

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

### Broadband dielectric relaxation study of 6CB and 6CB-aerosil dispersions in the nematic and isotropic phases

A. Hourri; P. Jamée; T. K. Bose; J. Thoen

Online publication date: 11 November 2010

**To cite this Article** Hourri, A. , Jamée, P. , Bose, T. K. and Thoen, J.(2002) 'Broadband dielectric relaxation study of 6CB and 6CB-aerosil dispersions in the nematic and isotropic phases', *Liquid Crystals*, 29: 3, 459 – 466

**To link to this Article:** DOI: 10.1080/02678290110114305

**URL:** <http://dx.doi.org/10.1080/02678290110114305>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# Broadband dielectric relaxation study of 6CB and 6CB—aerosil dispersions in the nematic and isotropic phases

A. HOURRI†‡, P. JAMÉE†, T. K. BOSE‡ and J. THOEN†\*

†Laboratorium voor Akoestiek en Thermische Fysica, Departement Natuurkunde, Katholieke Universiteit Leuven, Celestijnenelaan 200D, B-3001 Leuven, Belgium

‡Institut de Recherche sur l'Hydrogène, Département de Physique, Université du Québec à Trois-Rivières, Trois-Rivières, Québec, Canada G9A 5H7

(Received 13 August 2001; accepted 26 October 2001)

Experimental studies of dielectric relaxation in the nematic and isotropic phases of 6CB (4-hexyl-4'-cyanobiphenyl) and two mixtures of 6CB perturbed by 160 Å hydrophobic silica aerosil are presented. The measurements have been made from 1 MHz to 1 GHz in the temperature range from 19 to 40°C. For bulk 6CB, the dynamic aspect in the isotropic phase as well as the principal dielectric permittivities  $\epsilon_{\parallel}^*(\omega)$  and  $\epsilon_{\perp}^*(\omega)$  in the nematic phase have been fully explored. For the mixtures, measurements on the isotropic phase and also on homeotropically aligned samples in the nematic phase have been made, and these results are systematically compared with those for the bulk. The possible molecular reorientational movements corresponding to the different absorption domains in the dielectric spectrum are discussed and compared with the previously proposed interpretations.

## 1. Introduction

Much work has been done in the past few years on the effect of confinement of liquid crystals (LCs) in restricted geometries [1]. Included in such work are studies of LCs in silica aerogels [2, 3] and random porous media [4–7]. The interaction of a liquid crystalline compound with a solid surface depends on the nature of both the surface and the liquid crystalline material. Recently, dispersions of silica nano-particles covered with hydroxyl groups (aerosil) have been studied intensively [8–11]. These particles can hydrogen bond to form a gel network and allow the introduction of disorder in the LC.

In a previous article [11] we investigated the static and dynamic aspects of five mixtures of homeotropically aligned samples of 7CB perturbed by the dispersion of 70 Å diameter hydrophilic silica aerosil spheres. These measurements were made from 75 kHz to 30 MHz in the temperature range 30 to 60°C. The static dielectric permittivity in both the isotropic and nematic phase regions along with the evolution of the shift in the nematic–isotropic (N–I) transition temperature were analysed systematically as a function of silica aerosil density. Bulk-like relaxation processes connected with the molecular flips around the short axis were found to follow Arrhenius-type behaviour in the nematic phase

except in the vicinity of the N–I transition temperature. These processes are slightly faster in the mixtures than in the free phase. A new dielectric process in the low frequency range, absent in the bulk, was observed in samples with a very high silica concentration. It was suggested that this new process is due to the hindered rotation of molecules located in the surface layers formed by the 7CB molecules and the silica aerosil surface.

The present investigation involves a broadband dielectric study of 6CB (4-hexyl-4'-cyanobiphenyl) and 6CB perturbed by the dispersion of 160 Å diameter hydrophobic silica aerosil spheres (phobic sils) in the frequency range from 1 MHz to 1 GHz. In the case of hydrophobic silica aerosil with surface CH<sub>3</sub> groups, no specific interaction such as hydrogen bonding can occur for any LCs [12]. Results on 6CB and on two mixtures of 6CB + phobic sils are presented in order to probe the systematic effect of the phobic sil suspensions on the dynamic properties in the high frequency range of the 6CB molecules in the isotropic and in the nematic phases. Following a recently proposed molecular interpretation of the dielectric relaxation of nematic LCs [13], the complex dielectric permittivity for pure 6CB has been fully investigated for the nematic and the isotropic phase. For mixtures, the dynamical behaviour of the dielectric permittivity in the isotropic phase along with that of the longitudinal component ( $\epsilon_{\parallel}^*$ ) in the nematic phase have been explored and compared consistently with the results from the bulk phase.

\* Author for correspondence  
e-mail: Jan.Thoen@fys.kuleuven.ac.be

## 2. Experimental

The present experiment consists of measuring the real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of the complex dielectric permittivity ( $\epsilon^*$ ) of the liquid crystal 6CB and two dispersions of hydrophobic silica aerosil. The measurements were made in the frequency range 1 MHz to 1 GHz using a Hewlett-Packard 4291B RF Impedance/Material Analyzer. The dielectric test fixture, suitable for liquid crystal material measurements, was designed and fabricated in our laboratory. It takes complete advantage of the HP 4291B RF Impedance/Material Analyzer built-in compensation software and capabilities. The test fixture is properly centred inside a temperature controlled cylindrical cavity. This cavity is connected to the ground potential to be used as a shield against any noise pick up. Temperature control and measurement are, respectively, achieved by a circulatory fluid inside the walls of the cylindrical cavity and an HP 2850 quartz thermometer probe. The accuracy and stability of the temperature measurements is better than  $0.01^\circ\text{C}$ . In the nematic phase, the molecules were oriented by means of a magnetic field of 0.4 T.

