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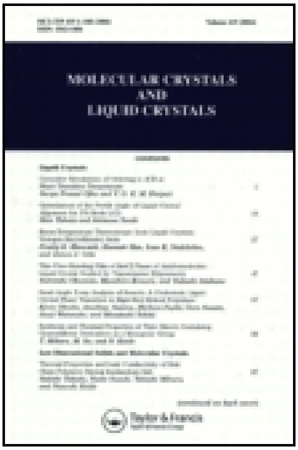

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Dynamic Light Scattering in Liquid Crystal Confined to Cylindrical Pores: Effect of Different Layer Thicknesses and Boundary Conditions

Sarmistha Basu [a] & Fouad Aliev* [a]
[a] Department of Physics, University of Puerto Rico, PR, USA

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DYNAMIC LIGHT SCATTERING IN LIQUID CRYSTAL CONFINED TO CYLINDRICAL PORES: EFFECT OF DIFFERENT LAYER THICKNESSES AND BOUNDARY CONDITIONS

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*Sarmistha Basu and Fouad M. Aliev**
Department of Physics, PO BOX 23343, University of Puerto Rico,
PR 00931, USA

Static and dynamic light scattering methods were applied to study the influence of boundary conditions and layer thickness of 8CB confined to cylindrical pores on phase transitions and relaxation of director orientational fluctuations. The pore surface influence on the properties of confined liquid crystal for radial orientation is stronger than it is for axial orientation. The separation between the first and the second (slow) relaxation processes observed in confined 8CB is clearer for thinner layers and the amplitude of slow process is greater for thinner layers. This suggests that the slow process is surface related director relaxation.

Keywords: confinement; dynamic light scattering; relaxation

INTRODUCTION

Studies of liquid crystals (LCs) confined in porous media have been very useful in exploring both the fundamental physics of condensed matter and in applications. Although a great success was achieved [1] in understanding the physical properties of LCs confined in porous media with different sizes and shapes of pores and different structure of porous matrix, little work has been done to characterize the influence of confinement on the dynamical behavior of LCs. Different aspects of the dynamical behavior of confined LCs can be investigated by photon correlation spectroscopy. It has been shown [2–8] using this method that different kind of confinement strongly influences dynamics of different fluctuations in LCs.

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*Corresponding author. Tel.: 1 (787) 764-0000, ext. 7554, Fax: 1 (787) 756-7717, E-mail: faliev@rrpac.upr.clu.edu

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Confinement has at least a two-fold impact on materials, which is the interaction of the materials with the pore surface and causes the finite size effect (both really strong for liquid crystals). Separating random field effects from finite size effects and from the effects of the influence of pore solid surface on the properties of liquid crystals is often a difficult problem in studying the dynamic process in confined systems. Using cylindrical porous matrices as a tool to change the thickness of confined LC layer permits us to control both the boundary conditions (orientation) of LC at interface and the size of the liquid crystal.

In the investigation of surface/interfacial effects in liquid crystals two important issues are: (1) boundary conditions (i.e. planar-axial or homeotropic-radial orientation of LC molecules on the surface of the solid pore walls of the matrices) and (2) the layer thickness (size of the confinement) of the LC inside cylindrical pores. Variation of the thickness of LC layer formed on pore walls then LC partially fills the pores, allows to control the confining size in a very wide range of scale from 200 nm up to the diameter of single molecule if monolayer is formed on the pore wall.

Investigations of LC in cylindrical pores makes it possible to minimize the role of random field effects dominant in random porous media in order to investigate LC-solid pore wall interface and finite size effect on phase transitions and the dynamic behavior of LC.

The fact that controlled molecular-size effective thickness liquid crystal surface deposition can be formed in the cylindrical cavities of Anapore membrane has been shown in [9,10]. A behavior of mesogenic molecules of 5CB forming thin layers formed on pore walls of Anapore membrane with pore size of 200 nm was investigated for the first time by means of deuteron nuclear magnetic resonance [9,10]. It was found that in the surface coverage range between 0.015 and 0.35 the bulk state and the surface layers coexist. In highly diluted surface deposition molecules lie flat on the surface with reorientation of their molecular axes with a rate within the time scale of 10^{-4} s. Simultaneously, molecules diffuse over the surface. We use the approach of sample preparation developed in [9,10] in order to obtain information on dynamics of cooperative origin–relaxation of director orientational fluctuations in liquid crystal under conditions established in [9,10]. Therefore we limit by 35% filling concentration of liquid crystal and for comparison study samples with pores completely filled with liquid crystal.

