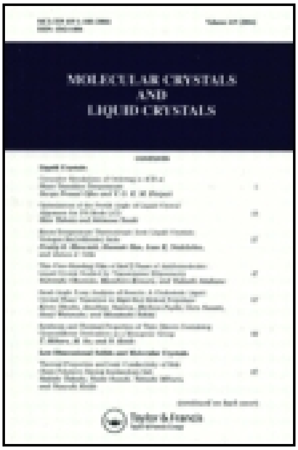

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Non-Debye Relaxation and Glass-Like Behavior of Confined Liquid Crystals

Fouad Aliev[a] & Ghanshyam Sinha[a]

[a] Department of Physics, UPR, San Juan, PR, 00931, USA

Version of record first published: 24 Sep 2006

To cite this article: Fouad Aliev & Ghanshyam Sinha (2001): Non-Debye Relaxation and Glass-Like Behavior of Confined Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 364:1, 435-442

To link to this article: http://dx.doi.org/10.1080/10587250108025013

Mol. Cryst. and Liq. Cryst., 2001, Vol. 364, pp. 435-442
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint,
a member of the Taylor & Francis Group.
Printed in the USA

Non-Debye Relaxation and Glass-Like Behavior of Confined Liquid Crystals

FOUAD ALIEV and GHANSHYAM SINHA

Department of Physics, UPR, San Juan, PR 00931, USA.

We report on non-Debye relaxation of fluctuations of director orientations observed in dynamic light scattering experiments for 5CB confined to random pores with average pore sizes of 100Å and in 5CB filled with Aerosil particles. The relaxation due to reorientations of molecules around short axes investigated by means of dielectric spectroscopy is also found to be of non-Debye type in confined 5CB. Deep supercooling of 5CB below the bulk crystallization temperature was observed in pores. 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 and shows glass-like temperature dependence.

Keywords: confinement; glass-like behavior; relaxation

INTRODUCTION

Despite of great success in the investigations of the physical properties of confined liquid crystals (LCs) [1], 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 LCs may be of a fundamental character. In the first study [2] of the nematic ordering of 8CB impregnating sintered porous silica by the dynamic light scattering (DLS) it was found that LC shows orientational glasslike dynamics. Later the non-Debye relaxation has been observed in different confined LC systems, such as: random pores [3,4]; cylindrical pores [5] and polymer-dispersed LCs [6,7]. Dielectric investigations [8,9] 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 this paper we present some evidence of glass-like relaxation behavior in confined and filled LCs. These systems are anisotropic (at least at short scales) and heterogeneous materials characterized by a very developed interface. Two techniques: DLS and dielectric spectroscopy (DS) were applied, providing a complementary information on dynamical properties of LC. DS probes the relaxation due to the reorientations of polar molecules of 5CB while DLS provides an information on the fluctuations of director orientations in this material.

EXPERIMENTAL

We used porous silica glass with randomly oriented and interconnected pores with mean pore size of 100 Å and volume fraction of pores 27% as matrix for confinement. The matrix was impregnated with 5CB at temperatures corresponding to isotropic phase. Additionally we have applied DLS for investigations of 5CB filled with 2.3 volume percent hydrophilic (A200) Aerosil particles with an average diameter $\simeq$ 10 nm. Bulk 5CB has a nematic phase in the temperature range of 22.5 - 35.0°C.

DLS measurements were performed using a $\lambda = 0.6328\mu m$ He-Ne laser and the ALV-5000/Fast Digital Correlator. In this experiment, one measures the intensity-intensity autocorrelation function $g_2(t) = \langle I(t)I(0)\rangle / \langle I(0)\rangle^2$. This function is related to dynamic structure factor $f(q,t)$ of the sample by $g_2(t) = 1 + kf(q,t)^2$, where k is a contrast factor and $q = 4\pi n \sin(\Theta/2)/\lambda$, ($n$ is the refractive index, Θ - the scattering angle). All dynamic light scattering data that we discuss below were obtained at $\Theta = 30^o$.

Dielectric measurements were performed using the broad band spectrometer based on SI 1260, Novocontrol Broad Band Dielectric Converter with active sample cell and HP4291A. For the quantitative analysis of the dielectric spectra the Havriliak-Negami function [10] has been used:

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

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 distribution of relaxation times.

DYNAMIC LIGHT SCATTERING

The decay function describing fluctuations of director orientations in bulk nematic phase is single exponential. The difference between the dynamic behavior of bulk, confined and filled 5CB can be seen by comparing curves (1), (2) and (3) in Fig. 1.

