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Critical behavior of director fluctuations in suspensions of ferroelectric nanoparticles in liquid crystals at the nematic to smectic-*A* phase transition

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By dynamic light scattering we studied the temperature dependence of scattered intensities and relaxation rates for pure twist and pure bend modes in a colloidal system of $BaTiO_3$ single domain nanoparticles and liquid crystal octylcyanobiphenyl (8CB) close to the nematic to smectic-*A* phase transition. From the experiments we obtained the critical exponents for the smectic correlation lengths, which in suspensions differ from the values for pure 8CB. The phase transition temperatures from isotropic to nematic phase (T_{NI}) and from nematic to smectic-*A* phase (T_{NA}) are both affected by the presence of the particles in two ways. The electric field around the ferroelectric particles increases the transition temperatures, whereas the disorder and probably also the excess of the surfactant cause a decrease of the transition temperatures compared to pure 8CB. The net effect is lower T_{NI} and almost unchanged T_{NA} in suspensions. After prolonged exposure to the external field the ferroelectric particles irreversibly aggregate, which results in the decrease of the internal electric field and, consequently, in the decrease of both transition temperatures.

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I. INTRODUCTION

Systems of colloidal particles dispersed in liquid crystals (LCs) present a rich variety of phenomena. Diluted LC colloids of very small ferroelectric particles show particularly interesting effects, such as change in switching behavior, dielectric properties, phase transition temperatures [1,2], and viscoelastic properties [3]. The dielectric constant anisotropy, for instance, can change by a factor of 2 or more [1,4]. 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. [2,5].

It has also been shown that the electrical prehistory of the cells imparts significant polarity sensitivity to the Freedericksz characteristics of the suspensions of the ferroelectric particles in nematic liquid crystals [6]. The threshold voltage for the Freedericksz transition is smaller when the sign of the voltage is the same as used last time compared to the threshold voltage of a virgin cell and is higher when it has the opposite sign. When cycling the sign of the voltage a hysteresis has been observed. This memory can be erased by heating the liquid crystal in the isotropic phase. These experiments show that the suspension in the *nematic* phase behaves as a true ferroelectric with nonzero spontaneous polarization.

The transition between nematic and smectic-*A* (the *N*-Sm*A*) phases is a nontrivial member of the three-dimensional (3D) *XY* universality class. The *N*-Sm*A* critical behavior is affected by the coupling between the smectic order parameter ψ and the nematic order parameter described by the scalar order parameter S and nematic director $\mathbf{n}$; in particular, this coupling affects the order of the phase transition. Owing to the coupling, there are two additional terms in the free energy expansion: the first is the so-called de Gennes coupling term between S and ψ [7], and the second represents the coupling between the nematic director fluctuations $\delta\mathbf{n}$ and ψ [8]. Both can cause the *N*-Sm*A* phase transition to be weakly first order. The critical behavior of the *N*-Sm*A* phase transition has been extensively studied in different liquid crystals by calorimetry, and x-ray and light scattering (for a review see Ref. [9]). These studies revealed a variety of critical exponents of the smectic correlation lengths due to a different magnitude of the coupling constants. Because of the need for systematic control of the coupling strength, many studies have focused on a controlled amount of mesogenic or nonmesogenic impurities incorporated in a chosen liquid crystal, mostly octylcyanobiphenyl (8CB).

The calorimetric studies, for example, have shown that by adding nonmesogenic impurities to liquid crystal 8CB the *N*-Sm*A* phase transition goes from second order in pure 8CB, reaches the Landau tricritical point at a certain concentration of impurities, and becomes a first-order phase transition above that concentration [10–12]. The addition of aerosil particles to liquid crystal 8CB has been shown to greatly reduce or completely suppress the de Gennes coupling [13,14]. While calorimetric studies suggests the *N*-Sm*A* phase transition in 8CB is of second order, the dynamics of propagation of the interface between the phases [15] and the intensity fluctuation microscopy [16] have shown the phase transition is weakly first order. Lelidis [17] has shown that the amplitude of director fluctuations in 8CB can be suppressed by the external electric field so that the second-order character of the transition is restored.