In this paper we report on investigations of the influence of different boundary conditions (planar-axial and homeotropic-planar) and the surface layer thickness of liquid crystal, confined in cylindrical pores matrices, on phase transitions and dynamics of director orientational fluctuations.

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EXPERIMENTAL

We have performed photon correlation (dynamic light scattering) measurements using a He-Ne laser operating at wavelength $\lambda = 632.8\,\mathrm{nm}$, and an ALV-5000/Fast digital multiple tau real time correlator with Thorn EMI 9130/100B03 photomultiplier, the ALV preamplifier and single mode optical fiber. The depolarized component of scattered light was investigated. In the dynamic light scattering experiment, one measures the intensity-intensity autocorrelation function $g_2(t) = \langle I(t)I(t+\Delta t)\rangle / \langle I(t)^2\rangle$. The intensity-intensity autocorrelation function $g_2(t)$ is related to the dynamic structure factor f(q,t) of the sample by $g_2(t) = 1 + k|f(t,q)|^2$, where k is a contrast factor that determines the signal-to-noise ratio and $q = (4\pi n/\lambda)\sin(\theta/2)$ (n is the refractive index, θ – the scattering angle). All the dynamic light scattering data discussed below were obtained at $\theta = 35^\circ$. These experiments were complemented with static light scattering measurements that provide information on phase transition.

We used matrices with parallel cylindrical pores (Anopore membranes with pore diameter of 200 nm). We investigated 8CB that has a smectic A phase in the temperature range of 294.2–306.8 K in addition to the nematic range of 306.8–314.4 K. The interaction between 8CB molecules and non-treated pore walls of Anapore membrane provides planar (axial) orientation of the molecules. To obtain homeotropic orientation, we treated the pore walls with lecithin molecules. For this purpose the matrix was dipped in a 2% concentrated solution of lecithin in hexane for an hour. After complete evaporation of hexane the matrix treated with lecithin was impregnated with liquid crystal. The long tail lecithin molecules forced the liquid crystal molecules to take position perpendicular to the pore wall.

Layers of different thickness are formed on the pore walls as a result of controlled impregnation [9,10] of porous matrices with 8CB from solutions of different liquid crystal concentration. When the matrix dried up the hexane molecules evaporated, leaving relatively long and heavy liquid crystal molecules at the surface of the pore wall. In this way, by varying the liquid crystal concentration in the hexane solution, we were able to obtain variable thickness of the surface layers of LC formed on the pore walls. It is natural to assume, at least qualitatively, that the lower the concentration of LC in solution the thinner the LC layer thickness on the surface of the pore wall.

RESULTS AND DISCUSSION

Light scattering is a powerful tool for investigations of bulk and interfacial properties of liquids as well as properties of very thin (of molecular size

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thickness) layers [11,12]. The experimental detection of scattered light in our samples is much simpler than light scattering measurements from flat thin layers of liquids [12] or liquid crystals [13,14] because they have a very developed area of the pore walls (this is what makes these samples an effective experimental tool for investigations of surface properties of liquid crystals) and the signal is collected from many pores inside the illuminated volume. Therefore the signal from the part of the sample that has fluctuations contributing to the light scattering can be detected without serious experimental problems. In the case of weak signals the signal accumulation time can be increased to several hours to provide reasonable averaging. In our samples, the length is unlimited in the direction of the pore axis and all fluctuations of the refractive index that appear within the scattering volume within layer of the thickness much less than the wavelength of probing light will contribute to the measured intensity of scattered light. Static light scattering was successfully applied [13] for investigations of layer thickness-dependent isotropic-nomadic phase transition in flat thin (the thinnest sample had a thickness less than 10 nm –much less than the wavelength of the incident light used in the experiments) layers of 8CB. The theory of nematic director fluctuations of a nematic liquid crystal confined to microcavities was developed [15] and later was modified for applications to light scattering by thin nematic liquid crystal films [16].

