

Dynamic light scattering in polymer-dispersed liquid crystals

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A polymer dispersed liquid crystal was studied by dynamic light scattering. In the experiments, where no electric field is applied, the system exhibits additional slow dynamics to the ones observed in bulk nematic liquid crystals. This slow dynamics gradually disappears with an increasing electric field. While the measured time intensity correlation function does not depend on the scattering vector in the system where no field is applied due to the multiple scattering, its dependence on the electric field shows expected size effects. In confined systems, with typical size d , there are no eigenmodes of the orientational fluctuations in droplets with the wave vectors less than the minimal wave vector $q_{\min} \sim \pi/d$. We observed a quadratic dependence of the inverse relaxation time on the scattering vector down to a certain scattering vector, below which the relaxation time remains constant. The size calculated from this minimal scattering vector is in agreement with the average droplet size obtained from scanning electron microscope photographs and the atomic force microscope images of our sample. The electric field changes the temperature behavior of the inverse relaxation time near the nematic-isotropic phase transition, which increases with the temperature when the electric field is applied, but decreases when the field is absent. [S1063-651X(97)02407-0]

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I. INTRODUCTION

Polymer dispersed liquid crystals (PDLCs) are interesting for applications as well as for fundamental research of surface and size effects in different phases of liquid crystals. Particular attention is given to the switching behavior of PDLC films for their applicability as light shutters or in electro-optical displays [1]. The transmittance of the PDLC films depends on the applied electric field that switches the films from opaque to clear state. Theoretically a calculated single scattering picture gives a good description of the film transmittance [2–4], but is insufficient to explain the angular dependence of the scattered intensity of light where multiple scattering effects seem to be important [5].

The dynamic behavior of the PDLC has been examined by several experimental means. Mostly the dielectric [6–8] and electro-optical properties in different PDLC films have been studied [9]. In the dielectric studies a discontinuous jump in the dielectric permittivity at the nematic-isotropic and smectic-nematic transitions was observed, as well as the lowering of the transition temperatures suggesting some contamination of liquid crystal by the polymer. The important parameters of the switching of the PDLC films are response times. The decay time for the composite to reach the opaque state when the voltage is switched off depends on the properties of the liquid crystal and the shape of the droplets [9], whereas the rise time for the composite to reach the clear state transmission when an alternating voltage is applied depends also on the amplitude of the applied voltage. While many experimental results show that increasing the temperature reduces the rise time, the effect of the temperature on the decay time differs from experiment to experiment [9]. Amundson [10] studied temperature dependence and phase behavior of electro-optic properties of the PDLC film. A few degrees below the nematic-isotropic phase transition temperature he observed a structural transition within droplets of

the film that gave rise to dramatic changes in electro-optical behavior.

The linear response of the nematic liquid crystals is determined by the decay time of thermal orientational fluctuations that also cause a strong scattering of light [11]. The spectrum of the scattered light depends on this orientational decay time, which has the same dependence on the elastic constant and viscosity as the switching decay time of the PDLC films. Although dynamic light scattering experiments can explain some of the open questions considering the response times of the PDLC, not many experiments have been carried out to date. Allia *et al.* [12] have measured stationary noise of the monochromatic light by a PDLC at room temperature. They observed expected size effects, but the distinctive features of the power spectra were not different from those for conventional slab-type samples of nematics and the obtained effective viscosity was comparable with the bulk viscosity.

Recently a lot of attention was given to the surface and finite-size effects in systems containing liquid crystals [13]. The presence of the surface seems to alter the dynamical behavior of liquid crystals. Gharbi, Fekih, and Durand [14] have studied the influence of the surface on the dynamics of surface anchoring breaking in a nematic liquid crystal. Their measurements suggest that the effective viscosity is larger in the presence of the surface than in the bulk nematic with the same scalar order parameter. Slower dynamics than in the bulk liquid crystals have also been observed in other confined systems [15–17] indicating the dynamical behavior of liquid crystals close to the surface is not yet clearly understood.

