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Liquid Crystals

Publication details, including instructions for authors and subscription information:
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Online publication date: 06 August 2010

To cite this Article Schlacken, H. and Schiller, P.(2001) 'Brownian reorientation in smectic phases', Liquid Crystals, 28: 5, 779 — 784
To link to this Article: DOI: 10.1080/02678290010025431
URL: http://dx.doi.org/10.1080/02678290010025431

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Liquid Crystals, 2001, Vol. 28, No. 5, 779–784

Brownian reorientation in smectic phases

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(*Received 31 July 2000; in final form 23 October 2000; accepted 10 November 2000*)

The rotation of molecules around their long axes is influenced by the in-plane order in smectic phases. Assuming a Brownian reorientation process, the effect of polar and quadrupolar order on the dielectric spectrum is investigated. In the case of quadrupolar order two modes should be visible, while only one mode arises if the order is polar.

1. Introduction

In smectic phases the rod-like molecules reorient around their short and long axes. As both reorientation modes have substantially different relaxation frequencies, these processes can be resolved by dielectric spectroscopy. The slower process, the rotation around the short axes, is usually detected in a frequency region between one and a few hundred kilohertz [1, 2], whereas the rotation around the molecular long axes produces a dispersion at much higher frequencies (up to one gigahertz) [3–5]. In addition to these molecular processes, cooperative low frequency modes appear in smectic phases with long range in-plane order. Especially, the relaxation of the ferroelectric ordering in the chiral smectic C phase leads to a strong dielectric response [6]. Slow cooperative processes also influence the dielectric relaxation of antiferroelectric and ferrielectric smectic liquid crystals.

The fast molecular rotations around the long axes in the uniaxial smectic A phase produce a Debye spectrum, which is characterized by a single relaxation time. The high frequency spectrum is not substantially changed in the smectic C phase, although the C phase is biaxial. This surprising result can be explained by the observation that the biaxiality in the smectic C phase is rather weak. The magnitude of the effective pair potential for the hindrance of the molecular rotation around the long axes is small compared with the mean thermal energy of a rotator. In this case the high frequency dielectric spectrum of a biaxial phase cannot be distinguished from the corresponding spectrum of the uniaxial smectic A phase. However, systematic torques resulting from the anisotropy of the molecular packing in the smectic layers are not necessarily weak in all biaxial phases. For example, if slab-like molecules form a biaxial smectic M phase (figure 1), the rotational hindrance could be rather strong. In this case the effective potential, which depends on the polar angle of the lateral molecular dipole direction, has two equal minima. Recently, ordered smectic phases with banana-like or chevron-like molecules were detected [7]. In the ordered state, the tips of the chevrons are uniformly aligned parallel to the smectic layers. Then the corresponding rotator potential has only one minimum. Since there should be a strong steric hindrance if two adjacent banana-like molecules adopt an antiparallel orientation, the potential barriers are expected to be much higher than barriers in the smectic C phase.

In this paper we investigate how a strong lateral order in a smectic layer can influence the high frequency dielectric spectrum, which is attributed to the molecular reorientation around the molecular long axes. This mode is supposed to be a molecular process clearly distinguishable from the cooperative modes at low frequencies. Each molecule can be considered as a uniaxial rotator with transverse dipole moment, which can couple to an

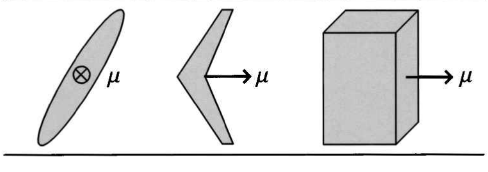

Figure 1. Rod-like, banana-like and slab-like molecules in a biaxial smectic layer.

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Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2001 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290010025431

external electric field perpendicular to the rotator axis. The Brownian motion of a rotator is influenced by the effective potential produced by the surrounding molecules. The deviations from a simple Debye spectrum are evaluated for potentials with one and two minima.

