POLYMERS
AND LIQUID CRYSTALS

Distribution Function of Relaxation Times
for a 4-*n*-Pentyl-4'-Cyanobiphenyl Liquid Crystal

B. A. Belyaev, N. A. Drokin, and V. F. Shabanov

Kirensky Institute of Physics, Siberian Division, Russian Academy of Sciences,
Akademgorodok, Krasnoyarsk, 660036 Russia
e-mail: belyaev@iph.krasn.ru
Received October 4, 2004

Abstract—The distribution function of relaxation times is reconstructed from the dielectric loss spectrum measured over a wide range of frequencies for a 4-*n*-pentyl-4'-cyanobiphenyl (5CB) liquid crystal. It is demonstrated that the distribution function for the isotropic and nematic phases is asymmetric in shape. Comparison shows that the reconstructed distribution function is in qualitative agreement with similar functions that are analytically derived from the Cole–Davidson and Havriliak–Negami empirical equations. The specific features observed in the behavior of the distribution function with a variation in the angle between the direction of polarization of a microwave electric field and the director of the liquid-crystal molecules are analyzed. A complex dependence of the permittivity for the liquid crystal in the range of ultrahigh frequencies is explained in terms of additional relaxation mechanisms associated with different motions of molecular fragments of alkyl chains. © 2005 Pleiades Publishing, Inc.

1. INTRODUCTION

As a rule, the dielectric spectra of liquid crystals measured over a wide frequency range cannot be adequately described by the Debye equation with one relaxation time. This is associated with the contributions from different relaxation mechanisms of motion of liquid-crystal molecules in alternating-current electric fields. These mechanisms have been extensively investigated in recent years. In particular, in our earlier works [1–3], we demonstrated that, in order to increase the accuracy in the approximation of the dispersion of the perpendicular component of the permittivity $\varepsilon'_{\perp}(\omega)$ in the high- and ultrahigh-frequency ranges, the Debye equation must take into account the continuous distribution of relaxation times over a sufficiently wide range. Such a continuous distribution of relaxation times for the perpendicular orientation of polarization of the microwave electric field with respect to the director of liquid-crystal molecules is most likely a characteristic property of liquid crystals and stems from the existence of flexible hydrocarbon groups (alkyl chains) in the molecular structure. As is known, the alkyl chain bonded to the rigid core of the molecule has a planar zigzag structure in which C–H methylene groups are located in planes perpendicular to the molecular axis [4]. In these liquid-crystal media, relaxation processes involve rotational motions of the molecules about their short and long axes, as well as rotational and translational motions of the rigid core and alkyl groups. It is these motions that are described by a continuous distribution of relaxation times over a wide range.

The so-called smeared dielectric spectra, as a rule, have been numerically analyzed by introducing a distribution function of relaxation times into the Debye dispersion relation in a specified time interval [5]. In our previous works [2, 3], the dielectric spectra of liquid crystals of the cyano derivative compounds were approximated using symmetric and asymmetric trial distribution functions of relaxation times. The distribution functions of relaxation times used in those studies were chosen without regard for the specific features of the liquid-crystal molecules. It is obvious that a more correct approach to the determination of the form of a distribution function of relaxation times should be based on a microscopic model of molecular motions. However, although the contribution of high-frequency molecular motions to the dispersion of the permittivity of a liquid crystal has been clearly revealed in experiments, it has never been studied theoretically. In this respect, the problem associated with the development and application of the appropriate methods for determining the distribution functions of relaxation times directly from the experimental dielectric spectra is of fundamental importance. Knowledge of the true distribution functions of relaxation times is required not only to approximate correctly the dielectric frequency spectra but also to gain a deeper insight into the nature of the characteristic relaxation times of intramolecular motions and to develop the relaxation theory of liquid crystals.

