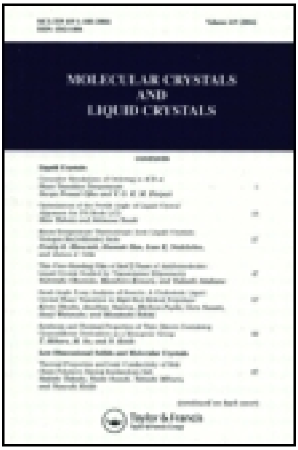

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Glass-Like Relaxation in Confined Liquid Crystals

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We have investigated the dynamics of reorientations of molecules due to their rotation around short axes and dynamics of director fluctuations (collective mode) in 5CB confined in porous matrices with randomly oriented, interconnected pores of average size 100 Å. The confinement strongly influences the dynamics of molecular and collective modes and has resulted in qualitative changes in 5CB properties. Deep supercooling of 5CB in pores up to 150 degrees below the bulk crystallization temperature was observed. The relaxation rate of the process due to the molecular rotation in deeply supercooled state is slower than at the temperatures corresponding to nematic phase by many orders of magnitude. This slowing down is accompanied by anomalous broadening of the spectra. The temperature dependencies of relaxation times of both processes obey the Vogel-Fulcher law suggesting that confined 5CB has dynamic features typical for glass-like behavior although in bulk it is a non glass former.

Keywords: confinement; glass-like behavior; relaxation

INTRODUCTION

The effect of confinement and the influence of a very developed interface in porous media on liquid crystals have brought about great deal of achievements and controversies over the past years. A variety of new properties and phenomena were discovered and studied in these materials. Although there has been great success in the investigations of the physical properties of confined liquid crystals [1,2], there are still open questions in the understanding of the influence of confinement on the dynamical behavior of anisotropic liquids.

The difference between dynamic behavior of bulk and confined liquid crystals may be of a fundamental character. In the first study [3] of nematic ordering of 8CB in sintered porous silica by the dynamic and static light scattering it was found that the confinement significantly changes the dynamic properties of LCs. Two new phenomena were observed. The system shows the slow relaxation process with wide spectrum of relaxation times and this slow dynamics is glasslike that is resulted in non-Debye relaxation and Vogel-Fulcher type temperature dependence of relaxation times. Later the slow process has been observed in different confined LC systems, such as: aerogel host [4,5]; cylindrical pores [6] and polymer-dispersed liquid crystals [7,8]. Dielectric investigations [9,10] of relaxation of molecular origin show that there is an evidence for broadening of dielectric spectra and deviations from Debye -like behavior in confined 5CB.

In present study the dynamic behavior of liquid crystals confined in porous matrix with randomly oriented, interconnected pores have been investigated by means of dielectric spectroscopy and photon correlation spectroscopy. These two methods provide complementary information on dynamical properties of material: dielectric spectroscopy probes the relaxation due to the reorientations of polar molecules of 5CB while the photon correlation spectroscopy provides an information on the fluctuations of director orientations in this material. The experimental results show that in confined LC there are qualitative changes resulted in the appearance of glasslike dynamical behavior, although bulk LC does not have glassy properties either in anisotropic or in isotropic phases.

EXPERIMENTAL

We used porous silica glass with randomly oriented and interconnected pores with mean pore size of 100 Å and volume fraction 27% as matrix for confinement. This matrix was a solid plate with polished surfaces. The sample was optically transparent and multiple scattering effects were observed in photon correlation experiments. We impregnated these porous glasses with 5CB at temperatures corresponding to isotropic phase. The bulk 5CB has a nematic phase in the temperature range of 22.5-35°C.

