

ARTICLES

Heat-diffusion central peak in the dielectric susceptibility of ferroelectric materials

M. Fally, W. Schranz, and D. Havlik

Institut für Experimentalphysik der Universität Wien, A-1090 Wien, Austria

(Received 24 July 1995; revised manuscript received 16 January 1996)

Recently, low-frequency measurements (0.1-Hz region) of the elastic susceptibility in KSCN near the order-disorder phase transition at $T_c=410$ K revealed a relaxation that could be explained by entropy fluctuations. We present a phenomenological theory describing the heat-diffusion central peak in the macroscopic ($q=0$) dielectric susceptibility. It results from the Landau free energy and the heat-diffusion equation. The model predicts a relaxation in the ferroelectric phase at low frequencies that depends on sample size. It does not follow a simple Debye behavior, but reveals a long high-frequency tail. [S0163-1829(96)00822-3]

I. INTRODUCTION

The low-frequency dynamics in the vicinity of phase transitions were studied intensively in the 1970s. The so-called central peak (CP) phenomena may have many different origins. Some are extrinsic (e.g., defects), others intrinsic (heat diffusion; HD). The interest in HD-CP was revived recently.¹⁻³ Though the work of Chaves *et al.*² on the dielectric dispersion in ferroelectric crystals at ultralow frequencies ($\frac{1}{10}$ –100 Hz) is very stimulating, the theory used for the explanation of the HD-CP phenomenon needs to be improved.

Here we deduce results directly from the Landau free energy and the heat-diffusion equation. The problem reduces to that of the crossover function between an isothermal susceptibility and an adiabatic one. In the case considered below [homogeneous field and $\epsilon(q=0,\omega)$] this crossover function $\mathcal{E}(\omega)$ is not a simple Debye function and is, as expected, sample geometry dependent.

II. PHENOMENOLOGICAL THEORY

In this approach, the temperature $T(\mathbf{x},t)$ and the order parameter $\eta(\mathbf{x},t)$ are taken as dynamical variables. One arrives, after linearization, at a system of coupled partial differential equations which are solved for the proper boundary conditions.

We start with the Landau free energy of a ferroelectric system [e.g., potassium dihydrogen phosphate (KDP) and triglycine sulfate] in its simplest form, neglecting coupling to strains or other variables, and assuming a second-order phase transition

$$F(\eta, T) = F_0(T) + \frac{a}{2} (T - T_0) \eta^2 + \frac{b}{4} \eta^4 - \eta f_\eta, \quad (1)$$

where f_η denotes the external conjugate field to the order parameter η . $F_0(T)$ is the background part of the free energy. The dynamics of the problem is obtained from the Lagrangian density \mathcal{L} . The Landau free energy plays the role of the potential-energy density. The kinetic-energy density \mathcal{T} is neglected as the soft mode frequency is many orders of

magnitude higher than the characteristic frequencies we are interested in. For the same reason, we neglect the Rayleigh dissipation term, so that $\mathcal{L} = -F$. Using Lagrange's equation for continuous systems, the equation of motion with respect to η is simply the equilibrium solution

$$a(T - T_0) \eta + b \eta^3 = f_\eta. \quad (2a)$$

However, both T and η are functions of time and space. For ferroelectric substances, η is the polarization and f_η is an electric field. The heat-diffusion equation reads

$$T \frac{dS}{dt} = \kappa \nabla \cdot (\nabla T), \quad (2b)$$

where κ denotes the thermal diffusivity. After linearizing with respect to small changes in the dynamical variables $\delta\eta$ and δT , and neglecting terms of second order (the dot denotes the time derivative), Eqs. (2) become

$$(\chi_\eta^0)^{-1} \delta\eta(z, t) + a \eta_0 \delta T(z, t) = \delta E(t), \quad (3a)$$

$$C^\eta \delta \dot{T}(z, t) - a \eta_0 \bar{T} \delta \dot{\eta}(z, t) - \kappa \frac{\partial^2 \delta T(z, t)}{\partial z^2} = 0. \quad (3b)$$

C^η denotes the specific heat at constant polarization, \bar{T} the equilibrium temperature, and χ_η^0 the static order-parameter

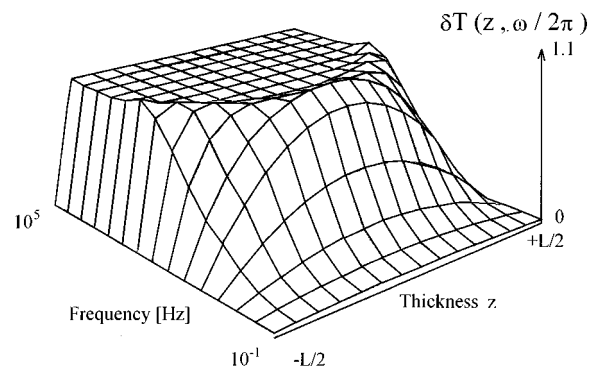


FIG. 1. Temperature profile $\delta T(z, \omega)$ according to Eq. (7).

