Reorientation in Random Potential: A Model for Glasslike Dynamics in Confined Liquid Crystals

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The dynamical behavior of polymer dispersed nematic liquid crystals was studied by quasielastic light scattering. In addition to fast intradroplet orientational fluctuations a slow stretched exponential relaxation with a stretching exponent $s \sim 0.2$ was observed. This process is modeled with a reorientation of the average director of the droplets in a random potential. The model can be used to describe the glasslike dynamics in similar systems, for example, in silica aerogel filled with liquid crystals. [S0031-9007(98)05352-6]

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Liquid crystals confined to structures with characteristic lengths below 1 μm, for example, in droplets dispersed in polymer (PDLC) or in silica aerogel, exhibit many new static and dynamic phenomena connected with the mesoscopic size, large surface to volume ratio, and strong elastic deformations imposed on the liquid crystal by the embedding matrix [1,2]. Most of the research focused on the structure and the effect of confinement on the phase transitions [3]. Some dynamic light scattering experiments, giving the fluctuations spectrum, were also performed, mainly on liquid crystals confined to porous glasses and silica aerogels [2,4]. The observed behavior shows generally a very wide distribution of the relaxation rates, different from the well defined exponentially relaxing modes in the bulk liquid crystals.

The understanding of these dynamical processes is rather incomplete. In particular, little is known how much of the changes are due to the effects of the confinement on the viscoelastic properties of the liquid crystals and how much to the surface dynamical processes at the interfaces of the liquid crystal with the solid matrix, which dominate the dynamics due to the very large surface to volume ratio of these systems.

In this Letter we report on the dynamical light scattering in polymer dispersed nematic liquid crystals, where liquid crystal is embedded in a polymer matrix in the form of more or less spherical droplets that form as a result of phase separation of the monomer-liquid crystal solution upon polymerization. The size of the droplets depends on the polymerization process and ranges from $\sim$0.3–10 μm [5]. The static properties and internal structure of PDLCs are well known and this makes PDLCs very suitable to study the effects of surface on orientational dynamics. Very few experiments on thermally driven dynamics of PDLCs have been performed [6–8].

Our experiments show that PDLCs and related systems of liquid crystals in confined structures can also serve as very convenient model systems to study random dynamics with very broad distribution of relaxation rates giving a highly nonexponential, in some cases nearly logarithmic, autocorrelation function. In the frequency domain this means that the noise spectrum is approximately proportional to $1/\omega$. This random dynamics can be easily changed by application of an external field. As we will show below, we are able to model this dynamics of the PDLCs with a diffusion process in a random potential for which a very simple and intuitive physical picture can also be given.

Dynamic light scattering was performed on a 20 μm thick PDLC foil sandwiched between two glass plates coated with indium-tin oxide electrodes. The liquid crystal was E7 mixture, embedded in the polymer matrix in droplets with average diameter around 0.5 μm, as measured by scanning electron microscopy and atomic force microscopy. The electron microscope picture also shows that droplets, while having relatively narrow size distribution, are not perfectly spherical, but have a somewhat irregular shape (Fig. 1). The system showed the transition from the nematic, scattering state, to the isotropic transparent state at 328 K. The scattered light intensity correlation function $g^{(2)}(\tau) = \langle I(t)I(t+\tau)\rangle / \langle I(t)\rangle \langle I(t+\tau)\rangle$ was measured with an ALV5000 correlator allowing correlation times to be sampled from 10^{-8}–10^{3} s. Measurements were performed at different scattering angles and temperatures and also as a function of applied field. To avoid screening by impurity charges an ac field with frequency of 44 kHz was used. The directions of the incoming and scattered light were chosen so that the scattering vector was in the plane of the sample, that is, perpendicular to the applied field. According to the selection rules the scattering on the orientational fluctuations in nematic is strongest for the orthogonal polarizations of incident and scattered light, so the incoming polarization was perpendicular to the scattering plane and the scattered polarization was in the scattering plane.

