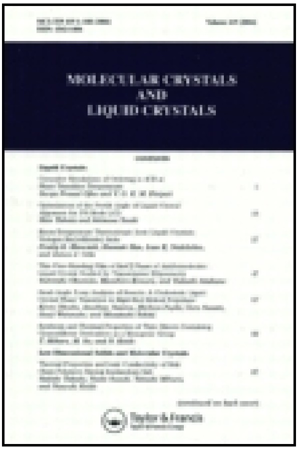

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Influence of Confining Geometries on Collective Dynamic Modes in Chiral Smectogens

S. A. Rozanski [a], L. Naji [b], F. Kremer [b] & R. Stannarius [b]

[a] Maria Sklodowska-Curie High School, W. Pola 11, 64-920, Pila, Poland

[b] Universität Leipzig, Fakultät für Physik und Geowissenschaften, Linnéstr. 5, D-04103, Leipzig, Germany

Version of record first published: 24 Sep 2006

Mol. Cryst. Liq. Cryst., 1999, Vol. 329, pp. 483-489
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S.A. ROZANSKI[a], L. NAJI[b], F. KREMER[b] and R. STANNARIUS[b]

[a]*Maria Sklodowska-Curie High School, W. Pola 11, 64–920 Pila, Poland and* [b]*Universität Leipzig, Fakultät für Physik und Geowissenschaften Linnéstr. 5, D-04103 Leipzig, Germany*

While confined nematogens have been extensively investigated in adsorbents of a large variety of cavity sizes, comparably little is known about smectogens under geometrical restraints. We study ferroelectric smectogens in porous material from nanometer to micrometer cavity sizes. No influences on the molecular dynamics but dramatic changes in the collective reorientation behaviour, in particular a disappearance of the collective modes in nanometer pores and in disordered cellulose membranes is observed.

Keywords: confining geometries; collective modes; ferroelectric liquid crystals

INTRODUCTION

The effects of geometrical confinement and surface interactions on liquid crystal (LC) order and molecular dynamics represent an area of growing interest, both theoretically and experimentally [1]. Studies of confined liquid crystal phases have been mostly performed with nematogens [2-7]. Adsorbents with different pore sizes and geometries were studied in the past, for example ANOPORE, NUCLEPORE [2, 4] and cellulose [8, 9] membranes, porous sol-gel glasses [3,5,6], and silica aerogels [7]. The behaviour of more complex mesophases like the ferroelectric SmC* in confined geometry, however, has been investigated only scarcely [10-13]. In these materials new collective dynamical reorientation modes (Goldstone and soft mode) are observed in the bulk in addition to the molecular processes found in nematics. The study of thermodynamics, structure and dynamics of ferroelectric liquid crystals (FLC) in restricted geometries is an attractive topic of research. For example, it is well known that the finite thickness of smectic films plays a considerable role in the SmA→SmC* phase transition [14].

Aliev [11] studied FLC in porous glass. In macropores (pore sizes ≈10^3 Å), he observed a suppression of the SmA→SmC* transition by about 15 K respective to the bulk phase, and confirmed the existence of the collective dynamical modes of the tilt angle, with slightly increased viscosity. In micropores (≈10^2 Å), neither Goldstone nor soft mode were detected. Xu et al.[10] investigated smectogens in aerogels and reported an additional dielectric process in the confined material which was attributed to an interfacial LC layer at the large inner surfaces of the system.

In our previous investigations we studied nematics [2, 3] and FLC [12] in sol-gel glass and ANOPORE membranes by means of dielectric and NMR spectroscopy. We found that in 200 nm ANOPORE filter pores the Goldstone mode is still present but shifted to lower frequencies. In 7.5 nm porous glass, the collective dynamic modes are completely suppressed. Molecular processes seem to be uninfluenced by confinement.

In this work we compare the influence of various adsorbents on the collective dynamics of confined enantiomeric smectogens. Dielectric spectroscopy is exploited. Possible explanations for the absence of the Goldstone mode in confined FLC are discussed.

EXPERIMENTAL

Dielectric measurements were performed in the range 10^{-2} to 10^9 Hz with a Solartron-Schlumberger frequency response analyser FRA 1260, a Novocontrol active sample cell BDC-S (10^{-2} Hz - $3\cdot10^{6}$ Hz) and a Hewlett Packard impedance analyser 4191A (10^{6} Hz- 10^{9} Hz). With this set-up, high conductivity electrodes (diameter 5 mm) must be used. Temperature control was achieved with a stability better than $\pm$ 0.05 K.

