PHYSICAL REVIEW A VOLUME 42, NUMBER 2 15 JULY 1990

Theoretical model of the frequency and temperature dependence of the complex dielectric constant of ferroelectric liquid crystals near the smectic-C^*–smectic-A phase transition

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(Received 15 August 1989)

Using the generalized Landau model [Phys. Rev. A **36**, 1484 (1987)], the temperature and frequency dependence of the complex dielectric constant of the ferroelectric smectic-C^* (Sm-C^*) phase and the corresponding smectic-A (Sm-A) phase is calculated. It is demonstrated how the dielectric response of the Sm-C^* phase generally consists of four modes—two high-frequency polarization modes and two modes of lower frequency that are connected to the reorientation of the director, commonly denoted the soft mode and the Goldstone mode. In the Sm-A phase only two modes are present—one doubly degenerate soft mode and one doubly degenerate polarization mode. The temperature dependences of the dielectric strengths and relaxation frequencies of the modes in question are calculated, and simplified expressions of these quantities are given. The most important feature of the generalized Landau model is the presence of a biquadratic coupling between tilt and polarization in the free-energy density of the system and we show how the general thermodynamic and dielectric properties of the system depend on the strength of this coupling. Comparing the results of the calculations with existing data, we finally conclude that the model provides a description of the Sm-C^*–Sm-A transition that takes all experimentally known features of the dielectric properties of the system into account in a qualitatively correct way.

I. INTRODUCTION

The possibility of developing electro-optical devices[1] by the use of ferroelectric smectic-C^* (Sm-C^*) liquid crystals[2] has increased the interest for these systems considerably during the past few years. Gradually, a vast number of experimental data has become available, and today at least the qualitative behavior of many-important quantities of the system can be considered to be established in the literature.[3] In a recent paper[4] we reported the measurements of the complex dielectric constant of a room-temperature ferroelectric liquid crystalline mixture close to the Sm-C^*–Sm-A transition. In the same paper we also showed how we, by a generalized Landau expansion of the free-energy density,[3,5] could develop a theory which enables us to calculate the temperature dependence of the static dielectric constant $\epsilon_0(T)$ of the system in agreement with experiment.

In order to describe the ferroelectric Sm-C^* phase one generally introduces two two-component order parameters [c.f. Eqs. (1)]. Thus, the dielectric response of the system consists (apart from the usual electronic contribution) of four modes—two high-frequency polarization modes and two modes of lower frequency connected to the relaxation of director fluctuations. The two latter modes are commonly denoted the soft mode and the Goldstone mode. In the Sm-A phase the system exhibits two degenerate modes—one high-frequency polarization mode and one (soft) mode of lower frequency connected to the relaxation of director fluctuations. In the present work we will calculate the dielectric strengths and the relaxation frequencies of the dielectric modes of the system as well in the Sm-C^* phase as in the Sm-A phase by the use of the generalized Landau model.

The soft mode is mostly connected to amplitude changes of the director but also to a certain extent to the phase changes. The reverse is true for the Goldstone mode. One difficulty when calculating the complex dielectric constant of the system is to establish in which way this mixing of phase and amplitude changes of the order parameters enters into the eigenmodes of the dielectric response. Solving this problem, and assuming a Debye-like relaxation, we consequently are presenting a complete theoretical calculation of the temperature- and frequency-dependent complex dielectric constant $\epsilon^*(\omega, T)$ of the Sm-C^* and Sm-A phases.

II. THE DIELECTRIC CONSTANT OF THE SMECTIC-C^* AND -A PHASES

The ferroelectric Sm-C^* phase represents a spatially modulated structure.[2,6,7] Because of the chirality of the molecules, the tilt locally breaks the axial symmetry along the long molecular axis and induces a transverse in-plane polarization perpendicular[2,3] to the direction of the tilt. Introducing the order parameters $\boldsymbol{\xi}=\xi_1\hat{\mathbf{x}}+\xi_2\hat{\mathbf{y}}$ and $\mathbf{P}=P_x\hat{\mathbf{x}}+P_y\hat{\mathbf{y}}$ to denote the tilt and the polarization, respectively, we can write

$$\begin{aligned}&\xi_1=\theta_0\cos(qz),\quad \xi_2=\theta_0\sin(qz)\ ,\\ &P_x=-P_0\sin(qz),\quad P_y=P_0\cos(qz)\ ,\end{aligned} \tag{1}$$

where z is the coordinate normal to the smectic planes (which are taken to be parallel to the xy plane) and $q=2\pi/p$ is the wave vector of the pitch. From Eqs. (1) we see that the average macroscopic polarization of the system is zero. In this paper we will be interested in the dielectric properties of the medium which are connected to electric fields which are applied parallel to the smectic layers.

Let us introduce the complex dielectric constant $\epsilon^*(\omega,T)=\epsilon(\omega,T)-j\epsilon''(\omega,T)$, where $\omega=2\pi f$ is the angular frequency of the applied electric field and T is the temperature of the system. In general several relaxation mechanisms, each of which is connected to a characteristic eigenfrequency f_i, are contributing to $\epsilon^*(\omega,T)$. In the case of ferroelectric liquid crystals in the Sm-C^* phase we expect two relaxation modes connected to the reorientation of the director, two polarization modes, and (at least) one mode connected to the electronic properties of the medium. For each mode, at a given temperature, the contribution to the dielectric constant decreases with increasing frequency of the field, from the low-frequency value ($f \ll f_i$) to zero, which is the value adopted when the frequency of the applied electric field is so high ($f \gg f_i$) that the mode cannot follow the electric field. The difference between the low- and high-frequency contribution of the mode to the total dielectric constant is called the dielectric strength of the mode and will be denoted $\Delta\epsilon_i(T)$. This quantity is related to the average induced polarization, $\langle P_i\rangle$, of the corresponding mode by

$$\varepsilon_0\Delta\epsilon_i(T)=\lim_{E\to 0}\frac{\langle P_i\rangle}{E}\ , \tag{2}$$

where E is the magnitude of a static applied electric field and ε_0 being the permittivity of free space. Except very close to T_c, the relaxation frequencies of the modes contributing to the dielectric constant of the Sm-C^* phase are well separated. In Fig. 1 we show the typical frequency dependence of ϵ in such a case.

The disturbance of the equilibrium order parameters which are given by Eqs. (1) when an electric field is applied to the system can be divided into two parts.[4] These are amplitude changes (magnitude of tilt and polarization) and phase changes (direction of tilt and polarization). In such a way the dielectric response of the system will consist of four parts (apart from the high-frequency electronic response $\Delta\epsilon_{\rm el}$)—two which are connected to director reorientations and two connected to reorientation of the polarization. Linear combinations of the former two are what commonly are denoted the soft mode ($\Delta\epsilon_{\rm S}$ is the dielectric strength and $f_{\rm S}$ the eigenfrequency) and the Goldstone mode ($\Delta\epsilon_{\rm G}$ is the dielectric strength and $f_{\rm G}$ the eigenfrequency). The relaxation frequency of these two modes are normally[4,8] of the order of $f_{\rm S}\sim 1-10^4$ kHz and $f_{\rm G}\sim 10-200$ Hz, respectively. The relaxation frequencies of the polarization modes have been reported by Benguigui[9] to be of the order of 500 MHz. This means that the study of these two modes are often beyond the experimentally feasible range. We will distinguish between the polarization soft mode ($\Delta\epsilon_{\rm PS}$ is the dielectric strength and $f_{\rm PS}$ the eigenfrequency) and the polarization Goldstone mode ($\Delta\epsilon_{\rm PG}$ is the dielectric strength and $f_{\rm PG}$ the eigenfrequency), respectively.

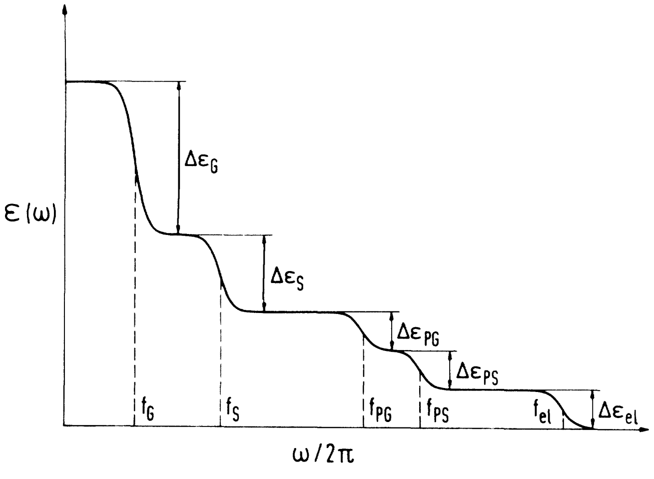

FIG. 1. Sketch of the frequency dependence of the real part of the dielectric constant of the Sm-C^* phase.