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 relaxation rates proportional to a ratio of the nematic elastic constants K and viscosity coefficients η [7]. By choosing the direction of the wave vector along or perpendicular to the nematic director, the relaxation of pure modes can be observed:

$$\frac{1}{\tau} = \frac{K_i}{\eta_i} q^2, \tag{1}$$

where q is the wave vector and $i = 1,2,3$ denotes splay, twist, and bend viscoelastic properties, respectively. 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, I_s, is proportional to the ratio of the square of the optical anisotropy $\Delta\varepsilon$ and elastic constants,

$$I_s \propto \frac{(\Delta\varepsilon)^2}{K_i q^2}. \tag{2}$$

Optical anisotropy linearly depends on the scalar order parameter $\Delta\varepsilon \propto S$, while elastic constants are proportional to the square of the S, $K_i \propto S^2$. So the temperature dependence of inverse intensity of a given mode at constant scattering vector q gives the temperature dependence of "bare" elastic constants, K_i/S^2. In the nematic phase the bare elastic constants are almost independent of temperature. From the temperature dependence of the relaxation rate the temperature dependence of viscosities can be obtained.

In the smectic-phase bend and twist deformations are expelled due to incompressibility of the smectic planes. In the nematic phase close to the phase transition to the smectic phase the correlation lengths of the smectic pretransitional fluctuations grow exponentially:

$$\xi_{\perp,\parallel} = \xi_{0\perp,0\parallel} \left(\frac{T - T_c}{T_c} \right)^{-\nu_{\perp,\parallel}} \tag{3}$$

and, consequently, the twist and bend elastic constants increase as [18]

$$K_2 = K_{20} + \frac{k_B T q_0^2}{24\pi} \frac{\xi_\perp^2}{\xi_\parallel}, \tag{4}$$

$$K_3 = K_{20} + \frac{k_B T q_0^2}{24\pi} \xi_\parallel, \tag{5}$$

where $q_0 = 2\pi/d$ with d being the thickness of the smectic layers, k_B the Boltzmann constant, and T the temperature. Similarly, also rotational viscosity (also called twist viscosity) diverges [19,20]:

$$\gamma_1 = \gamma_{10} + \frac{\gamma_{30} k_B T q_0^2}{16\pi} \frac{1}{A\xi_\parallel}, \tag{6}$$

where A is the leading coefficient in the Landau–de Gennes expansion of the free energy and γ_{30} is the bare viscosity associated with the relaxation of the smectic order parameter [20]. In the mean field theory $A = a'(T - T_c)$. However, near the N-SmA phase transition the fluctuations are important and critical exponents differ from the mean field theory prediction and, as already pointed out by de Gennes [21], the A in expressions for critical behavior should be replaced by $A \sim a'(T - T_c)^\gamma$. So by measuring the critical behavior of K_2, K_3, and γ_1 the critical exponents $\nu_\perp$, $\nu_\parallel$, and $\gamma \approx \nu_\parallel + \nu_{\gamma_1}$ can be measured. While in many experiments the critical behavior of elastic constants has been measured by static light scattering, the measurements of the critical behavior of rotational viscosity are sparse [22–24] and inconclusive.

The addition of ferroelectric nanoparticles in liquid crystal can affect the N-SmA phase transition in different ways; the electric field around the particles locally increases the scalar order parameter S, whereas the particles cause inhomogeneities that can have similar effects of quenched disorder as caused by aerosil particles, i.e., it reduces the de Gennes coupling.

In this paper we show that insertion of ferroelectric nanoparticles, even in small concentration, causes changes in the critical behavior at the N-SmA phase transitions. We measured the critical exponents of rotational viscosity, twist, and bend elastic constants by dynamic light scattering (DLS) in pure 8CB and in two suspensions of ferroelectric particles in 8CB. After an external ac electric field ($E = 10^6$ V/m, $\nu = 10$ kHz) was applied to the samples, a change of the phase transition temperatures was observed.