In dynamic light scattering we measure the normalized scattered intensity autocorrelation function $g^{(2)}(\tau)$. The amplitude of the decaying part of $g^{(2)}(\tau)$ was around 0.05,

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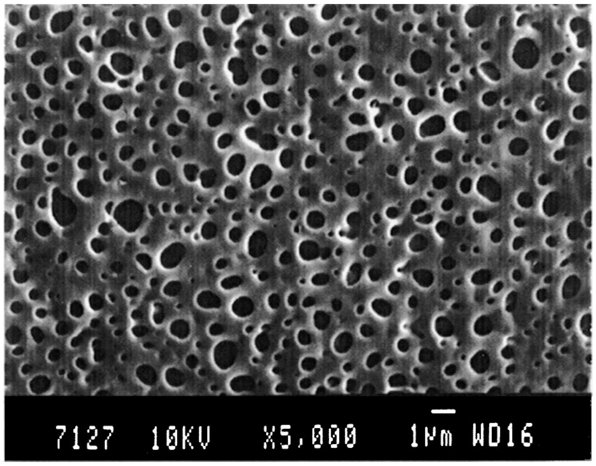

FIG. 1. The scanning electron microscope image of a part of the polymer matrix.

which means that our experiments were performed in the heterodyne regime, in which the statically scattered light acts as the local oscillator and $g^{(2)}(\tau) = [I_{LO}^2 + 2I_{LO}I_D g^{(1)}(\tau)]/I_{LO}^2 = 1 + 2g^{(1)}(\tau)I_D/I_{LO}$, where I_{LO} and I_D are the intensities of local oscillator and the dynamically scattered light, respectively, and $g^{(1)}(\tau)$ the normalized field autocorrelation function of the scattered light. So $g^{(2)}(\tau) - 1$ is proportional to $g^{(1)}(\tau)$. Figure 2 shows $g^{(1)}(\tau)$ at different strengths of the external field in the nematic phase. Two components are observed, a fast and a slow one. The fast component is due to the ordinary orientational fluctuations within the droplets. At zero field, when the sample is multiply scattering, it consists of distribution of relaxation rates due to the contributions at different scattering vectors. With the application of the electric field, this mode becomes monodisperse with increasing relaxation rate as expected for the orientational fluctuations of the director in external field. The behavior of this mode is thoroughly analyzed in a separate paper [7]. Here we want to focus on the slow mode which is highly nonexponential. Its decay extends over four or more decades, as seen in Fig. 2. Over that range it can be described as a stretched exponential function with a small stretching exponent $s \sim 0.2$, which means that the spectrum of this process has a $\sim 1/\omega^{1+s}$ form in the interval from $\sim 0.1 - 10^3$ Hz. The amplitude of the process decreases with the applied field but its general form remains unchanged.

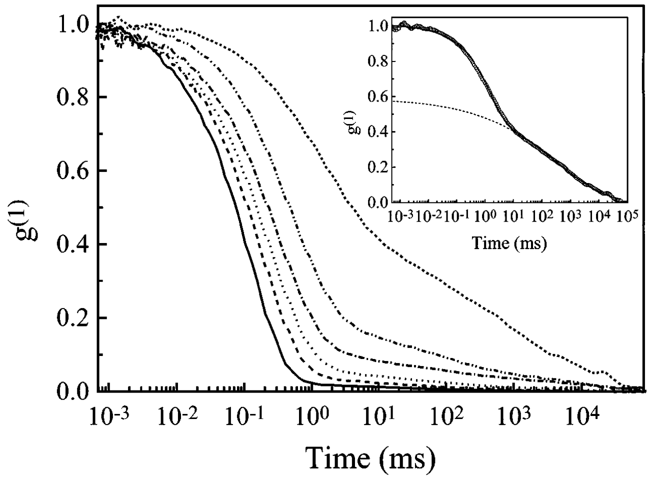

FIG. 2. The dependence of the normalized correlation function on the applied voltage, 0 V (short-dashed line), 64 V (dash-double-dotted line), 80 V (dash-dotted line), 100 V (dotted line), 120 V (dashed line), and 160 V (solid line). The temperature and outer scattering angle are 315 K and 30°, respectively. Inset: The measured zero field correlation function (circles), its fit (solid line) [7], and the stretched exponential part of the fit (dashed line) that describes the restricted rotational diffusion. The stretching exponent is 0.26.