In this paper we will present a theoretical calculation of the part of the dielectric constant of the Sm-C^* and Sm-A phases which is connected to fluctuations of the order parameters $\boldsymbol{\xi}$ and $\mathbf{P}$. This means that in order to obtain the total dielectric constant we have to add the (high-frequency) contribution $\Delta\epsilon_{\rm el}$. The complex dielectric constant of the Sm-C^* phase can be written

$$\begin{aligned}\epsilon^*(\omega,T)=&\frac{\Delta\epsilon_{\rm G}(T)}{1+j\omega t_{\rm G}}+\frac{\Delta\epsilon_{\rm S}(T)}{1+j\omega t_{\rm S}}+\frac{\Delta\epsilon_{\rm PG}(T)}{1+j\omega t_{\rm PG}}\\ &+\frac{\Delta\epsilon_{\rm PS}(T)}{1+j\omega t_{\rm PS}}+\Delta\epsilon_{\rm el}(T)\ ,\end{aligned} \tag{3}$$

where $t_i=1/2\pi f_i$ is the relaxation time of the corresponding mode. In the Sm-A phase only amplitude fluctuations are present and the system exhibits a doubly degenerate soft mode and a doubly degenerate high-frequency polarization mode. The complex dielectric constant can in this case be written

$$\epsilon^*(\omega,T)=\frac{\Delta\epsilon_{\rm SA}(T)}{1+j\omega t_{\rm A}}+\frac{\Delta\epsilon_{\rm PA}(T)}{1+j\omega t_{\rm PA}}+\Delta\epsilon_{\rm el}(T)\ . \tag{4}$$

III. THE GENERALIZED LANDAU MODEL OF THE FERROELECTRIC SMECTIC-C^* PHASE

In order to describe the thermodynamic properties of the ferroelectric Sm-C^* phase we have previously introduced a generalized Landau expansion of the free-energy density of the system.[3-5] By the use of this model we have shown that we are able to calculate most thermodynamical properties of interest in a qualitatively correct way. In one of these papers,[4] we showed explicitly how the generalized Landau model can take into account all the experimental features of the static dielectric constant of the system in contrast to previous calculations,[10,11] which were based on a too simple Landau expansion. In this work we will show that the generalized Landau model can also be used to calculate the dynamical properties of the Sm-C^* phase. A full review of the generalized Landau model can be found in any of the three papers quoted above.[3-5] Consequently, only a brief summary of the model is presented below.

The free-energy density $g_0(z)$ is given by a Landau expansion in the order parameters ξ and $\mathbf{P}$:

$$
\begin{aligned}
g_0(z)={}&\tfrac{1}{2}a(\xi_1^2+\xi_2^2)+\tfrac{1}{4}b(\xi_1^2+\xi_2^2)^2+\tfrac{1}{6}c(\xi_1^2+\xi_2^2)^3-\Lambda\left(\xi_1\frac{d\xi_2}{dz}-\xi_2\frac{d\xi_1}{dz}\right)+\frac{1}{2}K_3\left[\left(\frac{d\xi_1}{dz}\right)^2+\left(\frac{d\xi_2}{dz}\right)^2\right]\\
&+\frac{1}{2\epsilon}(P_x^2+P_y^2)-\mu\left(P_x\frac{d\xi_1}{dz}+P_y\frac{d\xi_2}{dz}\right)+C(P_x\xi_2-P_y\xi_1)-\tfrac{1}{2}\Omega(P_x\xi_2-P_y\xi_1)^2+\tfrac{1}{4}\eta(P_x^2+P_y^2)^2\\
&-d(\xi_1^2+\xi_2^2)\left(\xi_1\frac{d\xi_2}{dz}-\xi_2\frac{d\xi_1}{dz}\right),
\end{aligned}
\tag{5}
$$

where only the coefficient a is assumed to be temperature dependent: $a=\alpha(T-T_0)$. From Eqs. (1) and (5) we can derive[3] the equations governing the tilt, polarization, and pitch of the system to be

$$\tilde{a}\theta_0+\tilde{b}\theta_0^3+\tilde{c}\theta_0^5-\Omega\theta_0P_0^2-\left(\tilde{C}+\frac{3\mu d}{K_3}\theta_0^2\right)P_0=0\ , \tag{6}$$

$$\eta P_0^3+\left(\frac{1}{\tilde{\epsilon}}-\Omega\theta_0^2\right)P_0-\left(\tilde{C}+\frac{\mu d}{K_3}\theta_0^2\right)\theta_0=0\ , \tag{7}$$

$$q=\frac{1}{K_3}\left(\Lambda+\mu\frac{P_0}{\theta_0}+d\theta_0^2\right)\ , \tag{8}$$

where $\tilde{a}$, $\tilde{b}$, $\tilde{c}$, $\tilde{\epsilon}$, and $\tilde{C}$ are renormalized constants

$$
\begin{aligned}
&\tilde{a}=a-\frac{\Lambda^2}{K_3},\quad \tilde{b}=b-\frac{4\Lambda d}{K_3},\quad \tilde{c}=c-\frac{3d^2}{K_3}\ ,\\
&\frac{1}{\tilde{\epsilon}}=\frac{1}{\epsilon}-\frac{\mu^2}{K_3},\quad \tilde{C}=C+\frac{\Lambda\mu}{K_3}\ .
\end{aligned}
\tag{9}
$$

IV. THE TEMPERATURE AND FREQUENCY-DEPENDENT DIELECTRIC CONSTANT OF THE FERROELECTRIC SMECTIC-C^* PHASE

A. The dynamic equations

In order to write down the complex dielectric constant as it is given by Eq. (3), we must calculate the dielectric strengths and the eigenfrequencies of the four ferroelectric modes, which were introduced in Sec. II. A general disturbance of the equilibrium state of Eqs. (1) can be regarded to be composed of two parts. First, the amplitudes θ_0 and P_0 of the order parameters can change, and secondly the phase of the order parameters can change so that the sinosoidal *ansatz* of Eqs. (1) will no longer be valid. As a result of this, the relaxation behavior of the Sm-C^* phase consists of two director orientational modes—the soft mode (mostly amplitude changes) and the Goldstone mode (mostly phase changes)—and of two polarization modes. Denoting the amplitude changes by $\delta\theta_1$ and δP_1 and the phase changes by $\delta\theta_2$ and δP_2, respectively, we can write the order parameters in the presence of an electric field as[3,4]

$$
\begin{aligned}
&\xi_1=\theta_0\cos(qz)+\delta\theta_1\cos(qz)-\delta\theta_2\sin(qz)\ ,\\
&\xi_2=\theta_0\sin(qz)+\delta\theta_1\sin(qz)+\delta\theta_2\cos(qz)\ ,\\
&P_x=-P_0\sin(qz)-\delta P_1\sin(qz)-\delta P_2\cos(qz)\ ,\\
&P_y=P_0\cos(qz)+\delta P_1\cos(qz)-\delta P_2\sin(qz)\ .
\end{aligned}
\tag{10}
$$

We will only consider the case when the testing electric field is applied parallel to the smectic layers and assume that a homogeneous, time-dependent electric field $\mathbf{E}=E_0e^{j\omega t}\hat{\mathbf{x}}$ is applied in the x direction. Substituting the *ansatz* of Eq. (10) into Eq. (5), the free-energy density can be written as $g(z)=g_0+g_2(z)+g_E(z)$, where g_2 is the extra contribution due to the changes of the order parameters and g_E is the contribution due to the electric field. Only retaining terms quadratic in the changes we get (we introduce a prime to denote a derivative with respect to the z coordinate):

$$\begin{aligned} g_2(z)=&\delta\theta_1^2(\tfrac{1}{2}a+\tfrac{3}{2}b\theta_0^2+\tfrac{5}{2}c\theta_0^4-\Lambda q+\tfrac{1}{2}K_3q^2-\tfrac{1}{2}\Omega P_0^2-6\,dq\,\theta_0^2)+\delta\theta_2^2(\tfrac{1}{2}a+\tfrac{1}{2}b\theta_0^2+\tfrac{1}{2}c\theta_0^4-\Lambda q+\tfrac{1}{2}K_3q^2-2\,dq\,\theta_0^2)\\ &+\delta P_1^2\left[\frac{1}{2\epsilon}-\frac{1}{2}\Omega\theta_0^2+\frac{3}{2}\eta P_0^2\right]+\delta P_2^2\left[\frac{1}{2\epsilon}+\frac{1}{2}\eta P_0^2\right]-\delta\theta_1\delta P_1(\mu q+C+2\Omega P_0\theta_0)\\ &-\delta\theta_2\delta P_2(\mu q+C+\Omega P_0\theta_0)+\delta\theta_1\delta\theta_2'(-\Lambda+K_3q-3d\theta_0^2)+\delta\theta_1'\delta\theta_2(\Lambda-K_3q+d\theta_0^2)\\ &+\tfrac{1}{2}K_3(\delta\theta_1'^2+\delta\theta_2'^2)+\mu(\delta P_2\delta\theta_1'-\delta P_1\delta\theta_2')\ , \end{aligned} \tag{11}$$

$$g_E(z)=-\mathbf{E}\cdot\mathbf{P}=E_0[P_0\sin(qz)+\delta P_1\sin(qz)+\delta P_2\cos(qz)]e^{j\omega t}\ . \tag{12}$$