Measurements of the real (ϵ') and the imaginary (ϵ'') parts of the complex dielectric permittivity in the frequency range 10^{-3} Hz to 1.5 GHz were performed using two sets of devices. In the range from 10^{-3} Hz to 3 MHz we used the Schlumberger Technologies 1260 Impedance/Gain-Phase Analyzer in combination with Novocontrol Broad Band Dielectric Converter and an active sample cell (BDC-S). The sample was mounted between two gold plated parallel plates and placed in the shielded cell. For measurements in the frequency range 1 MHz-1.5 GHz we used Hewlett-Packard 4291A rf Impedance Analyzer. We focus on the results obtained in high frequency range that corresponds to the relaxation of molecular origin due to the rotation of molecules around their short axis. For the quantitative analysis of the dielectric spectra the Havriliak-Negami function [11] has been used. For the case of more than one relaxation process, taking into account the contribution of the dc conductivity to the imaginary part of dielectric permittivity, the Havriliak-Negami function is given by

$$\epsilon^* = \epsilon_\infty + \sum_j \frac{\Delta\epsilon_j}{[1 + (i2\pi f\tau_j)^{1-\alpha_j}]^{\beta_j}} - i\frac{\sigma}{2\pi\epsilon_0 f^n}, \qquad (1)$$

where ϵ_∞ is the high-frequency limit of the permittivity, $\Delta\epsilon_j$ the dielectric strength, τ_j the mean relaxation time, and j the number of the relaxation process. The exponents α_j and β_j describe the symmetric and asymmetric distribution of relaxation times. The term $i\,\sigma/2\pi\epsilon_0 f^n$ accounts for the contribution of conductivity σ, with

n as fitting parameter.

Photon correlation measurements were performed using a $\lambda = 0.6328 \mu m$ He-Ne laser and the ALV-5000/Fast Digital Multiple Tau Correlator (real time) operating over delay times from 12.5 ns up to 10^3 s with the Thorn EMI 9130/100B03 photomultiplier and the ALV preamplifier. In the dynamic light scattering experiment, one measures the intensity-intensity autocorrelation function

$$g_2(t) = \langle I(t)I(0)\rangle / \langle I(0)\rangle^2. \tag{2}$$

The intensity-intensity autocorrelation function $g_2(t)$ is related to the dynamic structure factor f(q,t) of the sample by

$$g_2(t) = 1 + kf^2(q,t), \tag{3}$$

where k is a contrast factor that determines the signal-to-noise ratio and $q = 4\pi n \sin(\Theta/2)/\lambda$, ($n$ is the refractive index, Θ - the scattering angle). We found that the intensity-intensity autocorrelation functions were q-independent for LC in porous glass, and almost q-independent in cylindrical pores. All dynamic light scattering data that we discuss below were obtained at $\Theta = 30^o$.

The lowest accessible temperature in dielectric experiment was about 130 K. In photon correlation spectroscopy experiment the lowest temperature was 265 K. The temperature stabilization in both experiments was better than 0.01°C.

DIELECTRIC RELAXATION

It is known that bulk 5CB is a non-glass former and does not have a glass transition. In the liquid crystalline phase of bulk 5CB there are two dielectrically active relaxation processes of molecular origin [12-16]. For a geometry in which the electric field **E** is parallel to the director **n** i.e. $\mathbf{E} \| \mathbf{n}$, the Debye type process due to the restricted rotation of the molecules about their short axis exists. The characteristic frequency of this process is ~ 5 MHz and the temperature dependence of the corresponding relaxation times obeys empirical Arrhenius equation. For the geometry in which the electric field **E** is perpendicular to the director **n**, $\mathbf{E}\perp\mathbf{n}$ the most prominent relaxation process with characteristic frequency about 70 MHz was observed, which has been attributed to the tumbling of the molecules about their molecular short axis [11]. No dielectrically active collective modes are present in bulk 5CB.

The dielectric spectroscopy investigations show that the behavior of 5CB confined in random pores is very different from its bulk behavior. At least four relaxation processes were identified. In the temperature range, corresponding to the bulk nematic phase, these processes are observed in the following frequency ranges: a broad low frequency relaxation process in the frequency range from 10^{-1} to 10^4 Hz, a second low frequency process in the frequency range from 10^4 to 10^6 Hz, a very clear process in the MHz frequency range and the last one in the frequency range f >30 MHz. All the four relaxation processes are of non-Debye-type. We suggest that the first (slowest) relaxation process is the relaxation of the interfacial polarization arising at the pore wall-LC interface. The second low frequency relaxation process in pores that does not exist in bulk LC is due to the rotation of molecules, located in the surface layer formed at the pore walls. This process is slower than the process due to rotation of molecules in bulk because the viscosity in surface layers is greater than the bulk viscosity.