The 6CB plus aerosil systems were prepared following the solvent preparation method described in [14]. After drying the aerosil powder at  $200^\circ\text{C}$  overnight, it is added to a solution of the LC in pure acetone ( $0.02\text{ g LC per cm}^3$  of solvent). Then the mixture is sonicated for 1 h to achieve good dispersion. Afterwards, the solvent is evaporated off slowly (15 h) above  $43^\circ\text{C}$  before the sample is placed in a vacuum system at  $10^{-3}$  torr and pumped continuously for one day at  $50^\circ\text{C}$ . The resulting density  $\rho_s$  denotes the grams of silica aerosil per  $\text{cm}^3$  of liquid crystal.

For the present experiment, a hydrophobic aerosil (type R972) was used as obtained from the Degussa Corp. [15]. This sil consists of  $160\text{ \AA}$   $\text{SiO}_2$  spheres, with a specific surface area of  $110\text{ m}^2\text{ g}^{-1}$  as determined from a Brunauer–Emmet–Teller adsorption isotherm [15]. The liquid crystal 6CB was obtained from the Merck Ltd. (UK) and was used without further purification.

## 3. Results and analysis

We have measured the dielectric properties of 6CB and 6CB perturbed by two dispersions of  $160\text{ \AA}$  hydrophobic silica aerosil spheres over the temperature range 19 to  $40^\circ\text{C}$ . The nematic to isotropic transition temperature ( $T_{\text{NI}}$ ) for pure 6CB is around  $29^\circ\text{C}$ . For the two mixtures, the silica aerosil concentrations in 6CB are  $\rho_s = 0.062\text{ g cm}^{-3}$  and  $\rho_s = 0.130\text{ g cm}^{-3}$ . Figure 1 presents typical frequency-dependence spectra of the real (a) and the imaginary (b) parts of the dielectric permittivities measured for pure 6CB on the isotropic phase

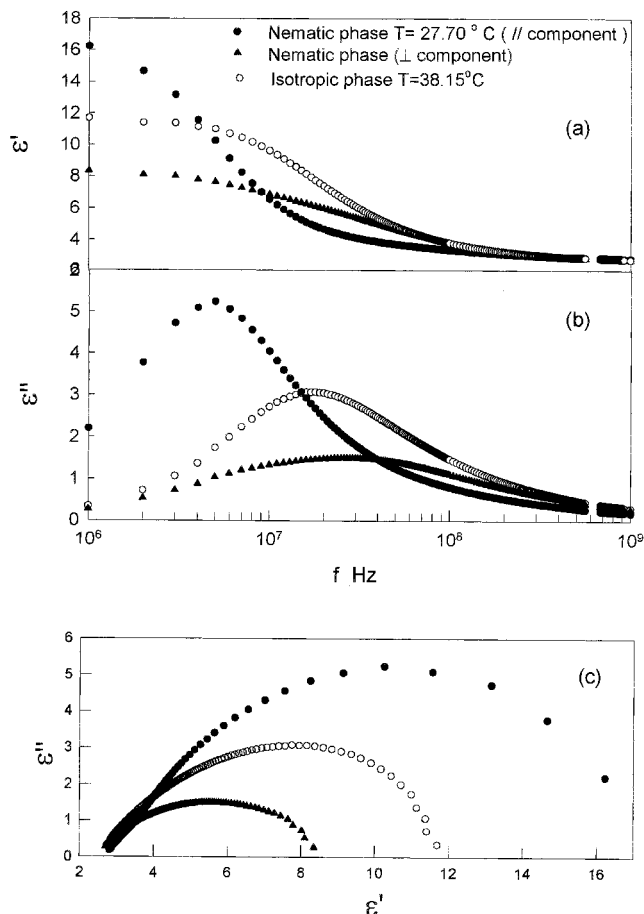


Figure 1. The frequency dependence of the real (a) and the imaginary (b) parts of the parallel and perpendicular components of the dielectric permittivity in the nematic phase and in the isotropic phase for 6CB. The dielectric data are presented in the form of Cole–Cole plots in (c).

( $T = 38.15^\circ\text{C}$ ) and on the nematic phase ( $\epsilon_{\parallel}$  and  $\epsilon_{\perp}$  at  $T = 27.70^\circ\text{C}$ ). In figure 1(c), the same results are presented in the form of Cole–Cole plots. For the sake of comparison and in order to characterize the influence of disorder and randomness introduced by the silica aerosil network on 6CB, figure 2 shows the imaginary part of the spectrum ( $\epsilon''$ ) for bulk 6CB along with that for two dispersions of silica aerosil in 6CB in the nematic phase at  $23.26^\circ\text{C}$ . As mentioned above, these measurements were taken in the frequency range from 1 MHz to 1 GHz. One can see from figure 2 that the maximum in the loss curve becomes flattened and decreases in magnitude with increasing silica concentration. A broadening of the loss curve is usually associated with the broadening of the spectrum of relaxation times associated with the dispersion.

