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

Influence of Confinement on Dynamics of Molecular Motion and Collective Modes of Liquid Crystal Dispersed in Pores

Fouad M. Aliev [a] & Ghanshyam P. Sinha [a]

[a] University of Puerto Rico, Department of Physics and Materials Research Center, San Juan, PR, 00931, USA

Version of record first published: 04 Oct 2006

To cite this article: Fouad M. Aliev & Ghanshyam P. Sinha (1997): Influence of Confinement on Dynamics of Molecular Motion and Collective Modes of Liquid Crystal Dispersed in Pores, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 303:1, 325-330

To link to this article: http://dx.doi.org/10.1080/10587259708039442

Mol. Cryst. Liq. Cryst., 1997, Vol. 303, pp. 325–330
Reprints available directly from the publisher
Photocopying permitted by license only

Amsterdam B.V. Published in The Netherlands
under license by Gordon and Breach Science Publishers
Printed in India

INFLUENCE OF CONFINEMENT ON DYNAMICS OF MOLECULAR MOTION AND COLLECTIVE MODES OF LIQUID CRYSTAL DISPERSED IN PORES

FOUAD M. ALIEV and GHANSHYAM P. SINHA
University of Puerto Rico, Department of Physics and Materials Research Center, San Juan, PR 00931, USA

Abstract We present the results of investigations of the influence of the confinement, interface, porous matrix structure, pore size and shape on the dynamic behavior of nematic liquid crystals (LC) dispersed in porous matrices with randomly oriented, interconnected pores (porous glasses) and parallel cylindrical pores (Anopore membranes) by photon correlation and dielectric spectroscopies. Investigations of LC in cylindrical pores together with studies in random porous matrices, makes it possible to separate the role of random structure and domain formation from the contributions due to existence of LC - solid pore wall interface and pure finite size effect in different relaxational processes. We suggest that slow relaxational process observed in photon correlation experiments is due to the formation of interfacial layers on the pore walls rather than due to the dynamics of domains.

INTRODUCTION

Studies of structure, phase transitions, as well as dynamic behavior of confined liquid crystals have often been very effective[1–4] for understanding the fundamental physics of condensed matter and at the same time puzzling and contradictory, requiring additional efforts to develop a comprehensive understanding of confined LC.

We used photon correlation and dielectric spectroscopies to study the influence of confinement on dynamics (molecular motion and collective modes) of nematic liquid crystals dispersed in porous matrices with different pore structure.

In the recent investigation[5] of the dynamic properties of 8CB in an aerogel host by dynamic light scattering, the observed dynamic behavior was different from that in sintered porous silica[6]. Nevertheless, according to Bellini *et al*[5] the spin glass interpretation given by these authors[5] and the random field interpretation given by Wu *et al*[6] are consistent if the geometrical differences between the two matrices are taken into account. An additional possible explanation (together with the pictures suggested in the Ref.[6] and domain picture[5]) may be the formation of interfacial layers on the pore walls[3,7].

In order to separate the role of random structure from the contributions due to existence of interface and pure finite size effect, we studied pentylcianobiphenyl (5CB) dispersed in porous matrices with randomly oriented, interconnected pores (porous glasses) and parallel cylindrical pores (Anopore membranes) with different pore sizes.

Since the volume of this paper is limited we restrict our consideration to the qualitative description of results obtained for different pores. Complete results of these investigations will be published separately.

EXPERIMENTAL

We performed photon correlation measurements using He-Ne laser (λ = 6328 Å) 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. Depolarized component of scattered light intesity was investigated. We found that for 5CB in porous glasses the intensity-intensity autocorrelation functions were independent of scattering angle Θ, and almost independent for 5CB in cylindrical pores. All dynamic light scattering data we discuss below were obtained at $\Theta = 30^o$.

Measurements of the real ϵ' and imaginary ϵ'' parts of the complex dielectric permittivity in frequency range 1 Hz - 3 MHz at different temperatures were carried out using computer controlled Schlumberger Technologies 1260 Impedance/Gain-Phase Analyzer. For the measurements in frequency range 1MHz-1.5GHz we used the HP 4291A RF Impedance Analyzer with a calibrated HP 16453A Dielectric Material Test Fixture.

We used porous glasses with average pore sizes of 100 Å and 1000 Å and Anopore membranes with parallel cylindrical pores having pore diameters of 200 Å and 2000 Å. The nematic liquid crystal we used was 5CB. The temperatures of phase transitions of 5CB in bulk are T_{CN}=295 K and T_{NI}=308.27 K.