The purpose of this work was to determine the distribution function of relaxation times for a 4-*n*-pentyl-4'-cyanobiphenyl (5CB) liquid crystal with the use of both the empirical equations approximating the dielec-
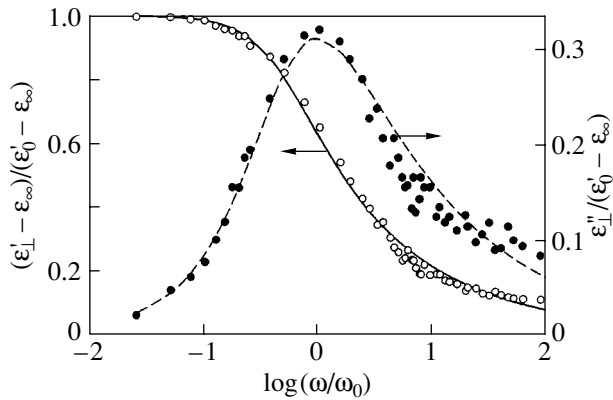
Fig. 1. Dispersion of the normalized real and imaginary components of the permittivity. Points are the experimental data, and the lines correspond to the approximations by the Havriliak–Negami equation.

tric spectra and a special algorithm that makes it possible to obtain this function directly from the dielectric loss spectra experimentally measured over a wide frequency range.

2. CALCULATIONS, RESULTS, AND DISCUSSION

The classical approach to the approximation of complex dielectric spectra for a large class of compounds, including liquid crystals, consists in determining the corresponding exponents in the empirical relationship proposed by Havriliak and Negami; that is,

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_0' - \varepsilon_\infty}{[1 + (i\omega\tau_0)^\alpha]^\gamma}. \quad (1)$$

Here, the exponents α and γ are the numerical parameters describing the degree of smearing and the asymmetry of the dielectric spectrum in the "low"- and "high"-frequency ranges, respectively; ε_0' is the static permittivity measured at the frequency $\omega = 0$; ε_∞ is the high-frequency permittivity at $\omega \gg 1/\tau_0$; and $\tau_0 = 1/(2\pi f_0)$ is the time constant corresponding to the effective relaxation time determined from the relaxation frequency $f_0 = \omega_0/2\pi$ at which the dielectric losses have a maximum. It should be noted that, in this case, the approximate equality $\varepsilon_\infty \approx n^2$ (where n is the optical refractive index) is satisfied. For anisotropic media, we have $\varepsilon_{\|\infty} \approx n_e^2$ and $\varepsilon_{\perp\infty} \approx n_o^2$ (where n_e and n_o are the extraordinary and ordinary refractive indices, respectively).

In this work, the Havriliak–Negami equation was used to approximate the measured dependences of the real and imaginary components of the perpendicular permittivity, $\varepsilon_\perp'(\omega)$ and $\varepsilon_\perp''(\omega)$, for the 5CB liquid crystal under investigation. The dielectric spectra were recorded using original microscopic resonance sensors

in the frequency range 1–5000 MHz at temperatures $T = 25$–60°C. The experimental technique was described in our previous work [6].

The experimental dependences of the normalized components of the permittivity $[\varepsilon_\perp'(\omega) - \varepsilon_\infty]/(\varepsilon_0' - \varepsilon_\infty)$ and $\varepsilon_\perp''(\omega)/(\varepsilon_0' - \varepsilon_\infty)$ on $\log(\omega/\omega_0)$ at $T = 30^\circ$C are shown by points in Fig. 1. The solid and dashed lines in this figure represent the results of approximating the dielectric spectra with the use of Eq. (1), in which the permittivity was separated into real and imaginary components. In the calculation, we used the following relationships [7]:

$$\frac{\varepsilon'(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty}$$
$$= \frac{\cos(\gamma\phi)}{\{1 + 2(\omega\tau_0)^\alpha \sin[\pi/2(1-\alpha)] + (\omega\tau_0)^{2\alpha}\}^{\gamma/2}}, \quad (2)$$

$$\frac{\varepsilon''(\omega)}{\varepsilon_0 - \varepsilon_\infty}$$
$$= \frac{\sin(\gamma\phi)}{\{1 + 2(\omega\tau_0)^\alpha \sin[\pi/2(1-\alpha)] + (\omega\tau_0)^{2\alpha}\}^{\gamma/2}}, \quad (3)$$

where

$$\phi = \arctan\left\{\frac{(\omega\tau_0)^\alpha \cos[\pi/2(1-\alpha)]}{1 + (\omega\tau_0)^\alpha \sin[\pi/2(1-\alpha)]}\right\}.$$

