Coupled director and polarization fluctuations in suspensions of ferroelectric nanoparticles in nematic liquid crystals

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In colloidal suspensions of nanosized ferroelectric particles and nematic liquid crystals a large increase in the isotropic-nematic transition temperature has been observed recently. By dynamic light scattering we measured the relaxation rate of the nematic director fluctuations in colloidal systems with $BaTiO_3$ and $Sn_2P_2S_6$ particles. A substantial increase in the bend-mode relaxation rate, attributed to an increase in the bend elastic constant, is observed. A mode with relaxation rate around $200\,000$ s^{-1}, independent of the scattering vector, is also observed. We propose that it represents the out-of-phase motion of the nematic director and average direction of the spontaneous polarization of the ferroelectric particles. No translation motion is observed, indicating that the particles may form chains.

I. INTRODUCTION

Systems of colloidal particles dispersed in liquid crystals present a rich variety of phenomena. The distortions of long-range liquid crystalline order around particles cause specific interparticle interactions, leading to a number of interesting phenomena [1–5]. In these situations the particles affect the liquid crystalline (LC) medium only inasmuch as the large distortions around the particles, which are due to specific boundary conditions, can decrease the amount of order in the vicinity of the particles and/or induce topological defect structures [2–5].

Recently diluted LC colloids of very small ferroelectric particles were developed [6]. They are so small ($\sim$30–70 nm) that they do not disturb the LC director. Therefore, the colloids look macroscopically the same as the matrix. At the same time the particles have a strong influence on the liquid crystal host. The transition temperature from the nematic to isotropic phase has been shown to increase by surprisingly large amounts, up to 40 K [7]. Other properties that are connected to the liquid crystal order parameter also show large changes. The dielectric constant anisotropy, for instance, can change by a factor of 2 or more [6,8].

The natural explanation for these phenomena is that the strong local electric field around the ferroelectric particles induces an increase in the nematic order parameter. On a phenomenological level this effect can be described by a Landau–de Gennes type of energy in which the square of the electric field acts as a force, conjugate to the nematic order parameter. A semimicroscopic explanation has been given in Refs. [7,9].

The nematic order parameter also affects other quantities like orientational elastic constants and nematic viscosities. These parameters govern the dynamic properties of the system, in particular the nematic orientational fluctuations. The ferroelectric particles should also add new degrees of freedom: namely, translational motion of the particles with respect to the background fluid and rotation of the polarization direction relative to the nematic director.

In pure nematic liquid crystals the orientational fluctuations are the fundamental hydrodynamic excitations of the director field. They have two dispersion branches, bend-twist and bend-splay, with the relaxation rates proportional to a ratio of the nematic elastic constants K and viscosity coefficients η [10]:

$$\frac{1}{\tau} = \frac{K}{\eta}q^2, \tag{1}$$

where q is the wave vector. These thermally excited fluctuations give rise to the turbidity of the nematic phase. The best way to observe them is by dynamic light scattering. The intensity of the scattering is proportional to the ratio of the optical anisotropy and elastic constants.

In this paper we show that insertion of ferroelectric nanoparticles, even in small concentrations, causes strong changes of the characteristics of dynamic light scattering that can be explained by a substantial increase in the nematic order parameter. The presence of the particles results also in an additional fluctuation mode where the nematic director and spontaneous polarization of the ferroelectric particles fluctuate in a counterphase.

II. EXPERIMENT

The ferroelectric particles were obtained by milling larger-($\sim$1-μm) sized particles together with heptane and oleic acid surfactant so that the resulting particle size, as determined by atomic force microscopy, was from 10 nm to 50 nm. At such sizes the ferroelectric properties of the particles, in particular the spontaneous polarization, remain essentially the same as in the bulk [11,12]. The milled ferroelectric particle suspension was mixed with the liquid crystal host and the solvent was evaporated. Cells with surfaces treated for planar or homeotropic orientation were filled with the mixture in the isotropic phase. Upon cooling well-aligned nematic samples were obtained.