For these reasons we decided to study PDLC films by photon correlation spectroscopy, a complementary technique to the one used by Allia *et al.* [12]. The average size of the droplets used in our measurements, however, is considerably smaller than in their samples and therefore the surface effects

are expected to be more pronounced. Moreover, we also investigated the temperature dependence of the orientational fluctuations of the nematic confined in droplets and found that it is significantly altered compared to the dependence in the bulk nematic.

Whereas to our knowledge no photon correlation experiments were performed in PDLCs, such experiments have been carried out in liquid crystals confined to various porous matrices [15–17]. In those cases the surface, finite size, and randomness affect the dynamic behavior of the liquid crystal and it is difficult, if not impossible, to distinguish these contributions in such systems. The effect of randomness is not so pronounced in our study of the dynamic light scattering in the droplets of the PDLC film and thus our results can also contribute to a better understanding of the results in random systems.

II. EXPERIMENT

The polymer dispersed liquid crystal used in our measurements was provided by the Liquid Crystal Institute, Kent State University. A thin film of the PDLC composed of the nematic liquid crystal E7 dispersed in the polymer matrix was placed between two indium-tin-oxide coated glass substrates.

We have studied orientational fluctuations of the liquid crystal droplets using quasielastic light scattering. 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 $g^{(2)}(\tau) = \langle I(t)I(t+\tau) \rangle / \langle I(t) \rangle \times \langle I(t+\tau) \rangle$ of light exiting the sample as a function of scattering angle, the amplitude of applied electric field and temperature. The frequency of the electric field was 44 kHz. In our scattering geometry the scattering vector was perpendicular to the electric field, therefore to the nematic director, when the applied field exceeded the threshold value, i.e., when the PDLC film was transparent. Following the selection rules, and to minimize the elastically scattered background, we chose orthogonal polarizations of incident and scattered light.

A significant difference was observed between the measured intensity correlation functions when the electric field was applied and when it was absent (Fig. 1). In the bulk nematics there are two independent orientational modes that decay exponentially [11]. Depending on the choice of the scattering geometry either of them or both can be observed in the dynamic light scattering experiments, each of them as a single exponential contribution to the correlation function. In the PDLC films in the experiments without the external electric field the system exhibits additional slow dynamics to one observed in the bulk nematic liquid crystals (Fig. 1). With the increasing external electric field the slow component decreases and, finally, disappears in higher fields leaving almost a single exponential correlation function. We explain this slow nonexponential part as due to restricted rotational diffusion of the average droplet orientation. The details are explained in [18]. The dependence of the inverse relaxation time of the single exponential part on the electric field is shown in Fig. 2. In the geometry we used, only the

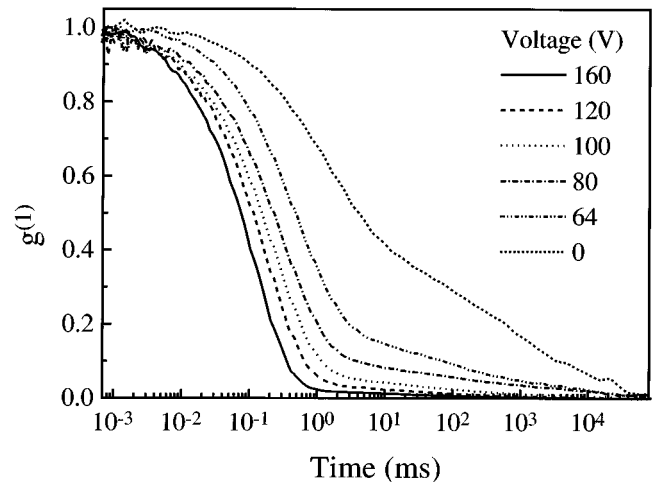


FIG. 1. Dependence of the normalized correlation function on the applied voltage. The temperature is 315 K. The outer scattering angle is 30° , i.e., the scattering vector is smaller than the wave vector of the first mode.

twist-bend mode was measured in the applied field, while without the field and at fields lower than a threshold field both the splay-bend and the twist-bend modes contributed to the correlation function.