This approximation leads to reasonable agreement between the calculation and the experiment (Fig. 1) for the following parameters: $\varepsilon_{0\perp} = 7$, $n_o = 1.54$, $\alpha = 0.95$, $\gamma = 0.48$, and $\tau_0 = 7.3 \times 10^{-9}$ s. It is worth noting that the exponent α appears to be close to unity. This means that the dispersion curves $\varepsilon_\perp'(\omega)$ and $\varepsilon_\perp''(\omega)$ can also be described by the Cole–Davidson equation with the sole parameter $\gamma = 0.48$. This equation is applicable to the dielectric spectra smeared only at high frequencies with respect to the frequency ω_0. To the Havriliak–Negami and Cole–Davidson empirical equations there correspond distribution functions of relaxation times at the aforementioned parameters α and γ. For the Cole–Davidson model, the distribution function $g(\tau)$ can be written in the form [8]

$$g(\tau) = \begin{cases} \dfrac{\sin(\pi\gamma)}{\pi}\left(\dfrac{\tau}{\tau_0 - \tau}\right)^\gamma, & 0 < \tau < \tau_0 \\ 0, & \tau > \tau_0. \end{cases} \quad (4)$$

For the Havriliak–Negami model, the distribution function $g(\tau)$ can be represented as follows [7]:

$$g(\tau) = \frac{1}{\pi}\frac{(\tau/\tau_0)^{\alpha\gamma}\sin(\lambda\theta)}{[(\tau/\tau_0)^{2\alpha} + 2(\tau/\tau_0)^\alpha\cos(\alpha\pi) + 1]^{\gamma/2}}, \quad (5)$$

where

$$\theta = \arctan\left[\frac{\sin(\gamma\pi)}{(\tau/\tau_0)^\alpha + \cos(\alpha\pi)}\right]. \qquad (6)$$

The distribution functions of relaxation times calculated from relationships (4) and (5) for the above models are presented in Fig. 2. It can be seen from this figure that, for the Cole–Davidson model, the distribution function of relaxation times is equal to zero at long relaxation times ($\tau > \tau_0$) and $g(\tau) \longrightarrow \infty$ at $\tau \longrightarrow \tau_0$. It can also be seen that the constructed functions are different in behavior. However, common to both functions is their asymmetry with respect to the axis passing through the point τ_0. Such a substantial difference between the functions complicates the physical interpretation of the dispersion dielectric properties of the liquid crystal, because the empirical coefficients α and γ are not related to specific physical models of a liquid-crystal medium. It is important to note that the true distribution function $g(\tau)$ reflecting relaxation processes in a particular liquid crystal can turn out to be considerably more complicated. Therefore, in order to describe the dispersion $\varepsilon(\omega)$ more correctly and then to analyze the mechanisms of relaxation processes in the liquid crystal, it is more expedient to determine the distribution function of relaxation times directly from the experimental data.

The complex permittivity that describes relaxation processes in materials with a broad distribution of relaxation times, as a rule, is written in the form

$$\varepsilon(\omega) = \varepsilon'_\infty + (\varepsilon'_0 - \varepsilon'_\infty)I(\omega). \qquad (7)$$

Here, $I(\omega)$ is the frequency-dependent function defined by the formula

$$I(\omega) = \int_0^\infty \frac{g(\tau)}{1 + i\omega\tau} d(\log\tau), \qquad (8)$$

which is normalized so that $I(0) = 1$.