The equations governing the static dielectric response have been derived by us previously.[3] The results of this derivation imply that the most general time and space dependence (in the limit of small electric fields) of the director and polarization changes defined by Eqs. (10) can be written as

$$\begin{aligned} &\delta\theta_1=\delta\theta_{10}\sin(qz)e^{j\omega t},\quad \delta\theta_2=\delta\theta_{20}\cos(qz)e^{j\omega t}\\ &\delta P_1=\delta P_{10}\sin(qz)e^{j\omega t},\quad \delta P_2=\delta P_{20}\cos(qz)e^{j\omega t}\ . \end{aligned} \tag{13}$$

From Eqs. (10)–(13) it is possible to show[3] that the equations governing the changes of the order parameters in the static limit ($\omega=0$) are given by

$$\begin{aligned} &b_1\delta\theta_{10}+b_2\delta\theta_{20}+b_3\delta P_{10}+b_4\delta P_{20}=0\ ,\\ &b_2\delta\theta_{10}+b_5\delta\theta_{20}+b_4\delta P_{10}+b_6\delta P_{20}=0\ ,\\ &b_3\delta\theta_{10}+b_4\delta\theta_{20}-b_7\delta P_{10}=E_0\ ,\\ &b_4\delta\theta_{10}+b_6\delta\theta_{20}-b_8\delta P_{20}=E_0\ , \end{aligned} \tag{14}$$

where the constants b_i are defined as

$$\begin{aligned} &b_1=-a-3b\theta_0^2-5c\theta_0^4+2\Lambda q-2q^2K_3+\Omega P_0^2+12\,dq\,\theta_0^2\ ,\\ &b_2=-2\Lambda q+2q^2K_3-4\,dq\,\theta_0^2\ ,\\ &b_3=\mu q+C+2\Omega P_0\theta_0\ ,\\ &b_4=-\mu q\ ,\\ &b_5=-a-b\theta_0^2-c\theta_0^4+2\Lambda q-2q^2K_3+4\,dq\,\theta_0^2\ ,\\ &b_6=\mu q+C+\Omega P_0\theta_0\ ,\\ &b_7=\frac{1}{\epsilon}-\Omega\theta_0^2+3\eta P_0^2\ ,\\ &b_8=\frac{1}{\epsilon}+\eta P_0^2\ . \end{aligned} \tag{15}$$

Equations (14) have been derived just by applying the Euler-Lagrange equations to the extra free-energy density contribution of Eqs. (11) and (12), which is due to the presence of the electric field. If we instead want to calculate the dielectric response at a finite ω we can reason in the following way. The dynamic equations can be formulated as a set of balance of torque equations, $\Gamma^{\text{elastic}}+\Gamma^{\text{viscous}}=0$. The left-hand side of Eqs. (14) (with the E terms of the two last equations moved to the left of the equality sign) is just the elastic torque Γ^{elastic}. The viscous torque Γ^{viscous} is related to the time derivatives of the order parameters as $\Gamma^{\text{viscous}}=-\gamma\dot{\delta\theta}_1=-j\omega\gamma\delta\theta_{10}\sin(qz)e^{j\omega t}$ and so on. We thus just have to add terms of the type $-j\omega\gamma\delta\theta_{10}$ to the left-hand side of Eqs. (14) in order to obtain the dynamic equations of the system:

$$\begin{aligned} &(b_1-j\omega\gamma_S)\delta\theta_{10}+b_2\delta\theta_{20}+b_3\delta P_{10}+b_4\delta P_{20}=0\ ,\\ &b_2\delta\theta_{10}+(b_5-j\omega\gamma_G)\delta\theta_{20}+b_4\delta P_{10}+b_6\delta P_{20}=0\ ,\\ &b_3\delta\theta_{10}+b_4\delta\theta_{20}-(b_7+j\omega\gamma_{PS})\delta P_{10}=E_0\ ,\\ &b_4\delta\theta_{10}+b_6\delta\theta_{20}-(b_8+j\omega\gamma_{PG})\delta P_{20}=E_0\ . \end{aligned} \tag{16}$$

To be general we have introduced four different viscosities in Eqs. (16). Two of these, γ_G and γ_S, are the ordinary rotational viscosities[12,13] connected to director reorientations. The way in which we have introduced γ_G and γ_S is such that close to T_c we can expect[13] $\gamma_G\simeq\gamma_S$. We should also point out that instead of our way[13] of defining the Goldstone mode rotational viscosity γ_G, some authors prefer to introduce[14,15] an effective rotational viscosity γ_G^{eff} which is related to our γ_G by the relation $\gamma_G^{\text{eff}}=\gamma_G\sin^2\theta$. The two viscosities γ_{PG} and γ_{PS} connected to the polarization modes are related to the rotation of the molecules around their long axis.

The fact that, concerning their order of magnitude, the relaxation frequencies of the four eigenmodes fall into two groups ($f_S,f_G\ll f_{PS},f_{PG}$) permits us to simplify the way of solving Eqs. (16). When studying the polarization modes we are dealing with frequencies which are so high that the director can no longer follow the electric field, and $\delta\theta_{10}$ and $\delta\theta_{20}$ can be put equal to zero. Mathematically this can be expressed in such a way that we are studying the system in the limit of infinite rotational viscosities γ_G and γ_S. On the other hand, when studying the low-frequency director modes we use the fact that the molecular rotation around the long axis is so fast that for each director configuration the polarization takes its corresponding equilibrium infinitely fast. Mathematically this can be expressed by putting γ_{PS} and γ_{PG} equal to zero in Eqs. (16). The accuracy of this approximative way of solving Eqs. (16) is of the order of $f_S/f_{PS}\sim\text{kHz/MHz}\sim10^{-3}$. This small loss of accuracy is negligible compared to experimental errors. Furtheron, the fact that the final expressions derived in this way are much more transparent will permit us to gain a better physical understanding of the system.

B. The polarization modes—high-frequency dielectric constant

As discussed above, when studying the polarization modes we are dealing with frequencies which are so high that the director can no longer follow the electric field, and $\delta\theta_{10}$ and $\delta\theta_{20}$ can be put to zero. The high-frequency response of δP_{10} and δP_{20} is then given by the last two equations of Eqs. (16)

$$\delta P_{10}^{\infty}=-\frac{E_0}{b_7+j\omega\gamma_{\mathrm{PS}}}, \quad \delta P_{20}^{\infty}=-\frac{E_0}{b_8+j\omega\gamma_{\mathrm{PG}}} . \tag{17}$$

The corresponding contributions to the dielectric constant can now be calculated by the use of Eqs. (2), (10), and (13) to be

$$\varepsilon_0\Delta\epsilon=\frac{\langle P_x\rangle}{E}=-\frac{P_0}{E}\langle\sin(qz)\rangle-\frac{\delta P_{10}}{E}\langle\sin^2(qz)\rangle-\frac{\delta P_{20}}{E}\langle\cos^2(qz)\rangle=-\frac{1}{2E_0}(\delta P_{10}+\delta P_{20}) , \tag{18}$$

where δP_{10} and δP_{20} are given by Eqs. (17). From Eqs. (15) and (18) we thus get the dielectric strengths and the eigenfrequencies of the polarization modes to be

$$\varepsilon_0\Delta\epsilon_{\mathrm{PS}}=\frac{1}{2\left[\dfrac{1}{\epsilon}-\Omega\theta_0^2+3\eta P_0^2\right]} , \qquad \varepsilon_0\Delta\epsilon_{\mathrm{PG}}=\frac{1}{2\left[\dfrac{1}{\epsilon}+\eta P_0^2\right]} , \tag{19}$$

$$f_{\mathrm{PS}}=\frac{1}{\pi\gamma_{\mathrm{PS}}}\left[\frac{1}{\epsilon}-\Omega\theta_0^2+3\eta P_0^2\right] , \qquad f_{\mathrm{PG}}=\frac{1}{\pi\gamma_{\mathrm{PG}}}\left[\frac{1}{\epsilon}+\eta P_0^2\right] . \tag{20}$$

Equations (19) and (20) imply a very simple result concerning the product of the dielectric strengths and the eigenfrequencies of the polarization modes

$$\varepsilon_0 f_{\mathrm{PS}}\Delta\epsilon_{\mathrm{PS}}=\frac{1}{2\pi\gamma_{\mathrm{PS}}}, \quad \epsilon_0 f_{\mathrm{PG}}\Delta\epsilon_{\mathrm{PG}}=\frac{1}{2\pi\gamma_{\mathrm{PG}}} . \tag{21}$$

Thus we see that it is possible to determine γ_{PS} and γ_{PG} directly from a measurement of the high-frequency complex dielectric constant of the system.

