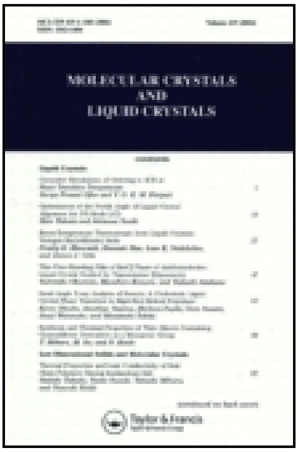

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MODEL FOR THE REORIENTATION OF MOLECULES AROUND THEIR LONG AXES IN BIAXIAL SMECTIC PHASES

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Abstract The reorientation of molecules around their long axes should be influenced by the biaxiality of smectic phases with tilted molecules. Assuming a brownian reorientation process, the effect of a quadrupolar ordering on high-frequency dielectric spectra is investigated.

INTRODUCTION

In smectic phases molecules can reorientate around their axes. The spinning motion around the long axis is a relatively fast process detectable in the high-frequency region of the dielecric spectrum[1]. In this region the spectrum reflects the dynamics of transverse dipoles attached to the molecular long axes and is related to the two-time correlation function for the transversal dipole moment.

The reorientation of a particle around its long axis depends on the interaction with neighbouring molecules. Supposing a molecular-field-approximation, this interaction is taken into account by an average potential $f(x)$, which depends on the rotation angle x enclosed by a molecular short axis and a symmetry axis of the smectic phase[2]. In FIGURE 1 the axis **u** is perpendicular to the tilt plane of the long molecules and the axis **a** is attached to a particle. Since the tilt of the molecules causes a biaxial ordering, a Fourier series of the effective potential has the leading (quadrupolar) term $f(x) = -h_2 \cos 2x$. If a ferroelectric ordering occurs, however, the dipolar term $h_1 \cos x$ should be included additionally[2]. On the other hand, it was found experimentally[3,4] that $|h_1|$ is small compared to $|h_2|$. In this case the dipolar contribution to $f(x)$ can be neglected when the dielectric spectrum is calculated[5].

The dielectric susceptibility for rotating dipoles has been considered previously[5,6] assuming the special case of a weak potential $f(x) = -h_1 \cos x - h_2 \cos 2x$ with $|h_1|, |h_2| << kT$ (k, Boltzmann constant; T, temparature). It was found that the quadrupolar term $-h_2 \cos 2x$ produces a splitting of a degenerated relaxation mode, so that two different relaxation times appear. But this splitting is rather small if $|h_2| << kT$.

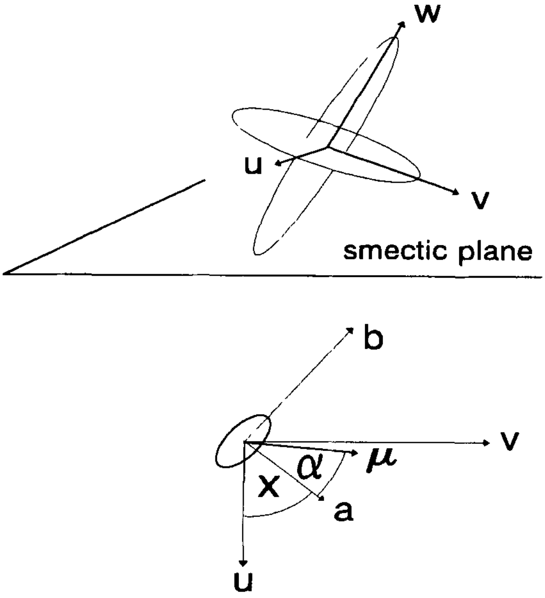


FIGURE 1 Smectic ordering with tilted molecules and cross-section of a particle. The angle α is enclosed by the short axis **a** and the transverse dipole μ of a particle.

In this paper the quadrupolar potential $f(x) = -h_2 \cos 2x$ is replaced by the step-potential

$$F(x) = \begin{cases} -H_2 \; for & -\pi/4 + n\pi < x < \pi/4 + n\pi \\ H_2 \; for & \pi/4 + n\pi < x < 3\pi/4 + n\pi \end{cases} \qquad (1)$$

where n is an integer. Using potential (1) the dielectric susceptibility can be calculated analytically even if H_2 is large. FIGURE 2 shows $F(x)$ for $H_2 > 0$.