Several approaches to the determination of the function $g(\tau)$ from experimental data on the dispersion of the real or imaginary components of the permittivity have been developed to date. Valenkevich *et al.* [9] proposed a method for calculating the function $g(\tau)$ that employs direct and inverse Fourier transforms applied to relationship (8). The advantage of this method is a high resolution of the distribution $g(\tau)$. However, the distribution function of relaxation times obtained in the framework of this approach appears to be distorted by subsidiary maxima that are not associated with the relaxation processes. Ktitorov [10] derived and justified expressions relating the function $g(\tau)$ to the dielectric loss function. However, the use of these expressions requires knowledge of the analytical properties of this function, but such properties cannot be uniquely established when the measurements are performed in a limited frequency range.
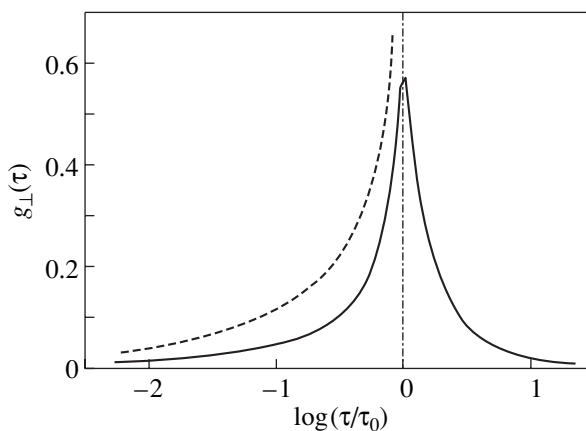

Fig. 2. Distribution functions of relaxation times calculated within the Cole–Davidson (dashed curve) and Havriliak–Negami (solid line) models.

It is known that expression (8) is a Fredholm equation of the first kind. This equation can be solved using a number of numerical methods for determining the distribution function of relaxation times from the experimental dependences $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ [7, 8, 11–13]. These algorithms as applied to solving integral equation (8) for determining the distribution function of relaxation times are the most promising at present. However, the proposed approaches require that the dielectric spectra be measured over a sufficiently wide range of frequencies. Moreover, the use of these approaches leads to a problem regarding the stability of the solutions obtained.

In this study, the distribution function $g(\tau)$ was determined from the measured dependences $\varepsilon''(\omega)$ by using the popular numerical algorithm, which is referred to as the histogram method [14]. In our opinion, the simplicity of this method and the possibility of determining even relatively narrow distributions of relaxation times render the histogram method more advantageous than the aforementioned approaches. In the histogram method, the initial dielectric spectrum $\varepsilon''(\omega)$ is represented in the form of a histogram that is constructed by dividing the chosen frequency range into a specified number of intervals. For each rectangle in the histograms there is a particular relaxation frequency ω_i with the corresponding relaxation time $\tau_i = 1/\omega_i$. As a result, integral equation (8) is transformed into the discrete form

$$\varepsilon''_{\mathrm{calcd}}(\omega) = K_1 \sum_{i=1}^{l} \sum_{k=1}^{l} g(\tau_k)\omega_i\tau_k/\{1 + \omega_i^2\tau_k^2\}. \qquad (9)$$

Here, $\varepsilon''_{\mathrm{calcd}}(\omega)$ is the calculated frequency dependence of the imaginary component of the permittivity, K_1 is the width of the interval in the histogram, l is the number of intervals in the histogram, and $g(\tau_k)$ is the set of weighting factors (the matrix containing one column
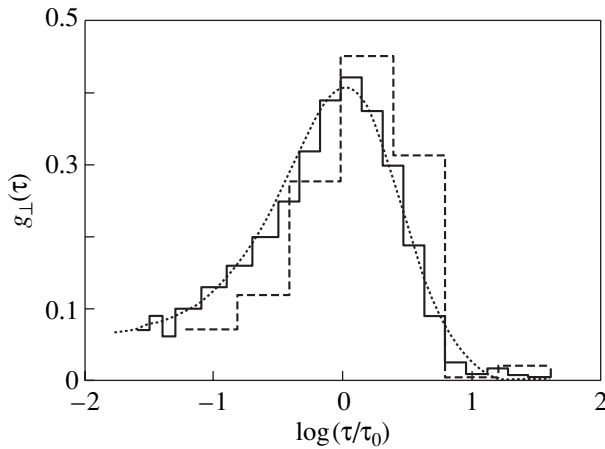
Fig. 3. Distribution functions of relaxation times obtained for the numbers of intervals $l = 8$, 20, and 80. The smoothed dotted line corresponds to the distribution function for $l = 80$.

