 40.5^\circ\text{C}$  signals an isotropic-nematic phase transition. This increase in  $I_{\perp}$  near the transition temperature is a result of enhanced nematic fluctuations and can be quantitatively described by  $I_{\perp} \sim \xi^2 \sim (T - T_c)^{-1}$  [9]. In comparison, the depolarized light scattering from 8CB+gel is qualitatively different. This is shown by the circles and squares in the same figure. The circles represent a heating run ( $\dot{T} = +4 \text{ mK/sec}$ ) and the squares represent a cooling run ( $\dot{T} = -2 \text{ mK/sec}$ ). The time interval between these runs was  $\sim 15 \text{ h}$ . The agreement between the two sets of data show that the system behaves reversibly over this temperature range, at least on this time scale.

The scattering intensity can be characterized by three distinct regimes: (I) For  $40^\circ\text{C} < T < 50^\circ\text{C}$ ,  $I_{\perp}$  from 8CB+gel is weak as a result of small nematic fluctuations and a short spatial correlation length. We also note that

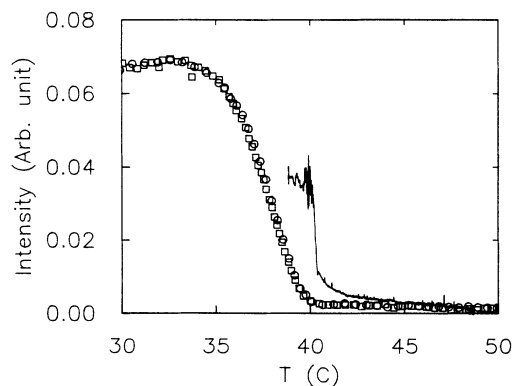


FIG. 1. Depolarized light scattering intensity vs temperature. The intensity is measured at  $\theta = 90^\circ$ . The circles and squares are heating and cooling measurements for 8CB in the silica gel. The solid line shows a measurement for a bulk 8CB sample.

$I_{\perp}$  has a weak temperature dependence in this regime. (II) In the interval  $34^\circ\text{C} < T < 40^\circ\text{C}$ ,  $I_{\perp}$  increases as the temperature is lowered. Accompanying such an increase, the angular distribution of scattered light intensity becomes anisotropic and appeared to peak in the forward direction at  $\sim 30^\circ\text{C}$ . The anisotropic scattering we observed implies the presence of nematic domains of size  $L$  which are comparable to the wavelength of light. The increase in the anisotropy also implies that  $L$  grows as the temperature is lowered. Nevertheless we failed to observe, with a  $50\times$  polarizing microscope, the familiar nematic textures down to  $20^\circ\text{C}$ , indicating that  $L$  is always less than  $10 \mu\text{m}$ . (III) For  $T < 34^\circ\text{C}$ ,  $I_{\perp}$  flattens out. In this regime, the sample has a uniform cloudiness which resembles the critical opalescence of a binary liquid mixture near the critical point. Since at  $\theta = 90^\circ$  the input laser beam is still visible, we believe that multiple scattering is of minor significance. According to the theory of critical phenomena, the temperature independence of  $I_{\perp}$  suggests  $qL \geq 1$ . However, this temperature independence may also be explained by the freezing of the size of the domains, as discussed below.

The above observations allow us to draw several important conclusions. First, the metastability and hysteresis usually associated with random-field behavior is absent for the liquid crystal in the gel. The scattering intensity swiftly and reversibly responds to temperature changes in the entire range  $30^\circ\text{C} < T < 50^\circ\text{C}$ . Second, the strength of the random "field" imposed on the liquid crystal is weak. In the high-temperature regime,  $T > 40^\circ\text{C}$ , the weak scattering suggests that the spatial fluctuations in the order parameter have a correlation length which is smaller than the pore size. In the low-temperature regime,  $T < 40^\circ\text{C}$ , when  $I_{\perp}$  becomes anisotropic, the nematic domains must span several pore diameters. Third, it appears that the isotropic-nematic transition is broadened by the gel and the transition temperature is displaced towards a lower value, if indeed it still exists.