The ANOPORE membranes from Anotech are inorganic aluminum oxide films with non-deformable and highly regular honeycomb structure. Cylindrical pores with 0.2 μm diameter penetrate the 60 μm thick sheets perpendicularly. Controlled porous sol-gel glass with pore sizes of 2.5 nm, 5.0 nm, and 7.5 nm was obtained from Geltech Inc., USA. The material has macroscopic cylindrical shape (diameter 10 mm, height 10 mm) and a huge inner surface (520 m^2/g to 610 m^2/g). SYNPOR membrane filters consist of pure cellulose nitrate films with spongelike interconnected pores and average membrane thickness $\approx$120 μm. These filters are available with pores sizes ranging from 0.23 to 0.85 μm. SYNPOR membranes are temperature stable up to 394 K. Both sol-gel glass and membrane filters are dielectrically inactive.

The porous glass, ANOPORE and SYNPOR membranes were cut to small (∅ 5-10 mm) disks and filled with the mesogens in the isotropic phase. The preparation technique was described earlier [2, 3]. The experiments were performed with standard ferroelectric liquid crystals 4 - (2′- methylbutyl) phenyl 4′-n-octylbiphenyl-4-carboxylate (CE8) and p-decyloxybenzylidene-p′-amino 2-methylbutyl-cinnamate (DOBAMBC).

RESULTS

The imaginary part of the complex dielectric function $\varepsilon^* = \varepsilon' + i\varepsilon''$ can be described by a superposition of Havriliak-Negami [15] functions and a conductivity contribution:

$$\varepsilon'' = \frac{\sigma_o}{\varepsilon_o} \cdot \frac{1}{\omega^s} - \sum_{k=1}^{N} \mathrm{Im}\left[\frac{\Delta\varepsilon_k}{\left(1+\left(i\omega\tau_k\right)^{\alpha_k}\right)^{\beta_k}}\right] \tag{1}$$

with the dielectric strengths $\Delta\varepsilon_k$ and relaxation times τ_k of each individual process k and conductivity parameter σ_0 (if $s = 1$, σ_0 corresponds to the Ohmic conductivity). Exponents α and β are empirical fit parameters which describe symmetric and unsymmetric broadenings of the relaxation peaks.

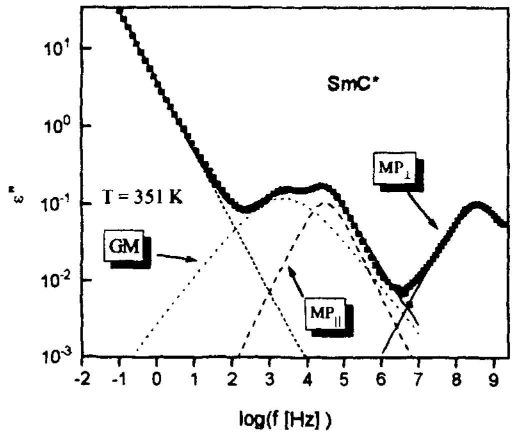

FIGURE 1 Dielectric loss spectrum in the SmC* phase of bulk CE8 together with dielectric processes and conductivity slope (solid, dashed and dotted lines) obtained from the fit.

Fig. 1 shows a typical spectrum with data analysis. The separation of strengths, frequencies and temperature characteristics of the individual processes yields information on collective and molecular dynamics.

Dielectric Bulk Data

The dielectric loss spectra in bulk samples show a pronounced low-frequency conductivity wing. We find a temperature dependent Ohmic conductivity σ_0.

For DOBAMBC (Fig. 2) in the frequency range 10^6 to 10^9 Hz we observe two absorption peaks in the isotropic (I) phase, assigned to molecular reorientation around the short axis ($MP_{\|}$) and long axis ($MP_{\perp}$).

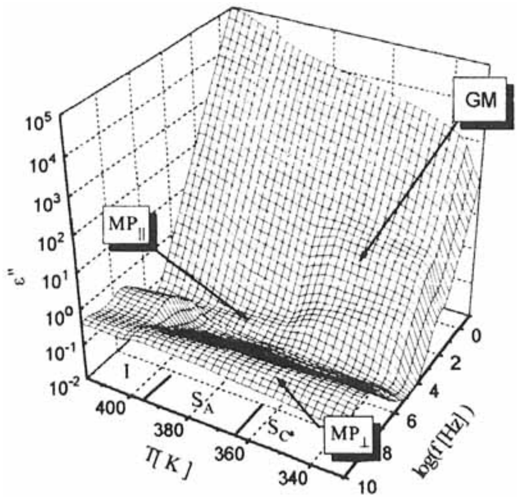

FIGURE 2 Dielectric loss of bulk DOBAMBC as a function of temperature and frequency.