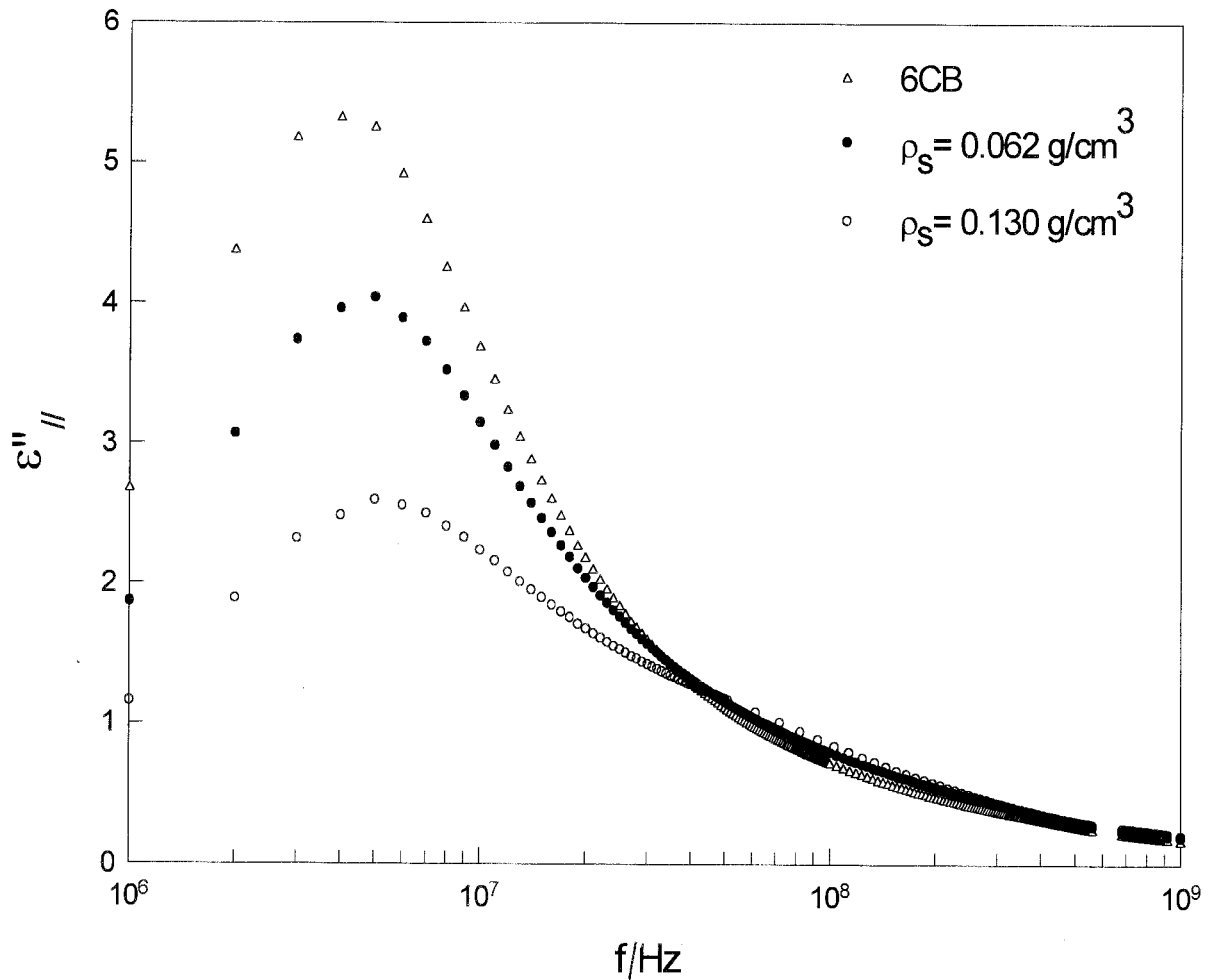


Figure 2. Comparative plots for the imaginary parts of the spectra of the parallel component of the dielectric permittivity for 6CB, and for the mixtures  $\rho_s = 0.062$  and  $0.130 \text{ g cm}^{-3}$  in the nematic phase at  $T = 23.26^\circ\text{C}$ .

For the quantitative analysis of the dielectric spectra, the Cole–Cole equation [16] has been used:

$$\begin{aligned} \varepsilon_a^*(\omega) &= \varepsilon_a'(\omega) - i\varepsilon_a''(\omega) \\ &= \varepsilon_\infty + \sum_j \frac{\Delta\varepsilon_j^a}{1 + (i\omega\tau_j^a)^{1-\alpha_j}}. \quad (a = \parallel, \perp) \end{aligned} \quad (1)$$

Here  $\varepsilon_\infty$  is the high frequency limit of the permittivity,  $\Delta\varepsilon_j$  the dielectric strength,  $\tau_j$  the mean relaxation time and  $j$  represents an index number for the relaxation processes. The exponent  $\alpha_j$  ( $0 \leq \alpha_j \leq 1$ ) represents the distribution of the relaxation times and goes to zero when a single relaxation is effective. Both the real and the imaginary parts of the dielectric permittivity have been analysed. The fitting of the Cole–Cole equation to the experimental spectrum has been performed using a least square fitting procedure. The resolution of the spectrum into elementary dielectric processes and the attribution of each process to a particular mode of

molecular motion are the most difficult tasks in dielectric relaxation studies. This has been a subject of numerous investigations [17, 18]. In the following, we analyse first the dynamical behaviour of 6CB and 6CB-silica aerosil mixtures in the nematic phase. Figure 3 presents the numerical decomposition of the experimentally obtained  $\varepsilon'$  and  $\varepsilon''$  for pure 6CB into components described by the Cole–Cole equation.

In our analysis of the dielectric data for the nematic phase for 6CB and also for the mixtures, we have followed the recently proposed model by Jazdyn *et al.* [13] for the interpretation of the molecular dynamics in oriented nematics. The molecules in the anisotropic phase rotate around three axes of symmetry. Two of these axes concern the molecule itself (the molecular long and short axes) and the third axis is the director  $\mathbf{n}$ . Figures 3(a) and 3(b) show, respectively, the resolution of the components  $\varepsilon_{\parallel}^*(\omega)$  and  $\varepsilon_{\perp}^*(\omega)$  for pure 6CB into three elementary absorption bands in accordance with