The usual effect of the multiple scattering on the autocorrelation function is a significant speeding up of the scattered intensity fluctuations as observed in diffusing wave spectroscopy [19]. We do not expect any such increase of the decay rate in our experiments, as most of the scattering in PDLCs is due to the static scattering on the surfaces of the droplets and only a small, dynamic part comes from the orientational fluctuations within the droplets. A similar situation is found in the scattering experiments in liquid crystals embedded in aerogels [16]. The static part of the scattered light acted as a local oscillator, so our dynamical measurements were performed in the heterodyne regime.

The static multiple scattering [5] hinders measurements of the wave vector dependence of the correlation function in the absence of the field. In this case the correlation function does not depend on the scattering vector and since the scattering

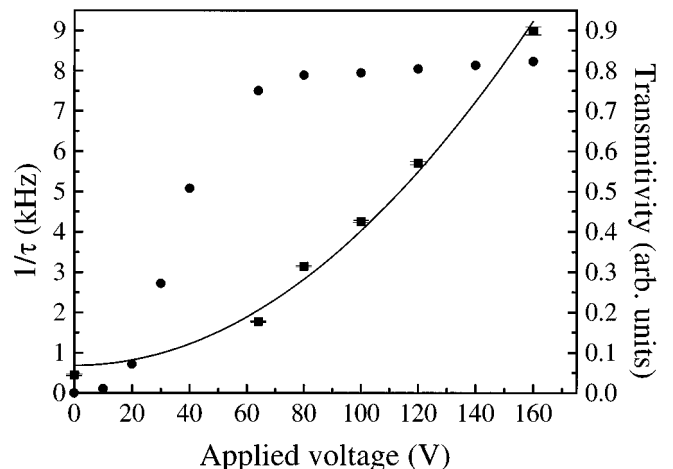


FIG. 2. Dependence of the relaxation rate of the orientational fluctuations on the applied voltage (squares) with a quadratic fitting function (line) and the corresponding transmittivity (circles). The experimental details are the same as in Fig. 1.

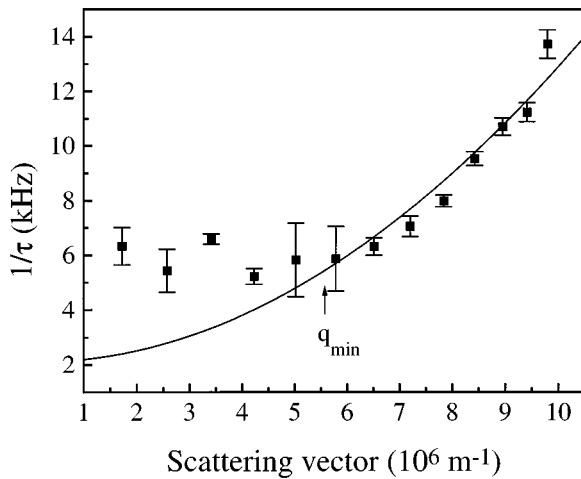


FIG. 3. Dependence of the relaxation rate of the orientational fluctuations on the scattering vector in the external field. The temperature is 295 K and the amplitude of the voltage is 160 V.

amplitudes of modes are proportional to $1/q^2$ mostly the lowest mode contributes to the correlation function. The situation is different, however, when the field is applied (Fig. 3). In fields higher than the threshold field the inverse relaxation time depends on the scattering vector. Above a certain scattering vector the dependence is strong and can be fitted well with a quadratic function, whereas below this scattering vector the inverse relaxation time has a constant value.