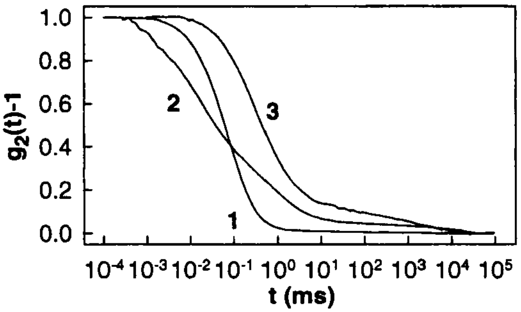

FIGURE 1: The normalized intensity/intensity autocorrelation functions for 5CB measured at 295.8 K: (1) - bulk, (2) - confined in 100 Å random pores and (3) - filled with Aerosil particles.

It is clear from Fig. 1 that the relaxation processes in confined and filled 5CB are nonexponential, as it is usually observed in glasslike systems. The relaxation process for 5CB in pores cannot 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 [2] of activated dynamical scaling with the scaling variable $x = lnt/ln\tau$. The decay function: $f(q,t) = a \cdot exp(-x^z)$, 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 autocorrelation functions of filled 5CB have been fitted by the superposition of three stretched exponential decays:

$$f(q,t) = \left[\sum_{i=1}^{n} a_i \cdot \exp(-(t/\tau_i)^{\bar{\beta}_i})\right],$$

where a_i, τ_i and $\bar{\beta}_i$ are the amplitude, relaxation time, and stretching exponent of i^{th} relaxation process respectively, and n is the number of processes. We assign the first decay to the bulk-like director fluctuations. This relaxation process is broader and slower than in bulk 5CB at the same temperature. The second relaxation process is most probably due to the director fluctuations in a thin LC layer formed on the surface of Aerosil particles. This relaxation process is notably slower than the bulk-like director fluctuations and broader than the bulk-like relaxation process with ($\bar{\beta} \approx 0.7$) appropriate to glass-like relaxation processes. The third (slowest) process could be due to a rotation of LC domains as a whole. However this process is masked by the first two processes and the quantitative analysis of the third process is difficult.

The relaxation times of the slow process for 5CB in 100 Å pores strongly increase with temperature decrease from 300 K to 270 K varying from 0.1 ms to 14 s (see Fig. 2). The temperature dependencies of the relaxation times of 5CB in 100 Å random pores and of the second process in filled 5CB (surface director relaxation) obey the Vogel-Fulcher law [11]: $\tau = \tau_0 exp(B/(T - T_0))$, with parame-

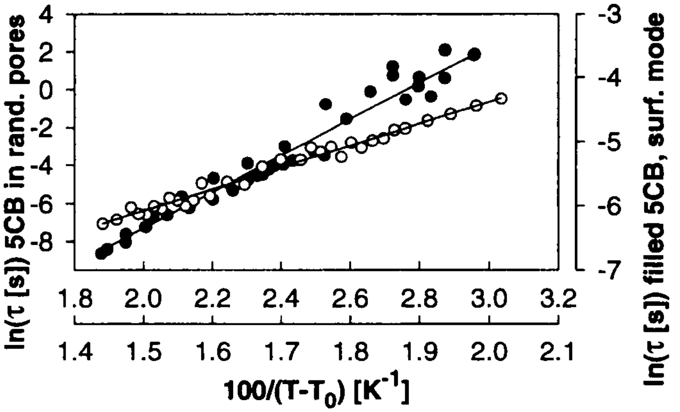

FIGURE 2: Temperature dependencies of relaxation times for 5CB confined in 100 Å random pores (filled circles) and filled 5CB (opened circles) measured by DLS. Symbols - experiment, solid lines - fitting.

ters: $\tau_0 = 3.1 \cdot 10^{-12}s$, $B = 960$ K and $T_0 = 246$ K for confined 5CB and $\tau_0 = 1.4 \cdot 10^{-3}s$, $B = 340$ K, $T_0 = 231$ K for filled 5CB. Both relaxation processes under discussion are characterized by the two main features typical for dynamics in conventional glass-forming fluids [11]: the stretched exponential relaxation is accompanied by the Vogel-Fulcher temperature dependence of the relaxation times.

DIELECTRIC RELAXATION

In the nematic phase of bulk 5CB there are two dielectrically active relaxation processes of molecular origin [12,13]. For a geometry in which the electric field **E** is parallel to the director **n** i.e. **E**||**n**, the Debye type process due to the restricted rotation of the molecules about their short axis exists. For the geometry in which **E**⊥**n** the relaxation due to librational motion of molecules is observed. Because of random distribution of the pores, there are molecules in confined 5CB oriented both parallel and perpendicular to the direction of probing electric field. Therefore both modes are 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 bulk like relaxation processes in pores. The parameter α varies in the limit from ≈ 0.5 to ≈ 0.3, ($\beta = 1$) when the temperature varies from T = 153 K to 303K. The dielectric function describing confined 5CB is similar to that for glass forming systems. This is clearly seen in the time domain representation (Fig. 3) of DS results. In this representation the 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 exponents.