Dynamic light scattering (DLS) measurements were also carried out in the same temperature interval. In DLS we measure the intensity-intensity autocorrelation function  $g_2(t) = \langle I(t)I(0) \rangle / \langle I(0) \rangle^2$ . For scattered light that obeys Gaussian statistics  $G_2(t) \equiv g_2(t) - 1$  directly measures the square of the order-parameter autocorrelation function  $\Psi(t) [= \sqrt{G_2(t)}]$ . Above  $40^\circ\text{C}$  [in regime (I)], the 8CB+gel behaves like the bulk 8CB and the relaxation time is very fast, with  $\tau_0 \sim 10^{-7} \text{ sec}$ .

The most interesting dynamics occurs at temperatures below the bulk transition temperature,  $T_{NI} = 40.5^\circ\text{C}$  [in regime (II)]. Figure 2 shows the intensity autocorrelation function,  $\sqrt{G_2(t)}$ , at temperatures  $T \simeq 40, 38,$  and  $36^\circ\text{C}$ . It is seen that  $\sqrt{G_2(t)}$  exhibits a pronounced slow decay in addition to the fast decay, which is barely observable. The relaxation time associated with the slow decay increases dramatically as the temperature is lowered and spans well over ten decades in time below

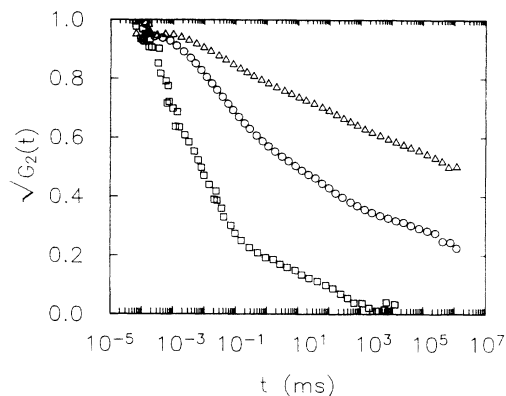


FIG. 2. Square root of autocorrelation functions,  $\sqrt{G_2(t)}$ , measured at three temperatures,  $T = 40$  (squares),  $38$  (circles), and  $36^\circ\text{C}$  (triangles).

$38^\circ\text{C}$ . We believe that over the above temperature range ( $36^\circ\text{C} < T < 40^\circ\text{C}$ ) and over long data accumulation time ( $> 12$  h) the system behaves ergodically [12]. Therefore no corrections for nonergodic behavior need to be made [13]. Because no hysteresis is observed in the intensity measurement as discussed above, it is reasonable to expect that the autocorrelation function  $G_2(t)$  measures the thermal equilibrium behavior of the system. This conjecture was further supported by the fact that the measured autocorrelation functions are repeatable over a period of at least one week and show no thermal history dependence.

It should be stressed that the slow dynamics shown in Fig. 2 corresponds to highly nonexponential decay. This slow relaxation is in marked contrast to the behavior of a bulk liquid crystals. Our data can be described by the equation  $G_2(x) = \text{const}/(1+x^2)$ , where  $x = \ln(t/\tau'_0)/\ln(\tau/\tau'_0)$  with  $\tau'_0$  and  $\tau$  being adjustable parameters. Because  $\tau'_0$  turns out to be of the order of  $\tau_0$ , we identify it with the relaxation time of the free liquid crystal. The longer time,  $\tau$ , is presumably associated with fluctuations of a size equal to the pore size of the gel or larger [14].

Using the above functional form for  $G_2(x)$ , all the correlation data could be collapsed onto a universal curve, as shown in Fig. 3, where the independent variable is  $\sqrt{G_2(x)}$ . The  $\ln t$  scaling is perhaps the most significant finding in this experiment and appears to be consistent with the notion of activated dynamics in quenched disordered systems [15–18]. However, our data are different from a computer simulation for a random-field Ising magnet (dashed line), where the order-parameter autocorrelation function was found to be  $\Psi(x) = \exp(-x^3)$  [15]. As shown in Fig. 3, this function decays much faster than the experimental curves, suggesting that the symmetry properties of the order parameter play an important role in the dynamics as well as the statics. Other functional forms for  $G_2(x)$ , such as single exponential and stretch