To precisely identify isotropic-nematic phase transition temperatures ($T_{I-N)}$ static light scattering experiments were performed first. The intensity of depolarized light scattering at the scattering angle 35° was measured as a function of temperature. The samples were heated to isotropic phase at a temperature of about 15°C above T_{I-N} and the temperature was stabilized until equilibrium was reached. Then we swept the temperature at the rate of 0.005 K/min. Each data point was measured for duration of 10 seconds with corresponding change in temperature of 0.008 K. Therefore these measurements could be considered as quasi-equilibrium. Figure 1 represents comparison of the temperature dependencies of the intensity of scattered light obtained from static light scattering experiment for bulk (curve 1) and confined 8CB for its axial (curve 2) and radial (curve 3) orientations. The figure shows a noticeable shift of T_{I-N} towards lower temperature from bulk to axial and then from axial to radial orientation in confined 8CB. Isotropic-Nematic phase transition temperatures T_{I-N} of bulk, nontreated and lecithin-treated confined 8CB completely filled pores are 314.4 K, 314.16 K and 313.9 K respectively. Figure 1 shows that confinement (both homeotropic and planar boundary conditions) affects I–N phase transition in 8CB liquid crystal and this effect is stronger for homeotropic boundary conditions.

Dynamic light scattering in bulk liquid crystals is well understood [17], and in the nematic phase the main contribution to the intensity of scattered

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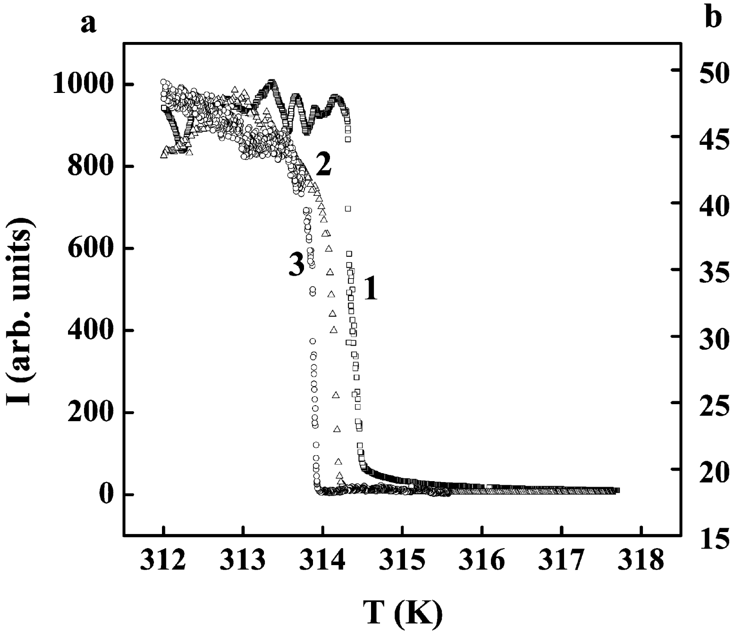

FIGURE 1 Temperature dependence of depolarized component of the intensity of scattered light in 8CB: 1 – bulk (a-axis), confined: 2 – axial orientation (a-axis), 3 – radial orientation (b-axis).

light is due to the fluctuations of director orientations. If, for simplicity's sake we assume that six Leslie coefficients have the same order of magnitude and are $\sim\eta_{\mathrm{eff}}$ (η_{eff} is the effective viscosity), and three elastic constants (bend, splay and twist) are equal to K_{eff} (K_{eff} is the effective elastic constant) then the relaxation time of director fluctuations according to [17] is

$$\tau = \eta_{\mathrm{eff}}/\left(K_{\mathrm{eff}}\mathrm{q}^2\right).$$

The corresponding decay function is single exponential: $f(t,q) = A\exp(-t/\tau)$, where A is the amplitude of the process and τ is the relaxation time.