The measurements were performed on suspensions of 1 wt % of $BaTiO_3$ and $Sn_2P_2S_6$ nanoparticles in a commercial liquid crystal mixture LC18523 (Merck) with the T_{NI} =55 °C. The number density of the ferroelectric particles in
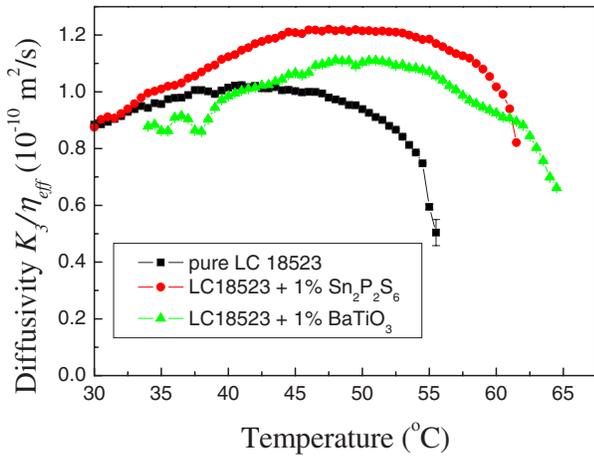
FIG. 1. (Color online) Diffusivity K_3/η of the pure bend mode as a function of temperature in pure liquid crystal and in both suspensions.

the suspensions is about 10^{20} m^{-3}. The ferroelectric phase transition of bulk $BaTiO_3$ is at $T=125$ °C while $Sn_2P_2S_6$ goes to the paraelectric phase at $T=66$ °C. The value of the spontaneous polarization for bulk $BaTiO_3$ monocrystal is $P_s=0.26$ A s/m^2 [13] and, for bulk $Sn_2P_2S_6$, $P_s=0.14$ A s/m^2 [14]. We could determine the transition temperature of the suspensions by observation under a polarizing microscope and also during the scattering measurements as the scattering intensity abruptly changes at the transition. For the mixture with $BaTiO_3$ we obtained $T_{NI}=63.5$ °C and, with $Sn_2P_2S_6$, $T_{NI}=61$ °C, close to the transition of $Sn_2P_2S_6$ to the paraelectric phase. Above the transition temperature in all cases (mixtures and pure liquid crystal) a coexistence region of about 5 °C of nematic and isotropic phases was observed.

In our experiment we used a standard photon correlation setup using a frequency-doubled diode-pumped Nd-YAG laser that has excellent power stability and an ALV-6010/160 correlator to obtain the autocorrelation functions of the scattered light intensity. The polarization of the incoming and detected light was chosen so that we observed either the splay-bend or twist-bend fluctuation mode. For instance, in a sample with planar orientation and the director in the scattering plane, the twist-bend mode is observed if the incoming light is ordinary polarized and the scattered light extraordinarily polarized (oe scattering), while the splay-bend mode is visible with both polarizations extraordinarily (ee scattering). By choosing the direction of the scattering vector parallel or perpendicular to the director we can observe pure bend or pure twist/splay mode, respectively. It is important to note that in ordinary-ordinary scattering the fluctuations of the nematic director are never observable.

III. RESULTS

Figure 1 shows the diffusivity—i.e., the ratio of the bend elastic constant K_3 and the effective rotational viscosity η—as a function of temperature in pure liquid crystal and in both suspensions. The measurements were obtained on pla-

nar samples in oe scattering. The general shape of the dependence is typical for many nematic liquid crystals and is due to several factors. The elastic constant is proportional to the square of the scalar order parameter S^2, while the temperature dependence of the viscosity is more complicated. The pure rotational viscosity γ_1 is proportional to S^2, while the other Leslie viscosities are either independent of S or proportional to S or S^2. In bend modes the effective viscosity includes the backflow effect so that it has a more complicated dependence on S. All viscosity coefficients have also an Arrhenius-type exponential temperature dependence [10]. At room temperature the diffusivity K_3/η of all three samples is nearly equal while closer to the transition temperature the diffusivity of the suspensions is considerably larger than in liquid crystal alone.

In our opinion the increase in the diffusivity of pure bend modes in the suspensions is due to an increase in the nematic order parameter S and an accompanying increase in the elastic constants. The alternative explanation that the rotational viscosity decreases with the addition of ferroelectric nanoparticles is unreasonable. Also, far below the transition the diffusivity is about equal ($Sn_2P_2S_6$ suspension) or even smaller ($BaTiO_3$ suspension) as in pure LC. As the order parameter in pure liquid crystal well below the T_{NI} is close to 1, the electric field due to the ferroelectric particles cannot substantially increase it so that the change in the elastic constant at low temperature is small. The particles probably cause some increase in viscosity which explains why at room temperature $BaTiO_3$ suspension has a slightly lower diffusivity.