To analyze the slow relaxation process we first note that the director configuration in the PDLC droplets in our sample is bipolar as was determined by optical observations and deuterium NMR measurements [9,10]. So in the interior of a droplet the director points predominantly along one direction **n**. At the surface of the droplet it is approximately parallel to the surface which requires at the poles two point defects. In the absence of an external electric or magnetic field, all the directions are equivalent and the average orientations of different droplets are random. The index of refraction of the polymer matrix is close to the ordinary index of the liquid crystal while extraordinary is considerably larger. Therefore, for a generally oriented droplet and light polarization, the light scattering cross section of a droplet is rather large, so in a sample with a thickness of 20 μm light is multiply scattered.

In strongly scattering systems the usual single scattering approximation used in analysis of photon correlation spectroscopy experiments is not applicable and the approach of diffusing wave spectroscopy (DWS) [11] has to be used. In the regime of DWS, the observed decay of $g^{(1)}(\tau)$ is shifted to shorter times. This effect can be understood in the following way: The total amount of frequency shift is a sum of random contributions over all the scattering events in a particular path of light through the sample. Also, obviously even if only a single relaxation rate is present in the system, multiple scattering will cause a distribution of relaxation rates in $g^{(1)}(\tau)$.

Formally, in DWS $g^{(1)}(\tau)$ is obtained by

$$g^{(1)}(\tau) \propto \int P(t) \exp[-\mu(\tau)t]\, dt\,, \tag{1}$$

where $P(t)$ is the distribution of times for transit of light through the sample and $\mu(\tau)$ is the dynamic absorption coefficient [12], which is proportional to $g^{(1)}(0) - g^{(1)}(\tau)$. As only short times are important for a single scattering event, $\mu(\tau)$ can be approximated by the first term in its power expansion. When light is scattered many times in traveling through the sample, the diffusion approximation for light transport is valid and $P(t)$ is peaked at $t_D = L^2/D = \pi L^2/l^* c$, where L is the sample thickness and l^* is the light transport length in the sample. L/l^* is the effective number of scattering events on the average light path. So for a process with an autocorrelation function of the stretched exponential form $\exp[-(t/\tau_0)^s]$, $g^{(1)}(\tau)$ for multiple scattering in the diffusion limit can be approximated by [11]

$$g^{(1)}(\tau) \simeq \exp\left[-\sqrt{6}\,\frac{L}{l*}\left(\frac{\tau}{\tau_0}\right)^s\right]. \qquad (2)$$

The main effect of multiple scattering is therefore to decrease characteristic relaxation time to $\tau_0(l^*/L)^{1/s}$.

The transport length l^* is related to the mean free path l by $l/l^* = \langle 1 - \cos\vartheta\rangle = \langle q^2\rangle/2k_0^2$, where q is the magnitude of the scattering vector (momentum transfer), k_0 the wave number of light, and the average is taken over all the scattering events [13]. So $l^{*-1} = \pi/2k_0^4 \int q^3 B(q)\,dq$, where $B(q)$ is the optical structure function of the PDLC foil. Assuming that nematic director in the droplets is homogeneous and randomly oriented, and that the droplets are independent, we get

$$l^{*-1} \simeq 4\pi^3 N\langle\Delta\varepsilon^2\rangle R^2 \int (qR)^3 f^2(qR)\,d(qR)\,, \qquad (3)$$

where $f(qR) = \pi(\sin qR - qR\cos qR)/(qR)^3$ is the single droplet form factor, N the droplet density, $\langle\Delta\varepsilon^2\rangle$ the square dielectric anisotropy averaged over all droplet orientations and directions of scattered polarization, and R the droplet radius. We get $l^* \sim 5\ \mu$m, so for our sample thickness $L/l^* \sim 4$. That the sample is several l^* thick can of course also be inferred from its milky look.

