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A phenomenological model for dielectric relaxation processes in the B_2 phase

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A simple model based on the Landau theory is used to describe the dielectric relaxation modes of the antiferroelectric B_2 phase. The model allows us to explain the occurrence of two separated dielectric modes based on particle rotation about the molecular long axes.

1. Introduction

The investigation of smectic phases with chevron- or banana-shaped molecules has revealed a rich polymorphism [1]. Several new phases have been elucidated by X-ray experiments combined with optical, electro-optical and dielectric observations. The alignment of the banana-shaped molecules within the smectic layers offers new possibilities for the formation of ferroelectric and antiferroelectric smectic phases. The electro-optic response of switchable smectic phases provides some insight into the orientational order of the chevrons [2, 3]. In particular, the B_2 phase has been clearly identified as an antiferroelectric phase. Each smectic layer has a spontaneous polarization in the direction of the bent cores. The polarization vectors of adjacent smectic layers are directed antiparallel so that no net polarization occurs. Most surprising is the helical alignment of the molecular axes, which occurs even if the molecules are non-chiral [4]. This observation can be explained by taking into account a weak tilt of the molecules with respect to the smectic layer planes in such a way that the two-fold rotation axis (C_2 symmetry) is retained, while the mirror plane perpendicular to the smectic layers no longer exists. Similarly to the chiral smectic C* phase, the helix period is much larger than the length of a molecule.

Recently Schmalfuss *et al.* [5] investigated the dielectric response of the smectic B_2 phase. Two adsorption modes attributed to the rotation of the molecules around their long axes were found in a frequency range up to 10 MHz. The relatively large value of the dielectric permittivity indicates that the molecular reorientation, at least for one of the modes, is a cooperative process. In this paper we present a simple model demonstrating that both modes can be related to the antiferroelectric order in the B_2 phase. To characterize the dielectric relaxation, a simplified version of the Landau theory for antiferroelectric liquid crystals [6–8] is used. The Landau–Khalatnikov equations for this model yield two Debye-like modes which can compared with the experimental results [5]. Relaxation effects attributed to the helical structure are neglected, because the pitch of the helix is much larger than the layer spacing. We consider only uniform processes with correlation lengths smaller than the pitch.

2. Model

2.1. *Theory*

The chevron-like molecules can be regarded as steric dipoles which tend to align each other for achievement of a better packing [9]. Let ξ define the projection of the chevrons onto the smectic layer plane. ξ is parallel to the two fold rotation axis in the B_2 phase. The vectors ξ_1 and ξ_2 for two adjacent layers are aligned antiparallel, whereas both vectors are oriented randomly in the smectic A phase. Similarly, the polarization vectors $\mathbf{P}_1$ and $\mathbf{P}_2$ are introduced to describe the electric polarization within the smectic layer planes. Assuming a firm connection between the steric dipoles and the polarization leads to the relations $\mathbf{P}_1 = C\xi_1$ and $\mathbf{P}_2 = C\xi_2$, where C is a constant. Then the order parameters $\mathbf{P}_1$ and $\mathbf{P}_2$ are sufficient to describe the free energy in the framework of a Landau expansion. It is useful to introduce modified vectors [6]

$$\mathbf{P}_a = \frac{1}{2}(\mathbf{P}_1 - \mathbf{P}_2) \quad \text{and} \quad \mathbf{P}_f = \frac{1}{2}(\mathbf{P}_1 + \mathbf{P}_2) \qquad (1)$$

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where $\mathbf{P}_f$ and $\mathbf{P}_a$ account for ferroelectric and antiferroelectric order, respectively. Using these order parameters the free energy expansion reads

$$F=\frac{\alpha}{2}\mathbf{P}_a^2+\frac{\beta_a}{4}\mathbf{P}_a^4+\frac{1}{2\chi_f}\mathbf{P}_f^2+\frac{\beta_f}{4}\mathbf{P}_f^4 + \frac{c_1}{2}\mathbf{P}_a^2\mathbf{P}_f^2+\frac{c_2}{2}(\mathbf{P}_a\ \ \mathbf{P}_f)^2. \tag{2}$$

By varying the coefficients in the free energy expansion (2), four different phases can be described, namely the disordered state (smectic A phase: $\mathbf{P}_a=\mathbf{P}_f=\mathbf{0}$), the ferroelectric ($\mathbf{P}_a=\mathbf{0}$, $\mathbf{P}_f\neq\mathbf{0}$), the antiferroelectric ($\mathbf{P}_a\neq\mathbf{0}$, $\mathbf{P}_f=\mathbf{0}$) and the ferrielectric phase ($\mathbf{P}_a\neq\mathbf{0}$, $\mathbf{P}_f\neq\mathbf{0}$). If an electric field $\mathbf{E}$ directed parallel to the smectic layer planes is applied, the free energy F is replaced by $G=F-\mathbf{P}_f\ \ \mathbf{E}$. The response of the order parameters to an alternating electric field is described by the Landau–Khalatnikov equations

$$-\Gamma_f\frac{d\mathbf{P}_f}{dt}=\frac{\delta G}{\delta \mathbf{P}_f}\quad\text{and}\quad-\Gamma_a\frac{d\mathbf{P}_a}{dt}=\frac{\delta G}{\delta \mathbf{P}_a}\tag{3}$$

where both Γ_f and Γ_a are 2×2-diagonal matrices and t is the time. The dielectric susceptibility is defined by

$$\chi=\lim_{\mathbf{E}\to 0}\frac{\delta P}{E}\tag{4}$$

where δP denotes the induced polarization.