II. EXPERIMENT

The stressed ferroelectric particles were obtained by milling larger ($\sim 1\ \mu$m) sized particles together with heptane and oleic acid surfactant so that the resulting particle size was 12 ± 2 nm. The particles were harvested as described elsewhere [25]. It has been shown that the spontaneous polarization of such single domain particles is significantly larger than in the bulk [26,27]. 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 0.2 and 0.4 wt % of $BaTiO_3$ nanoparticles in a liquid crystal 8CB (Synthon GmbH). The number density of the ferroelectric particles in the suspensions was about 3×10^{20} m^{-3} and 6×10^{20} m^{-3}. The value of the spontaneous polarization for the particles is approximately $P_s \simeq 1$ A s m^{-2} [26], while for the bulk $BaTiO_3$ monocrystal $P_s = 0.26$ A s m^{-2} [28]. We could determine the transition temperatures of the suspensions by observation under a polarizing microscope and also during the scattering measurements as the scattering intensity abruptly changes at the transitions. The temperature dependence of the anisotropy of the index of refraction was measured using a polarized microscope in planar cells with a thickness of 20 μm. The sample between the cross polarizers was rotated by 45° and the intensity of monochromatic light transmitted through the sample was measured to determine the phase difference between the ordinary and extraordinary light. An interference filter for $\lambda = 632.8$ nm was used to filter the light from the halogen lamp used in the microscope.

In our DLS 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 measured intensity autocorrelation function $g_2(t)$ is related to the field autocorrelation function $g_1(t)$ by the relation $g_2 = 1 + 2(1 - j_d) j_d g_1 + j_d^2 g_1^2$, where

j_d is the ratio between the intensity of the light that is scattered inelastically and the total scattered intensity. In our measurements j_d was close to 1. The relaxation rate of the electric field autocorrelation function is the relaxation rate of the mode of the director fluctuations [Eq. (1)]. The direction of the scattering vector and the polarization of the incoming and detected light was chosen such that we observed either pure splay, pure twist, or pure 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). By choosing the direction of the scattering vector parallel or perpendicular to the director we can observe pure bend or pure twist modes, respectively. The splay bend mode is visible with both polarizations extraordinarily (ee scattering). Both pure splay and pure twist modes are visible in oe scattering when the director is perpendicular to the scattering plane. In this geometry the ratio of the amplitudes between both pure modes strongly depends on the scattering angle, which can be chosen so the amplitude of one of the modes is much larger than that of the other.

We measured the temperature dependence of the scattered intensity and relaxation rates of the pure modes at a given scattering vector. We started the measurements at a temperature of about 1.5–2 K above the phase transition temperature $T_c = T_{NA}$ and slowly cooled the system so that every 0.01 K the correlation function was measured. Using Eqs. (1) and (2), the temperature dependence of diffusivities, elastic constants, and viscosities were obtained. The viscosity of the twist mode is just the rotational viscosity γ_1, while the viscosities of the bend and splay modes are smaller than γ_1 due to the backflow [7]:

$$\eta_1 = \gamma_1 - \frac{\alpha_3^2}{\eta_b}, \tag{7}$$

$$\eta_3 = \gamma_1 - \frac{\alpha_2^2}{\eta_c}, \tag{8}$$

where $\alpha_{2,3}$ are Leslie viscosities and $\eta_{b,c}$ are Miesowicz viscosities. In pure 8CB the backflow reduces the viscosity of the bend mode by more than a factor of 2, while reduction of the splay viscosity due to the backflow is much smaller (0.7 K above the N-SmA transition, $\gamma_1 = 0.074$ Pa s, $\eta_1 = 0.067$ Pa s, $\eta_3 = 0.036$ Pa s [29,30]).

The effect of the external electric field was studied in homeotropic samples with thickness of 20 μm to which an ac field with frequency $f = 10$ kHz was applied.