2. Linear response of the dipoles

The effect of an alternating field $E(\omega)$ on rotating dipoles is described by the linear relation $p(\omega) = \chi(\omega)E(\omega)$, where $p(\omega)$ is the dipole moment induced by the electric field and $\chi(\omega)$ is the susceptibility. We consider an ensemble of uniaxial rotators with transverse dipole moments μ. The orientation of a rotator is defined by a polar angle φ $(-\pi \leqslant \varphi < +\pi)$. In a smectic sample, the molecular long axes may be macroscopically oriented due to constraints imposed by the smectic layers and by boundary conditions, which fix the director to the substrate surfaces of a sandwich cell consisting of plane parallel plates. But the preferred direction (angle φ) of the transverse dipoles is usually different in various domains of a smectic sample. Assuming that these domains are arbitrarily aligned, the susceptibility can be expressed as [8]

$$\chi(\omega) = \chi_0 \left[K(0) + \mathrm{i}\omega \int_0^\infty \mathrm{d}t K(t) \exp(\mathrm{i}\omega t) \right] \tag{1}$$

where $\chi_0 = \beta\rho\mu^2/2$, $\beta = 1/(kT)$, ρ is the particle density, ω is the frequency and $K(t) = \langle \cos(\varphi(t) - \varphi(0)) \rangle$ is the two-time correlation function attributed to the reorientation of the lateral dipole. The correlation function $K(t)$ is obtained from the relation [9]

$$K(t) = \int_{-\pi}^{+\pi} \mathrm{d}\varphi \int_{-\pi}^{+\pi} \mathrm{d}\varphi' P(\varphi, t|\varphi', 0) P_{\mathrm{eq}}(\varphi') \cos(\varphi - \varphi') \tag{2}$$

where $P_{\mathrm{eq}}(\varphi')$ denotes the Boltzmann distribution for the rotator ensemble and $P(\varphi, t|\varphi', 0)$ is the transition probability of a stationary Markovian process.

3. Brownian reorientation model

We suppose that the reorientation of the molecular dipoles is a Brownian motion influenced by deterministic forces, which reflect the symmetry of the molecular packing in the smectic layers. The effective pair potential for a molecular rotator depends on a polar angle φ $(-\pi \leqslant \varphi < +\pi)$ of the lateral dipole moment. A Fourier expansion for this mean field potential reads $U^*(\varphi) = h_1 \cos(\varphi) + h_2 \cos(2\varphi)$, where h_1 and h_2 are potential barriers characterizing the polar and quadrupolar order, respectively. For slab-like molecules arranged in the smectic M phase, the first Fourier term vanishes ($h_1 = 0$), whereas for phases with banana-like molecules the polar term dominates ($|h_1| \gg |h_2|$). There are serious mathematical problems in evaluating the transition probability $P(\varphi, t|\varphi', 0)$ for rotator models with cosine potentials like $U^*(\varphi)$. For $\beta U^* \ll 1$ a perturbation expansion is appropriate [10], but for $\beta U^* \gg 1$ numerical methods [9] must be used. Therefore, we use modified potentials, which also reproduce polar and quadrupolar order (figure 2). These model potentials are formally written as

$$\beta U_\nu(\varphi) = (-1)^\nu \left[\frac{2H_1}{\pi}\varphi - H_1(2\nu - 1) \right] \quad \text{for} \quad (\nu - 1)\pi \leqslant \varphi < \nu\pi \tag{3}$$

and

$$\beta U_\nu(\varphi) = (-1)^\nu \left[\frac{4H_2}{\pi}\varphi - H_2(2\nu - 1) \right] \quad \text{for} \quad (\nu - 1)\frac{\pi}{2} \leqslant \varphi < \nu\frac{\pi}{2} \tag{4}$$

where $H_1 \geqslant 0$, $H_2 \geqslant 0$. In both formulae (3) and (4), ν is an integer indicating a region between two deflection points. The transition probability $P(\varphi, t|\varphi', 0)$ for the Brownian reorientation satisfies the Fokker–Planck equation [9]

$$\frac{\partial P}{\partial t} = D_{\mathrm{R}} \frac{\partial^2 P}{\partial \varphi^2} + \frac{\partial}{\partial \varphi}(\Omega P) \tag{5}$$