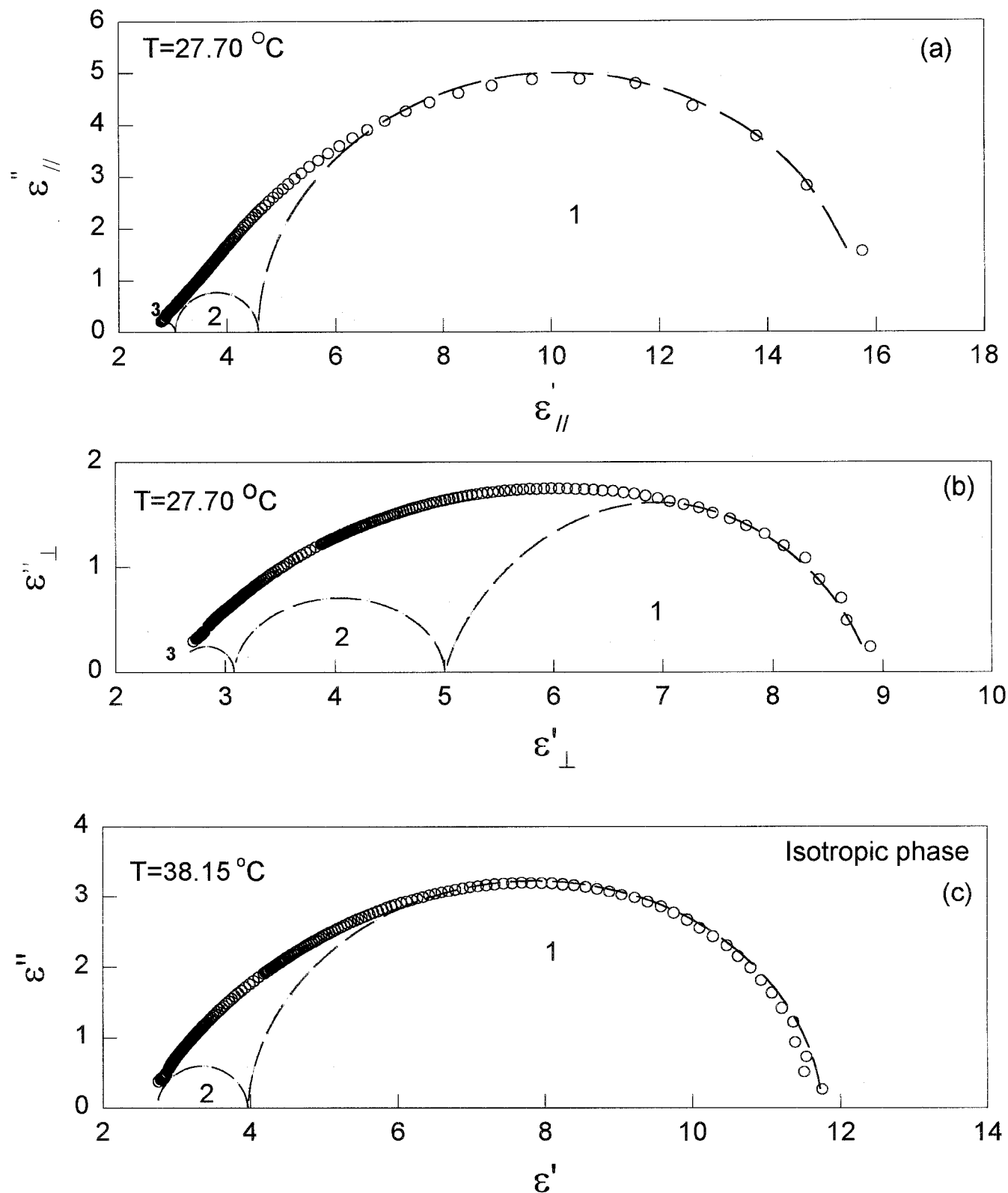


Figure 3. Cole-Cole plots for bulk 6CB. The dashed lines represent the elementary contributions to the total dielectric absorption spectra corresponding to the molecular motion in the nematic (a, b) and isotropic (c) phases.

Jadzyn's interpretation. These bands, i.e. 1, 2 and 3 [see figures 3(a) and 3(b)], with characteristic frequencies, respectively, in the range of 10 MHz, 100 MHz and 1 GHz, are to a good approximation of the Debye type ( $\alpha_j \approx 0.01$ ). They correspond to different modes of molecular motion: band 1 corresponds to the rotation around the molecular short axis and band 2 is related to molecular rotation on the cone around the director  $\mathbf{n}$ , while band 3 originates from the molecular rotation around the molecular long axis.

Figures 4 and 5 present, respectively, the temperature dependence of the relaxation times and the corresponding dielectric strengths for bulk 6CB. From these figures and in concordance with the above-mentioned model, the shortest relaxation time ( $\tau_3$ ) appears in both  $\epsilon_{\parallel}^*(\omega)$  and  $\epsilon_{\perp}^*(\omega)$  with approximately the same strength. As pointed out by many workers [19, 20], the molecular rotation around the short axis, i.e. ( $\tau_{\perp}^{\parallel}$ ) and ( $\tau_{\perp}^{\perp}$ ), is the only movement which shows significant differences when investigated for both orientations in the nematic phase. This effect could be due to the occurrence in the low frequency range of a temporary orientation defect. Druon and Wacrenier [20] have supposed that this defect is

related to the existence of small groups of associated molecules with a lifetime of the same order of magnitude as  $\tau_{\perp}^{\parallel}$ .

For 6CB + aerosil mixtures, figure 6 displays comparative plots with bulk 6CB for the temperature dependence of the relaxation times. In the nematic phase, only the longitudinal component  $\epsilon_{\parallel}^*(\omega)$  for the mixtures has been measured. One can see in figure 6 that all the processes for the mixtures are bulk-like processes which compare well with those for bulk 6CB. It is worth mentioning that during our quantitative evaluation of the dielectric permittivity of the mixtures, the same analysis as for pure 6CB has been followed. Nevertheless, eventualities where the appearance of a new relaxation process or the suppression of a bulk-like process in the mixtures have been systematically investigated in our measuring frequency range.