RESULTS AND DISCUSSION

In the dynamic light scattering experiment, one measures the intensity-intensity autocorrelation function $g_2(t) = \langle I(t)I(0)\rangle / \langle I(0)\rangle^2$. The intensity-intensity autocorrelation function $g_2(t)$ is related to the dynamic structure factor f(q,t) of the sample by $g_2(t) = 1 + kf(q,t)^2$, where k is a contrast factor that determines the signal-to-noise ratio, $q = 4\pi n \sin(\Theta/2)/\lambda$ and n is the refractive index. Dynamic light scattering in bulk liquid crystals is very well understood, and in the nematic phase the main contribution to the intensity of scattered light is due to the director fluctuations. If for simplicity we assume that six Leslie coefficients have the same order of magnitude and are $\sim \eta$ (η is an average viscosity), and three elastic constants (bend, splay and twist) are equal (K) then the decay function $f(q,t)$ is single exponential with the relaxation time $\tau = \eta/Kq^2$ and $\tau \sim 10^{-5}s$. The influence of confinement on the dynamic behavior in both random and cylindrical pores is clearly observed from Fig. 1 and Fig. 2. Note that autocorrelation function for 5CB in 1000 Å random pores is measured at temperatures much below the crystallization temperature ($\simeq$ 294 K) of bulk 5CB. We observed that 5CB does not crystallize in the pores up to 270 K (lowest temperature available in our experiments). The decays in Fig. 1 and Fig. 2 are strongly non-exponential in contrast to the bulk behavior. It is clear from Fig. 1 and Fig. 2 that the slow relaxational process which does not exist in bulk LC and a broad spectrum of relaxation times appear not only for random pores but in cylindrical pores as well. We found that the decay function :

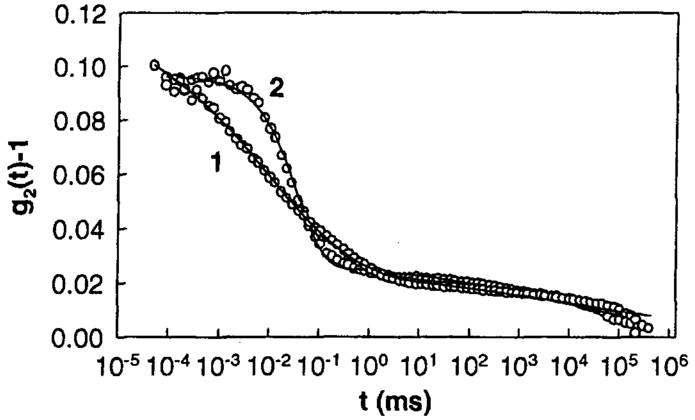

FIGURE 1 Intensity/intensity autocorrelation functions for 5CB in random pores: 1 - 5CB in 100 Å pores, 295.8 K; 2 - 5CB in 1000 Å pores, 280.8 K.

$$f(q,t) = a \cdot exp(-(t/\tau_1)^{\beta}) + (1-a) \cdot exp(-x^z), \qquad (1)$$

where $x = ln(t/\tau_0)/ln(\tau_2/\tau_0)$, and in our case $\tau_0 = 10^{-8}s$ provides reasonably good fitting for 5CB in pores. For 5CB in 100 Å random pores the second term in relationship (1) dominates, whereas for 200 Å and 2000 Å cylindrical pores as well as 1000 Å random pores the contribution from the first term is much more visible. The fitting parameters corresponding to (1) and (2) in Fig. 1 are: (1) - τ_1=0.03 ms, β=0.27, z=4.0; (2) - τ_1=0.49 ms, β=0.9, z=4. In Fig. 2 these parameters are: (1) - τ_1=0.028 ms, β=0.85, z=4.0, (2) - (a) - τ_1=0.036 ms, β=0.69, z=4.0. The second relaxation times for all curves in Fig. 1 and Fig. 2 are of the order of 10^3 s.