where $D_{\mathrm{R}} = kT/\zeta_{\mathrm{R}}$ is the effective diffusion coefficient for the rotational motion, $\Omega = \zeta_{\mathrm{R}}^{-1}(\mathrm{d}U/\mathrm{d}\varphi)$ is the angular velocity and ζ_{R} is the rotational friction coefficient. The transition probability satisfies the initial condition $P(\varphi, 0|\varphi', 0) = \delta(\varphi - \varphi')$. Equation (5) can be written in the short-hand notation $\partial P/\partial t = \mathbf{L}\, P$. Then the ansatz $P \sim \Psi(\varphi)\exp(-\lambda t)$ leads to the eigenvalue problem $\mathbf{L}\Psi_n = -\lambda_n \Psi_n$, where the operator $\mathbf{L}$ is non-hermitean. The replacements $\exp(W/2)\mathbf{L}\exp(-W/2) \rightarrow \mathbf{L}$ and $\exp(W/2)\Psi_n \rightarrow \Psi_n$ with $W = \beta U/2$ lead to a modified

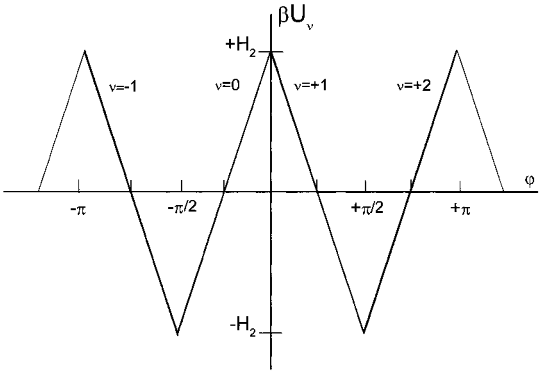

Figure 2. Triangular model potential. The integers ν denote regions between the deflection points.

equation with hermitean operator

$$\left(D_{\mathrm{R}}\frac{\mathrm{d}^2}{\mathrm{d}\varphi^2} - V\right)\Psi_n = -\lambda_n\Psi_n \tag{6}$$

where $V = D_{\mathrm{R}}[(1/2\beta\mathrm{d}U/\mathrm{d}\varphi)^2 - 1/2\beta\mathrm{d}^2U/\mathrm{d}\varphi^2]$. At the deflection points of the potential U the solutions of equation (6) must obey the conditions [9]

$$[\exp(+\beta U/2)\Psi_n]_{\varphi_0-0} = [\exp(+\beta U/2)\Psi_n]_{\varphi_0+0} \tag{7}$$

and

$$\left[\exp(-\beta U/2)\left(\frac{\mathrm{d}\Psi_n}{\mathrm{d}\varphi} + \frac{1}{2}\Psi_n\frac{\mathrm{d}(\beta U)}{\mathrm{d}\varphi}\right)\right]_{\varphi_0-0} = \left[\exp(-\beta U/2)\left(\frac{\mathrm{d}\Psi_n}{\mathrm{d}\varphi} + \frac{1}{2}\Psi_n\frac{\mathrm{d}(\beta U)}{\mathrm{d}\varphi}\right)\right]_{\varphi_0+0} \tag{8}$$

Choosing normalized eigenfunctions

$$\int_{-\pi}^{+\pi}\mathrm{d}\varphi\,\Psi_m\Psi_n^* = \delta_{mn} \tag{9}$$

the transition probability has the representation [9]

$$P(\varphi, t|\varphi', 0) = \frac{\Psi_0(\varphi)}{\Psi_0(\varphi')}\sum_n \Psi_n(\varphi)\Psi_n^*(\varphi')\exp(-\lambda_n t) \tag{10}$$

and the ground state function attributed to the eigenvalue $\lambda_0 = 0$ is given by $\Psi_0(\varphi) = [P_{\mathrm{eq}}(\varphi)]^{1/2}$. Combining the expansion (10) and formula (2) the correlation function is written as

$$K(t) = K_0 + \sum_{n\neq 0} K_n\exp(-\lambda_n t) \tag{11}$$

where the coefficients are defined by

$$K_n = \int_{-\pi}^{+\pi}\mathrm{d}\varphi\int_{-\pi}^{+\pi}\mathrm{d}\varphi'\,\Psi_0(\varphi)\Psi_0(\varphi')\Psi_n(\varphi)\Psi_n(\varphi') \times \cos(\varphi - \varphi'), \quad (n = 0, \pm 1, \pm 2, \ldots). \tag{12}$$