The temperature dependence of the correlation function also differs for the cases with and without electric field (Figs. 4 and 5). In the absence of the field the contribution of the slow dynamics, due to the rotational diffusion of the average droplets' orientation, to the correlation function increases

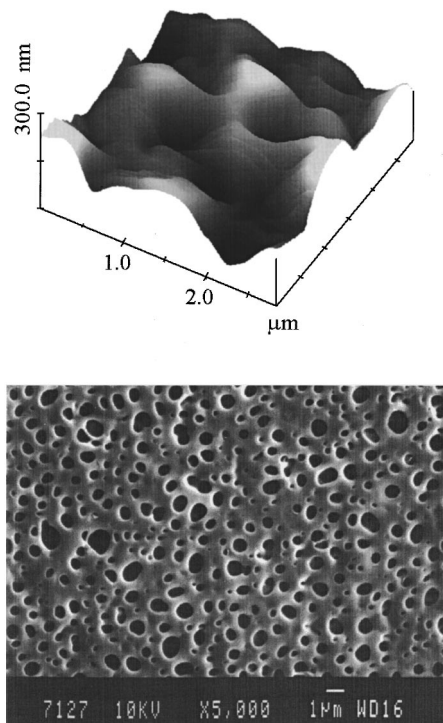


FIG. 4. Atomic force microscope (up) and scanning electron microscope (down) images of parts of the polymer matrix.

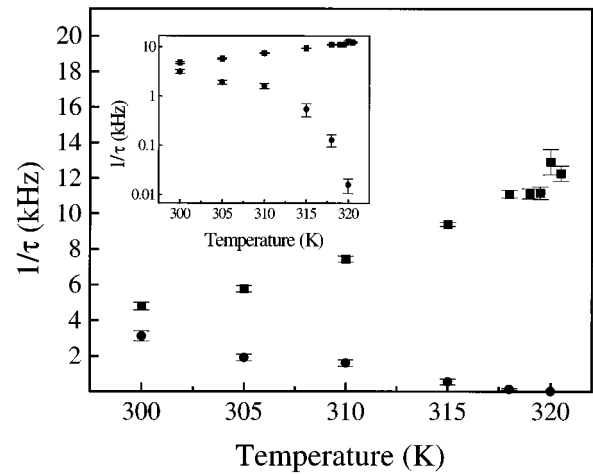


FIG. 5. Temperature dependences of the relaxation rate of the orientational fluctuations with and without an external electric field. Outer scattering angle is 30° , i.e., the first mode is observed. Inset: the same plot on the logarithmic scale.

with the temperature and close to the nematic-isotropic phase transition temperature it prevails upon the contribution of the faster orientational fluctuations (Fig. 6). This can be understood considering the results of Amundson [10]. He observed that a few degrees below the phase transition to the isotropic phase the droplets became biphasic. The birefringent nematic sphere in the center of each droplet was surrounded by an isotropic fluid shell. With increasing temperature the nematic cores gradually melted and finally vanished. So the rotational diffusion of the average droplet orientation becomes less restricted in this temperature region, giving a larger and faster signal, as well as a considerably more exponential contribution to the correlation function (Fig. 6). There is a knee in the temperature dependence of the transmittivity at 322 K (inset of Fig. 6) and at approximately the same temperature the part of the correlation function due to the rotational diffusion

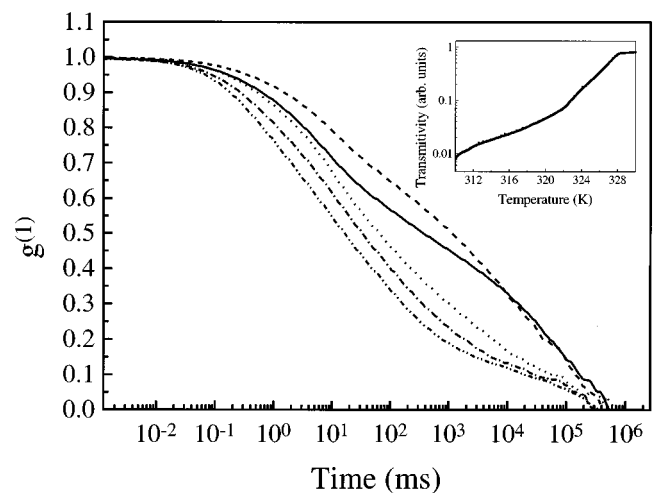


FIG. 6. Temperature dependence of the correlation function in the temperature region where droplets start to melt. Temperature: 321 K (line), 322 K (dash), 323 K (dots), 324 K (dash-dotted), and 324.6 K (dash-double-dotted). Outer scattering angle is 30° . Inset: the temperature dependence of the transmittivity of the sample.

prevails upon the part due to the orientational fluctuations, so the melting of the droplets in our sample probably starts at this temperature. The temperature at which the whole liquid crystal is in the isotropic phase can be determined from the saturation of the transmittivity and is 328 K.