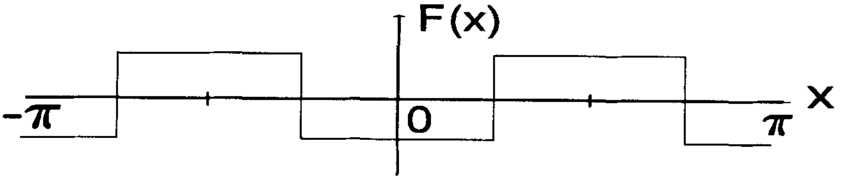


FIGURE 2 Effective potential $F(x)$.

For an equilibrium configuration the single particle distribution is defined by

$$P(x)=\frac{\exp\left(-F(x)/kT\right)}{2\pi\cosh\left(H_2/kT\right)} \tag{2}$$

CORRELATION FUNCTIONS

The reorientation of the molecules around their long axes is characterized by the correlation functions $K_{cc}(t)=\langle\cos x(t)\cos x(0)\rangle$ and $K_{ss}(t)=\langle\sin x(t)\sin x(0)\rangle$, which depend on the time t. The brackets $\langle\ \rangle$ define the averaging over a stationary statistical ensemble. Using the notation $x(t)=x$ and $x(0)=y$, the correlation functions are obtained from

$$\begin{pmatrix} K_{cc}(t) \\ K_{ss}(t) \end{pmatrix}=\int_0^{2\pi}\int_0^{2\pi} dxdy P(x,t|y,0)P(y)\begin{pmatrix} \cos x\cos y \\ \sin x\sin y \end{pmatrix} \tag{3}$$

where $P(y)$ is defined by Eq. (2) and $P(x,t|y,0)$ is the transition probability satisfying the initial condition $P(x,t|y,0)=\delta(x-y)$ for $t=0$. The joint probability density $P(x,t;y,0)=P(x,t|y,0)P(y)$ has the representation[7]

$$P(x,t;y,0)=\psi_o(x)\psi_o(y)\sum_n \psi_n{}^*(x)\psi_n(y)\exp(-\lambda_n t) \tag{4}$$

for a brownian reorientation process. The functions $\psi_n(x)$ in the series (4) are obtained from the simple eigenvalue problem

$$D\psi''=-\lambda\psi \tag{5}$$

where $\psi(x)$ is a periodic function with period 2π. The solutions of Eq. (5) are discontinuous at a point x_o where the potential $F(x)$ jumps. In the special case $F'(x_o+0)=F'(x_o-0)=0$ the jump conditions[7]

$$\psi\exp\left(\frac{F(x)}{2kT}\right)\Bigg|_{x_o+0}=\psi\exp\left(\frac{F(x)}{2kT}\right)\Bigg|_{x_o-0}$$

and (6)

$$\frac{d\psi}{dx}\exp\left(-\frac{F(x)}{2kT}\right)\Bigg|_{x_o+0}=\frac{d\psi}{dx}\exp\left(-\frac{F(x)}{2kT}\right)\Bigg|_{x_o-0}$$

are satisfied. Equation (5) is solved by using the ansatz

$$\psi_n(x) = a_n(l)\exp(Ik_n x) + b_n(l)\exp(-Ik_n x) \tag{7}$$

where $I = \sqrt{-1}$ and n is the number of an eigenfunction. The coefficients $a_n(l)$ and $b_n(l)$ are defined separately for each section between two jumps. (l is the number of a section with constant value of $F(x)$ in the range between -π and +π.) Inserting ansatz (7) in equation (5) yields

$$\lambda_n = Dk_n^{\,2} \tag{8}$$

Both λ_n and $\psi_n(x)$ are determined by the jump conditions (6) which lead to linear equations for the coefficients $a_n(l)$ and $b_n(l)$. λ_n is obtained from the condition that the whole set of those equations has nontrivial solutions only in this case if its determinand is equal to zero. In such a way the complete spectrum of eigenvalues and the corresponding eigenfunctions are accessible by applying a simple mathematical procedure. The explicit expressions for $\psi_n(x)$ will be published elsewhere[8]. Using the eigenfunctions $\psi_n(x)$ with the normalization condition

$$\int_0^{2\pi} \psi_m(x)\,\psi_n(x)dx = \delta_{mn} \tag{9}$$

the correlation functions $K_{cc}(t) = \langle\cos x(t)\cos x(0)\rangle$ and $K_{ss}(t) = \langle\sin x(t)\sin x(0)\rangle$ are obtained from the relation (3).