Figure 2 shows a comparative study of the autocorrelation functions of bulk 8CB in nematic and SmA phases. Consider the autocorrelation functions at T = 306.97 K (in nematic phase – curve 1), and at T = 306.75 K (in SmA phase – curve 2). These temperatures are very close to the nematic-SmA boundary. From these two autocorrelation functions it is clearly seen that for a small difference in temperature ($\Delta T = 0.22$ K) the contrast of the auto correlation function just at SmA phase (at T = 306.75 K) decreases by 60% than that of the autocorrelation function in nematic phase (at T = 306.97 K). The auto correlation function obtained

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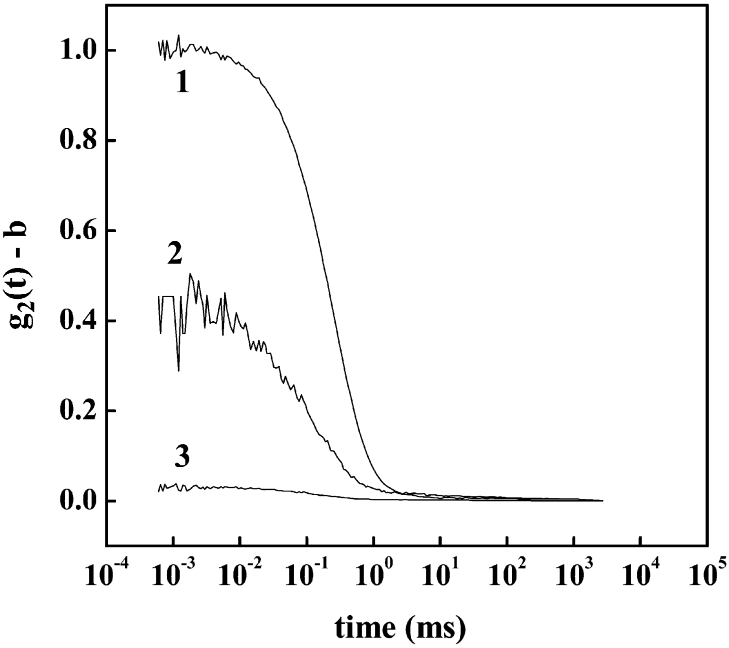

FIGURE 2 Intensity/intensity autocorrelation functions for bulk 8CB: 1 – nematic phase, T = 306.97 K; 2 and 3 – smectic-A phase, T = 306.75 K, T = 300.28 K respectively.

at T = 300.28 K (curve 3) corresponds to deep SmA phase and shows "freezing" of the process due to director reorientational fluctuations. In the nematic phase of bulk 8CB the observed relaxation process due to director fluctuations is single exponential (curve 1) with relaxation time $\tau = 0.64$ ms, in agreement with the theory [10].

The process due to the director orientational fluctuations in the SmA phase is almost frozen and therefore the contrast is drastically reduced. This is because in the SmA phase a layered structure is formed that is rigid and more viscous than nematic phase. Therefore in the SmA phase the molecular fluctuations as well as director fluctuations are more hindered than they are in the nematic phase, resulting in substantial "freezing" of director fluctuations.

The experiments show significant changes in the physical properties of confined LC. The difference between the dynamic behavior of confined and bulk LC in nematic phase, observed in photon correlation experiments, can be seen by comparing curves (a)–(c) in Figure 3. Due to the large pore size of the matrix it is obvious that some bulk-like properties will be observed in confined 8CB. Indeed the first relaxation process in confined 8CB (curves b