The slow part of the zero field data in Fig. 2 can be well fit with a stretched exponential with $s \sim 0.26$, while the corresponding time cannot be determined with any precision due to masking by the fast fluctuations within the droplets. From the data in Fig. 2 we get a very rough estimate for $[l^*/(\sqrt{6}L)]^{1/s}\tau_0 \sim 1$ s.

To explain the highly stretched correlation function of the slow part of the dynamics of PDLC, we propose the following model. In the absence of external field, the average direction of the nematic director in perfectly spherical droplet can freely diffuse. The mechanism for this diffusion is motion of the point defects; the torque needed to turn the director is approximately γV, where γ is the rotational viscosity and V the volume of the droplet. The diffusion time is then approximately $1/\tau_{\text{diff}} = k_B T/\gamma V$, that is, of the order of 1 s^{-1}. Thermally induced reorientation in samples with droplet size a few micrometers has been actually observed visually under the microscope by Amundson [8]. As those droplets were larger than in our sample, the reorientation was observed only close to the isotropic phase, where the effective viscosity is smaller and the characteristic time a few seconds.

Free rotational diffusion gives a simply exponentially decaying correlation function. The droplets, however, are not of perfectly spherical shapes and also the anchoring of the director on the surface is probably not perfectly homogenous. In our model, based on the theories of $1/f$ noise and stretched exponential relaxation in condensed matter [14], in particular on the random walk in random potential [15], these irregularities are modeled by a random potential in which the average director of each droplet moves.

To see what is the effect of the random potential, we performed a model simulation for the diffusion of a point on a lattice on the sphere. The lattice was taken to be vertices of the dodecahedron. In each vertex a value V_i for the random potential was assigned. They were taken to have Gaussian distribution with zero mean and variance v_0. Then the single step transition probabilities were calculated according to an adaptation of the Metropolis scheme, that is, the transition probability to a neighboring vertex with a lower potential was $\frac{1}{3}$ and to a vertex with a higher potential $\frac{1}{3}\exp(V_i - V_j)$. This assures detailed balance and the correct (canonical) equilibrium distribution. Other slightly more complicated schemes were also tried and, as long as they obeyed the requirement of detailed balance, the results were essentially the same. Different random generators were tried with no change in the results. For each sample of the values V_i, $i = 1,\ldots,20$, we get a 20 dimensional Markow chain, which is computed in powers 2 to 2^m steps, with m from 20–30. The director $\mathbf{n}$ is determined by the coordinates (x,y,z) of the currently occupied vertex, so as the component of the dielectric tensor which gives the main contribution to the scattering is ε_{xz}, we compute $\langle n_x(0)n_z(0)n_x(\tau)n_z(\tau)\rangle$, with τ taking values 2^i. This quantity should be proportional to $g^{(1)}(\tau)$.

The correlation function must be averaged over the distribution of the random potential, which we do by repeating the calculation for 100–1000 samples of the random potential. The necessity to average both over time and over the ensemble of droplets of course implies that the system is nonergodic. Experimentally that means that a sufficient number of droplets must contribute to scattering to ensure a true ensemble average.