The relaxation rate of the faster orientational fluctuations decreases with temperature. In the applied field we observed a drastic decrease of the intensity of the scattered light a few degrees below the clearing point, while in the bulk the intensity of the scattered light from the orientational fluctuations only weakly depends on the temperature [11]. The reason for such a decrease in the PDLC is in melting of the droplets, i.e., the reduction of the effective scattering volume. In the PDLC the inverse relaxation time of the orientational fluctuations in the field increases, but less than in the bulk.

III. DISCUSSION

The temperature and electric field dependence of the inverse relaxation time of the faster part, i.e., the orientational fluctuations, can be explained within the nematodynamics. The inverse relaxation time of the orientational fluctuations in the bulk nematic liquid crystal in the external electric field E is given by [11]

$$\frac{1}{\tau} = \frac{Kq_n^2}{\eta_{\text{eff}}} + \frac{\varepsilon_a E^2}{2\eta_{\text{eff}}}, \quad (1)$$

where q_n is the wave vector, K the Frank elastic constant, η_{eff} the effective viscosity, and ε_a the dielectric anisotropy. While in the bulk the eigenmodes of orientational fluctuations are plane waves with arbitrary wave vectors, confinement changes both the structure of the modes as well as the set of allowed wave vectors. In the most simple case of a nematic liquid crystal confined to a box, the eigenmodes become standing plane waves. The wave vectors have only discrete values that are determined by the size of the box and the boundary conditions. The allowed values of their components are approximately

$$q_{ni} = \frac{(n+1)\pi}{d_i}, \quad (2)$$

where d_i ($i=x,y,z$) is the dimension of the box and $n=0,1,2,\dots$. The minimal wave vector q_{0i} is therefore determined by the dimension of the box. In the light scattering experiment at a given scattering vector \mathbf{q} one probes modes with the wave vector equal to the scattering vector, if the scattering volume is much larger than the wavelength of light λ . When the scattering volume is comparable to λ , the scattering vector need not match any mode wave vector and several modes contribute to scattering. In rectangular geometry the contribution of the mode with the wave vector \mathbf{q}_n is proportional to

$$\prod_{i=x,y,z} \frac{\sin^2[(q_i - q_{ni})d_i/2]}{[(q_i - q_{ni})d_i/2]^2}. \quad (3)$$

In such cases, the intensity correlation function is no longer a single exponential. In our experiments, however, the measured correlation function deviates from the single exponential decay function also due to scattering from droplets with

different sizes. Clearly, when the scattering vector is smaller than the wave vector of the first mode, the largest contribution to the scattered intensity comes from this mode. The situation is similar to the case of a spherical nematic droplet, except that the mode structure is more complicated. Still the lower limit of the wave vectors in the droplet is limited by the size of the droplet d , $|\mathbf{q}_0| \sim A/d$. The numerical factor A depends on the boundary conditions and the droplet configuration, but is also of the order of π . So the droplet size can be extracted from the dependence of the relaxation time on the scattering vector (Fig. 3). At scattering vectors larger than the wave vector of the first mode \mathbf{q}_0 , mostly the mode with minimal $|\mathbf{q}_n - \mathbf{q}|$ contribute to the correlation function with relaxation time proportional to $|\mathbf{q}_n|^2$ (Fig. 3), while at scattering vectors smaller than the \mathbf{q}_0 , as already said, the main contribution comes from the first mode and the relaxation time obtained is independent of the scattering vector. Therefore, the limiting scattering vector q_{min} at which the dependence of the relaxation time on the scattering vector changes from quadratic dependence to a constant value can be attributed to the wave vector of the lowest mode of the liquid crystal droplet. This also allows us to analyze the situation when there is no field applied and due to multiple scattering all modes contributes to the correlation function with amplitudes proportional to $1/q_n^2$. Obviously in such a case mostly the first mode is observed. To verify these assumptions we have measured the droplets' size with the atomic force microscope and the scanning electron microscope (Fig. 4). Both methods give the same average size of approximately $0.5 \mu\text{m}$ and this is also in agreement with the size obtained from the limiting scattering vector as π/q_{min} .