Figure 2 shows the temperature dependence of the diffusivity of pure twist fluctuations. The twist diffusivity K_2/γ_1 of both suspensions is slightly lower than in pure liquid crystal throughout the whole temperature range. This shows that in the twist mode the S^2 dependence of both K_2 and γ_1 cancel and again that in suspensions we get some increase in the rotational viscosity γ_1. The temperature dependence of K_2/γ_1 is due to the Arrhenius type of temperature dependence of γ_1.
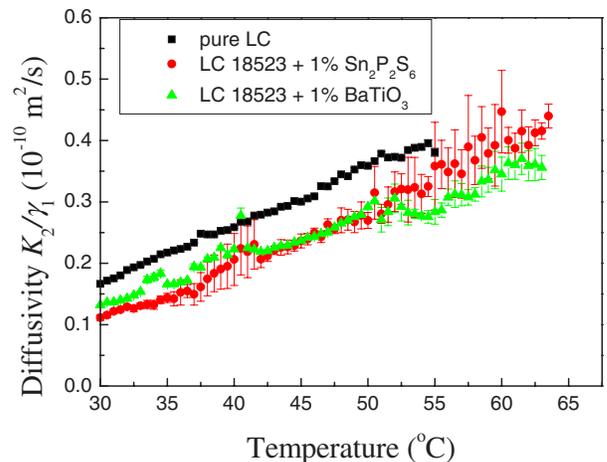

FIG. 2. (Color online) Diffusivity K_2/γ_1 of the pure twist mode as a function of temperature in pure liquid crystal and in both suspensions.
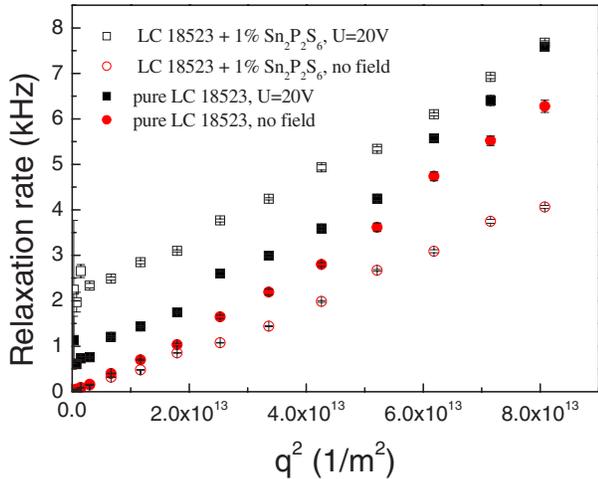
FIG. 3. (Color online) Relaxation rate of the twist-bend mode versus the square of the scattering vector q^2 for pure liquid crystal and $Sn_2P_2S_6$ suspension at zero field and at 1.7 MV/m ($f=50$ kHz, $U=20$ V, thickness of the samples around 12 μm) measured in a homeotropic cell at room temperature.

We also measured the dependence of the fluctuations on the external electric field ($f=50$ kHz). Figure 3 shows the relaxation rate of the twist-bend mode versus the square of the scattering vector q^2 for pure liquid crystal and $Sn_2P_2S_6$ suspension at zero field and at 1.7 MV/m ($U=20$ V, thickness of the samples around 12 μm) measured in a homeotropic cell. The relaxation rate of orientational fluctuations in an external field in a pure liquid crystal in one elastic constant approximation is [10]

$$\frac{1}{\tau} = \frac{K}{\eta}q^2 + \frac{\epsilon_a\epsilon_0 E^2}{\eta}. \qquad (2)$$

The relaxation rate increases as expected but the increase at $q=0$ in the $Sn_2P_2S_6$ suspension is larger by a factor of about 2.5. This means that the anisotropy of dielectric tensor ϵ_a also increases at least as much, as we expect that there is also some increase of the effective viscosity, which partly compensates for the increase in ϵ_a. That ϵ_a increases in suspensions of ferroelectric particles has also been reported in Refs. [6,8,9]. There the observed increase of dielectric anisotropy was also of the same order.