III. RESULTS

In Fig. 1 the temperature dependence of the anisotropy of the index of refraction is shown for pure liquid crystal and both suspensions. While the isotropic-to-nematic phase transition temperature T_{NI} decreases in suspensions by 1.5 ± 0.2 K and 2.5 ± 0.2 K for 0.2 wt % and 0.4 wt % $BaTiO_3$, respectively (Table I), we observe no decrease in the N-SmA phase transition temperature T_{NA}. In the 0.2 wt % suspension the N-SmA phase transition temperature even increases by 0.4 ± 0.2 K, while in the 0.4 wt % suspension the transition temperature is within the same experimental error as in pure 8CB. The range of the nematic phase T_{NI}–T_{NA} for this particular liquid crystal decreases with increasing concentration of $BaTiO_3$. The orientational fluctuations in the nematic phase reduce the anisotropy of the index of refraction, Δn. By applying a sufficiently large external field the orientational fluctuations can be suppressed so that they no longer affect Δn and similarly, since the twist and bend fluctuations are expelled in the SmA phase, there is a jump in Δn at the N-SmA phase transition as is clearly visible in Fig. 1 and its inset [17]. We estimated the increase of Δn at the SmA phase transition by fitting the temperature dependence of $\Delta n(T)$ in the nematic phase with $a + b(T_0 - T)^c$. We fixed the parameters b, T_0, and c and then fit the $\Delta n(T)$ just below the N-SmA phase transition to obtain the increase in a, i.e., the increase in the Δn at the phase transition (inset of Fig. 1). In pure 8CB and in both suspensions the Δn increases by the same value of 0.006.

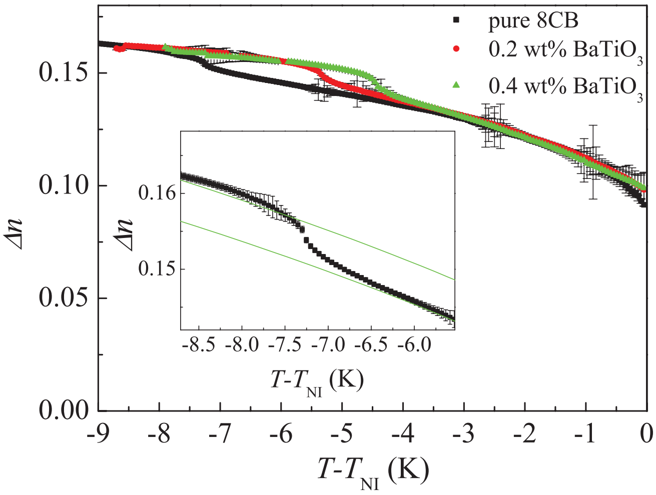

FIG. 1. (Color online) Temperature dependence of the anisotropy of the index of refraction for pure 8CB and both suspensions for $\lambda = 632.8$ nm. Inset: Enlarged region of the N-SmA phase transition for pure 8CB. Lines are the fits (see text).

Figure 2 shows the splay, twist, and bend diffusivity, i.e., the ratio of the elastic constant K_i and the effective rotational viscosity η_i, as a function of temperature close to the N-SmA phase transition in pure liquid crystal and in both suspensions. The measurements were obtained on planar samples in oe scattering. While the values of splay and twist diffusivities in pure 8CB and suspension are almost the same, a decrease of bend diffusivities is observed in suspensions. The reason for that is probably the reduced backflow in suspensions. The nanoparticles in suspensions hinder the backflow, so the viscosities in suspensions are larger [Eqs. (8) and (7)]. Since in pure 8CB only the bend viscosity is significantly smaller than γ_1 due to backflow, only bend diffusivities in suspensions are significantly affected.

We have fit the temperature dependencies of twist and bend elastic constants and viscosities with $a + b(T - T_c)^{-\nu_i}$. The pairs of data for elastic constant and corresponding viscosity were fit simultaneously with the parameter T_c shared. In Figs. 3 and 4 the critical behavior of the twist and bend elastic constants and viscosities with the fits are shown. The critical exponents $\nu_\parallel$, $\nu_\perp$, ν_{γ_1}, and ν_{η_3} are summarized in Table I.