Using formula (1) for the susceptibility we arrive at

$$\chi(\omega) = \chi_0\sum_{n\neq 0}\frac{1 + \mathrm{i}\tau_n\omega}{1 + (\tau_n\omega)^2}K_n \tag{13}$$

with the relaxation times $\tau_n = 1/\lambda_n$, $(n = \pm 1, \pm 2, \ldots)$. It is easily proved that the condition $K_0 + \Sigma_{n\neq 0}K_n = 1$ is satisfied.

4. Evaluation of the eigenfunctions

In the regions between two deflection points the potential U is a linear function of the angle φ. Then the potential entering into equation (6) reduces to $V = D_{\mathrm{R}}(1/2\mathrm{d}\beta U/\mathrm{d}\varphi)^2$. For $n \neq 0$ the eigenvalue problem is solved by using the ansatz

$$\Psi_n(\varphi) = a_{n,v}\exp(+\mathrm{i}k_n\varphi) + b_{n,v}\exp(-\mathrm{i}k_n\varphi) \tag{14}$$

where v denotes a region between two deflection points. Inserting equation (14) in (6) yields the eigenvalues

$$\lambda_n = D_{\mathrm{R}}k_n^2 + V. \tag{15}$$

There is always a solution for the eigenvalue $\lambda_0 = 0$, namely $\Psi_0 = C_0\exp(-\beta U/2)$ with the normalization constant $C_0 = 1/[2\pi\sinh(H_i)/H_i]^{1/2}$, $(i = 1, 2)$. The conditions (7, 8) lead to a set of linear equations for the coefficients $a_{n,v}$ and $b_{n,v}$. These equations allow evaluation of k_n from the condition that this linear system has non-trivial solutions.

4.1. *Dipolar order*

The linear equations resulting from potential (3) and conditions (7) and (8) yield $k_n = n$ where n runs over all integers $-\infty < n < \infty$. For $n \neq 0$ the eigenvalues are

$$\lambda_n = D_{\mathrm{R}}n^2 + D_{\mathrm{R}}\left(\frac{H_1}{\pi}\right)^2. \tag{16}$$

Taking into account the degeneracy $\lambda_{-n} = \lambda_n$ the corresponding eigenfunctions can be expressed as

$$\Psi_n(\varphi) = C_n[\cos(n\varphi) - r_n^*\sin(n\varphi)] \quad \text{for} \quad -\pi < \varphi < 0 \tag{17}$$

$$\Psi_n(\varphi) = C_n[\cos(n\varphi) + r_n\sin(n\varphi)] \quad \text{for} \quad 0 < \varphi < +\pi \tag{18}$$

where

$$C_n = 1/[\pi(1 + r_nr_n^*)]^{1/2}$$

and

$$r_n = \frac{H_1}{\pi n} + \mathrm{i}\left[1 + \left(\frac{H_1}{\pi n}\right)^2\right]^{1/2} \tag{19}$$

(r_n^* is the conjugate complex of r_n). Using these eigenfunctions the evaluation of the coefficients K_n in the susceptibility (13) yields

$$K_0 = 64\pi^2C_0^4\frac{H_1^2}{(4H_1^2 + \pi^2)^2}\cosh^2(H_1),$$

$$K_1 = 128\pi^4C_0^2C_1^2\frac{H_1^2 + 2\pi^2}{(H_1^2 + 4\pi^2)^2H_1^2}\sinh^2(H_1/2)$$

and

$$K_n = 32 C_0^2 C_n^2 H_1^2 \pi^4 \frac{H_1^2 + \pi^2(n^2+1)}{[H_1^2 + \pi^2(n-1)^2]^2 [H_1^2 + \pi^2(n+1)^2]^2} \times [\exp(H_1/2) + (-1)^n \exp(-H_1/2)]^2 \quad (n \geq 2).$$