On homeotropically oriented samples with the incident wave vector along the director and when the incident polarization is in the scattering plane and the scattered polarization is perpendicular to the scattering plane (oo scattering), we observed another mode with the relaxation rate in the region around 2×10^5 s^{-1}. In this scattering geometry the orientational fluctuations of the nematic director are not observable. The temperature dependence of this mode for $Sn_2P_2S_6$ suspension is shown in Fig. 4. The relaxation rate of this mode does not depend on the scattering vector.

We propose that this mode represents the out-of-phase motion of the average orientation of the ferroelectric polarization with respect to the nematic director. In ordinary hydrodynamic nematic fluctuations the orientation of the polar-
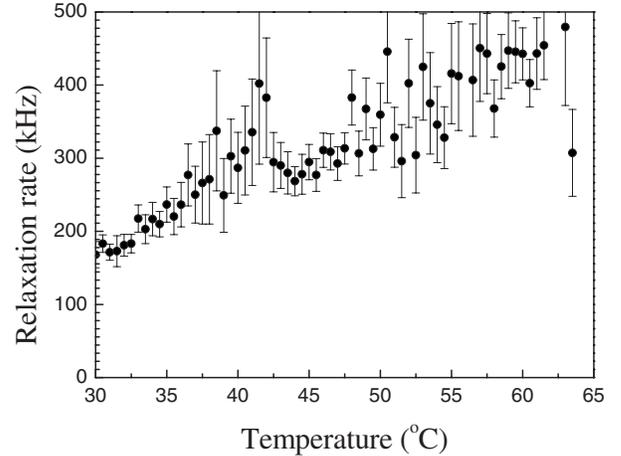

FIG. 4. Relaxation rate of the optic mode versus temperature ($q=6.9\times10^5$ m^{-1}). The relaxation rate does not depend on the scattering vector.

ization of the particles must fluctuate in phase with the nematic director. Obviously in the situation in which the system is described by two vector quantities—nematic director and spontaneous polarization of the ferroelectric particles—there must exist a mode of the nonhydrodynamic optic type where the two vector directions fluctuate in a counterphase.

IV. DISCUSSION

The somewhat naive picture of well-dispersed oriented ferroelectric particles needs some comments. The first is that in the liquid crystal host there are certainly some ions which screen the electric field. We have measured the conductivity of our samples which is not affected by the presence of ferroelectric particles. The ion mobility can be estimated from the known viscosity. We can then estimate that the ion concentration density is $\sim 2\times10^{20}$ m^{-3} and the corresponding Debye screening length about 300 nm. The average distance between the ferroelectric particles is about 200 nm so that the electric field is not substantially screened.

The second problem is the interaction between the electric dipoles of the particles. The interaction caused by director distortion around the particles can be neglected due to the small particle size [16,17] or is an order of magnitude smaller than the electrostatic dipole-dipole interaction between particles. The electrostatic attractive energy between two particles of radius 10 nm and spontaneous polarization of 0.1 A s/m^2, separated by 0.1 μm, is of the order of 1 eV—i.e., much larger than the energy of the thermal motion. Therefore, the ferroelectric particles should aggregate into chains which are on average antiferroelectrically ordered. That the particles may be aggregated in chains is also corroborated by the fact that we were not able to observe translational diffusion of the particles in the nematic or isotropic phase. Translational motion should be visible in the polarized scattering, where we get no signal.

The electric field around a linear chain of polarized spheres decays approximately exponentially with a characteristic length comparable to the particle diameter. This

means that the average internal field is much smaller than in the case of separated particles which is considered below and in [7]. At the same time, the field very close to the chains is still large enough to increase the local nematic order parameter. This local ordering could then propagate from the chains by intermolecular interactions which are enhanced by the increased local order and increase the phase transition temperature T_{NI}, as observed in Ref. [7].

A possible explanation how the particles can remain separated is that they are charged. In such a case the monopolar part of the electric field would additionally enhance the magnitude of the order parameter S, while the dipolar component is responsible for the coupling between the director and **P**. The strong electrostatic potential also restricts the translation motion of the particles so that we cannot observe it. Further experimental and theoretical studies are necessary to clarify the existence and the role of the chains and charge on the particles.