The temperature dependence of the relaxation time is hidden in the temperature dependences of the elastic constant, viscosity, and dielectric anisotropy through the scalar order parameter $S(T)$. The elastic constants and the orientational viscosity γ_1 that mainly contributes to the effective viscosity are proportional to the square of the order parameter, while the dielectric anisotropy is linear in $S(T)$ [11]. Therefore, in the bulk nematic liquid crystal in the absence of the electric field, the inverse relaxation time remains almost constant although the temperature, i.e., order parameter changes. However the dissipation processes due to the surface can change the temperature behavior of the effective viscosity as already observed in other confined systems [14,17,20]. An increase of the effective viscosity can be understood by considering it has two contributions. Besides the rotational viscosity there is a term due to the backflow effect that reduces effective viscosity. At the surface the fluid cannot flow freely as in bulk, therefore the backflow is smaller, i.e., the effective viscosity larger. However, this effect alone cannot change the temperature dependence of the relaxation time since the backflow term is also roughly proportional to the square of the order parameter. Since the fluid velocity is zero at the surface and is equal to its bulk value some distance away from it, obviously there are gradients in velocity that cause additional dissipation in the region close to the surface. The viscosity connected to these losses is the usual fluid viscosity which is in nematic liquid crystal almost independent of the order parameter. And indeed, Petrov *et al.* [20] have observed that the contribution of the dissipation processes due to the surface to the energy dissipation already became com-

parable to the volume contribution below penetration depths of the order of $0.2 \mu\text{m}$. Since the surface contribution is not expected to have the same temperature behavior as the bulk contribution, i.e., it is not expected to decrease so drastically when approaching the phase transition, that could explain the decrease of the inverse relaxation time with temperature in the absence of the field.

In the external electric field the situation is different. The inverse relaxation time in the bulk increases with the square of the electric field. Our measurements can be indeed fitted well with a quadratic function and obtained effective orientational diffusivity K/η_{eff} is a few times smaller than the same diffusivity in the bulk E7 [21]. This is not surprising since the decrease of the nematic-isotropic phase transition temperature by about 5 K indicates the liquid crystal is contaminated by the polymer which can reduce the diffusivity [21] and as already mentioned, the effective viscosity is larger than in the bulk because of dissipation close to the droplet surface. The increase of the relaxation rate with temperature is the consequence of temperature behavior of the order parameter. In Eq. (1) we have two terms, the usual q^2 dependent and a field term, the first decreases with temperature as explained in the previous paragraph, while the second, field term is proportional to $1/S(T)$. Therefore, in the

bulk nematic in the external field the increase of the relaxation rate with temperature is expected. Since near the nematic-isotropic phase transition the average order parameter in the small droplets decreases more and on larger temperature interval than in the bulk nematic [22], the field term prevails upon the first decreasing term and this results in an increase of the inverse relaxation time with the temperature. The increase is smaller than in the bulk nematic liquid crystal.

IV. CONCLUSION

To conclude, the orientational diffusivity of the nematic liquid crystal in the droplets is smaller and has different temperature behavior than in the bulk nematic liquid crystal. The effect can be attributed to the dissipation processes close to the droplet surface that increase the effective viscosity and have different temperature dependence. The droplet size can be extracted from the angular dependence of the relaxation time of the orientational fluctuations and it agrees with the average droplet size obtained from scanning electron microscope photographs and the atomic force microscope images of our sample.

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