TABLE I. Summary of the results for pure 8CB and both suspensions. The shift of the *N-I* phase transition temperatures in suspensions, nematic range, McMillan's ratio, the critical exponents for correlation lengths parallel and perpendicular to the director, the critical exponents for the rotational and bend viscosity, and $\gamma \approx \nu_\parallel + \nu_{\gamma_1}$ are shown.

	8CB	8CB+0.2 wt % BaTiO$_3$	8CB+0.4 wt % BaTiO$_3$
$T_{NI\text{pure}LC} - T_{NI}$ (K)	0	1.5 ± 0.2	2.5 ± 0.2
$T_{NI} - T_{NA}$ (K)	7.3 ± 0.2	5.4 ± 0.2	4.6 ± 0.2
$\frac{T_{NA}}{T_{NI}}$	0.977	0.983	0.985
$\nu_\parallel$	0.72 ± 0.07	0.48 ± 0.09	0.59 ± 0.1
ν_{K_2}	0.32 ± 0.06	0.65 ± 0.04	0.61 ± 0.06
$\nu_\perp$	0.53 ± 0.07	0.56 ± 0.07	0.57 ± 0.08
ν_{γ_1}	0.44 ± 0.07	0.56 ± 0.1	0.70 ± 0.07
ν_{η_3}	0.52 ± 0.07	0.39 ± 0.09	0.53 ± 0.1
$\nu_{\gamma_1} + \nu_\parallel$	1.16 ± 0.14	1.04 ± 0.19	1.29 ± 0.17

We also measured the dependence of the fluctuations on the external electric field in pure 8CB and in the 0.2 wt % BaTiO$_3$ suspension. An external field was applied to homeotropic cells, so that the direction of the external field was along the director. In the external field in homeotropic cells we have only measured the properties of the twist mode, while the scattered intensity of the bend mode was too low to obtain reliable results. The relaxation rate of the twist mode in the external field in a pure liquid crystal is [7]

$$\frac{1}{\tau} = \frac{K_2}{\gamma_1} q^2 + \frac{\varepsilon_a \varepsilon_0 E^2}{\gamma_1}, \tag{9}$$

where ε_a is the dielectric anisotropy and E the electric field. We have measured the temperature dependence of relaxation rates in pure 8CB using an ac field of amplitude $E_0 = 1$ MV/m and frequency $f = 10$ kHz. The calculated increase of the relaxation rate from Eq. (9) in this case is 480 s^{-1} [Eq. (9)], which is in agreement with the measured value of 540 ± 54 s^{-1} (0.7 K above the *N*-Sm*A* transition). The scattered intensity in the external field decreases as

$$I_s \propto \frac{(\Delta\varepsilon)^2}{K_i q^2 + \varepsilon_a \varepsilon_0 E^2}. \tag{10}$$

The calculated ratio $I_s(E = 0)/I_s(E_0 = 1\text{MV/m}, f = 10\,\text{kHz}) = 1.14$ is the same as the measured one of 1.14 ± 0.01. The critical exponent $\nu_{K_2}(E_0 = 1\text{MV/m}) = 0.56 \pm 0.06$.

We have also measured the relaxation rate and scattered intensity in the 0.2 wt % suspension in the external field of $E_0 = 0.5$ MV/m and $E_0 = 1$ MV/m ($f = 10$ kHz). When the field of $E_0 = 1$ MV/m was switched on, the scattered intensity decreases [$I_s(E = 0)/I_s(E_0 = 1\text{MV/m}, f = 10\,\text{kHz}) = 1.05$) and the relaxation rate increases by 430 ± 43 s^{-1}. However, during the measurement, i.e., continuous exposure to the ac external field, the sample irreversibly changed, as observed in a decrease of both *I-N* and *N*-Sm*A* phase transition temperatures. After the external field was switched off, the phase transition temperatures were also lower than before the exposure to the field by more than 1 K (see Fig. 5). The temperature interval of the nematic range decreases in the external field. In pure 8CB the *N*-Sm*A* phase transition temperature in the field is about 0.1 K lower than without the field, and after the field is switched off the phase transition temperature is the same as before exposure to the field.