In the isotropic phase, despite numerous studies on the subject, the situation is still not clear. Using the logarithmic distribution functions of relaxation times  $G(\ln \tau)$ , earlier dielectric studies of 7CB and 8CB by Bose *et al.* [18, 21] showed the existence of three relaxation frequencies in the isotropic phase. They localized one

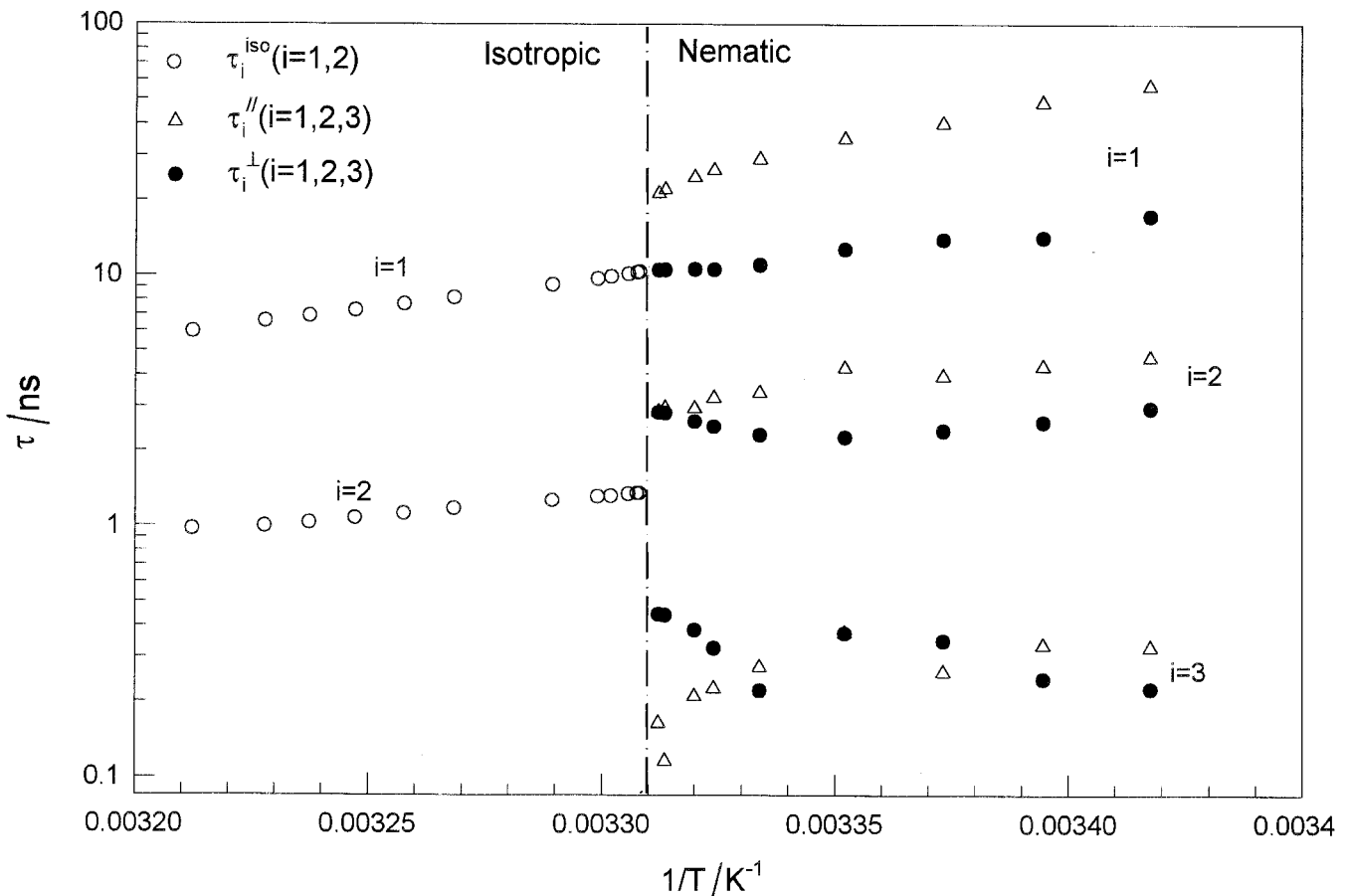


Figure 4. Temperature dependence of the relaxation times corresponding to the different molecular processes of 6CB molecules.