Fig. 4. Distribution functions of relaxation times at different angles φ of the microwave field orientation with respect to the director.

formed by l components of trial values of the desired distribution function). As seed (initial) values of $g(\tau_k)$, it is possible to choose, for example, zero values. The desired distribution function $g(\tau)$ can be reconstructed using the following iterative procedure:

$$g(\tau) \longleftarrow g(\tau) + K_2 \Delta\varepsilon, \qquad (10)$$

where $\Delta\varepsilon$ is the difference between the experimental and calculated values $\varepsilon''_{exp}(\omega)$ and $\varepsilon''_{calcd}(\omega)$ and the factor $K_2 \approx 0.3$–0.5 provides the stability of the iterative procedure. In our work, this algorithm was implemented with the Mathcard software package. The distribution function of relaxation times was determined after completion of the iterative procedure, when the specified maximum difference $\Delta\varepsilon$ was reached. As a result, the distribution function of relaxation times thus obtained ensures that the experimental and calculated frequency dependences of the imaginary component of the permittivity $\varepsilon''_{exp}(\omega)$ and $\varepsilon''_{calcd}(\omega)$ coincide to within a specified value $\Delta\varepsilon$.

When determining the distribution function of relaxation times, the spectrum $\varepsilon''_{exp}(\omega)$ can be divided into an arbitrary number of identical intervals. Figure 3 shows the distribution function $g_\perp(\tau)$ determined for the 5CB liquid crystal at $T = 30°C$ with the use of different numbers of intervals in the histogram ($l = 8$, 20, 80). Note that, at $l < 8$, the algorithm works poorly, because some intervals in the histogram contain negative values of $g(\tau)$. It can be seen from Fig. 3 that, in principle, the shape of the distribution function of relaxation times does not depend on the number of intervals in the histogram. As is also seen from this figure, all the dependences obtained are asymmetric with respect to the ordinate axis and are extended toward short relaxation times. It should be noted that the specified equidistant relaxation times are not associated with the particular relaxation models of liquid crystals. Therefore, the
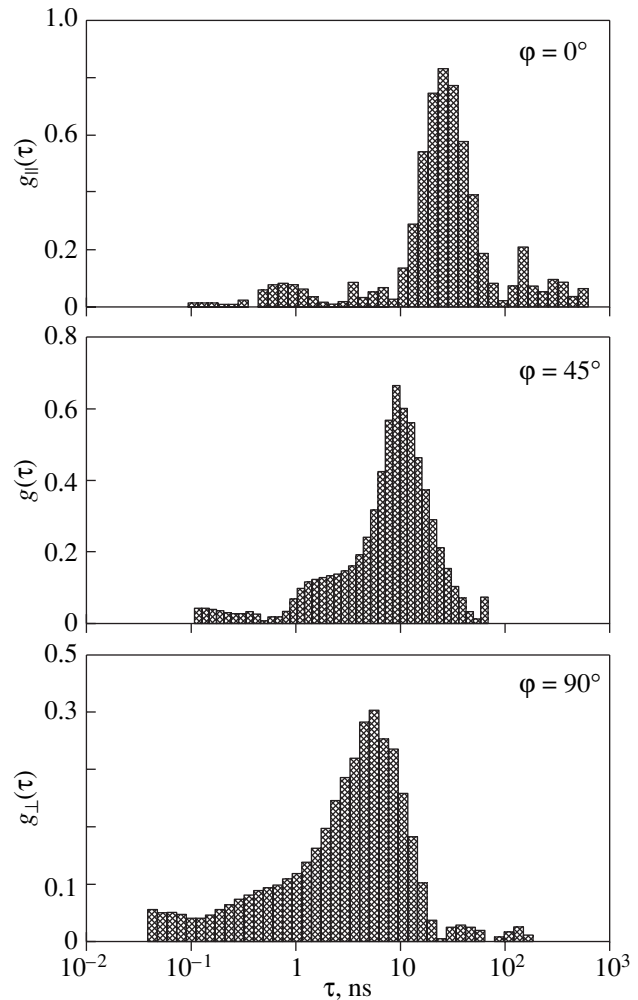
division into a specified number of intervals is governed by the problem under investigation rather than by the physical models. For example, in order to obtain a well-resolved distribution of relaxation times $g_\perp(\tau)$, the spectrum $\varepsilon''_{exp}(\omega)$ should be divided into intervals with the use of a small step, whereas the analysis of the relaxation in a narrow time interval can be performed using a large step.