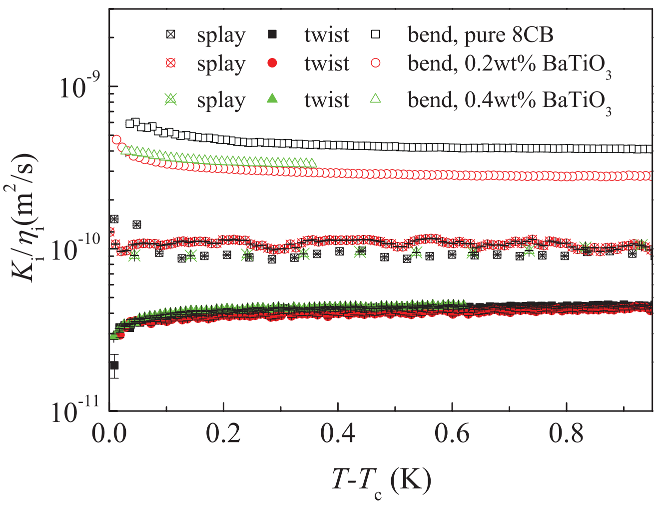

FIG. 2. (Color online) Temperature dependence of the diffusivities for pure 8CB and both suspensions close to the *N*-Sm*A* phase transition.

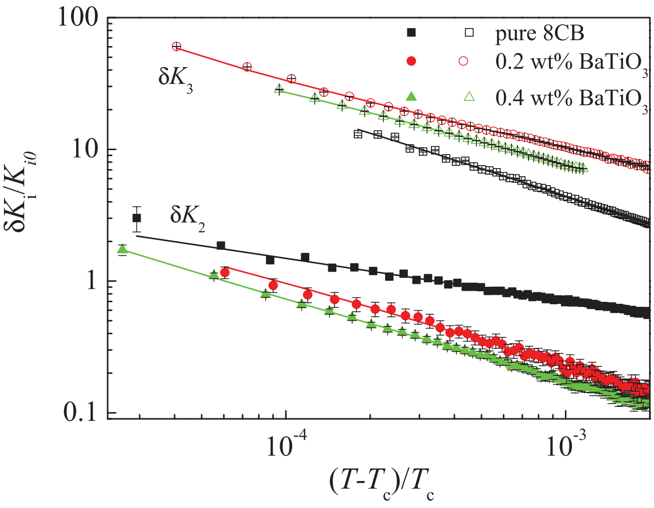

FIG. 3. (Color online) Temperature dependence of the diverging parts of the twist (solid symbols) and bend (open symbols) elastic constants for pure 8CB and both suspensions close to the *N*-Sm*A* phase transition. Lines are the fits (see text).

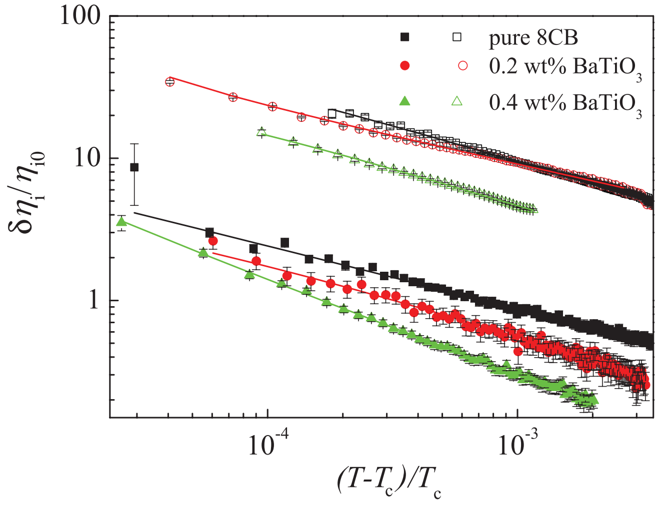

FIG. 4. (Color online) Temperature dependence of the diverging parts of the twist (solid symbols) and bend (open symbols) viscosities for pure 8CB and both suspensions close to *N*-Sm*A* phase transition. Lines are the fits (see text).