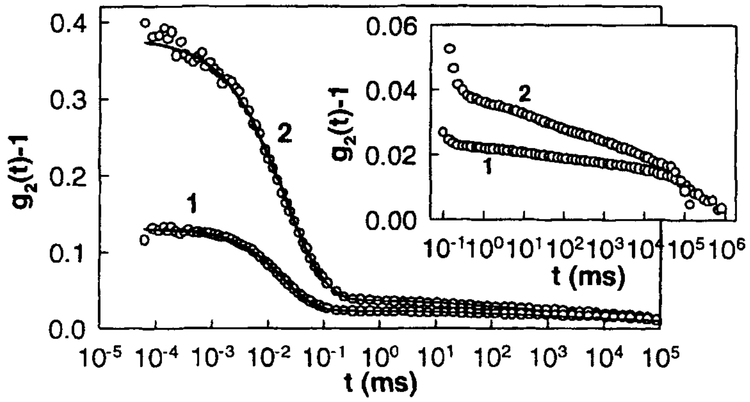

FIGURE 2 Intensity/intensity autocorrelation functions for 5CB in cylindrical pores: 1 - 5CB in 200 Å pores, 305.4 K; 2 - 5CB in 1000 Å pores, 306.1K. Solid line-fitting according to eqn.(1). Inset shows long time decay.

Data analysis shows that the relaxation time of the slow process for 5CB in 100 Å pores strongly increases when temperature decreases from 300 K up to 276 K and it's temperature dependence is satisfactorily described by the Vogel-Fulcher law[8]: $\tau = \tau_0 exp(B/(T - T_0))$, with the parameters: $\tau_0 = 1.4 \cdot 10^{-11} s$, $B = 847K$ and $T_0 = 246K$. This is characteristic of glass-like behavior. Since the slow decay previously observed[5-7] in pores with random structure also exists in cylindrical pores where the domain formation is very difficult and for which the the random-field approach[6] is not applicable, it is reasonably to assume that observed slow decay is due to the formation of interfacial layers on the pore wall. The slow dynamics detected by dynamic light scattering and a broad spectrum of relaxation times still remain unexplained and further systematic investigations are needed.

In the dielectric experiments a slow relaxational process absent in bulk 5CB was also detected for both random and cylindrical pores. The example of this slow process is given in Fig. 3 where the frequency dependencies of the real and imaginary parts of dielectric permittivity for 5CB in 2000 Å cylindrical pores are presented. For 5CB in both porous matrices we observe three relaxational processes. Two of them are clearly indicated in the Fig. 3 (first - in the frequency range 0.1Hz - 1kHz and the second process has characteristic relaxational frequency ~1 MHz). The third process with characteristic relaxational frequency ~50 MHz is out of the scale we are using. All observed processes were active up to 267 K in confined 5CB.

We analyzed data using the Debye equation for complex permittivity ϵ^*, modified by Cole and Cole[10]. According to Cole and Cole the frequency dependence of complex dielectric permittivity of a system which has more than one relaxational process is described by the equation:

$$\epsilon^* = \epsilon_\infty + \sum_{j=1}(\epsilon_{js} - \epsilon_\infty)/(1 + i2\pi f\tau_j)^{1-\alpha_j} - i\sigma/2\pi\epsilon_0 f^n, \qquad (2)$$

where ϵ_∞ is the high-frequency limit of the permittivity, ϵ_{js} the low-frequency limit, τ_j the mean relaxation time, and j the number of the relaxational process. The term $i\sigma/2\pi\epsilon_0 f^n$ takes into account the contribution of conductivity σ and n is a fitting parameter ($n \simeq 1$). The Cole-Cole (Fig. 3) diagrams indicate that for LC in pores the parameter α, which empirically represents the spectrum of relaxation times, varies from 0.1 to 0.4; hence there is a spectrum of relaxation times. It should be noted that in bulk[9] 5CB $\alpha = 0$.