Figure 4 presents the distribution function $g(\tau)$ determined from the experimental data obtained at different angles φ between the director of liquid-crystal molecules and the direction of polarization of the microwave electric field. In measurements, the liquid-crystal molecules were oriented by a static magnetic field $H = 2.5$ kOe applied at a specified angle with respect to the polarization of the microwave field. Note that, at $\varphi = 0°$, the long axes of the liquid-crystal molecules are oriented along the electric field, so the measured dielectric spectrum corresponds to the parallel
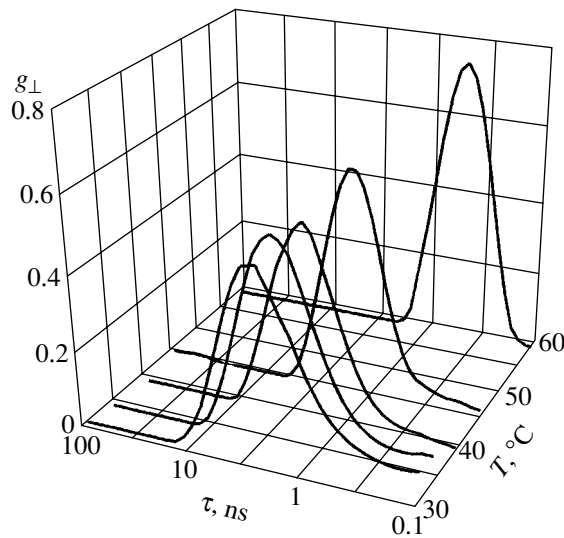
Fig. 5. Evolution of the distribution function of relaxation times with variations in the temperature.

permittivity and, hence, $g(\tau) = g_\parallel(\tau)$. In the case under consideration, the liquid-crystal molecules in the microwave field rotate about the short axis and this process is characterized by long relaxation times. This is confirmed by the distribution function $g_\parallel(\tau)$ (Fig. 4), whose maximum is shifted toward the range of long relaxation times. It is worth noting that the distribution function itself is almost symmetric in shape and exhibits its low-intensity additional maxima to the left and the right of the principal maximum.

As the angle φ increases to 45°, the maximum of the distribution function $g(\tau)$ shifts toward the range of shorter relaxation times and the distribution function itself becomes asymmetric (the left slope flattens). At $\varphi = 90°$, the long axes of the liquid-crystal molecules are oriented perpendicular with respect to the microwave electric field, so the measured dielectric spectrum corresponds to the perpendicular permittivity and, hence, $g(\tau) = g_\perp(\tau)$. With such director orientation, the liquid-crystal molecules in the microwave field rotate about the long axis and this process is characterized by short relaxation times. This is confirmed by the distribution function $g_\perp(\tau)$, whose maximum is shifted toward the range of short relaxation times (Fig. 4). The distribution function is strongly asymmetric in shape due to the gentle left slope.

It is of interest to investigate the behavior of the distribution function of relaxation times not only in the nematic phase but also in the isotropic phase of the liquid crystal. For this purpose, the dielectric spectra were measured at different temperatures. The distribution functions $g_\perp(\tau)$ determined from these dielectric spectra are shown in Fig. 5. As can be seen from Fig. 5, the distribution functions of relaxation times are asymmetric both in the nematic phase and in the isotropic phase up to temperatures $T \sim 50°C$. However, with a further

increase in the temperature of the liquid crystal, the distribution function becomes symmetric in shape. It should be noted that, in the nematic phase, an increase in the temperature leads to an insignificant shift in the maximum of the distribution function of relaxation times toward the range of short relaxation times. Upon transition from the nematic state to the isotropic state ($T_{ni} = 35°C$), this shift becomes more pronounced.