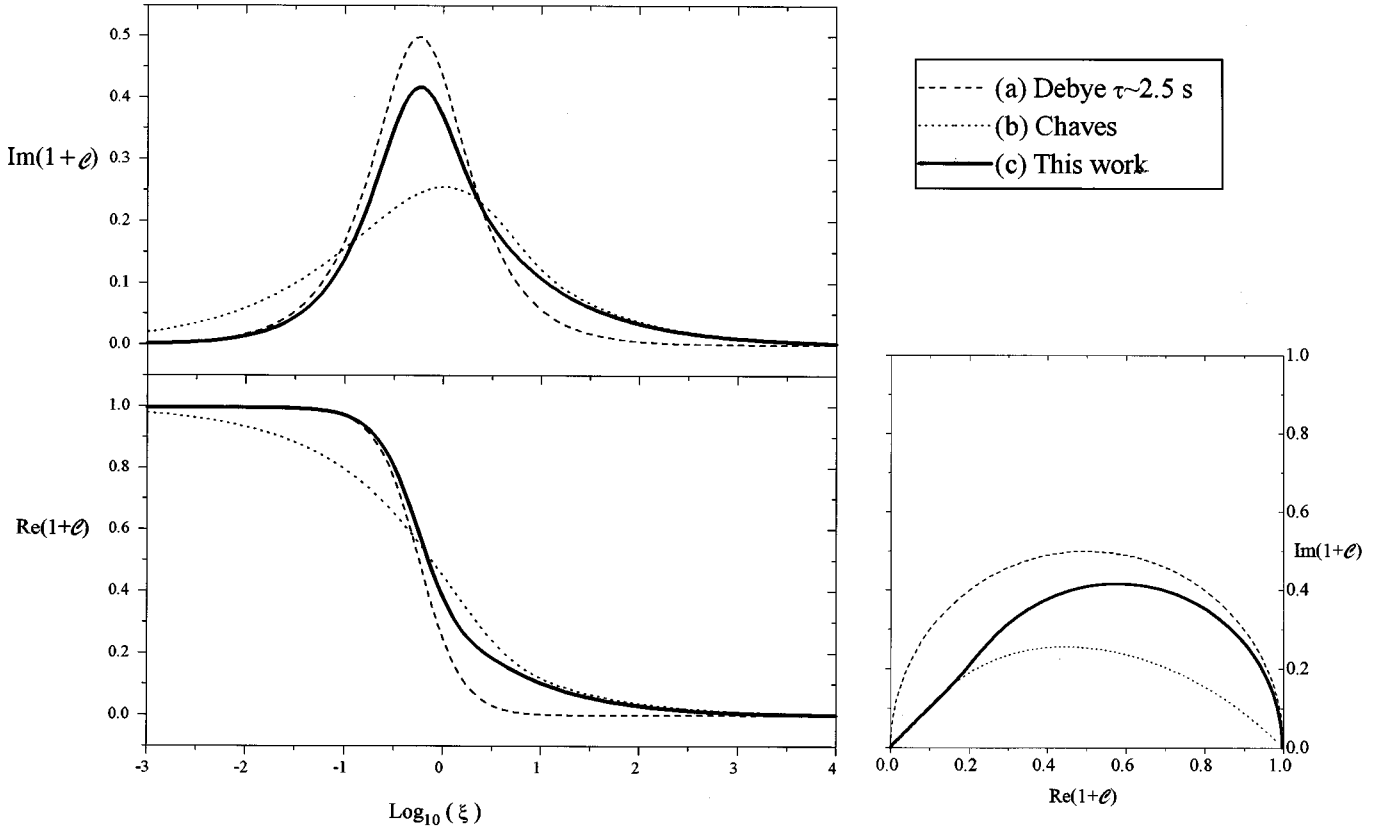


FIG. 2. ξ dependence of various crossover functions [$\xi = \omega(L^2/2D)$, $D = 3 \times 10^{-3}$ cm²/s, and $L = 0.1$ mm]: (a) Debye relaxator (one relaxation time $\tau \approx 2.5$ s). (b) After Chaves (Ref. 2) [Eq. (11)]. (c) According to this work [Eq. (10a)].

susceptibility. The problem treated is that of a thin sample in the direction of polarization, which is parallel to z .

At this point, one should shortly discuss the physics of a system obeying Eqs. (3). According to the coupling $T\eta^2$ in the Landau free energy (1), the order-parameter fluctuations create temperature fluctuations propagating through the crystal by diffusion. If a very low-frequency field is applied, the system has sufficient time to exchange heat with its surroundings, and one measures $\chi^T = \chi_\eta^0$ (in the limit $t \rightarrow \infty$) and $\delta T(z) = 0 \forall z$. In contrast, when applying high frequencies no heat exchange is possible and χ^S is measured. The temperature changes $\delta T(z)$ occur then in the crystal, whereas for the boundaries we assume an ideal thermal contact with metal electrodes and the thermal bath, i.e., infinite thermal conductivity what is a reasonable approximation. With this assumption we set the boundary conditions $\delta T(z = \pm L/2) = 0$, where L is the thickness of the sample.