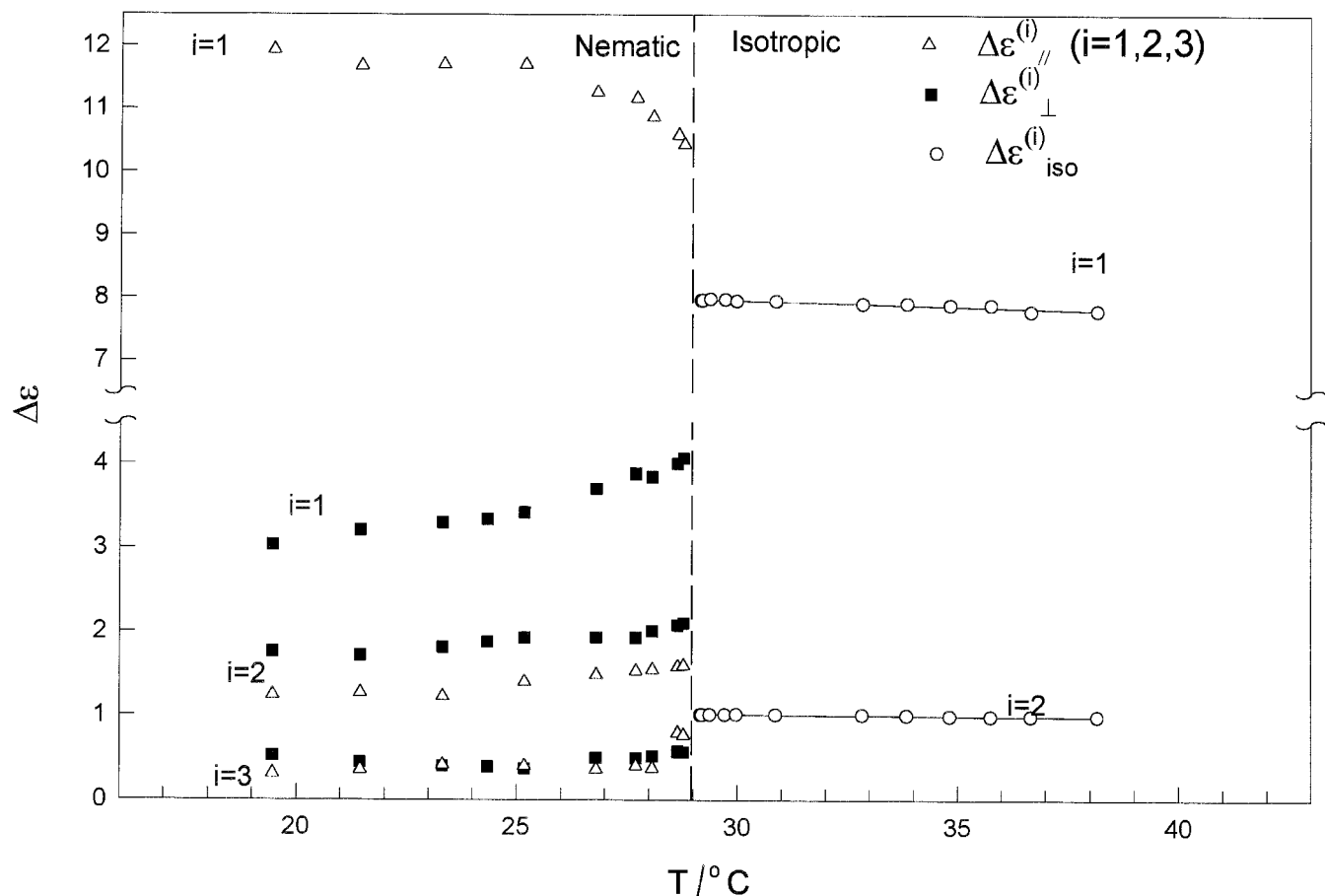


Figure 5. Temperature dependence of the dielectric strengths for the different absorption bands for 6CB molecules.

low frequency process in the 30 MHz range and two high frequency processes in the 200 and 600 MHz ranges. It is worth mentioning that by using the distributions functions, one does not need prior knowledge about how many relaxations processes there may be in a given phase before fitting the experimental data. In their recent work on 6CHBT, Jadzyn *et al.* [22] showed the existence of only two relaxation times in the isotropic phase. One low frequency relaxation process was due to the rotation of the molecules around the molecular short axis and a high frequency relaxation process in the 1 GHz range, which goes deep into the nematic phase, related to the rotation of the molecules around the molecular long axis. In the present study, fits of our isotropic dielectric data with three relaxation times seem to reject the high frequency relaxation (near 1 GHz), probably because of its small strength, resulting in two longer relaxation times than when fitted with two relaxation times with all the parameters free. We also obtained a reasonable fit with two relaxation times by leaving the parameters of the low frequency process free and fixing the high frequency relaxation time around 900 MHz.

In an attempt to resolve the dielectric spectrum into elementary contributions based on the best fit in the isotropic phase, we took into account both the absorption and the dispersion curves to obtain the minimum value for

$$S = \sum_1^m \{ [\epsilon'_{\text{obs}}(\omega_1) - \epsilon'_{\text{calc}}(\omega_1)]^2 + [\epsilon''_{\text{obs}}(\omega_1) - \epsilon''_{\text{calc}}(\omega_1)]^2 \} \quad (2)$$

where  $m$  is the number of data points. The most appropriate number of elementary processes involved is determined by the minimum of the standard deviation  $\sigma_{\text{min}} = [S/(m-2p)]^{1/2}$  which takes into account the quality of the fit (value of  $S$ ) and the number of degrees of freedom ( $m-2p$ ). From our analysis, the fits of the experimental data with two relaxations in the Cole–Cole equation with all the parameters free were the best. Figure 3(c) shows the resolution of the Cole–Cole plot at  $T = 38.15^\circ\text{C}$  into two elementary contributions for the bulk 6CB. From the results of our fits, the values of the Cole–Cole