3. CONCLUSIONS

Thus, it was demonstrated using the 5CB liquid crystal as an example that the distribution function of relaxation times can be reconstructed from the measured frequency dependence of the imaginary component of the permittivity. The validity of the chosen approach and the algorithm for determining the distribution function of relaxation times was confirmed by the following circumstances. First, the distribution functions of relaxation times determined from the experimental data and those analytically calculated in the framework of the Cole–Davidson and Havriliak–Negami models are in qualitative agreement and correspond to the same time interval. Second, the numerically calculated distribution functions of relaxation times adequately describe the corresponding frequency dependences of both the imaginary component $\varepsilon''_\perp(\omega)$ and the real component $\varepsilon'_\perp(\omega)$ of the permittivity. The specific features in the evolution of the distribution function of relaxation times for the 5CB liquid crystal with a variation in the temperature were investigated for the first time. These results are particularly important for the understanding of the molecular dynamics in liquid crystals. The distribution function of relaxation times $g_\perp(\tau)$ is asymmetric because additional relaxation processes occur in the 5CB liquid crystal due to the dynamic change in the conformational equilibrium of alkyl chains of liquid-crystal molecules in response to a microwave field. Certainly, it is more advisable to reconstruct the distribution function of relaxation times from the experimental data on the real component of the permittivity $\varepsilon'(\omega)$, because the accuracy in recording these spectra by the resonance technique of dielectric measurements is higher than that of the spectra $\varepsilon''(\omega)$. In the future, we hope to perform such investigations.

REFERENCES

1. B. A. Belyaev, N. A. Drokin, V. F. Shabanov, and V. N. Shepov, Fiz. Tverd. Tela (St. Petersburg) **45** (3), 567 (2003) [Phys. Solid State **45** (3), 598 (2003)].

2. B. A. Belyaev, N. A. Drokin, V. F. Shabanov, and V. A. Baranova, Fiz. Tverd. Tela (St. Petersburg) **46** (3), 554 (2004) [Phys. Solid State **46** (3), 574 (2004)].

3. B. A. Belyaev, N. A. Drokin, and V. F. Shabanov, Fiz. Tverd. Tela (St. Petersburg) **46** (3), 559 (2004) [Phys. Solid State **46** (3), 579 (2004)].

4. E. M. Aver'yanov, *Local Field Effects in Optics of Liquid Crystals* (Nauka, Novosibirsk, 1999) [in Russian].

5. H. Fröhlich, *Theory of Dielectrics*, (Oxford Univ. Press, Oxford, 1958; Inostrannaya Literatura, Moscow, 1960).

6. B. A. Belyaev, N. A. Drokin, V. F. Shabanov, and V. N. Shepov, Zh. Tekh. Fiz. **72** (4), 99 (2002) [Tech. Phys. **47** (4), 470 (2002)].

7. F. Alvarez, A. Alegria, and H. Colmenero, Phys. Rev. B **44** (14), 7306 (1991).

8. F. D. Morgan and D. P. Lesmes, J. Chem. Phys. **100** (1), 671 (1994).

9. V. A. Valenkevich, M. S. Mitsek, and O. I. Gudkov, Izv. Vyssh. Uchebn. Zaved., Fiz. **25** (3), 37 (1982).

10. S. A. Ktitorov, Pis'ma Zh. Tekh. Fiz. **29** (22), 74 (2003) [Tech. Phys. Lett. **29** (11), 956 (2003)].

11. M. A. Leshchenko and Yu. M. Poplavko, Ukr. Fiz. Zh. **73** (6), 898 (1992).

12. J. R. Macdonald, J. Chem. Phys. **102** (15), 6241 (1995).

13. A. Bello, E. Laredo, and M. Grimau, Phys. Rev. B **60** (18), 12764 (1999).

14. Y. Imanishi, K. Adachi, and T. Kotaka, J. Chem. Phys. **89** (12), 7593 (1988).

Translated by O. Borovik-Romanova