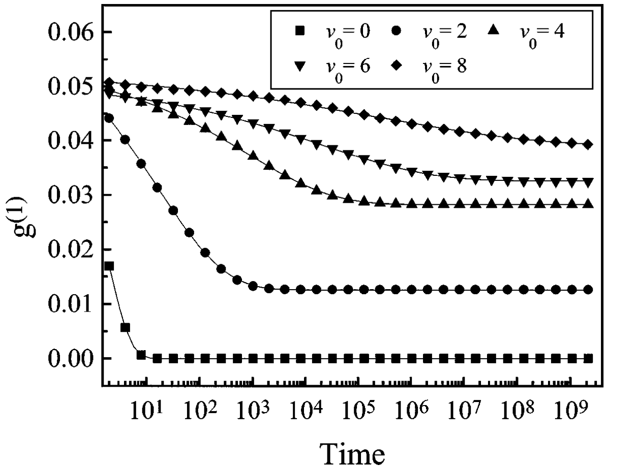

FIG. 3. $\langle n_x(0)n_z(0)n_x(\tau)n_z(\tau)\rangle$ computed from the model of droplet reorientation in random potential for different variances of the potential v_0 (in units of k_BT). At $v_0 = 6$, $s = 0.2$. Lines are the fits to the stretched exponential function.

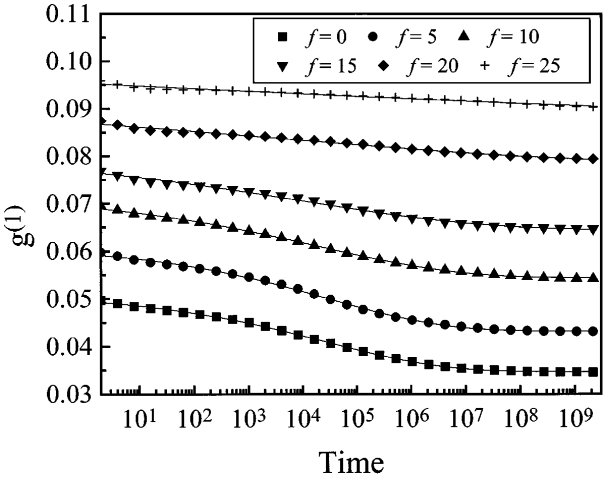

FIG. 4. $\langle n_x(0) n_z(0) n_x(\tau) n_z(\tau) \rangle$ computed from the model of droplet reorientation in random potential in an external field F (in units of $k_B T$) at $v_0 = 6$. Lines are the fits to the stretched exponential function.

The resulting correlation functions for different choices of the variance of the potential distribution v_0 (in units of $k_B T$) are shown in Fig. 3. The time unit is of the order of the free diffusion time τ_{diff}, as can be seen from the $v_0 = 0$ curve. The decay can be very well described with a stretched exponential, with a stretching exponent s from $s = 0.45$ for $v_0 = 2$ to $s = 0.12$ for $v_0 = 8$. The best agreement with the measurements is obtained for $v_0 = 5$, where $s = 0.25$. The corresponding parameter τ_0 is $\sim 3000 \tau_{\mathrm{diff}}$. The experimental value from the zero field data in Fig. 2 is roughly $2000 \tau_{\mathrm{diff}}$, so the agreement is quite good.

The effect of external field on the rotational diffusion process can also easily be simulated with a term in a potential of the form $f n_z^2$, which is added to the random part. The results are shown in Fig. 4. As can be expected, at field energies somewhat larger than the random potential, the rotational diffusion is quenched and the amplitude of the decaying part of the correlation function nearly completely disappears. This is in accordance with our observations presented in Fig. 2. There the slow extended part of the correlation function disappears at the orienting field, that is, just at the field needed to enforce orientation of the droplets.

A similar extended relaxation process can also be observed in other systems, related to PDLCs, for example, in silica aerogels, filled with nematic liquid crystal [2]. There the authors attribute the slow glasslike part of the correlation function to motions which are coupled from pore to pore. They propose that a possible mechanism is hindered rotational diffusion. We think that our model of thermally driven jumps of director field configuration in a random potential is also appropriate in this case, where the individual pores are much more irregular than in PDLCs and form a complex interconnected network. The reorientation may occur either in individual pores, or in several neighboring pores, which are elastically coupled, concurrently.

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