IV. DISCUSSION

The electric field around the ferroelectric particles locally induces an increase of nematic order. To evaluate the internal electric field in the liquid crystal we need to consider two things. 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 affected by the presence of the ferroelectric particles. The ion mobility can be estimated from the known viscosity. We can then estimate that the ion concentration density is $\sim 5 \times 10^{21}$ m^{-3} and the corresponding Debye screening length is about 50 nm. The average distance between the ferroelectric particles is about 150 nm so the electric dipole field is screened.

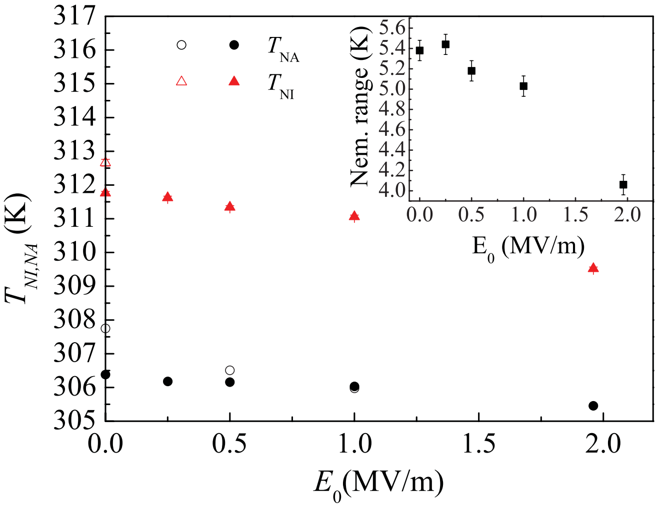

FIG. 5. (Color online) The *I*-*N* and *N*-Sm*A* phase transition temperatures in the external field for the 0.2 wt % suspension. Open symbols show the transition temperatures in zero field before any exposure and at $E = 0.5$ MV/m during the first long exposure to the field. Solid symbols show the transition temperatures during the next exposures to the external field. Inset: The nematic range as a function of external field.

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 [31] or it is an order of magnitude smaller than the electrostatic dipole-dipole interaction between particles. Electrostatic attractive energy between two equally oriented particles of radius 6 nm and spontaneous polarization of 1 A s m^{-2}, separated by 0.15 μm, is in spite of ion screening of the order of 1 eV [32], i.e., much larger than the energy of the thermal motion. It becomes comparable to $k_B T$ at distances of around 300 nm. However, if the direction of the polarization of the particles is random, the average interparticle interaction of the particles is smaller. The ferroelectric particles at least partially aggregate into clusters which are on average antiferroelectrically ordered, as was shown in Ref. [27]. While in the absence of the external field the shape of the clusters depends on the shape of the particles, the aggregates in the external field strong enough to orient the dipoles are chains of the particles or chainlike elongated structures. Aggregates of other shapes have been shown to disaggregate after the application of strong enough external field [27]. 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 in the case of the chains is much smaller than in the case of separated particles.

If we assume that the particles are well separated and there is no ion screening, we can estimate that the average internal field is of the order of

$$E_{\text{int}} = \frac{c P_s}{\varepsilon\varepsilon_0} \approx 4 \times 10^6 \text{ V/m}, \qquad (11)$$

where c is the volume concentration of the particles and ε the dielectric constant of the liquid crystal. At the surface of the particles the field is roughly about 1000 times stronger. In our case the actual average internal field is affected by the screening of the ions and is an order of magnitude smaller. That is why it does not affect the amplitude and the relaxation rate of the fluctuations considerably.