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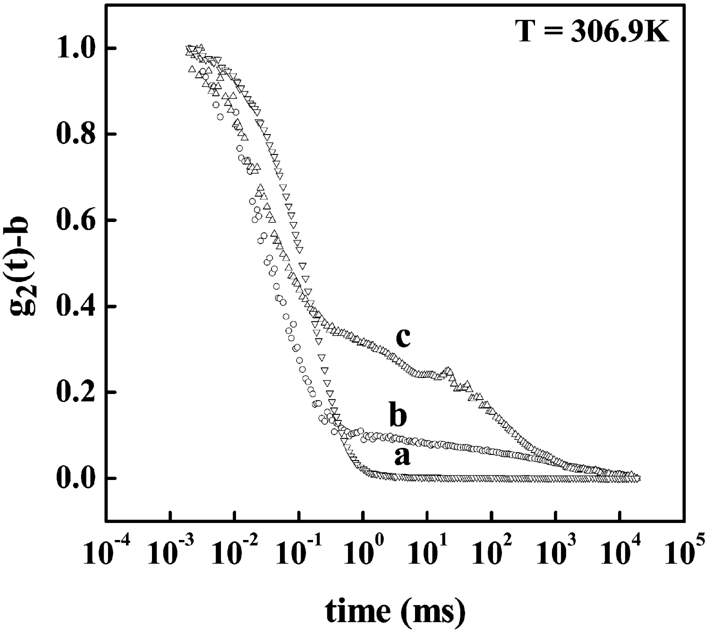

FIGURE 3 Normalized intensity/intensity autocorrelation functions of 8CB in nematic phase: (a) bulk, (b) confined – axial orientation, (c) confined – radial orientation.

and c) is close to the relaxation due to director orientational fluctuations in bulk 8CB (curve a) and it has the same physical origin. However the bulk-like relaxation process in confined 8CB the bulk-like relaxation process is different from to the process observed inbulk 8CB. The decay of autocorrelation functions in bulk 8CB was single exponential but in confined 8CB the process was broaden and stretched exponential. Moreover, in the confined 8CB slow relaxation process, which does not exist in the bulk LC, a broad spectrum of relaxation times appear for both axial and radial orientations. The second relatively slow relaxation process is most likely due to the fluctuations of director orientations in liquid crystal layers nearest the pore wall surface. It is clear from Figure 3 that the relaxation processes in confined 8CB are highly nonexponential, as it is usually observed in glasses and glass-like systems. The autocorrelation functions for confined 8CB can be described by superposition of two stretched exponential functions

$$\mathrm{f(t, q) = A\exp[-(t/\tau_1)_1^{\beta}] + (1 - A)\exp[-(t/\tau_2)_2^{\beta}]},$$

where A is the amplitude of the first process due to of the contribution from relaxation of bulk-like director reorientational fluctuations (we use $A = A_1$)

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and $A_2 = (1 - A)$ is the amplitude of the slow process (because $A_1 + A_2 = 1$). The amplitude of the relaxation process is proportional to the volume fraction of the material contributing to this process.

The relaxation times τ_1 and τ_2 characterize the first and the slow (second) relaxation processes respectively, and the fitting parameters β_1 and β_2 determine the degree of the stretching of the decay function. The values of β_1 and β_2 for confined 8CB are about 0.7 and 0.3 respectively. The relaxation times of the second slow process are of order of magnitude of 1 second for both samples. The amplitude of the slow decay and its contribution to the measured autocorrelation function is greater for radial orientation ($A_2 = 0.4$) than it is for axial ($A_2 = 0.18$) orientation. Thus, from Figure 3 we can conclude that for homeotropic boundary conditions of confined 8CB, the influence of pore wall-liquid crystal interactions on the properties of the surface layer is stronger than it is for the axial boundary conditions.

Figure 4 illustrates the influence of different boundary conditions on smectic ordering in confined liquid crystal from the dynamic point of view. To show this influence on the relaxation processes we choose two