The dielectric spectra for last two "bulklike" processes in MHz and 100 MHz frequency range are presented in Fig. 1. The first of those, most well established process, is due to the rotation of molecules about their short axis and the second one is due to the tumbling of the molecules about their molecular short axis. Because of random

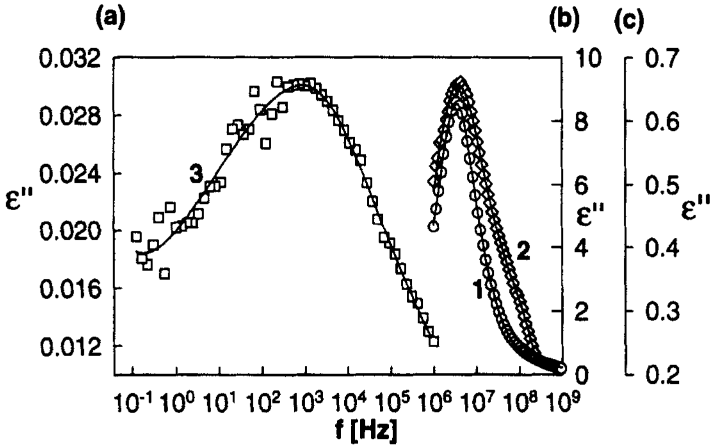

FIGURE 1: Dielectric spectra of 5CB: (1) - bulk, T = 303 K, (2) and (3) - confined in 100 Å random pores at T = 303 K and T = 153 K respectively.

distribution of the pores in the matrices, there are molecules oriented both parallel as well as perpendicular to the direction of probing electric field, independently of alignment of LC on pore walls. Therefore the dielectric behavior typical for two geometries **E**||**n** and **E**⊥**n** is detected in the same experiment. These two processes are strongly modified by confinement, while they are due to the same mechanism as in bulk. The Debye relaxation function ($\alpha = 0$ and $\beta = 1$ in eqn. 1) does not describe bulklike relaxation processes in pores and the parameters α were ≈ 0.5 at T = 153 K and ≈ 0.3 at 303K while for bulk 5CB $\alpha = 0$. The parameter β was equal to 1 for all cases.

The dielectric function describing confined 5CB is similar to that for glass forming systems. This is clearly seen in the time domain representation. Figure 2 (a) shows the experimental data for 5CB in 100 Å pores obtained by the frequency domain measurements converted to the time domain representation. These data are described by the dipole moment/dipole moment autocorrelation function $\Psi(t) = \langle\mu(t)\mu(0)\rangle/\langle\mu(0)\rangle^2$ that in our case is a superposition of two stretched exponential functions:

$$\Psi(t) = a \cdot exp(-(t/\tau_1)^{\beta_1}) + (1-a) \cdot exp(-(t/\tau_2)^{\beta_2}). \qquad (4)$$