THE SUSCEPTIBILITIES

A susceptibility $\chi(\omega)$ can be defined by the relation $p(\omega) = \chi(\omega)E(\omega)$, where $p(\omega)$ is the dipole moment per unit volume induced by the alternating local electric field $E(\omega)$. Let us regard the response of rotating particles which possess a transverse dipole **μ** (see Figure 1). The alternating electric field is assumed to be parallel to the axis **u** or to the axis **v**. The corresponding susceptibilities $\chi_{uu}(\omega)$ and $\chi_{vv}(\omega)$ are principal values of the dielectric susceptibility tensor. They are obtained by a half-sided Fourier transformation

$$\chi_{rr}(\omega) = \frac{1}{kT}\left[\phi_{rr}(0) + I\omega\int_0^{\infty}\phi_{rr}(t)\exp(I\omega t)dt\right] \tag{10}$$

(ω, frequency, $r = u, v$ and $I = \sqrt{-1}$) of the macroscopic correlation functions $\phi_{uu}(t)$ and $\phi_{vv}(t)$. Taking into account that the transverse dipole **μ** is not necessarily parallel to a molecular short axis (FIGURE 1), these functions are defined by[5]

$$\begin{aligned} &\phi_{uu}(t) = \rho\mu^2\left[\cos^2\alpha\, K_{cc}(t) + \sin^2\alpha\, K_{ss}(t)\right] \quad \text{and} \\ &\phi_{vv}(t) = \rho\mu^2\left[\sin^2\alpha\, K_{cc}(t) + \cos^2\alpha\, K_{ss}(t)\right], \end{aligned} \tag{11}$$

where ρ is the particle density. In all further expressions we assume $H_2 \geq 0$ and use the definition

$$\phi = \arctan\left[\exp(-H_2 / kT)\right] \qquad (0 \leq \phi \leq \pi / 4)$$

The explicit calculation of the correlation functions (11) reveals that only two terms associated with the relaxation times

$$\tau_c = \frac{\pi^2}{16D\phi^2} \quad \text{and} \quad \tau_s = \frac{\pi^2}{D(4\phi - 2\pi)^2} \tag{12}$$

have a remarkable contribution[8]. Thus the susceptibilities are obtained by the formulae

$$\begin{aligned} &\chi_{uu}(\omega) = \chi_{cc}(\omega)\cos^2\alpha + \chi_{ss}(\omega)\sin^2\alpha \\ &\chi_{vv}(\omega) = \chi_{cc}(\omega)\sin^2\alpha + \chi_{ss}(\omega)\cos^2\alpha \end{aligned} \tag{13}$$

where

$$\chi_{cc}(\omega) = \frac{\rho\mu^2}{kT}\frac{\left[A_{11}\exp(H_2 / 2kT) + A_{12}\exp(-H_2 / 2kT)\right]^2}{\cosh(H_2 / kT)}\frac{1 + I\omega\tau_c}{1 + (\omega\tau_c)^2}$$

and

$$\chi_{ss}(\omega) = \frac{\rho\mu^2}{kT}\frac{\left[A_{21}\exp(H_2 / 2kT) + A_{22}\exp(-H_2 / 2kT)\right]^2}{\cosh(H_2 / kT)}\frac{1 + I\omega\tau_s}{1 + (\omega\tau_s)^2}$$

with the coefficients

$$A_{11} = \frac{2(\pi\cos\phi - 4\phi\sin\phi)}{\pi^2 - 16\phi^2}, \quad A_{12} = \frac{2(-\pi\sin\phi + 4\phi\cos\phi)}{\pi^2 - 16\phi^2}$$

$$A_{21}=\frac{2(-\pi\cos\phi+2\pi\sin\phi-4\phi\sin\phi)}{16\phi^2-16\phi\pi+3\pi^2} \text{ and } A_{22}=\frac{2(\pi\sin\phi-2\pi\cos\phi+4\phi\cos\phi)}{16\phi^2-16\phi\pi+3\pi^2}.$$