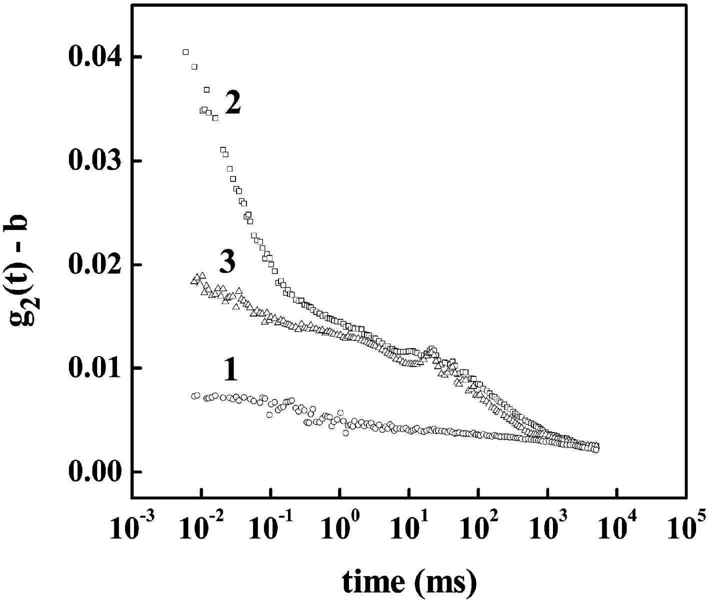

FIGURE 4 Intensity/intensity autocorrelation functions of confined 8CB: 1 – axial orientation, T = 306.7 K; 2 – radial orientation, T = 306.7 K; 3 – radial orientation, T = 305.5 K.

autocorrelation functions for confined 8CB in axial (curve 1) and radial (curve 2) orientations at a particular temperature T = 306.7 K that corresponds to bulk SmA phase of 8CB. For the axial boundary condition the first bulk-like relaxation process is almost frozen (curve 1) due to formation of smectic layers in liquid crystal. In lecithin treated sample with radial boundary conditions, at the same temperature, we can see substantial relaxation (amplitude of which is about 4%) caused by director fluctuations, which is typical for nematic phase (curve 2). In this sample the contribution from the first process decreases (curve 3) due to smectization of LC at a lower temperature (T = 305.5 K) than it does for the sample with axial boundary conditions. Therefore one might conclude that confined 8CB with radial orientation switches from the nematic to the SmA phase at a lower temperature than confined 8CB with axial orientation and that different boundary conditions differently affect N-SmA phase transition in confined 8CB.

If the slow process is associated with director relaxation in surface layers then it is naturally to assume that this relaxation should be affected by the liquid crystal layer thickness. To investigate this influence samples with 8CB partially filling cylindrical pores [9] were prepared. We filled pores with 8CB from its solution in hexane of different concentrations: 35%, 16%, 10% and 3.5%. The samples were identified as per as their concentrations in the respective solutions. For example, the sample identifier 8CB(n%) means that the filling concentration was n%. It is obvious that the lower the concentration the thinner liquid crystal layer on the pore wall. We have undertaken the static light scattering measurements for all four samples keeping all experimental conditions (e.g. scattering angle, cooling rate of the samples) the same. Figure 5 shows the temperature dependencies of depolarized intensity of scattered light for 8CB(35%) along with 8CB(100%) – axial boundary conditions. While presenting the data, selective temperature range was plotted to clearly show the allied peaks. Samples with pores partially filled with 8CB exhibit interesting features that are very different from the features of 8CB(100%) and bulk 8CB. The phase transition (I–N) appeared as a peak on the temperature dependence of the intensity of scattered light for matrices with pores partially filled with 8CB, which is typical for the second order phase transition. The temperature of I–N phase transition (irrespective to the order of this transition) decreased with the decrease in layer thickness of liquid crystals. The possible change of the order of the phase transition, as observed in our experiment, is a new phenomenon. Further research is needed to obtain a additional insight into this observation.

Figure 6 shows the normalized intensity/intensity autocorrelation functions (at T = 309.0 K) for the above samples with five different filling concentrations. Note that the separation between the first and the second