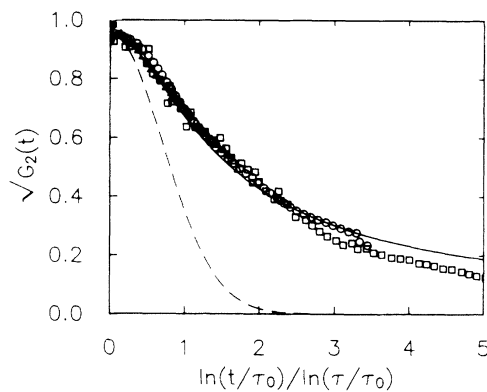


FIG. 3. Dynamic scaling of  $\sqrt{G_2(t)}$ . The three curves in Fig. 2 have been collapsed onto a single curve by rescaling  $t$  according to  $x = \ln(t/\tau_0)/\ln(\tau/\tau_0)$ . The resulting functional form,  $\sqrt{G_2(x)} = 1/\sqrt{1+x^2}$ , appears as the solid line. Also shown is  $\Psi(x) = \exp(-x^3)$  (dashed line) predicted by a computer simulation for the random-field Ising magnet [15].

exponential, do not fit our data.

A plot of  $\ln \tau$  vs  $1/(T - T^*)$  yields a straight line, as shown in Fig. 4. Thus the relaxation time of the order parameter is consistent with the Vogel-Fulcher law,  $\tau = \tau_0 \exp[A/(T - T^*)]$ . Here  $T^*$  defines a transition temperature below which the relaxation time becomes essentially infinite. This behavior is expected in the conventional random-field systems, if the domain size grows as  $(T/T^* - 1)^{-\nu'}$ , so that  $\ln \tau \sim L^\psi = (T/T^* - 1)^{-\nu'\psi}$ , where  $\psi$  and  $\nu'$  are critical exponents [16–18]. Using a linear fit to the data in Fig. 4, we obtained  $A \simeq 100 \text{ K}^{-1}$  and  $T^* \simeq 32.2^\circ\text{C}$ . It is interesting that the transition temperature ( $T^* \simeq 32.2^\circ\text{C}$ ) determined in the dynamic measurement seems to coincide with the temperature at which  $I_\perp$  levels off as shown in Fig. 1. The saturation in the static light scattering below  $T^*$  therefore can be a result of two effects, namely,  $qL \geq 1$ , as mentioned before, and a freezing of the size of the domains. In this sense  $T^*$  may be identified as a glass transition temperature.

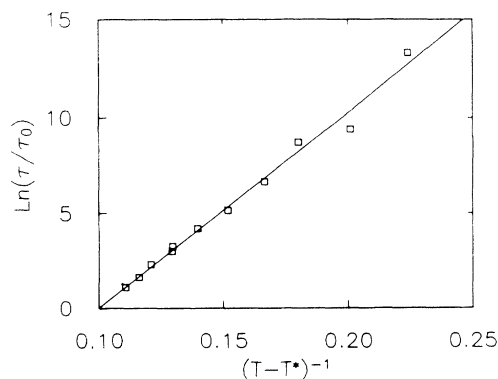


FIG. 4. Vogel-Fulcher plot of the relaxation time.

We also studied the  $q$  dependence of  $G_2(t)$  at  $39^\circ\text{C}$ , where the optical signal is reasonably strong and the autocorrelation function decays to zero in the time window of our correlator. The measurements, which were made at  $\theta = 45^\circ, 75^\circ$ , and  $100^\circ$  (corresponding to  $1/q = 88, 55$ , and  $40$  nm), showed  $G_2(t)$  to be independent of  $q$ . The absence of  $q$  dependence for  $G_2(t)$  is intriguing. Since  $qL \geq 1$  for the measurement, it is plausible that the dynamics occurs locally and on a length scale much less than the average domain size [19]. Motions of nematic defects may very well be the source of the dynamics we observed. The liquid-crystal system behaves very differently from a binary liquid mixture in Vycor, which was studied by Dierker and Wiltzius [20]. They found that both fast and slow relaxation times depend on  $q$ , and that the slow relaxation process dominates the autocorrelation function in the large- $q$  limit.