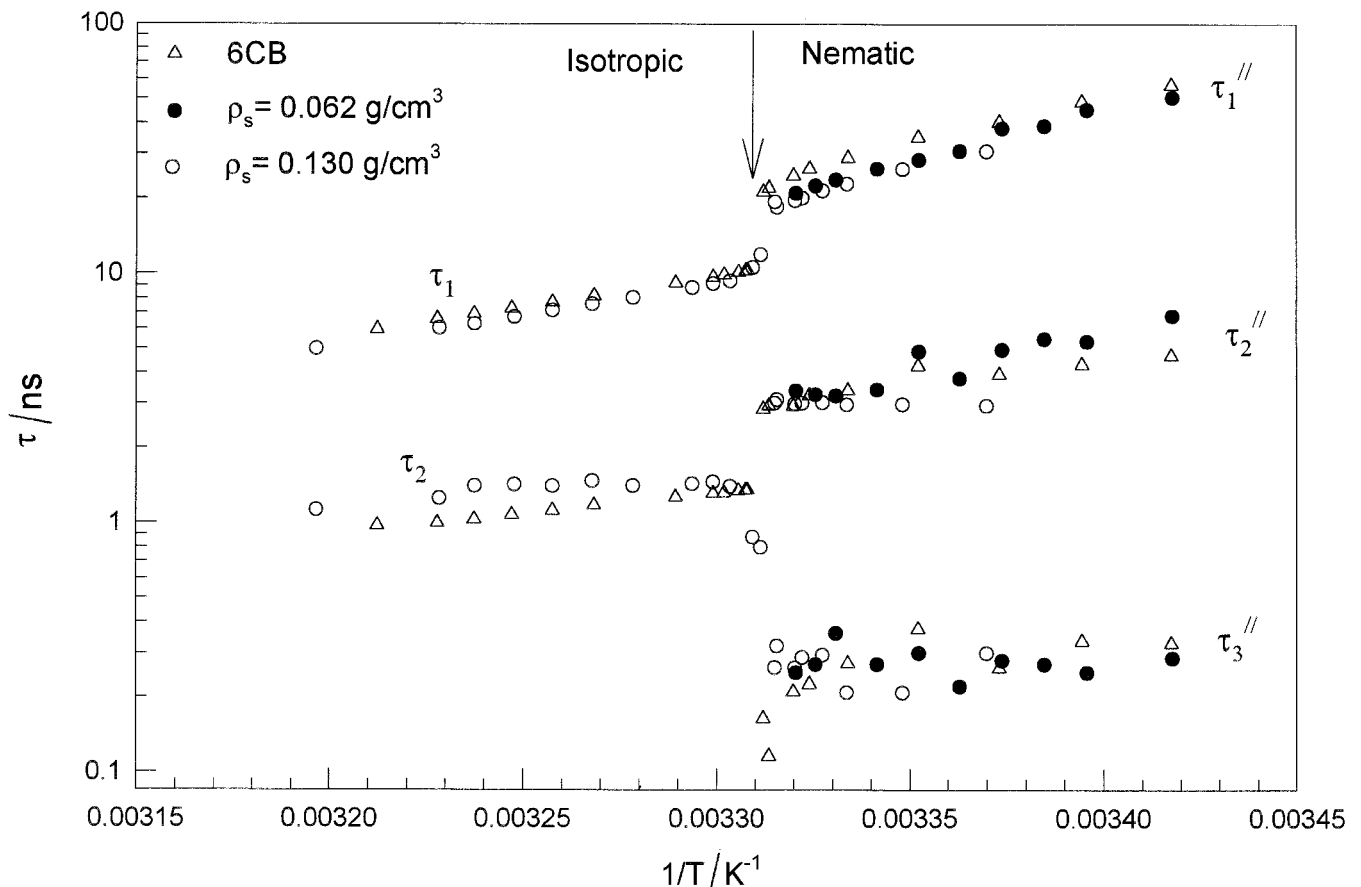


Figure 6. Comparative plot of the temperature dependence of the longitudinal relaxation times for the different modes of molecular rotation of 6CB molecules in the bulk and in the mixtures  $\rho_s = 0.062 g cm^{-3}$  (in the nematic phase only) and  $\rho_s = 0.130 g cm^{-3}$ .

distribution parameter  $\alpha_j$  ( $j = 1, 2$ ) for the two contributions varies between 0.026 at  $38.15^\circ C$  to a value of 0.08 at the lowest temperature in the isotropic phase. The second relaxation mechanism, i.e. band 2 in figure 3(c), has a characteristic frequency in the range from 117 MHz at  $29.15^\circ C$  to 164 MHz at  $38.15^\circ C$  (see figure 6). As a director does not exist in the isotropic phase (disordered phase), this relaxation process could not be due to molecular rotation on the cone around the director  $\mathbf{n}$ . It is therefore probably connected with some sort of a weighted average of all relaxation processes where the measuring electric field sees simultaneously relaxations of molecular rotation along the short and long axes.

Figure 7 presents for comparison the temperature dependence of the dielectric strengths in the isotropic phase and in the nematic phase for the longitudinal component of the dielectric permittivity for 6CB and the mixture  $\rho_s = 0.130 g cm^{-3}$ . At a given temperature in the isotropic phase, the dielectric strengths  $\Delta\epsilon^{(i)}$  ( $i = 1, 2$ ) for both processes are lower for the mixture than for the bulk 6CB. However, as seen in the figure, the isotropic strength  $\Delta\epsilon^{(2)}$  seems to decrease with decreasing tem-

perature towards the relaxation strength  $\Delta\epsilon^{(3)}$  in the nematic phase, which is connected with the rotation of the molecules around the molecular long axis. At fixed temperature in the nematic phase, the dielectric strength of the first process  $\Delta\epsilon^{(1)}$  is also higher for pure 6CB than for the  $\rho_s = 0.130 g cm^{-3}$  mixture. This behaviour may be due to the silica aerosil network, which induces disorder and defects that degrade the orientational order. For the strengths  $\Delta\epsilon^{(2)}$  and  $\Delta\epsilon^{(3)}$ , no noticeable differences between bulk 6CB and the mixture with  $\rho_s = 0.130 g cm^{-3}$  can be inferred from their temperature dependences. This is probably because of their small values and an estimated error of around 30% in their determination from the fits.

One of us (A.H.) gratefully acknowledges the post-doctoral fellowship of the Québec-Flanders cooperation. This work was supported by the National Fund for Scientific Research Flanders (Belgium) (FWO, project: G.0264.97N) and by scientific and technological cooperation between Flanders and Québec (Project: BIL 96/45-A1460).