2.2. *Response of the antiferroelectric structure*

The conditions $\alpha<0$ and $\beta_a>0$ are necessary for the stability of the antiferroelectric phase. For $\mathbf{E}=\mathbf{0}$ the order parameters of the antiferroelectric structure are expressed as vectors $\mathbf{P}_{f,o}=(0,0)$ and $\mathbf{P}_{a,o}=(P_{a,x},0)$, which are parallel to the smectic layer planes. Assuming that $\beta_a>0$, the order parameter $P_{a,x}$ satisfies the equation $\alpha+\beta_a P_{a,o}^2=0$. Let us consider the response $\delta\mathbf{P}_a(t)=[\delta\tilde{P}_{a,x}\exp(i\omega t),\ \delta\tilde{P}_{a,y}\exp(i\omega t)]$ and $\delta\mathbf{P}_f(t)=[\delta\tilde{P}_{f,x}\exp(i\omega t),\ \delta\tilde{P}_{f,y}\exp(i\omega t)]$ of the order parameters to an alternating electric field $\mathbf{E}(t)=[\tilde{E}_x\exp(i\omega t),\ \tilde{E}_y\exp(i\omega t)]$. Using the linearized Landau–Khalatnikov equations (3) we arrive at

$$\left[\frac{1}{\chi_f}+c_1P_{a,o}^2+i\omega\Gamma_{f,1}\right]\delta\tilde{P}_{f,y}=\tilde{E}_y\tag{5}$$

and

$$\left[\frac{1}{\chi_f}+(c_1+c_2)P_{a,o}^2+i\omega\Gamma_{f,2}\right]\delta\tilde{P}_{f,x}=\tilde{E}_x.\tag{6}$$

Two additional equations for modes resulting from the equations (3) are not considered here, because they do not couple to the external electric field. Using equations (5) and (6) and the definition (4) for the susceptibility, two Debye-like modes $\chi_k=\chi_{k,o}/(1+i\omega\tau_k)$, ($k=1,2$) are obtained. The corresponding amplitudes and relaxation times are

$$\chi_{1,o}=\frac{\chi_f}{1+c_1\chi_fP_{a,o}^2}\quad\text{and}\quad\tau_1=\chi_{1,o}\Gamma_{f,1}\tag{7}$$

for the first mode and

$$\chi_{2,o}=\frac{\chi_f}{1+(c_1+c_2)\chi_fP_{a,o}^2}\quad\text{and}\quad\tau_2=\chi_{2,o}\Gamma_{f,2}\tag{8}$$

for the second mode. For the smectic A phase ($P_{a,o}=0$, $\Gamma_{f,1}=\Gamma_{f,2}$) both modes coincide and only one Debye process is visible.

3. Conclusion

The symmetry of the dielectric modes is shown in the figure. Mode 1 is accompanied by a rotation of the polarization vector towards the direction of the electric field. The direction of this rotation alternates from layer to layer due to the antiferroelectric order. This type of scissoring motion has already been proposed by Heppke *et al.* [10]. In the case of mode 2, however, the

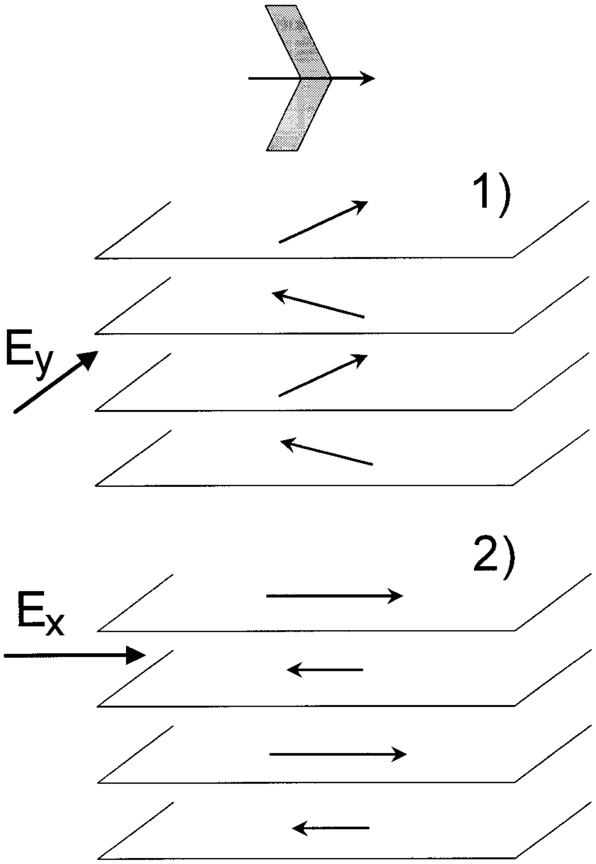

Figure. Dielectrically active reorientation modes of the model. The arrows indicate the electric polarization vectors for the smectic layers.

polarization vectors of each layer retain their initial orientations, but the amplitude of the polarization changes. The polarization of a layer is reduced or enhanced dependent upon the mutual orientation of the electric field and the spontaneous polarization (see the figure). Both modes are expected to be visible in a disordered sample. We suggest that mode 1 should have a lower frequency than the second mode, since a rotation of the local electric polarization in liquid crystals is accomplished much more easily than changing its amplitude.

The results of the simple model could explain recent dielectric observations for the B_2 phase [5]. Two clearly separated relaxation modes attributed to the reorientation about the molecular long axes were found. The large dielectric permittivity of the low frequency process indicates that the motion is cooperative in agreement with the assumptions of our model. We suggest that this relaxation mode should be identified as the scissoring motion (mode 1). The second process (mode 2) may be less correlated, because the dielectric permittivity related to this high frequency relaxation was found to be relatively small. In this case rotational diffusion models based on the Smoluchovsky equation for rotating dipoles in an effective potential should provide an alternative description [11].

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