The latter (polarisation mode [16]) is present in all mesophases without discontinuities at phase transitions. Its frequency shows Arrhenius behaviour. In contrast, the strength of the $MP_{\|}$ drops remarkably in SmA and it slows down by about one decade. Three processes are seen in the ferroelectric SmC* phase: the two molecular processes and one collective process in the kHz range, the Goldstone mode (GM). Its relaxation strength is by about two orders of magnitude higher than the molecular process. Its frequency is almost temperature independent. A soft mode is probably hidden in the large conductivity wing.

Spectra of Adsorbed Samples

In the previous work [12] we have shown the existence of the Goldstone mode in ANOPORE samples. Its relaxation frequency is lowered by about one decade with respect to the bulk. However, in the cellulose membranes as well as in nanoporous glass we observe a complete disappearance of the Goldstone mode. Fig. 3 shows the 3D plot of $\varepsilon''(T, f)$ for DOBAMBC.

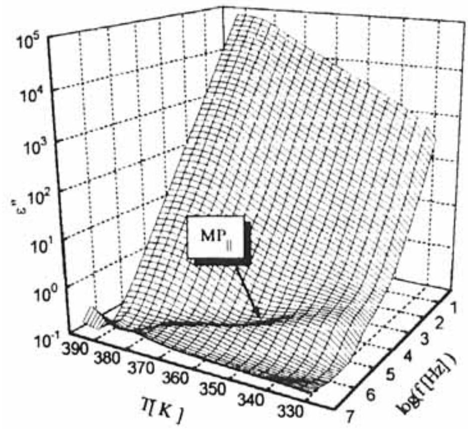

FIGURE 3 DOBAMBC in SYNPOR filters: Dielectric loss as a function of temperature and frequency. The spectrum of CE8 is qualitatively similar. The GM peak has disappeared completely.

In the nanoporous glass the absence of the GM was explained by the very small pore sizes [12]. The cellulose membranes combine the size properties of a microporous system (like ANOPORE) with a disordered cavity structure as present in a nanoporous glass. It is highly suprizing that in this large-pore system the GM is also suppressed (Figs. 3, 4). We suggest the following explanation: defects induced in the smectic layer structure from the irregular SYNPOR network play the dominant role. The state of disorder induced by these defects leads to a frustration of the layer structure and prevents the free reorientation of the director, resulting in the suppression of the collective dynamic modes. The geometry of the porous material determines the orientational order of the confined molecules while it leaves phase transitions, order parameters and molecular dynamics unchanged. This has already been found [8] for confined nematic LC in spongelike SYNPOR membranes.

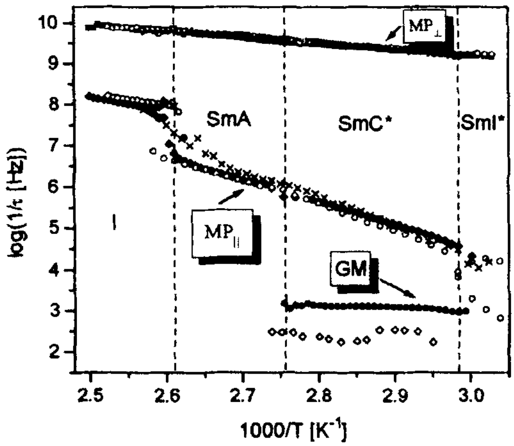

FIGURE 4 Dielectric relaxation rates for DOBAMBC in adsorbents with different pore geometries: solid symbols - bulk, open symbols - ANOPORE, (×) - SYNPOR. Note the absence of the GM in SYNPOR membranes.

CONCLUSIONS

The dielectric properties of ferroelectric liquid crystals confined in different porous materials have been measured in the frequency range from 10^{-2} Hz to 10^{9} Hz. It has been shown that the molecular processes are nearly unchanged but the influence of geometrical restrictions on the collective dynamics in the SmC* phase is dramatic. In samples confined in non-ordered cellulose membranes and nanoporous glass (7.5 nm) we observe the suppression of the Goldstone mode.

Acknowledgements

The authors acknowledge support by the State Committee for Scientific Research in Poland under Grant No. 2 P03B 085 12, the Organizing Committee of 16th ILCC, Kent, USA, and the Deutsche Forschungsgemeinschaft within SFB 294.

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