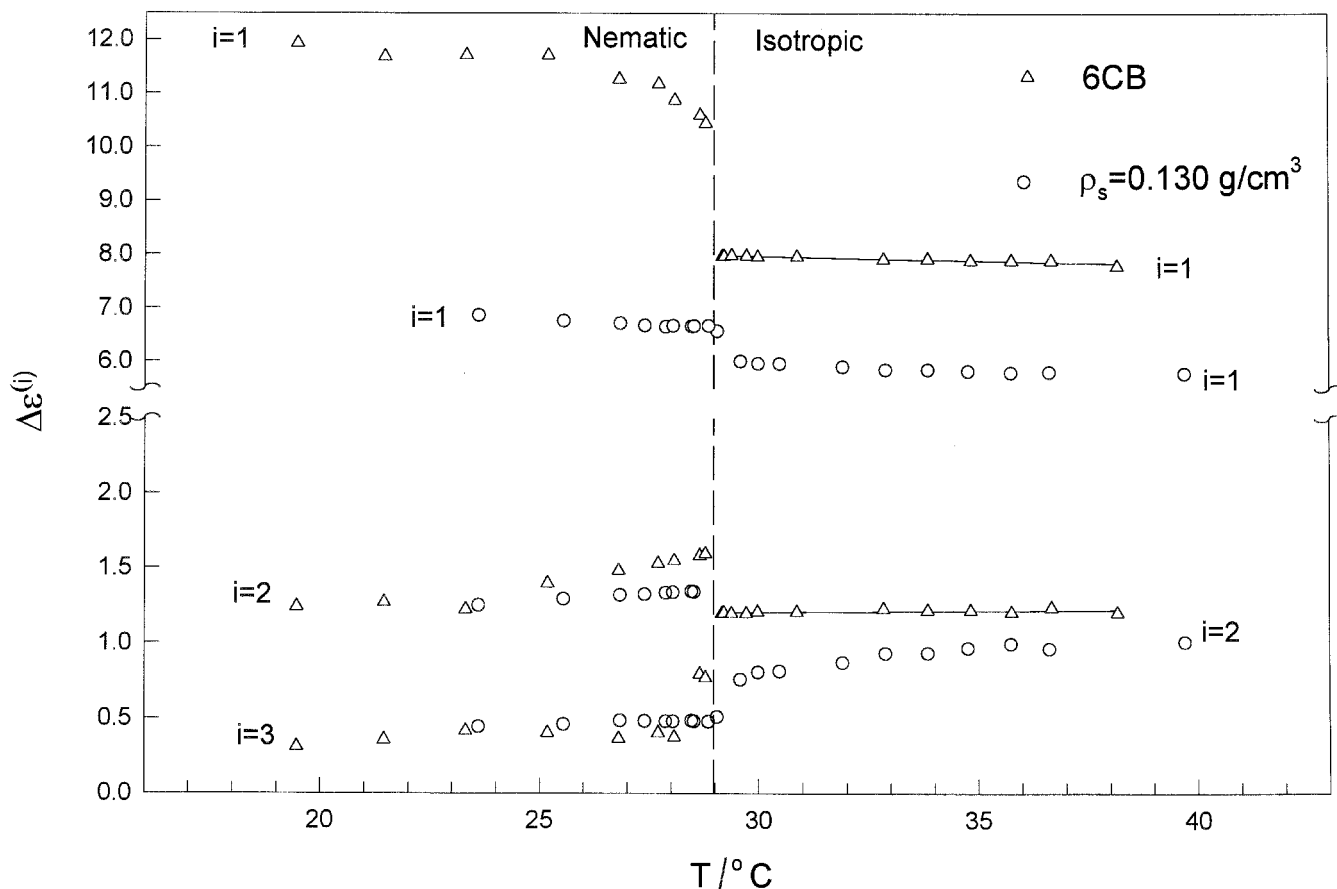


Figure 7. Comparative plot of the temperature dependence of the longitudinal dielectric strengths for the different modes of the molecular processes for bulk 6CB and the mixture with  $\rho_s = 0.130 \text{ g cm}^{-3}$ .

### References

- [1] CRAWFORD, G. P., and ZUMER, S., 1996 *Liquid Crystals in Complex Geometries Formed by Polymer and Porous Networks* (London: Taylor & Francis) and references therein.
- [2] BELLINI, T., CLARK, N. A., and SCHAEFER, D. W., 1995, *Phys. Rev. Lett.*, **74**, 2740.
- [3] WU, L., ZHOU, B., GARLAND, C. W., BELLINI, T., and S. SCHAEFER, D. W., 1995, *Phys. Rev. E*, **51**, 2157.
- [4] SINHA, G. P., and ALIEV, F. M., 1998, *Phys. Rev. E*, **58**, 2001.
- [5] ALIEV, F. M., 1995, in *Access in Nanoporous Materials*, edited by T. J. Pinnavia and M. F. Thorpe (New York: Plenum Press), pp. 335–354.
- [6] CRAMER, C., CRAMER, T., KREMER, T., and STANNARIUS, R., 1997, *J. chem. Phys.*, **106**, 3730.
- [7] WERNER, J., OTTO, K., ENKE, J., PELZL, G., JANOWSKI, F., and KRESSE, H., 2000, *Liq. Cryst.*, **27**, 1295.
- [8] ZHOU, B., IANNACHIONE, G. S., and GARLAND, C. W., 1997, *Liq. Cryst.*, **22**, 275.
- [9] HAGA, H., and GARLAND, C. W., 1997, *Phys. Rev. E*, **56**, 3044.
- [10] ABD.-EL-MESSIEH, S. L., WERNER, J., SCHMALFUS, H., WEISSFLOG, W., and KRESSE, H., 1999, *Liq. Cryst.*, **26**, 535.
- [11] HOURRI, A., BOSE, T. K., and THOEN, J., 2001, *Phys. Rev. E*, **63**, 0517706.
- [12] HAGA, H., and GARLAND, C. W., 1997, *Liq. Cryst.*, **23**, 645.
- [13] JADZYN, J., CZECHOUSKI, G., DOUALI, R., and LEGRAND, C., 1999, *Liq. Cryst.*, **26**, 1591.
- [14] IANNACHIONE, G. S., GARLAND, C. W., MANG, J. T., and RIEKER, T. P., 1998, *Phys. Rev. E*, **58**, 5966.
- [15] Degussa Corp., Silica Division, 65 Challenger Road, Ridge-Field Park, N.J. 07660 USA. Technical data and properties are given in the manufacturer's booklet *AEROSIL*.
- [16] COLE, K. S., and COLE, R. H., 1949, *J. chem. Phys.*, **9**, 341.
- [17] THOEN, J., and BOSE, T. K., 1999, in *Handbook of Low and High Dielectric Constant Materials and Their Applications*, Vol. 2, edited by H. S. Nalwa (Academic Press), pp. 501–561.
- [18] BOSE, T. K., CAMPBELL, B., YAGIHARA, S., and THOEN, J., 1987, *Phys. Rev. A*, **36**, 5767 and references therein.
- [19] LIPPENS, D., PARNEIX, J. P., and CHAPOTON, A., 1977, *J. Phys. (Paris)*, **38**, 1645.
- [20] DRUON, C., and WACRENIER, J. M., 1978, *Ann. Phys.*, **3**, 199.
- [21] BOSE, T. K., CHAHINE, R., MERABET, M., and THOEN, J., 1984, *J. Phys. (Paris)*, **45**, 1329.
- [22] JADZYN, J., HELLMANS, L., CZECHOUSKI, G., LEGRAND, C., and DOUALI, R., 2000, *Liq. Cryst.*, **27**, 613.