4.2. *Quadrupolar order*

The linear set of equations resulting from the conditions (7) and (8) at the deflection points of the potential (4) has non-trivial solutions if the condition

$$\sin\left(k_n \frac{\pi}{2}\right)\left[\cos\left(k_n \frac{\pi}{2}\right) + \frac{2H_2}{\pi k_n} \sin\left(k_n \frac{\pi}{2}\right)\right] \times \left[\cos\left(k_n \frac{\pi}{2}\right) - \frac{2H_2}{\pi k_n} \sin\left(k_n \frac{\pi}{2}\right)\right] = 0 \qquad (20)$$

is satisfied. Two types of solution obeying the condition $\Psi_{2n}(\varphi + \pi) = +\Psi_{2n}(\varphi)$ and $\Psi_{2n+1}(\varphi + \pi) = -\Psi_{2n+1}(\varphi)$ can be distinguished. The first one is connected with the zeros $k_n = 2n$ of the first term in equation (20) and provides the eigenvalues

$$\lambda_{2n} = D_R (2n)^2 + D_R \left(\frac{2H_2}{\pi}\right)^2 \qquad (21)$$

($1 \leq n < \infty$, n integer). The corresponding eigenfunctions are

$$\Psi_{2n}(\varphi) = C_n[\cos(2n\varphi) + r_n \sin(2n\varphi)] \quad \text{for} \quad -\pi \leq \varphi < -\pi/2 \quad \text{and} \quad 0 \leq \varphi < +\pi/2 \qquad (22)$$

and

$$\Psi_{2n}(\varphi) = C_n[\cos(2n\varphi) - r_n^* \sin(2n\varphi)] \quad \text{for} \quad -\pi/2 \leq \varphi < 0 \quad \text{and} \quad +\pi/2 \leq \varphi < +\pi \qquad (23)$$

where the coefficients C_n and r_n are evaluated by the formulae (19) replacing H_1 by H_2. The second type of eigenfunction has two sets of eigenvalues

$$\lambda_{2n+1} = D_R k_n^2 + D_R \left(\frac{2H_2}{\pi}\right)^2 \quad \text{with} \quad H_2 = -\frac{k_n \pi}{2} \cot\left(\frac{k_n \pi}{2}\right) \qquad (24)$$

and

$$\tilde{\lambda}_{2n+1} = D_R \tilde{k}_n^2 + D_R \left(\frac{2H_2}{\pi}\right)^2 \quad \text{with} \quad H_2 = +\frac{\tilde{k}_n \pi}{2} \cot\left(\frac{\tilde{k}_n \pi}{2}\right) \qquad (25)$$

($0 \leq n < \infty$, n integer). Note, that $k_n = 2n + 1$ for $H_2 = 0$. The eigenfunctions connected with λ_{2n+1} are

$$\Psi_{2n+1}(\varphi) = D_n[+\exp(-\mathrm{i}k_n\varphi) - \exp(-\mathrm{i}k_n(\varphi + \pi))] \quad \text{for} \quad -\pi \leq \varphi < 0 \qquad (26)$$

and

$$\Psi_{2n+1}(\varphi) = D_n[-\exp(-\mathrm{i}k_n(\varphi - \pi)) + \exp(-\mathrm{i}k_n\varphi)] \quad \text{for} \quad 0 \leq \varphi < +\pi \qquad (27)$$

with the normalization constants

$$D_n = \frac{1}{2} \Big/ \left[\pi\left(1 - \frac{\sin(k_n \pi)}{k_n \pi}\right)\right]^{1/2}. \qquad (28)$$