In the special case $H_2=0$ both relaxation times (12) coincide ($\tau_c=\tau_s=1/D$) and Eq. (13) is simplified to

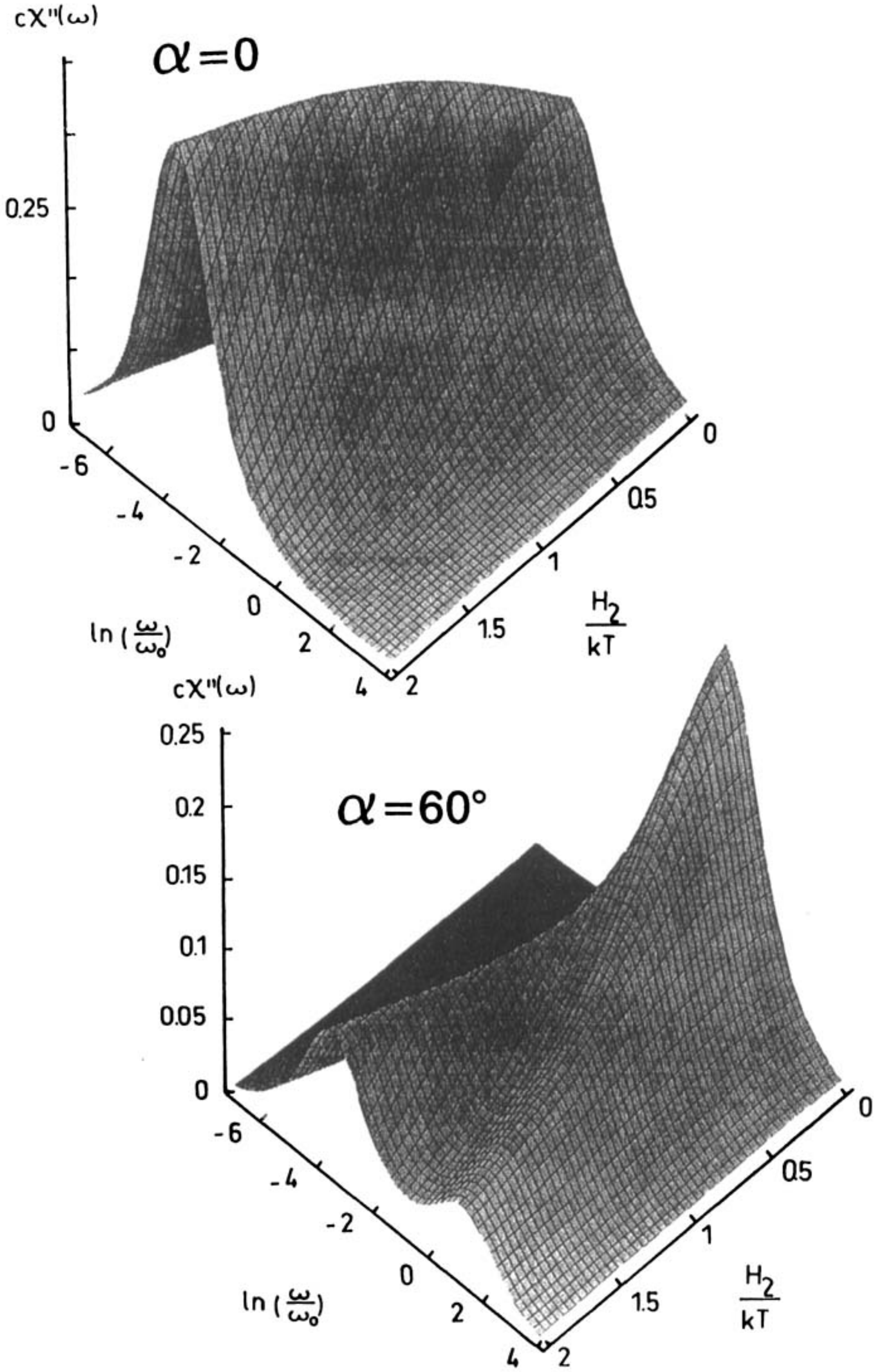
$$\chi_{uu}(\omega)=\chi_{vv}(\omega)=\frac{\rho\mu^2}{2kT}\frac{1+I\omega D^{-1}}{1+\left(\omega D^{-1}\right)^2} \tag{14}$$