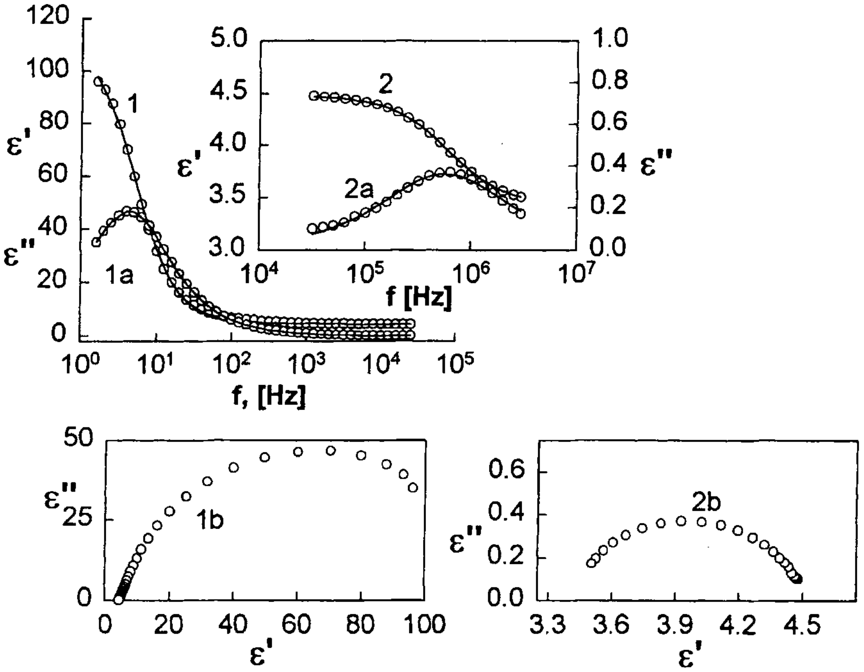

FIGURE 3 Frequency dependencies of ϵ' (1,2) , ϵ'' (1a), (2a) and Cole-Cole plots (1b), (2b) for 5CB in 2000 Å cylindrical pores at T=-2.6°C. Solid lines - fitting according to eqn. (2): τ_1=0.06 s, α_1=0.1 (curves 1 and 1b) and τ_2=2.8·10^{-7} s, α_2=0.1 (curves 2 and 2b).

Possibly at low frequencies we observe the relaxation of interfacial polarization due to formation of surface layers with polar ordering on the pore walls. In this case a new cooperative and slow process may arise.

We attribute relaxation times for the process in MHz frequency range (curves 2 and 2a in Fig. 3) to the molecular rotation around short axis. This process is the main relaxational process in bulk 5CB[9]. Howerver the temperature dependence of these relaxation times in pores is different from the bulk behavior.

For 5CB in 1000 Å random pores we attribute the temperature range $34.5°C < T < 20°C$ to nematic phase. We found that the activation energy for 5CB in these pores $U_p = 0.74eV$ in nematic phase is greater than the bulk value $U_b = 0.61eV$. This is because the pore wall imposes additional potential due to pore wall - molecule interaction. This potential is 0.13 eV ($2 \cdot 10^{-13} erg$), and taking into account that number of molecules per unit area is $(2-3) \cdot 10^{14} cm^{-2}$ we estimate the surface potential of molecule-wall interaction $U_{surf} \sim 50 erg/cm^2$.

CONCLUSION

From qualitative point of view the influence of confinement on the dynamics of molecular reorentational motion and low frequency relaxational process of LC observed in dielectric experiment in random and cylindrical pores is similar. The slow relaxational process detected by photon correlation spectroscopy which does not exist in bulk LC and a broad spectrum of relaxation times $(10^{-6} - 10)s$ appear not only for LC in random pores but in cylindrical as well. We conclude that differences in dynamical behavior of confined LC from that in the bulk are due to finite-size effects and the existence of interface. Random porous structure has secondary importance.

ACKNOWLEDGEMENTS

This work was supported by US Air Force grant F49620-95-1-0520 and NSF grant OSR-9452893.

REFERENCES

1. D. Finotello and J. Iannacchione, Int.Journ. Mod.Phys., B9, 109, 1995.
2. G.P. Crawford and S. Zumer, Int.Journ. Mod.Phys., B9, 331, 1995.
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. Liquid Crystals in Complex Geometries, edited by G.P. Crawford and S. Zumer (Taylor and Francis, London, 1996).
5. T. Bellini, N.A. Clark, and , D.W.Schaefer, Phys. Rev. Lett., **74**, 2740 (1995).
6. X-l. Wu, W.I. Goldburg, M.X. Liu, and J.Z Xue, Phys.Rev.Lett., 69, 470, (1992).
7. F.M. Aliev and V.V. Nadtotchi in: Disordered Materials and Interfaces, edited by H.Z. Cummins, D.J. Durian, D.L. Johnson, and H.E. Stanley, (Mater. Res. Soc. Proc., 407, Pittsburgh, PA, 1996), pp. 125-130.
8. G. Williams, J. Non-Cryst. Solids, 31-133, 1 (1991).
9. P.G. Cummins, D.A. Danmur, and D.A. Laidler, MCLC, 30, 109, (1975).
10. Scaife, B.K.P., Principles of Dielectrics, Oxford: Clarendon Press (1989).