C. The director modes—low-frequency dielectric constant

We now go on to study the director modes, which are of much lower frequency[9] than the polarization modes. This fact will be used in order to simplify the calculations, which we will perform in the limit when the eigenfrequencies of the polarization modes are assumed to be infinite. This assumption simply means that the molecular rotation around the long axis is so fast, that for each director configuration the polarization takes its corresponding equilibrium value infinitely fast. As discussed at the end of Sec. IV B, mathematically this can be expressed by putting γ_{PS} and γ_{PG} equal to zero in the dynamic equations (16). Thus we can write the two last equations of Eqs. (16) as

$$\delta P_{10}=\frac{1}{b_7}(-E_0+b_3\delta\theta_{10}+b_4\delta\theta_{20}) , \tag{22a}$$

$$\delta P_{20}=\frac{1}{b_8}(-E_0+b_4\delta\theta_{10}+b_6\delta\theta_{20}) . \tag{22b}$$

Substituting these two equations into the first two of Eqs. (16) we can write

$$(X+j\omega\gamma_S)\delta\theta_{10}+qZ\delta\theta_{20}=-E_0\left[\frac{b_3}{b_7}+\frac{b_4}{b_8}\right] , \tag{23a}$$

$$qZ\delta\theta_{10}+(Y+j\omega\gamma_G)\delta\theta_{20}=-E_0\left[\frac{b_4}{b_7}+\frac{b_6}{b_8}\right] , \tag{23b}$$

where we have introduced the quantities X, Y, and Z

$$X=-b_1-\frac{b_4^2}{b_8}-\frac{b_3^2}{b_7} , \tag{24a}$$

$$Y=-b_5-\frac{b_4^2}{b_7}-\frac{b_6^2}{b_8}=q^2\left[K_3-\frac{\mu^2}{\dfrac{1}{\epsilon}-\Omega\theta_0^2+3\eta P_0^2}\right]=q^2\tilde{K}_3 , \tag{24b}$$

$$qZ=-b_4\left[\frac{b_2}{b_4}+\frac{b_3}{b_7}+\frac{b_6}{b_8}\right] . \tag{24c}$$

When deriving the second equality of Eq. (24b) we have utilized Eqs. (6)–(8). Furtheron, in Eq. (24b), we have introduced a renormalized elastic constant $\tilde{K}_3=K_3-\mu^2/(1/\epsilon-\Omega\theta_0^2+3\eta P_0^2)$. For the set of parameters we are using in the numerical calculations of Sec. VI this renormalization is negligible.

Before we proceed to solve Eqs. (23) we shall estimate the magnitudes of the coefficients which enter these equations. To do so we need the values of the material parameters which enter the Landau expansion of Eq. (5). These have been estimated elsewhere[3] by us for DOBAMBC and here we will use these values as a set of "typical" parameters of the Sm-C^* phase. The temperature dependence of Eqs. (23) lies in X. For estimation purpose we neglect the term proportional to $c\theta^6$ in X and get approximately $X\sim 2\alpha(T_c-T)$ where we have used the approximate relation $\theta^2\simeq\alpha/2b(T_c-T)$. Furtheron, the terms qZ and $Y=\tilde{K}_3q^2$ are of the same order of magnitude except close to T_c where Z approaches zero. Taking $\tilde{K}_3 \sim 5\times10^{-12}$ N, $2\pi/q \sim 2$ μm and $\alpha \sim 5\times10^4$ N/m^{2}K, we see that X is much larger than both Y and qZ except in a narrow temperature interval $\Delta T \sim 0.01$ K just below T_c.

When diagonalizing Eqs. (23) in order to obtain the eigenmodes of the system, as an intermediate step by putting the determinant of the system of equations equal to zero, we get the following equation determining the eigenfrequencies:

$$(X+j\omega\gamma_S)(Y+j\omega Y_G)-q^2Z^2=0 \ . \tag{25}$$

Excluding the small-temperature interval ΔT estimated above we can safely neglect the term q^2Z^2 in this equation ($T_c - T \gg \Delta T \Longrightarrow q^2Z^2 \ll XY$), the solution of which is then given by putting each of the two parantheses equal to zero. The eigenfrequencies of the soft mode and the Goldstone mode are then obtained by identifying $X+j\omega\gamma_S = X(1+j\omega\gamma_S/X) = X(1+j\omega t_S)$ and so on. We thus get the corresponding eigenfrequencies $f_i = 1/2\pi t_i$ as

$$f_S = \frac{X}{2\pi\gamma_S} \ , \tag{26a}$$

$$f_G = \frac{Y}{2\pi\gamma_G} = \frac{q^2\tilde{K}_3}{2\pi\gamma_G} \ . \tag{26b}$$

Also observing that the coefficient b_4 is much smaller than both b_3 and b_8, the solution of Eqs. (23) can be written as

$$\frac{1}{E}\delta\theta_{10} \simeq -\frac{b_3}{b_7 X}\frac{1}{1+j\omega t_S} + \frac{b_6 qZ}{b_8 Y\left[X-\dfrac{\gamma_S}{\gamma_G}Y\right]}\frac{1}{1+j\omega t_G} \ , \tag{27a}$$

$$\frac{1}{E}\delta\theta_{20} \simeq -\frac{b_6}{b_8 Y}\frac{1}{1+j\omega t_G} + \frac{b_3 qZ}{b_7 Y\left[X-\dfrac{\gamma_S}{\gamma_G}Y\right]}\frac{1}{1+j\omega t_G} \ , \tag{27b}$$

where we have only retained terms of the order of $1/X$ in the solution. From Eq. (27a) we see that the amplitude fluctuation $\delta\theta_{10}$ consists of two parts comparable in magnitude, the first of which contributes to the soft mode while the second is contributing to the Goldstone mode. This last term should thus be compared with the two terms in the expression of $\delta\theta_{20}$ of Eq. (27b), which also contribute to the Goldstone mode. Of the three terms contributing to the Goldstone mode two are smaller than the third one by a factor of the order $1/X$ and can thus safely be neglected in the temperature interval $T_c - T > \Delta T$. From Eqs. (18) and (22) we can write the contribution to the dielectric constant as

$$\varepsilon_0\Delta\epsilon \simeq \frac{1}{2}\left[\left[\frac{1}{b_7}+\frac{1}{b_8}\right] - \frac{b_3}{b_7}\frac{\delta\theta_{10}}{E} - \frac{b_6}{b_8}\frac{\delta\theta_{20}}{E}\right] , \tag{28}$$

where we again have utilized the fact that $b_4 \ll b_3, b_6$. The first of these three terms represents the high-frequency part of the dielectric constant and is just the sum of the dielectric strengths of the polarization modes which were already given by Eqs. (19). By substituting Eqs. (27) into Eq. (28), only retaining the leading terms of each mode, we get

$$\varepsilon_0\Delta\epsilon = \frac{1}{2}\left[\left[\frac{1}{b_7}+\frac{1}{b_8}\right] + \frac{b_3^2}{Xb_7^2}\frac{1}{1+j\omega t_S} + \frac{b_6^2}{Yb_8^2}\frac{1}{1+j\omega t_G}\right] \tag{29}$$

and the dielectric strengths of the soft mode and the Goldstone mode are then given by

$$\varepsilon_0\Delta\epsilon_S = \frac{b_3^2}{2Xb_7^2} \ , \tag{30a}$$

$$\varepsilon_0\Delta\epsilon_G = \frac{b_6^2}{2Yb_8^2} \ . \tag{30b}$$

By the use of Eqs. (7) and (9) we can prove the identity

$$\frac{b_6^2}{b_8^2} = \left[\frac{P_0}{\theta_0}\right]^2 \tag{31}$$

and consequently we can write the Goldstone mode dielectric strength as

$$\varepsilon_0\Delta\epsilon_G = \frac{1}{2\tilde{K}_3}\left[\frac{P_0}{q\theta_0}\right]^2 \ . \tag{32}$$

Equations (26), (30a), and (32) represent our final expressions of the soft mode and Goldstone mode relaxation frequencies and dielectric strengths. We notice from these equations that if we multiply the relaxation frequency with the dielectric strength of each mode we obtain two particular simple expressions which are suitable to use if we want to measure the rotational viscosities of the system

$$\varepsilon_0\Delta\epsilon_S f_S = \frac{1}{4\pi\gamma_S}\left[\frac{b_3}{b_7}\right]^2 , \tag{33a}$$

$$\varepsilon_0\Delta\epsilon_G f_G = \frac{1}{4\pi\gamma_G}\left[\frac{P_0}{\theta_0}\right]^2 . \tag{33b}$$

The result of Eq. (33b) thus shows that it is possible to experimentally determine the Goldstone mode rotational viscosity by a measurement of the four quantities $\Delta\epsilon_G$, f_G, P_0, and θ_0 without the need of doing any assumption of the material parameters which enter the model. Such an evaluation of γ_G has been done by us and has been presented elsewhere.[16]

Finally we will show how the expressions of $\Delta\epsilon_G$ and f_G can be derived in a different way using the "switching" equation, i.e., the equation which is normally used when analyzing the electro-optical switching[1] of the ferroelectric Sm-C^* phase, as a starting point. With the present choice of coordinates, this equation[13,14] can be written

$$\mathrm{PE}\cos\varphi - \tilde{K}_3\theta^2\varphi'' = -\gamma_G\theta^2\dot{\varphi} \ . \tag{34}$$

We should notice in connection to Eq. (34) that the way in which we introduce[12,13] the rotational viscosity γ_G differs from the convention of some other authors[14,15] who prefer to introduce an effective rotational viscosity $\gamma_G^{\mathrm{eff}}=\gamma_G\sin^2\theta\simeq\gamma_G\theta^2$. We again introduce a time dependence of the electric field as $E=E_0e^{j\omega t}$ and expand $\varphi(z)$ to first order

$$\varphi(z)\simeq qz+\delta\varphi \ . \tag{35}$$

Assuming $\delta\varphi$ to have the time and space dependence $\delta\varphi=\delta\varphi_0\cos(qz)e^{j\omega t}$ we can linearize Eq. (34) and arrive at an equation determining $\delta\varphi_0$

$$\mathrm{P}\mathrm{E}_0+\tilde{K}_3\theta^2q^2\delta\varphi_0=-j\omega\gamma_G\theta^2\delta\varphi_0 \ . \tag{36}$$