According to Eq. (13) the relaxation time $\tau=D^{-1}$ of the smectic A-phase splits into two different relaxiation times, if the potential barrier H_2 becomes non-zero in a higher ordered smectic phase. If $H_2\Rightarrow\infty$ the time τ_c tends to infinity, but τ_s remains finite ($\tau_s\Rightarrow(4D)^{-1}$).

Imaginary Part of the Susceptibility for Different Angles α

Most experimental results for microwave spectra refer to the dielectric loss $\chi''(\omega)$. Therefore, only the imaginary part of the susceptibility will be considered. The susceptibilities $\chi_{uu}(\omega)$ and $\chi_{vv}(\omega)$ depend on the angle α, which is enclosed by the transverse dipole **μ** and the molecular short axis **a** (FIGURE 1). Obviously, there is a relation between the susceptibilities, namely $\chi_{uu}(\omega;\alpha)=\chi_{vv}(\omega;\pi/2-\alpha)$. The axis **a** is chosen in such a way that the effective potential obeys $F(x=0)=-H_2<0$ as shown in FIGURE 2. The electric field is supposed to be parallel to the axis **u** (FIGURE 1). According to formula (13) the dielectric loss $\chi_{uu}''(\omega)$ does not change if the angle α is replaced by $\alpha+m\pi$ or $-\alpha+m\pi$, where m is an integer. Thus we assume without loss of generality that $0\le\alpha\le\pi/2$.

In the following diagrams the imaginary part of the normalized susceptibility $c\chi_{uu}''(\omega)$ is plottet versus the frequency ω and the reduced potential barrier H_2/kT, where the coefficient c is defined by $c=kT\left(\rho\mu^2\right)^{-1}$ and $\omega_o=D$. If $H_2/kT>1$ the dielectric susceptibility is strongly influenced by the angle α. If the short axis **a** and the dipole **μ** are parallel ($\alpha=0$) only one mode is visible in the spectrum (plot 1). The amplitude of $c\chi_{uu}''(\omega)$ increases slightly and the relaxation time decreases when the potential barrier H_2 grows. For $\alpha=60°$ (plot 2) and $H_2>kT$ a second mode is visible by an additional crest. If α is further increased ($\alpha=75°$; plot 3), the amplitude of the high-frequency mode becomes more pronounced in comparison to the amplitude of the low-frequency mode. Finally, if $\alpha = 90°$, only the high-frequency mode has survived (plot 4).