It has been shown that nonmesogenic impurities or aerosil particles in the liquid crystal matrix cause both the *I*-*N* and the *N*-Sm*A* phase transition temperatures to shift to lower values [12,13], while ferroelectric particles can either increase or decrease the *I*-*N* transition temperature [33]. While the increase of the *I*-*N* transition temperature is due to the strong internal field around the ferroelectric particle that increases the nematic order parameter S at given temperature [2], the main reason for a decrease of the *I*-*N* transition temperature, as suggested in Ref. [33], is probably an excess of oleic acid. Our results show that both mechanisms are present in the investigated suspensions and similarly affect both phase transitions. The *N*-Sm*A* phase transition temperature decreases in suspensions only after long exposure (48 h) to external electric field. The external field orients the spontaneous polarization of the nanoparticles and so enhances the attractive interaction between them, which causes, similarly as in the magnetic fluids [34], the formation of chains of particles. Since the interaction between the ferroelectric particles at contact is orders of magnitude larger than k_BT, the particles remain aggregated also after the field is switched off. As already mentioned the average internal field in the suspension of chains is much smaller than in the suspension of separated particles, so the consequence of the formation of the chains is a significant decrease of the average internal field. Since we observe significant decrease of both the *I*-*N* and the *N*-Sm*A* phase transition temperatures after the exposure to the external field, we can conclude that the internal field before the exposure indeed caused the increase of the transition temperatures.

The anisotropy of the index of refraction is proportional to the scalar order parameter S. Unlike in suspension of ferroelectric particles in 5CB [33], where the order parameter in suspensions is the same as in pure 5CB when plotted as a function of $T - T_{NI}$, there are some differences between the order parameter in our suspension and in pure 8CB (Fig. 1). First, at T_{NI} the order parameter in suspensions is slightly larger than in pure 8CB, and second, the order parameter in suspensions increases more steeply with decreasing temperature than in pure 8CB. The equilibrium value of S is given by a minimization of the free energy in the nematic phase, which in the systems with the Sm*A* phase includes also the terms due to the coupling between the nematic and smectic order parameters. The de Gennes coupling increases S by $\delta S = \chi(T)C|\psi|^2$, where C is the strength of the coupling and χ is a response function, which is large close to T_{NI} and smaller farther away from the *I*-*N* phase transition [7]. So a possible explanation for larger S at the *I*-*N* phase transition in the suspensions is larger C. Larger C would also promote the transition to the Sm*A* phase, which explains the smaller nematic range in suspensions. It has been shown that in some mixtures of 8CB and nonmesogenic compounds the coupling between the smectic and nematic order parameter was indeed larger [11].

Our results show that the amplitude of fluctuations is not significantly different in suspensions and pure 8CB. However, the difference between the critical exponents of the correlation lengths along and perpendicular to the director is smaller in the suspensions, which could be a sign that the coupling between the nematic director fluctuations and the phase of the smectic order parameter is weaker in suspensions, similarly as in aerosil gels [14]. But unlike aerosil gels, the values of critical exponents in suspensions are close to the predictions of the mean field theory.

We have also measured the critical exponent of the rotational viscosity. In pure 8CB the critical exponent of the bend viscosity should be the same as for rotational viscosity, since neither α_2 nor η_c are expected to diverge at the *N*-Sm*A* phase transition [19]. Within experimental error our results are the same and are close to the mean field value as was also observed in other measurements [23,24]. The value of the critical exponent γ in pure 8CB of 1.26 [14] can be compared to our results $\gamma \approx \nu_\parallel + \nu_{\gamma_1} = 1.16 \pm 0.14$; however, the experimental error is large, so this point remains inconclusive.

To conclude, we have presented the results of dynamical light scattering on the colloidal system of nanosized ferroelectric particles in a liquid crystal host near the *N*-Sm*A* phase transition. The critical exponents in the suspensions differ from those of pure liquid crystal and their values approach the predictions of the mean field theory. Because of the ferroelectric particles there is an internal electric field in the system. Our results show that the ferroelectric particles during prolonged exposure to the ac external electric field irreversibly aggregate, which results in a decrease of the internal electric field in the system and, consequently, in the decrease of the phase transition temperatures. In suspensions the nematic range is smaller than in pure 8CB, which is probably due to larger coupling between the nematic and smectic order parameters.

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