For the eigenvalues $\tilde{\lambda}_{2n+1}$ we obtain

$$\tilde{\Psi}_{2n+1}(\varphi) = -2\mathrm{i}\tilde{D}_n \sin(\tilde{k}_n(\varphi + \pi)) \quad \text{for} \quad -\pi \leq \varphi < -\pi/2, \qquad (29)$$

$$\tilde{\Psi}_{2n+1}(\varphi) = +2\mathrm{i}\tilde{D}_n \sin(\tilde{k}_n\varphi) \quad \text{for} \quad -\pi/2 \leq \varphi < +\pi/2 \qquad (30)$$

and

$$\tilde{\Psi}_{2n+1}(\varphi) = -2\mathrm{i}\tilde{D}_n \sin(\tilde{k}_n(\varphi - \pi)) \quad \text{for} \quad +\pi/2 \leq \varphi < +\pi. \qquad (31)$$

After replacing k_n by $\tilde{k}_n$ the formula for the normalization constants $\tilde{D}_n$ coincides with that for D_n. It should be mentioned that the value of $\tilde{k}_0$ is imaginary if $H_2 > 1$

5. Discussion

The isotropic state with $H_1 = 0$, $H_2 = 0$ and $P_{\mathrm{eq}} = 1/2\pi$ corresponds to the symmetry of the smectic A phase. In this case the model leads to a simple Debye spectrum

$$\chi(\omega) = \chi_0 \frac{1 + \mathrm{i}\tau_1 \omega}{1 + (\tau_1 \omega)^2} \qquad (32)$$

with the relaxation time $\tau_1 = 1/D_R$. The static susceptibility varies only slightly if the temperature T is changed.

The dielectric spectrum obtained from the rotator model is modified for configurations with quadrupolar order. For example, the smectic M phase possesses a twofold rotation axis perpendicular to the layer planes. In this case the effective potential (4) is consistent with the symmetry requirements. If the potential barrier H_2 is low or moderately high only two relaxation modes make a substantial contribution to the dielectric spectrum. Neglecting modes with small amplitudes we obtain

$$\chi(\omega) \approx \chi_0 \left[\frac{1 + \mathrm{i}\tau_1 \omega}{1 + (\tau_1 \omega)^2} K_1 + \frac{1 + \mathrm{i}\tilde{\tau}_1 \omega}{1 + (\tilde{\tau}_1 \omega)^2} \tilde{K}_1\right] \qquad (33)$$

where $\tau_1 = 1/\lambda_1$, $\tilde{\tau}_1 = 1/\tilde{\lambda}_1$, and K_1, $\tilde{K}_1$ are defined by the relation (12). If $H_2 \to 0$ the relation (32) for the isotropic case is obtained ($K_1 \to 1/2$, $\tilde{K}_1 \to 1/2$ and

$\tilde{\tau}_1 \rightarrow \tau_1$). The relaxation time τ_1 slightly diminishes, while $\tilde{\tau}_1$ strongly increases with increasing potential barriers $H_2 > 0$. If H_2 is sufficiently large, both modes are well separated in a Cole–Cole plot (figure 3).

Finally, we consider the spectrum for dipolar order. If $H_1 \neq 0$, polar order with parallel oriented dipole moments appears. The alignment is not necessarily accompanied by the formation of a ferroelectric phase, since the direction of the molecular dipole moments μ can alternate in such a way that an antiferroelectric structure is formed. For example, an antiferroelectric order occurs in the smectic B_2 phase, which consists of banana- or chevron-like molecules. In this phase the dipole moments are antiparallel in adjacent smectic layers. The strength of the dipole orientational order in the smectic layers can be characterized by the first term K_0 of the correlation function. For the triangular potential (3) this term can be written as $K_0 = \langle \cos \varphi \rangle^2$, where

$$\langle \cos \varphi \rangle = -\frac{4H_1^2}{4H_1^2 + \pi^2} \coth(H_1) \tag{34}$$

is the order parameter for the dipole alignment. The polar order becomes more pronounced if the temperature is reduced, or if the potential barrier H_1 is increased. For $H_1 \rightarrow \infty$ the values of $\langle \cos \varphi \rangle$ and K_0 tend to one. Because of $\Sigma_{n \neq 0} K_n = 1 - K_0$ the static susceptibility can be expressed as $\chi(\omega = 0) = \chi_0(1 - \langle \cos \varphi \rangle^2)$. Obviously, the susceptibility decreases with increasing polar order or increasing potential barrier H_1. As $K_1 \gg K_n$ ($n = 2, 3, \ldots$), the main contribution to the dielectric spectrum results from a single relaxation process. As shown in figure 4, even for large values of H_1 the dielectric spectrum remains well approximated by a simple Debye spectrum. For $H_1 \rightarrow \infty$ both the susceptibility $\chi(\omega)$ and the relaxation time τ tend to zero.