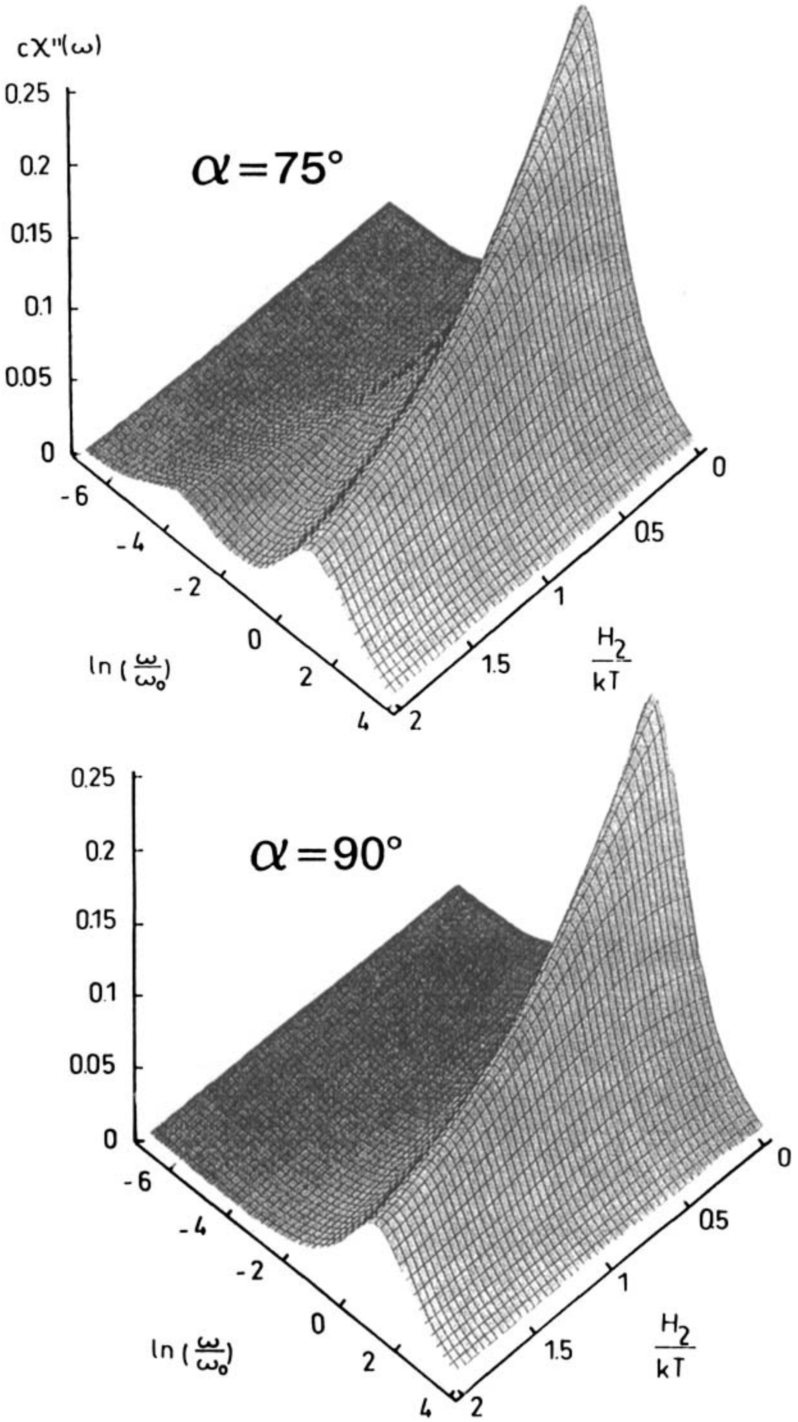


FIGURE 3 The dielectric loss $\chi_{uu}''(\omega)$ for different angles α.

CONCLUDING REMARKS

Equations (13) are useful for investigating how the quadrupolar ordering in smectic phases with tilted molecules have an effect on the high-frequency dielectric spectrum. The replacement of the potential $-h_2 \cos 2x$ by the simplified model potential (1) does not influence the general conclusions.

The relaxation mode accompanied with the spinning motion is found to be double degenerated for $h_2, H_2 = 0$ (smectic A-phase). This degeneracy is lifted if a quadrupolar ordering appears $(h_2, H_2 \neq 0)$, as expected to occur in some smectic phases with tilted molecules. Two different relaxation times should be clearly detectable if the potential barrier h_2 (H_2) is compareable to kT and if $\alpha \neq m\pi/2$, where m is an integer (see plots 2 and 3 in FIGURE 3). Unfortunately, most experimental results concerning the microwave region refer to the smectic C-phase[1,9,10]. In this case the splitting of the relaxation spectrum is not visible, since the potential barrier is rather low $(h_2, H_2 << kT)$[3,4]. But the potential barrier is expected to be much larger in some strongly ordered low-temperature smectic phases with tilted molecules.

The interpretation of microwave spectra could be difficult, since most molecules which form a smectic phase possess more than only one transverse electric dipole. Then intramolecular reorientations lead to several relaxation times, which are accompanied with a broadening of the dielectric spectrum.

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