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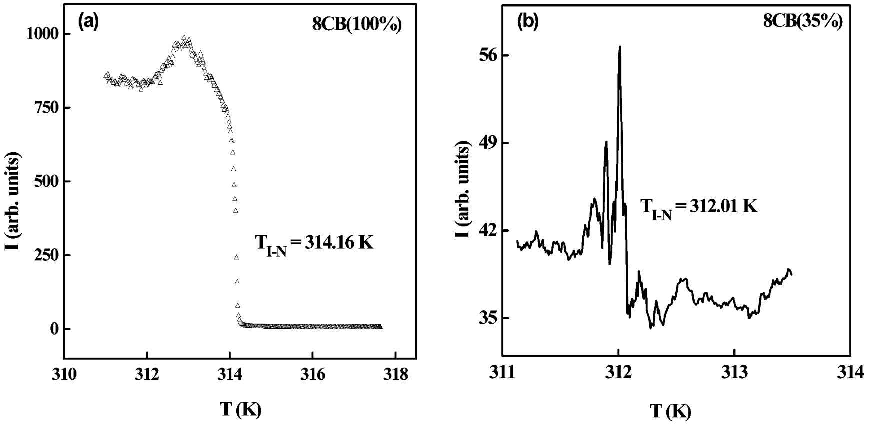

FIGURE 5 Temperature dependence of depolarized intensity of scattered light in confined 8CB – axial orientation completely and partially filling pores: (a) – 100%, and (b) –35%.

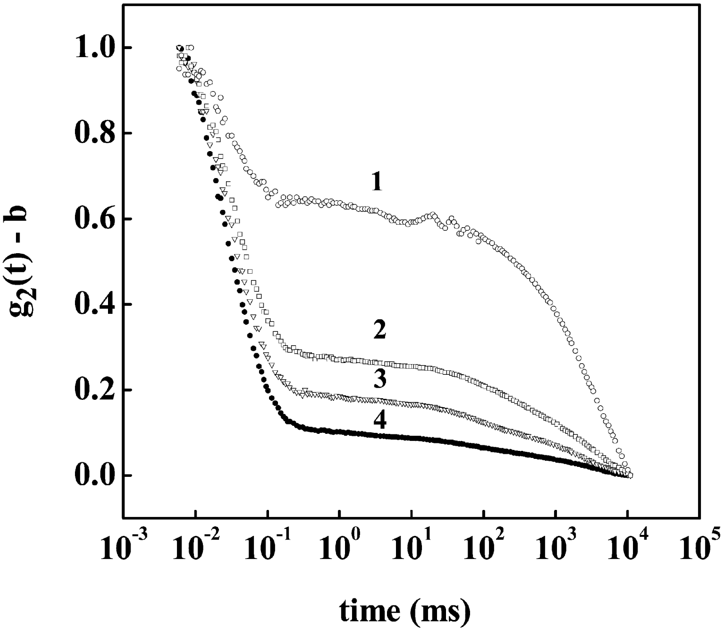

FIGURE 6 Normalized intensity/intensity autocorrelation functions confined 8CB – axial orientation, partially filling pores: 1–3.5%, 2–10%, 3–16%, and 4–35% concentrations of liquid crystal at T = 309.0 K.

(slow) processes is more distinct for thinner layers and the amplitude of the contribution of the slower process increases with the decrease of liquid crystal layer thickness. The slow process is most prominent for the sample with the lowest filling concentration of 8CB – the thinnest layers of LC formed on the pore walls.

CONCLUSION

Variations of both the boundary conditions on pore walls and the thickness of liquid crystal layers formed on pore walls allow investigations of the details of the interfacial properties of confined liquid crystals. The phase transition temperatures of confined liquid crystal depend on the molecular orientation as well as the LC layer thickness on pore walls: the temperature of I–N phase transition decreased with the decrease in liquid crystal layer thickness inside the pore. The influence of both boundary conditions and LC layer thickness on *N-SmA* phase transition is stronger than on *I–N* phase transition.

Two well-defined relaxation processes were observed in DLS experiments for confined LCs in the nematic phase. The first process is qualitatively associated with bulk-like nematic director fluctuations. The second relaxation process (with relaxation time slower than the first one) is most likely due to the fluctuations of director orientations in layers nearest to the pore wall surface. For homeotropic (radial) boundary conditions of confined liquid crystal, i.e. if the molecules of liquid crystal are oriented perpendicular to the pore walls, the influence of the pore wall-liquid crystal interactions on the properties of the surface layers is stronger than it is for axial orientation. For samples with pores partially filled with 8CB the amplitude of slow process is greater for thinner layers. This suggests that the slow process is surface-related relaxation of fluctuations of director orientations.

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