This equation implies

$$\delta\varphi_0=-\frac{E_0P_0}{\tilde{K}_3q^2\theta^2}\,\frac{1}{1+(j\omega\gamma_G/\tilde{K}_3q^2)} \ . \tag{37}$$

The induced polarization is calculated as

$$\langle P_x\rangle=-P_0\langle\sin(qz+\delta\varphi)\rangle=-\tfrac{1}{2}P_0\delta\varphi_0E_0e^{j\omega t} \ . \tag{38}$$

From Eqs. (36) and (37) we get the Goldstone mode part of the dielectric constant

$$\varepsilon_0\Delta\epsilon_G=\frac{1}{E}\langle P_x\rangle=\frac{P_0^2}{2\tilde{K}_3q^2\theta^2}\,\frac{1}{1+(j\omega\gamma_G/\tilde{K}_3q^2)} \ . \tag{39}$$

From Eq. (39) we directly get f_{G} and $\Delta\epsilon_{\mathrm{G}}$ and by comparing with Eqs. (26b) and (32) we see that the result of the present analysis agrees with the previous one. We can thus conclude that our expressions of f_{G} and $\Delta\epsilon_{\mathrm{G}}$ are exact results as long as Eq. (34) is applicable for describing the Goldstone mode dynamics of the system.

V. THE TEMPERATURE- AND FREQUENCY-DEPENDENT DIELECTRIC CONSTANT OF THE CHIRAL SMECTIC-*A* PHASE

In this section we will study the complex dielectric constant of the chiral Sm-*A* phase. In this phase only amplitude fluctuations are present and the system exhibits a doubly degenerated soft mode and a doubly degenerated high-frequency polarization mode. The complex dielectric constant has in this case the form given by Eq. (4). In order to make the presentation complete, we will give below a brief derivation of the expressions of $\Delta\epsilon_{\mathrm{SA}}$, $f_{\mathrm{SA}}=1/2\pi t_{\mathrm{A}}$, $\Delta\epsilon_{\mathrm{PA}}$, and $f_{\mathrm{PA}}=1/2\pi t_{\mathrm{PA}}$, i.e., the dielectric strengths and eigenfrequencies of the Sm-*A* soft mode and the Sm-*A* polarization mode, respectively.

We expand the free-energy density in the order parameters ξ and $\mathbf{P}$ and take $g_0(z)$ to be the one given by Eq. (5). In the Sm-*A* phase ξ and $\mathbf{P}$ are zero in equilibrium so the fluctuations corresponding to $\delta\theta_i$ and δP_i, which were introduced by Eqs. (10), can here be taken to be the components of ξ and $\mathbf{P}$ themselves. The dielectric response is by definition the response taken in the limit of zero electric field, and thus we only retain terms of second order in ξ and $\mathbf{P}$ in Eq. (5). Furtheron, the system being in the Sm-*A* phase, a homogeneous electric field will couple to spatially uniform changes of the order parameters and accordingly we put $d/dz\equiv0$ in the expression of the free-energy density. In this way we get

$$\begin{aligned}g={}&\tfrac{1}{2}a(\xi_1^2+\xi_2^2)+\frac{1}{2\epsilon}(P_x^2+P_y^2)\\&+C(P_x\xi_2-P_y\xi_1)-E_0e^{j\omega t}P_x \ ,\end{aligned} \tag{40}$$

where the last term is the contribution to the free-energy density from a time-dependent electric field $\mathbf{E}=E_0e^{j\omega t}\hat{\mathbf{x}}$. The equation of motion, which we will write down as a set of torque balance equations, can now be written

$$-\frac{\partial g}{\partial\xi_i}-\gamma_{\mathrm{SA}}\dot{\xi}_i=0,\quad -\frac{\partial g}{\partial P_i}-\gamma_{\mathrm{PA}}\dot{P}_i=0 \ , \tag{41}$$

where γ_{SA} and γ_{PA} are the rotational viscosities of the two modes in question. Introducing a time dependence of the order parameters as $\xi_i=\xi_{i0}e^{j\omega t}$ and $P_i=P_{io}e^{j\omega t}$ Eqs. (40) and (41) give

$$-(a\xi_{10}-CP_{y0})-j\omega\gamma_{\mathrm{SA}}\xi_{10}=0 \ , \tag{42a}$$

$$-(a\xi_{20}+CP_{x0})-j\omega\gamma_{\mathrm{SA}}\xi_{20}=0 \ , \tag{42b}$$

$$-\left[\frac{1}{\epsilon}P_{x0}+C\xi_{20}-E_0\right]-j\omega\gamma_{\mathrm{PA}}P_{x0}=0 \ , \tag{42c}$$

$$-\left[\frac{1}{\epsilon}P_{y0}-C\xi_{10}\right]-j\omega\gamma_{\mathrm{PA}}P_{y0}=0 \ . \tag{42d}$$

Equations (42a) and (42d) imply $\xi_{10}=0$ and $P_{y0}=0$, while Eqs. (42b) and (42c) can be rearranged to read

$$(a+j\omega\gamma_{\mathrm{SA}})\xi_{20}+CP_{x0}=0 \ , \tag{43a}$$

$$C\xi_{20}+\left[\frac{1}{\epsilon}+j\omega\gamma_{\mathrm{PA}}\right]P_{x0}=E_0 \ . \tag{43b}$$

When solving Eqs. (43) we will proceed in the same way as when we solved the dynamic equations (16) of the Sm-C^* phase. Using the fact that the polarization mode frequency is much higher than that of the director mode, we first study Eq. (43b) in the limit of such high frequencies that the director can no longer follow the electric field. As discussed at the end of Sec. IV B, mathematically this can be expressed by putting $\gamma_{\mathrm{SA}}=\infty$ in Eq. (43a) implying $\xi_{20}=0$. In this case Eq. (43b) has the solution

$$P_{x0}=\frac{\epsilon}{1+j\omega\epsilon\gamma_{\mathrm{PA}}}E_0 \ . \tag{44}$$

From Eq. (44) we get the relaxation frequency and the dielectric strength of the Sm-*A* polarization mode to be

$$f_{\mathrm{PA}}=\frac{1}{2\pi\epsilon\gamma_{\mathrm{PA}}} \ , \tag{45a}$$

$$\varepsilon_0\Delta\epsilon_{\mathrm{PA}}=\epsilon \ . \tag{45b}$$

We now proceed by studying the director relaxation for frequencies which are much lower than the polarization mode relaxation frequency. Just like when studying the director modes in the Sm-C^* phase the fact that the relaxation frequency of the polarization mode is much larger than that of the director mode can be expressed by putting γ_{PA} equal to zero in Eq. (43b). Doing so we solve Eqs. (43) for P_{x0}

$$P_{x0}=\left[\epsilon+\frac{\epsilon^2C^2}{a-\epsilon C^2}\frac{1}{1+j\omega\gamma_{\mathrm{SA}}/(a-\epsilon C^2)}\right] . \qquad (46)$$

The constant a in Eq. (46) is given by $a=\alpha(T-T_0)$. Introducing[3] the wave vector of the pitch at T_c, $q_0=q(T=T_c)=(\Lambda+\epsilon\mu C)/(K_3-\epsilon\mu^2)$ and the expression of the Sm-C^*-Sm-A phase transition temperature $T_c=T_0+1/\alpha(\Lambda^2/K_3+\tilde{C}^2\tilde{\epsilon})$ we can derive the following equality:

$$a-\epsilon C^2=\alpha(T-T_c)+(K_3-\epsilon\mu^2)q_0^2 . \qquad (47)$$

From Eqs. (46) and (47) we now get the Sm-A phase soft mode dielectric strength and relaxation frequency

$$f_{\mathrm{SA}}=\frac{1}{2\pi\gamma_{\mathrm{SA}}}[\alpha(T-T_c)+(K_3-\epsilon\mu^2)q_0^2] , \qquad (48a)$$

$$\varepsilon_0\Delta\epsilon_{\mathrm{SA}}=\frac{\epsilon^2C^2}{\alpha(T-T_c)+(K_3-\epsilon\mu^2)q_0^2} . \qquad (48b)$$

Finally we derive from Eqs. (45) and (48) the expressions of the products of the relaxation frequencies with the corresponding dielectric strengths of the two modes

$$\varepsilon_0 f_{\mathrm{SA}}\Delta\epsilon_{\mathrm{SA}}=\frac{\epsilon^2C^2}{2\pi\gamma_{\mathrm{SA}}} , \qquad (49a)$$

$$f_{\mathrm{PA}}\Delta\epsilon_{\mathrm{PA}}=\frac{1}{2\pi\gamma_{\mathrm{PA}}} . \qquad (49b)$$