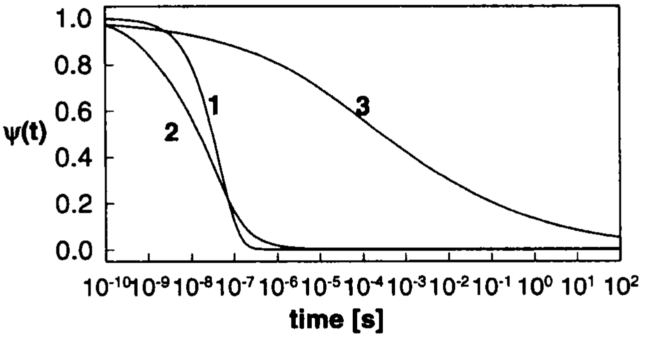

FIGURE 3: Dipole moment/dipole moment autocorrelation functions of 5CB: (1) bulk, T= 303 K, (2) and (3) confined in 100 Å random pores at T= 303 K and 153 K respectively.

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. Figure 3 shows 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 temperatures cor-

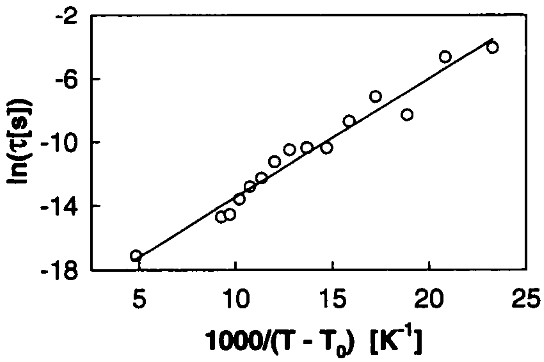

FIGURE 4: Temperature dependence of relaxation times for 5CB confined in 100 Å random pores measured by dielectric spectroscopy. Symbols - experiment, solid lines - fitting.

responding to the nematic phase. This slowing down is accompanied by a considerable broadening of the decay function. The temperature dependence of the relaxation times (Fig. 4) of the process due to reorientations of molecules around their short axes obeys the Vogel-Fulcher law with the fitting parameters: $\tau_0 = 8.3 \cdot 10^{-10} s$, $B = 745$ K and $T_0 = 90$ K.

CONCLUSION

The DLS and DS experiments show significant changes in the physical properties of LC confined in random porous medium and filled with Aerosil particles. The collective relaxation processes due to fluctuations of director reorientations as well as relaxation due to reorientation of molecules around their short axis are of non-Debye type and the temperature dependencies of relaxation times obey Vogel-Fulcher law. The small pore size (surface effects) and random pore structure (geometrical disorder) stimulate partial disorder (at least at long scales) and prevent crystallization. Therefore LC supercooled in small random pores has properties typical for glass forming liquids.

Acknowledgement

This work was supported by NRO grant N00014-99-1-0558. F.A. acknowledges support from Japan S&T Corporation, Tsukuba RC.

References

[1] *Liquid Crystals* in *Complex Geometries Formed by Polymer and Porous Networks*, edited by G.P. Crawford and S. Zumer (Taylor & Francis, London, 1996).
[2] X-1. Wu, W.I. Goldburg, M.X. Liu, and J.Z. Xue, *Phys. Rev. Lett.* **69**, 470 (1992).
[3] F.M. Aliev, in *Access in Nanoporous Materials*, edited by T.J. Pinnavaia and M.F. Thorpe, (Plenum Press, New York, 1995), pp. 335–354.
[4] T. Bellini, N.A. Clark, and D.W. Schaefer, *Phys. Rev. Lett.* **74**, 2740 (1995).
[5] A. Mertelj and M. Copic, *Phys. Rev. E* **55**, 504 (1997).
[6] F.M. Aliev, *Mol. Cryst. Liq. Cryst.* **329**, 1129 (1999).
[7] A. Mertelj, L. Spindler, and M. Copic, *Phys. Rev. E* **56**, 549 (1997).
[8] S.R. Rozanski, R. Stanarius, H. Groothues, and F. Kremer, *Liq. Cryst.* **20**, 59 (1996).
[9] G.P. Sinha and F.M. Aliev, *Phys. Rev. E* **58**, 2001 (1998).
[10] S. Havriliak and S. Negami, *Polymer* **8**, 101 (1967).
[11] *Disorder Effects on Relaxational Processes*, edited by R. Richert and A. Blumen (Springler Verlag, Berlin 1994).
[12] J.M. Wacrenier, C. Druon, and D. Lippens, *Mol. Phys.* **43**, 97 (1981).
[13] T.K. Bose, B. Campbell, S. Yagihara, and J. Thoen, *Phys. Rev. A* **36**, 5767 (1987).