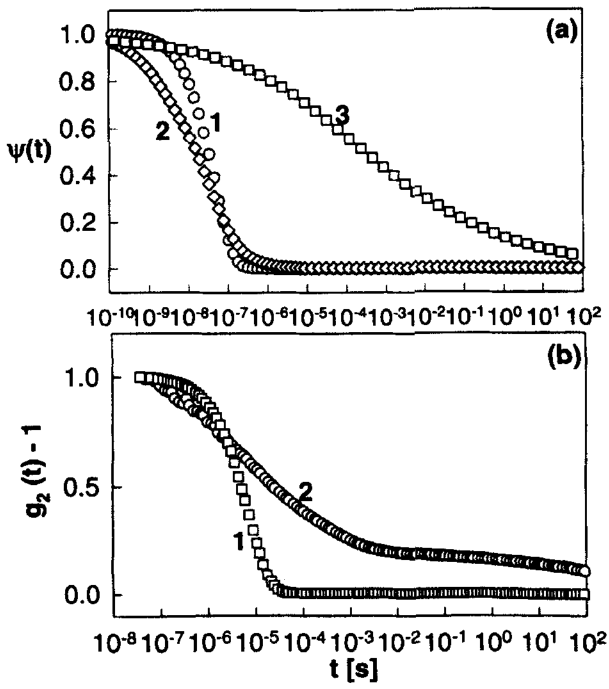

FIGURE 2: (a) - Autocorrelation functions of 5CB. (a) - Dipole moment/dipole moment autocorrelation function: (1) bulk, T= 303 K, (2) and (3) confined in 100 Å random pores at T= 303 K and 153 K respectively. (b)- The normalized intensity/intensity autocorrelation functions measured at 295.8 K: (1) bulk, (2) - confined.

The transformation to the time domain is done by using the step answer function

$$\Psi(t) = \int_0^\infty G(\tau)\exp\left(-\frac{t}{\tau}\right)d\tau, \tag{5}$$

where the relaxation time distribution function $G(\tau)$ for a superposition of j Havriliak-Negami terms is calculated by

$$G(\tau) = \frac{\sum_{i=1}^{j}\Delta\epsilon_i g_i(\tau)}{\sum_{i=1}^{j}\Delta\epsilon_i}. \tag{6}$$

The relaxation time distribution function for a single Havriliak-Negami term with parameters $\alpha_i, \beta_i, \tau_{0i}, \Delta\epsilon_i$, is obtained as

$$g_i(\tau) = \frac{(\tau/\tau_{0i})^{\beta_i\alpha_i}\sin(\beta_i\Theta_i)}{\pi\tau[(\tau/\tau_{0i})^{2\alpha_i} + 2(\tau/\tau_{0i})^{\alpha_i}\cos(\pi\alpha_i) + 1]^{\beta_i/2}}, \tag{7}$$

where

$$\Theta_i = \arctan\left(\frac{\sin(\pi\alpha_i)}{\tau/\tau_{0i} + \cos(\pi\alpha_i)}\right), \tag{8}$$

and $0 \le \Theta \le \pi$.

The values of $\bar{\beta}_1$ and $\bar{\beta}_2$ are varying form 0.5 to 0.2 depending on the temperature indicating broadening of the dielectric spectra in confinement.

Figures 1 and 2 (a) show dramatic changes in the rate of the molecular relaxation processes in supercooled state. The relaxation times of molecular process in the supercooled state change by many orders of magnitude compared to τ obtained at the temperature corresponding to the nematic phase. This slowing down is accompanied by the considerable broadening of dielectric spectra and the decay function.

Rigorous data analysis shows that the temperature dependence (Fig. 3 a) of the relaxation times reorientations of molecules due to their rotation around short axes obeys the Vogel-Fulcher law [17]:

$$\tau = \tau_0 exp(B/(T - T_0)), \tag{9}$$

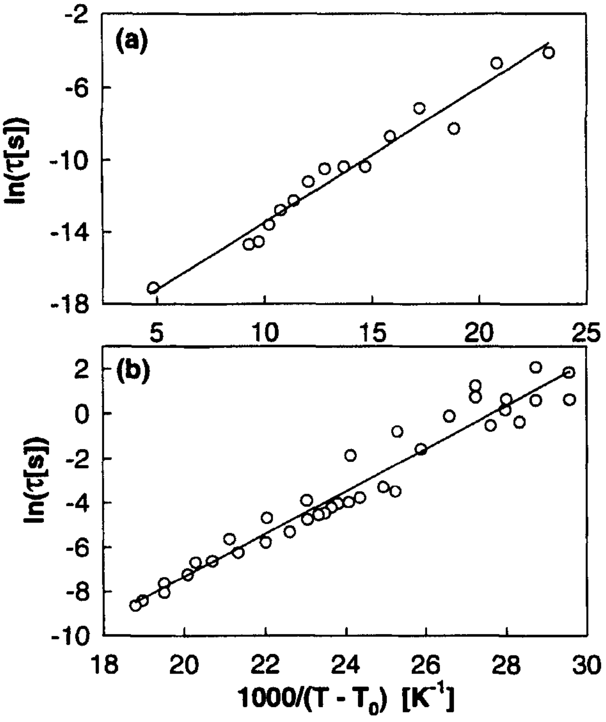

FIGURE 3: Temperature dependencies of relaxation times. (a) - dielectric spectroscopy, (b) - photon correlation spectroscopy. Symbols - experiment, solid lines - fitting.

with the fitting parameters: $\tau_0 = 8.3 \cdot 10^{-10} s$, $B = 745$ K and $T_0 = 90$ K. The temperature dependencies of the relaxation times corresponding to the most low frequency process and to the surface process (τ_1 and τ_2) are also of non Arrhenius type and obey the Vogel-Fulcher law. The fitting parameters describing the temperature dependence of τ_1 and τ_2 are: $\tau_{01} = 4.7 \cdot 10^{-6}$ s, $B_1 = 1105$ K, $T_{01} = 198$ K and $\tau_{02} = 8.5 \cdot 10^{-10}$ s, $B_2 = 960$ K, $T_{02} = 188$ K.

PHOTON CORRELATION SPECTROSCOPY

Dynamic light scattering in bulk LCs is well understood [18], and in the nematic phase the main contribution to the intensity of scattered light is due to the director fluctuations. In the single constant approximation, the relaxation time of director fluctuations is $\tau = \eta_{eff}/K_{eff}q^2$, there η_{eff} is the effective viscosity, and K_{eff} is the effective elastic constant. The corresponding decay function is single exponential.

The experiments show significant changes in the dynamic 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 (1) and (2) in Fig. 2 (b).

In nematic phase of bulk 5CB the observed relaxation process due to director fluctuations is single exponential (curve 1) in agreement with the theory [18]. The slow relaxation process which does not exist in the bulk LC and a broad spectrum of relaxation times appear for confined 5CB. It is clear from Fig. 2 (b) that the relaxation process in confined 5CB is highly nonexponential, as it is usually observed in glasslike systems. The long time tail of relaxation process for 5CB in pores can not be described by using standard form of dynamical scaling variable (t/τ) and the decay function cannot be reduced to a superposition of finite number of exponential terms. It is reasonable for so slow dynamics and such a wide spectrum of relaxation times to use ideas [3,19] of activated dynamical scaling with the scaling variable $x = lnt/ln\tau$. The decay function:

$$f(q,t) = a \cdot exp(-x^z), \tag{10}$$

where $x = ln(t/\tau_0)/ln(\tau_2/\tau_0)$, and in our case $\tau_0 = 10^{-8}s$ provides suitable fitting for confined 5CB. The relaxation time of the slow process for 5CB in 100 Å pores strongly increases with temperature decrease from 300 K up to 270 K varying from 0.1 ms to 14 s in this temperature range (see Fig.3 b).

The data analysis shows that the temperature dependence of the relaxation times for 5CB in 100 Å random pores measured in photon correlation spectroscopy experiment, in the temperature interval (270-300) K, obeys the Vogel-Fulcher law: with parameters: $\tau_0 = 3.1 \cdot 10^{-12} s$, $B = 960$ K and $T_0 = 246$ K.

CONCLUSION

The dielectric and photon correlation spectroscopy experiments show significant changes in the physical properties of liquid crystal confined in porous media. The slow relaxation process that does not exist in the bulk phase and the process due to the presence of surface layer at the solid pore-wall liquid crystal interface, in which the dynamics of molecular motion is different from that in the bulk, were observed. Two bulklike molecular relaxation processes were found considerably modified by confinement. All the observed relaxation processes are non-Debye-type processes and have features typical for glasslike behavior.

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