VI. NUMERICAL RESULTS

A. Some general features of the generalized Landau model

Before we shall evaluate the results in the preceding section numerically, we want to discuss briefly some general properties of the generalized[3,5] Landau model which we used as a basis for the calculations. The most essential feature of the generalized Landau model, in contrast to the simpler "classical" one introduced[6] by Pikin and Indenbom, is the presence of the biquadratic coupling (the Ω term) between tilt and polarization in the free-energy density of Eq. (5). That this biquadratic coupling is important has been verified by NMR measurement[17,18] and can also be understood[19] from sterical reasoning. In order to show how the presence of the Ω term in the free-energy density takes the predictions of the model from the trivial ones given by the classical Landau model to the more realistic ones given by the generalized Landau model, we will introduce a dimensionless parameter β

$$\beta=\frac{\eta^{1/2}\tilde{C}\tilde{\epsilon}}{\Omega^{1/2}} . \qquad (50)$$

The important feature of this parameter is that it is a measure of how important the biquadratic coupling (the Ω term) between tilt and polarization is compared with the bilinear one (the C term), i.e., the smaller β is the more important is the biquadratic coupling. In Fig. 2 we show the quantities $P_0/\theta_0, b_3/b_7$, and q for five different values of β. The calculations have been performed by rewriting the equations into dimensionless[3,5] form and thus the scales on the vertical axes are not related to any physical units, but should be considered as arbitrary units, and we should only pay attention to the shapes of the calculated curves. The values of the material parameters used in the calculations are those introduced by us as a standard set of parameters of the Sm-C^* phase (Ref. 3, Table II), only β and d are changed from these values. Experimentally,[20] the ratio P_0/θ_0 adopts one value at T_c and increases monotoneously towards a saturated value away from T_c. The classical Landau model just predicts P_0/θ_0 to be constant. From Fig. 2(a) we see that the curve calculated for $\beta=1$ (where we have also put $d=0$) corresponds to this classical limit. By lowering β (and at the same time increasing d), i.e., allowing the biquadratic coupling to become more important, we see how the P_0/θ_0 curves are gradually taken into more realistic ones. Concerning the pitch $p=2\pi/q$, it is an experimental

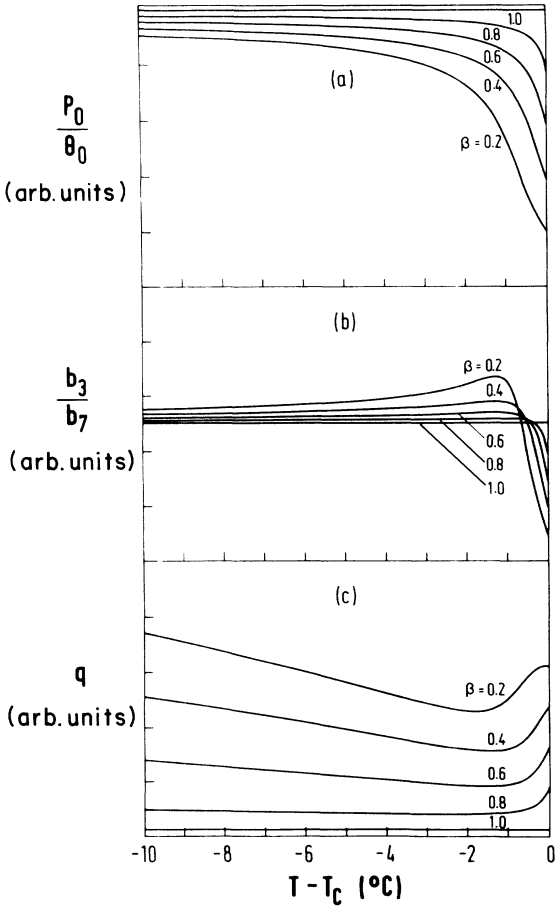

FIG. 2. Temperature dependence of P_0/θ_0, b_3/b_7 [cf. Eqs. (15) and (30a)] and q (the wave vector of the pitch) calculated by the generalized Landau model. The parameter β is a measure of how important the biquadratic coupling between tilt and polarization is compared with the bilinear one.

fact[21] that it slowly increases with increasing temperature, reaches a maximum at approximately 1 K below T_c and then sharply drops to a finite value at T_c. Again the classical Landau model just predicts the pitch to be temperature independent. From Fig. 2(c) we again see how the introduction of the biquadratic coupling makes possible to describe the temperature dependence of the pitch in a qualitatively correct way (here we have plotted q). In conclusion we thus state that the presence of the biquadratic coupling between tilt and polarization in the free-energy density permits us to describe the general features of the Sm-C^* phase in a qualitatively correct way in contrast to the classical Landau model. This biquadratic coupling is introduced through the parameter β. Values of β between approximately 0.2 and 0.7 seems to be adequate in order to describe the system in agreement with experiment. As is seen from Fig. 2 the value $\beta=1$ corresponds to bringing the model back into the classical one.

B. Numerical results for the complex dielectric constant

In this paper we have presented a theoretical calculation of the complex dielectric constant of the ferroelectric Sm-C^* phase as well as of the corresponding Sm-A phase. Assuming that each dielectric mode is characterized by one single relaxation frequency (Debye relaxation), the complex dielectric constant can be given the form of Eqs. (3) and (4) for the Sm-C^* and the Sm-A phases, respectively. As a starting point of the calculations we have used the generalized Landau model [Eq. (5)] introduced and reviewed elsewhere.[3,5,20,22] In Figs. 3 and 4 we show the calculated dielectric strengths and relaxation frequencies, respectively, of the different modes as they are given by Eqs. (19), (20), (26), (30a), (32), (45), and (48). We have chosen to perform the calculations with the same set of parameters which was used for the calculations presented in Fig. 2. We have not considered any temperature dependence of the rotational viscosities, but just adjusted those in such a way that the calculated frequencies fall into the correct range. To do so we have chosen $\gamma_G=\gamma_S=\gamma_{SA}=0.25$ PaS and $\gamma_{PG}=\gamma_{PS}=\gamma_{PA}=7400$ V m/C s. We give the results for three different values of the parameter β in order to demonstrate how the strength of the biquadratic coupling between tilt and polarization have influence on the calculations.

In Figs. 3(c), 3(d), 4(c), and 4(d) we have plotted the calculated temperature dependence of the dielectric strengths and relaxation frequencies of the polarization modes. Today, to our knowledge, the experimental data available in the literature concerning these modes is very scarce. Most dielectric experiments of the Sm-C^* phase

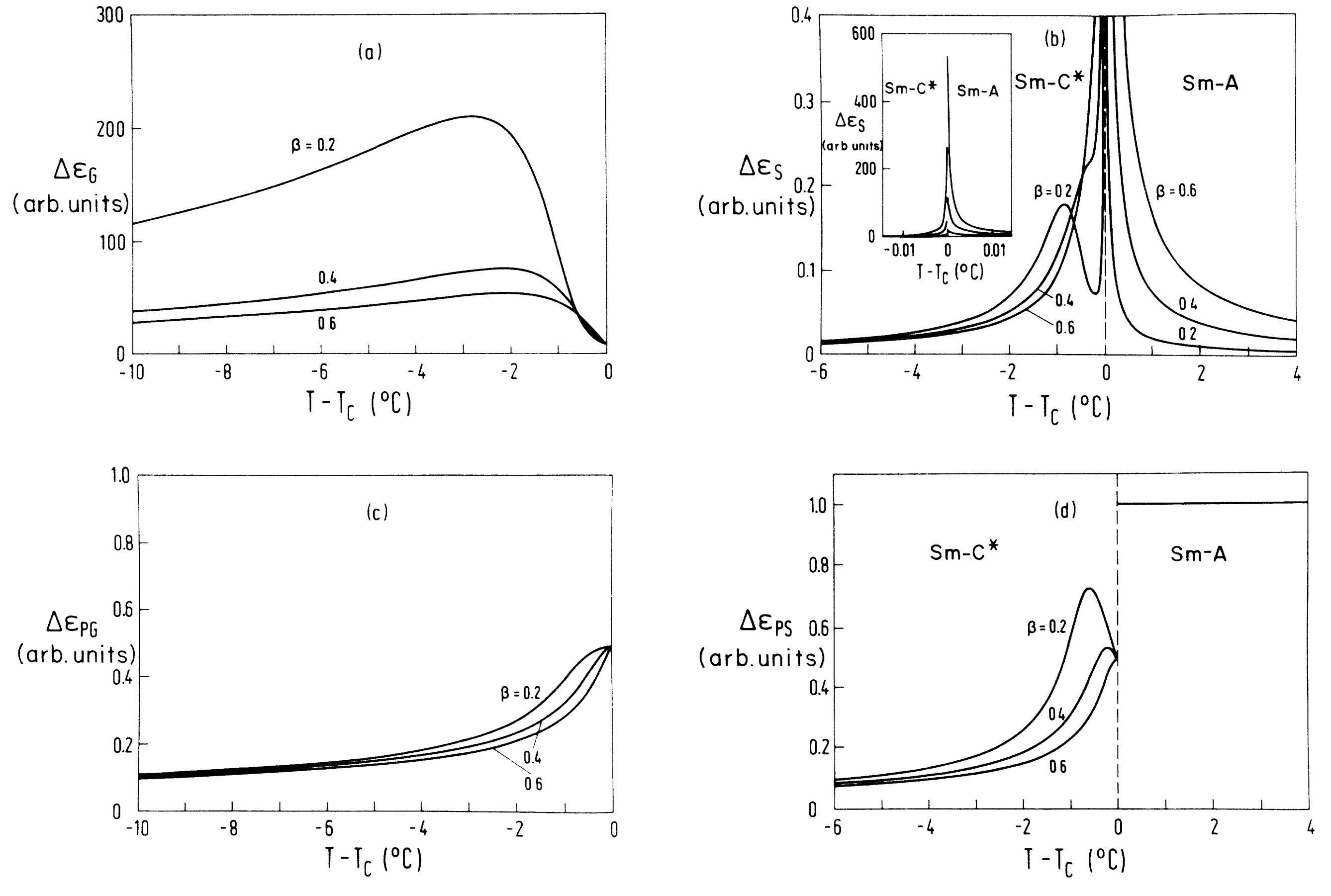

FIG. 3. The calculated dielectric strengths as a function of temperature of the four dielectric modes of the Sm-C^* phase which are included in our model. The parameter β is a measure of how important the biquadratic coupling between tilt and polarization is compared with the bilinear one.