Aside from the absence of hysteresis, our observations are consistent with the view that the gel imposes a random uniaxial field on the liquid crystal. The equilibrium phase transition is smeared out by the randomness and the domains larger than the pore size are the major contributor to the scattering. Dynamically, the system shows the kind of self-similarity that is associated with the conventional random-field behavior [15, 17], namely,  $G_2(t) = G_2(x)$ , where  $x = \ln t / \ln \tau$ , with  $\tau$  being a sensitive function of temperature. However, at present we are not aware of any theory which can account for the functional form of  $G_2(t)$  observed in our experiment.

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- [1] Ping Sheng, Phys. Rev. Lett. **37**, 1059 (1976).
  - [2] J.H. Erdmann, S. Zumer, and J.W. Doane, Phys. Rev. Lett. **64**, 1907 (1990).
  - [3] A. Golemme, S. Zumer, D.W. Allender, and J.W. Doane, Phys. Rev. Lett. **61**, 2937 (1988).
  - [4] K. Miyano, Phys. Rev. Lett. **43**, 51 (1979).
  - [5] Y. Imry and S.k. Ma, Phys. Rev. Lett. **35**, 1399 (1975).

- [6] Y.Y. Goldschmidt and A. Aharony, Phys. Rev. B **32**, 264 (1985); Y.Y. Goldschmidt, in *Recent Progress in Random Magnets*, edited by D.H. Ryan (World Scientific, Singapore, 1992).
- [7] P.C. Hohenberg and B.I. Halperin, Rev. Mod. Phys. **49**, 435 (1977).
- [8] H. Hsiung, Th. Rasing, and Y.R. Shen, Phys. Rev. Lett. **57**, 3065 (1986).
- [9] P.G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974).
- [10] Silica gel was purchased from Geltech Inc., Alachua, FL 32615. For more details about the preparation of the silica gels, see W.L. Vasconcelos, R.T. Dehoff, and L.L. Hench, in *Proceedings of the Fourth International Conference on Ultrastructure Processing of Ceramics, Glasses and Composites, Tucson, Arizona, 1989*, edited by D.R. Uhlmann et al. (Wiley, New York, 1991).
- [11] B. Chu, C.S. Bak, and F.L. Lin, Phys. Rev. Lett. **28**, 1111 (1972).
- [12] Even though fluctuations are slow in the temperature range  $36^\circ\text{C} < T < 40^\circ\text{C}$ , the system still behaves ergodically as indicated by the observation that there is no appreciable degradation in the the coherency factor,  $f(A)$ , for the light scattering (see Ref. [15]). However, for temperature much lower than  $36^\circ\text{C}$ , the nonergodic behavior seems to be significant. We will discuss this effect in a separate paper.
- [13] P.N. Pusey and W. Van Meegen, Physica (Amsterdam) **157A**, 705 (1989).
- [14] It is natural to ask if mechanical instability could be the source of the slow decay of the autocorrelation function. We know that this is not the case because no such slow decay is observed when the gel is saturated with water instead of the liquid crystal.
- [15] A.T. Ogielski and D.A. Huse, Phys. Rev. Lett. **56**, 1298 (1986).
- [16] J. Villain, J. Phys. (Paris) **46**, 1843 (1985).
- [17] D. Fisher, Phys. Rev. Lett. **56**, 416 (1986).
- [18] D.A. Huse, Phys. Rev. B **36**, 5383 (1987).
- [19] The situation is similar to the reptation dynamics in entangled polymer solutions. In these systems the dynamic structure factor is also independent of  $q$  when  $qR_G \gg 1$ , where  $R_G$  is the radius of gyration of a polymer. The absence of  $q$  dependence in this case is again due to local dynamics. Namely, fluctuations arise only at the free ends of the polymer chain [see M. Doi and S.F. Edwards, *The Theory of Polymer Dynamics* (Clarendon, Oxford, 1986)].
- [20] S.B. Dierker and P. Wiltzius, Phys. Rev. Lett. **58**, 1865 (1987).