The model with polar order ($H_1 \neq 0$) should be appropriate for the antiferroelectric B_2 phase. Experimental results [7] indicate two relaxation modes accompanied with rotation around the molecular long axes. The ratio of both relaxation times exceeds two orders of magnitude. Only the high frequency mode is to be related to the molecular reorientation process considered in this paper. The low frequency mode is assumed to be cooperative and probably reflects the response of the antiferroelectric long range order to the external electric field.

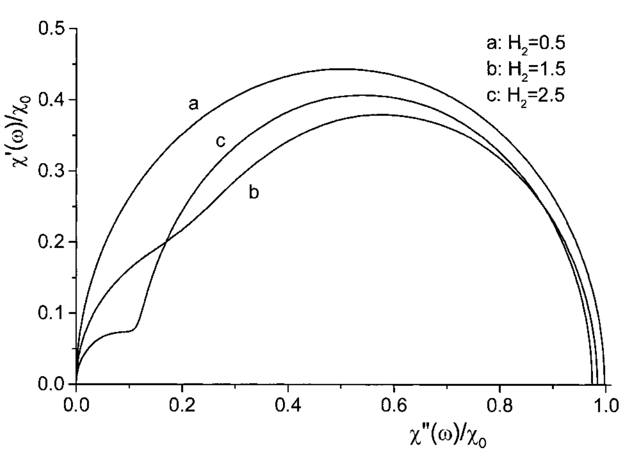

Figure 3. Cole–Cole plot for the potential (4). For a sufficiently large potential barrier H_2 two well separated modes occur.

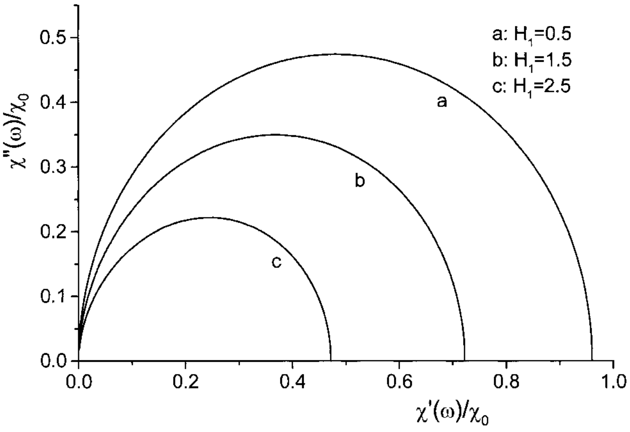

Figure 4. Cole–Cole plot for the potential (3). Even for large values of H_1 the spectrum remains Debye-like.

It should be mentioned that dipolar and quadrupolar order also exist in the ferroelectric smectic C* phase. Using a Landau theory, Carlsson *et al.* [11] predicted a splitting of the high frequency dielectric relaxation mode (polarization mode) attributed to the hindered rotation of the molecules around their long axes. However, experimental investigations did not reveal such a splitting. The spectra of the smectic C* and the adjacent smectic A* phase were not found to be significantly different. Our Brownian reorientation model predicts two separated relaxation modes if the potential barrier H_2 (accompanied with quadrupolar order) is sufficiently high. But in the ferroelectric C* phase, the barrier is much lower than the mean thermal energy kT [12]. Therefore both relaxation times nearly coincide and the splitting of the spectrum cannot be resolved experimentally.

Financial support by the Fonds der Chemischen Industrie and the Kultusministerium Sachsen-Anhalt (project 2828A) is gratefully acknowledged.

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