Our results can be explained by assuming that the internal electric field due to the ferroelectric particles couples to the nematic order parameter. If we keep the assumption that the particles are well separated, we can estimate that the average internal field is of the order of

$$E_{int} = \frac{cP_s}{\varepsilon\varepsilon_0} \approx 10^7 \text{ V/m}. \tag{3}$$

At the surface of the particles the field is roughly about 100 times stronger. Such a strong field acts as a generalized thermodynamic force conjugate to the order parameter. So the Landau expansion of the free energy in the scalar order parameter S has the form

$$F = F_0 + \frac{1}{2}\alpha S^2 - \frac{1}{3}\beta S^3 + \frac{1}{4}\gamma S^4 - \delta_1 S E_{int}^2 - \frac{1}{2}\delta_2 S^2 E_{int}^2, \tag{4}$$

where F_0 is the free energy in the isotropic case and α, β, γ, δ_1, and δ_2 the coefficients in the expansion. The first three terms are the usual nematic free energy, which gives a slightly first-order transition. The first coupling term, linear in S, drives the transition to a critical point [15], while the last term simply increases the transition temperature. Both terms increase the magnitude of the order parameter at a given temperature.

As the elastic constants are proportional to S^2 and the dielectric anisotropy to S, this simple model seems to roughly explain the results of the experiment. The above free energy is also a phenomenological version of a more microscopic argument presented in Ref. [7].

The observed high-frequency relaxation rate mode, presented in Fig. 4, can be explained by the following simple model. If we assume that the ferroelectric particles are well dispersed, we can get an estimate for the relaxation rate of the optic mode. The average magnitude of the internal electric field due to the spontaneous polarization P_s is about $cP_s/\varepsilon\varepsilon_0$, where c is the volume concentration of the particles and ε the dielectric constant of the liquid crystal. The free energy density has the form

$$f = f_{nem} + \frac{P_s^2}{2\varepsilon\varepsilon_0} - \frac{\epsilon_a c^2}{2\varepsilon^2\varepsilon_0}(\mathbf{n} \cdot \mathbf{P}_s)^2. \tag{5}$$

The second term is the electric energy while the last one represents the coupling of the nematic director with the internal field. Let Ψ be the angle between $\mathbf{P}_s$ and $\mathbf{n}$; then, for small Ψ we can write

$$f = f_{nem} + \frac{P_s^2}{2\varepsilon\varepsilon_0} - \frac{\epsilon_a c^2 P_s^2}{2\varepsilon^2\varepsilon_0}(1 - \Psi^2). \tag{6}$$

The Ψ^2 term gives rise to an elastic restoring torque for the angle Ψ. Assuming that the viscous drag for the relaxation of Ψ is also governed by the effective viscosity η and using the Landau-Khalatnikov formalism, we get for the optic-mode relaxation rate (at $q=0$)

$$\frac{1}{\tau} = \frac{\epsilon_a c^2 P_s^2}{\varepsilon^2\varepsilon_0\eta}. \tag{7}$$

Assuming $P_s \approx 0.1$ A s/m^2 [14], $\epsilon_a \approx 3$, $\varepsilon \approx 7$, $\eta \approx 0.3$ P, and $c=0.01$, we get for the relaxation rate $\frac{1}{\tau}=2\times10^5$ s^{-1}, which agrees rather well with the experiment.

This model for the observed high-frequency optic mode should be valid also in the case of ordered chains. The nematic director can still fluctuate in the opposite phase with respect to fluctuations of the chains. As the chains should be quite stiff on the length scale of 0.1 μm, the relaxation rate should be governed by the effective anchoring of the director to the chains. This is primarily due to the electric field at the surface of the chains, so we still expect a relaxation rate of the order of 10^5 s^{-1}.

V. CONCLUSIONS

We have presented the results of dynamical light scattering on the colloidal system of nanosized ferroelectric particles in a nematic liquid crystal host. Our results point to a substantial increase in the nematic order parameter in agreement with other measurements in similar systems. We also observe an additional fluctuation mode of optic character—that is, independent of the wave vector—which we interpret as an out-of-phase motion of the nematic director with respect to the ordering of the ferroelectric particles. Arguments on the energetics of the system suggest that the particles should be ordered in chains, which makes an explanation of the observed properties more difficult. Further experiments, primarily small-angle x-ray scattering, are needed to clarify the actual structure of these systems.

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