which have been reported are performed only at frequencies well below the relaxation frequencies of the polarization modes. The only exception known by us is the work by Benguigui,[9] but he only discusses the eigenfrequencies in a qualitative way and not the corresponding dielectric strengths in his report. What normally is experimentally determined as ϵ_∞ is thus the sum $\Delta\epsilon_{PS}+\Delta\epsilon_{PG}+\Delta\epsilon_{el}$, where $\Delta\epsilon_{el}$ is the general electronic background which is not included into the model. In order to resolve these three contributions one has to increase the frequency range of the measurements well beyond the 500 MHz which is the value Benguigui has given for the eigenfrequencies of the polarization modes. Thus there exists presently no experimental data with which we can compare the outcome of the calculations concerning these modes.

The two director reorientational modes of the Sm-C^* phase are commonly denoted the soft mode and the Goldstone mode. These two modes generally consist of linear combinations of amplitude and phase fluctuations of the director. Solving the dynamic equations (23) we showed that if we exclude a temperature interval $\Delta T \sim 0.01$ K below T_c this mixing is negligible and we can consider the soft mode to consist only of amplitude fluctuations while the Goldstone mode consists only of phase fluctuations to a high degree of accuracy. We should, however, observe that the reverse is not true because not all the amplitude fluctuations go into the soft mode as can be seen from Eq. (27a). The part of the amplitude fluctuations which goes into the Goldstone mode can, however, be neglected compared to the large contribution which is given by the first term in Eq. (27b). As good approximations of the soft mode and the Goldstone mode dielectric strengths we thus can use the expressions given by Eqs. (30a) and (32), respectively. From these equations we see that the quantity b_3/b_7 plays an analogous role for the soft mode as does P_0/θ_0 for the Goldstone mode. In Fig. 2 we see that in the classical limit these quantities are the same, but as β is lowered, i.e., as the biquadratic coupling between tilt and polarization is becoming more important, b_3/b_7 develops a pronounced maximum approximately 1 K below T_c. This maximum is responsible for the bump in $\Delta\epsilon_S$, which can be seen in Fig. 3(b). From a theoretical point of view the existence of this maximum can be understood because it appears in a temperature interval where the calculated polarization shows[3,5] a very sharp increase with $T_c - T$, an increase which is more pronounced the stronger is the biquadratic coupling. By plotting $1/\Delta\epsilon_S$ versus temperature, as is done in Fig. 5, we see that for a strong biquadratic cou-

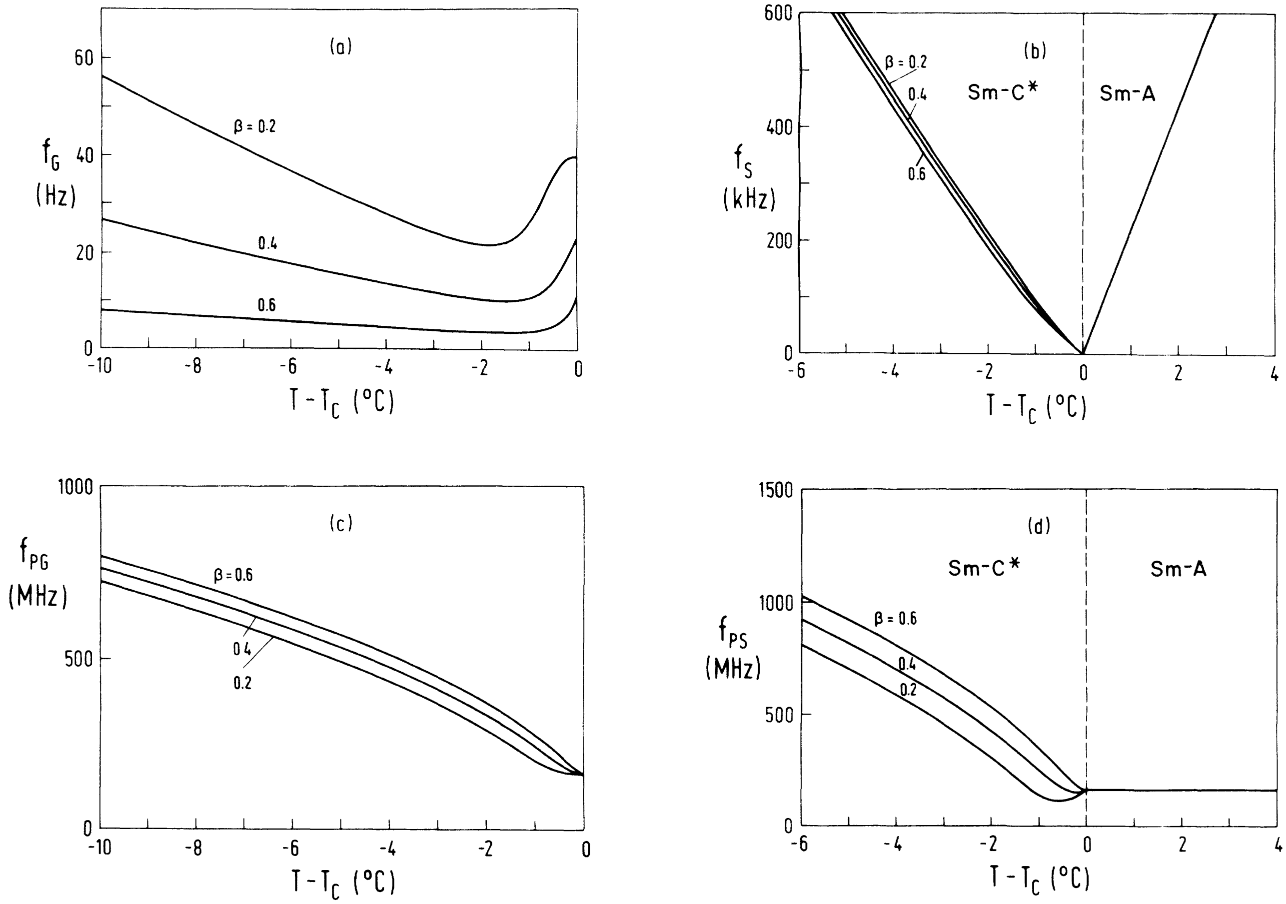

FIG. 4. The calculated relaxation frequency as a function of temperature of the four dielectric modes of the Sm-C^* phase which are included in our model. The parameter β is a measure of how important the biquadratic coupling between tilt and polarization is compared with the bilinear one.

pling we get one linear behavior close to T_c and another one far away from T_c. By extrapolating this last line we see that this line will not cross the corresponding line obtained in the Sm-A phase at $T=T_c$ and for a small finite value of $1/\Delta\epsilon_S$ as is the case in the classical limit, but the crossing of the lines will occur for $T<T_c$ and for a negative value of $1/\Delta\epsilon_S$. As is seen from Figs. 3(a) and 3(b) the intensity of the soft mode is rapidly drowned in that of the Goldstone mode as the temperature of the system is lowered from T_c. This makes it possible to separate[4,8,23] the contribution from the two modes only in a temperature interval which is of the order of a few tenths of a degree just below T_c. One way[24–26] to study the soft mode in a broader temperature interval into the Sm-C^* phase is to apply a static electric bias field parallel to the smectic layers. If the bias field is strong enough the helix of the system is unwound and thus the Goldstone mode is suppressed. In a recent study of this type performed by F. Gouda[27] the soft mode was studied in a 4-K broad temperature interval below T_c. By plotting $1/\Delta\epsilon_S$ versus temperature a behavior was obtained which agrees with the crossover behavior of $1/\Delta\epsilon_S$ which we calculate for a system with strong biquadratic coupling, and thus the theoretical behavior of the soft mode dielectric strength displayed in Fig. 3(b) is confirmed by experiment.

In Fig. 3(a) we have plotted the dielectric strength of the Goldstone mode as a function of temperature. By comparing the magnitude of the four dielectric strengths displayed in Fig. 3 we see that concerning the low-frequency part of the dielectric constant almost all contribution comes from the Goldstone mode. In order to get a physical understanding of the Goldstone mode dielectric strength we make the following reasoning. The coupling of the polarization to the external field increases with P_0. This suggests $\Delta\epsilon_G \sim P_0^2$ as the response cannot depend on the sign of P_0. Furthermore, the elastic energy associated with the pitch is given by $g_K = K_3 q^2 \theta_0^2/2$ as can be seen from Eq. (5). This suggests $\Delta\epsilon_G \sim 1/K_3 q^2 \theta_0^2$. All together we thus expect $\Delta\epsilon_G \sim P_0^2/K_3 q^2 \theta_0^2$ which is exactly what is given by Eq. (32). In Fig. 2 we showed the temperature dependences of the pitch $p=2\pi/q$ and the ratio P_0/θ_0 calculated by the use of Eqs. (6)–(8). By comparing this figure and Fig. 3(a) we see that the pronounced maximum of $\Delta\epsilon_G$ a few degrees below T_c can be understood to be connected to the maximum of the pitch (minimum of q). Furtheron the factor $(P_0/\theta_0)^2$ which enters the expression of $\Delta\epsilon_G$ is emphasizing the sharp decrease of the Goldstone mode dielectric strength close to T_c. We finally point out that the calculated performance of $\Delta\epsilon_G$ which is displayed in Fig. 3(a) is well in accordance with existing experimental data.[4,23,28]

In Fig. 4(b) the relaxation frequency is plotted of the soft mode as a function of temperature. We notice that this has a very strong temperature dependence, showing a cusplike minimum at T_c. In solid ferroelectrics the slope of the $f_S(T)$ line is twice as large in the low-symmetry phase than in the high-symmetry phase[29] close to T_c. This result is also valid in our case. We should also note that the calculated value of f_S at T_c is finite. By symmetry considerations we must demand $\gamma_S(T_c)=\gamma_{SA}(T_c)$ and from Eqs. (26a) and (48a) we get

$$f_S(T_c)=f_{SA}(T_c)=\frac{(K_3-\epsilon\mu^2)q_0^2}{2\pi\gamma_S(T_c)} . \tag{51}$$

[Here we should point out that Eqs. (26) are exact at T_c because of the fact that the quantity Z equals zero at T_c]. Only the response to a modulated external field with a wave vector equal to q_0 can exhibit[30] a relaxation frequency of the soft mode which goes to zero at T_c.

The calculated Goldstone mode relaxation frequency is shown in Fig. 4(a). The way in which this varies with temperature can be qualitatively understood in the following way. The restoring force of the Goldstone mode is the twist elasticity of the system. The corresponding elastic energy is proportional to $K_3 q^2$. Thus the corresponding relaxation frequency should be proportional to this quantity. That this is the case is seen from Eq. (26b). From Fig. 4(a) we also notice how the calculated curves gradually transform into the results of the classical Landau model as β is increased towards unity. As a conclusion we thus notice that the general behavior of the results of the calculations, using a value of the parameter β of the order of approximately 0.2–0.7, is well in agreement with existing experimental data.[4,8,23,28]

In the present calculation we have excluded a small-temperature interval $\Delta T \sim 0.01$ K just below T_c. This temperature interval is, of course, insignificant as long as we only want to achieve a theoretical guidance to experiments. From a principle point of view it is, however, interesting to know how the solutions to the dynamic equations (23) look like also in the very vicinity of T_c. Here the mixing of amplitude and phase fluctuations in the eigenmodes becomes larger and the exact solution to the

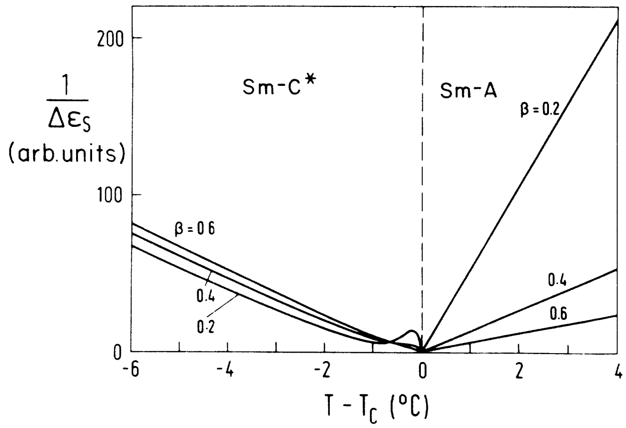

FIG. 5. The calculated temperature dependence of the inverse of the dielectric strength of the soft mode. The parameter β is a measure of how important the biquadratic coupling between tilt and polarization is compared with the bilinear one. For a small biquadratic coupling (β=0.6), $1/\Delta\epsilon_S$ displays a straight line in both phases. If the biquadratic coupling gets larger (β=0.2), $1/\Delta\epsilon_S$ displays a crossover behavior in the Sm-C^* phase with one linear behavior close to T_c and another one far away from T_c.

dynamic equations gets rather involved. At T_c, however, everything simplifies because it is possible to prove that here the two eigenmodes are degenerate and both consist of equal parts of amplitude and phase fluctuations. As by the symmetry of the system amplitude and phase fluctuations are degenerate at T_c we must demand $\gamma_S(T_c)=\gamma_G(T_c)$. Thus from Eq. (26b) we get

$$f_G(T_c)=\frac{(K_3-\epsilon\mu^2)q_0^2}{2\pi\gamma_G(T_c)} \tag{52}$$

showing by comparing with Eq. (51) that $f_G(T_c)=f_S(T_c)=f_{SA}(T_c)$.

The experimental verification of this degeneracy of the two modes at T_c is, however, a very subtle task due to the different frequency scales of the modes. As the slope of the $f_S(T)$ graph is of the order of 10 kHz/K, it is obvious that a very accurate determination of T_c is needed in order to answer this question. From a theoretical point of view it is, however, clear that as far as a Landau model, simple or complicated, is used to describe the system we always get as a result that the soft mode and the Goldstone mode are degenerate at T_c.

VII. DISCUSSION

In this paper we have shown how we by the generalized[3,5] Landau model, which is introduced by Eq. (5), can calculate the temperature-dependent complex dielectric constant in agreement with its experimental behavior for ferroelectric liquid crystals near the Sm-C^*–Sm-A phase transition. We have shown how the results depend on the parameter β, which is a measure of how important is the biquadratic coupling between tilt and polarization and conclude that values of β between approximately 0.2–0.7 are relevant in describing the system.

Previous calculations[7,31–33] of the dielectric constant of the Sm-C^* phase based on the classical Landau model introduced by Pikin and Indenboom[6] have failed to describe its experimental behavior in a proper way. These calculations predict a constant value of the Goldstone mode dielectric strength $\varepsilon_0\Delta\epsilon_G=C^2\epsilon^2/2(K_3-\epsilon\mu^2)q_0^2$. By comparing this expression with Eq. (32) we see the similarities and differences between the two models. Whereas the wave vector of the pitch adopts a constant value within the classical model, the generalized one describes the temperature dependence of q in a correct way. Furtheron, the constant $C^2\epsilon^2$, which in the classical model equals the (constant) ratio between polarization and tilt, is, in our expression, replaced by P_0/θ_0, which in the generalized model has been given a realistic temperature dependence. The soft mode dielectric strength is given as $\varepsilon_0\Delta\epsilon_S=C^2\epsilon^2/2[(K_3-\epsilon\mu^2)q_0^2+2\alpha(T_c-T)]$ by the classical Landau model. The denominator in this expression corresponds to our X [cf. Eq. (24a)]. These two quantities do only differ by some minor details. The large difference between the generalized model and the classical one lies in the fact that we have replaced the constant $C^2\epsilon^2$ by the quantity $(b_3/b_7)^2$, a quantity which we have plotted in Fig. 2(b). This factor can, in some sense, be regarded to play the same role for the soft mode as the quantity $(P_0/\theta_0)^2$ does for the Goldstone mode and permits us to describe the crossover effects in $1/\Delta\epsilon_S$ (cf. Fig. 5) which has also been recently observed.[27]

In Figs. (2)–(5) we have demonstrated that our model, which in the limit $\beta=1, d=0$ is identical to the classical one, gradually transforms the two simple predictions of the classical model into more realistic ones. The essential feature of the generalized Landau model is, as discussed before, the presence of the biquadratic coupling (the Ω term) between tilt and polarization in the free-energy density of Eq. (5). The larger is the biquadratic coupling, the smaller is β. We thus see that in order to describe the dielectric properties (and also the basic thermodynamic quantities) of the Sm-C^* phase in a correct way the presence of the biquadratic coupling is essential. All the observed anomalies in the thermodynamic behavior of ferroelectric liquid crystals approximately 1 K below T_c can be explained as crossover effects between the regime close to T_c where the bilinear coupling (the C term) between tilt and polarization is dominant to the regime far from T_c where the biquadratic coupling is the most important one.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation through the United States—Yugoslav Joint Fund for Scientific Cooperation under Grant No. NSF JF 845. Supports from the Research Council of Slovenia and the Swedish Science Research Council are also acknowledged.

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