Substitution of $\delta\eta = \chi_\eta^0[\delta E - a\eta_0\delta T]$ from Eq. (3a) into Eq. (3b) leads to (the double prime denotes second space derivative)

$$\underbrace{[C^\eta + (a\eta_0)^2\bar{T}\chi_\eta^0]}_{c^E(\bar{T})} \delta\dot{T} = \kappa\delta T'' + a\eta_0\bar{T}\chi_\eta^0\delta\dot{E}. \quad (4)$$

Rewriting Eq. (4), we obtain

$$\delta\dot{T}(z,t) = D(\bar{T})\delta T''(z,T) + h(\bar{T},t), \quad (5)$$

where $D(\bar{T}) = \kappa/C^E(\bar{T})$ is the temperature-dependent thermal diffusivity.

Applying a sinusoidal electric ac field $\delta E(t) = E_0 \exp(-i\omega t)$, the effective generalized field $h(\bar{T},t)$ is

$$h(\bar{T},t) = -i\omega\delta E(t) \frac{a\eta_0\bar{T}\chi_\eta^0}{C^E(\bar{T})}. \quad (6)$$

Now, one is interested in the solution of Eq. (5) under the boundary conditions $\delta T(z = \pm L/2) = 0$.

The general solution of this partial differential equation can be found, e.g., in Ref. 4 or 5 (also see the Appendix). Taking the steady-state limit $t \rightarrow \infty$, one obtains

$$\begin{aligned} \delta T(z,t) = & -\frac{a\eta_0\bar{T}\chi_\eta^0}{C^E(\bar{T})} \sum_{j=0}^{\infty} (-1)^j \frac{4}{Lq_j} \cos(q_j z) \\ & \times \frac{i\omega}{D(\bar{T})q_j^2 - i\omega} \delta E(t), \end{aligned} \quad (7)$$

with $q_j = (2j+1)(\pi/L)$ and $\tau_j = 1/[D(\bar{T})q_j^2]$. The temperature profile of a ferroelectric system under an applied electric field described by Eq. (7) is depicted in Fig. 1. Inserting Eq. (7) into Eq. (3a), and averaging over the sample size, leads to the dielectric susceptibility

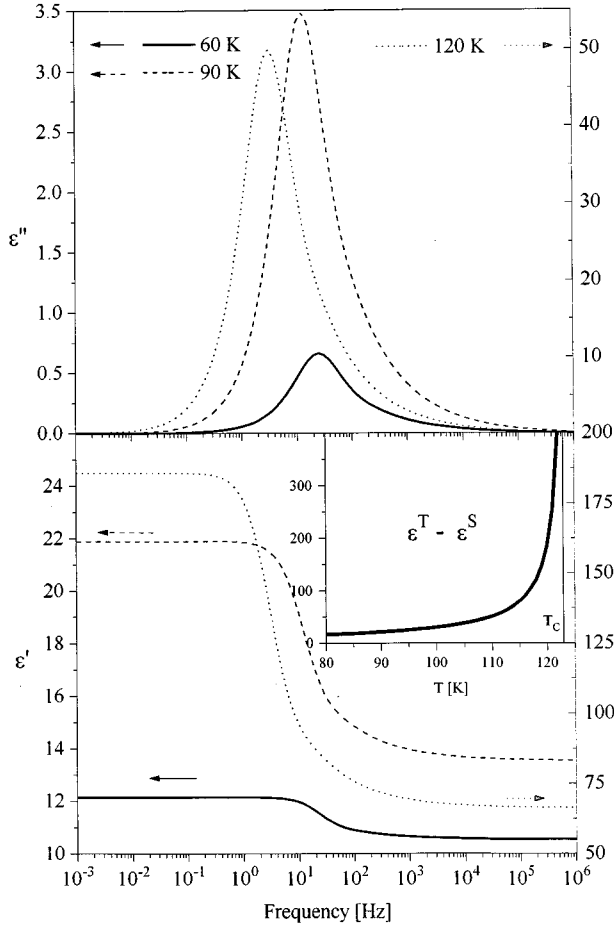


FIG. 3. Calculated frequency dependence of the dielectric constant for KDP (with parameters from Ref. 6 and $L=1$ mm) for three temperatures below the phase transition ($T_c=123$ K). The right axis is used for ϵ' at $T=120$ K. The inset shows the strength $[\epsilon^T(T) - \epsilon^S(T)]$ of the relaxation. The sample is assumed mechanically “free.”

$$\chi_\eta(\omega, \bar{T}) = \chi_\eta^0(\bar{T}) \left(1 + \frac{8}{L^2} \frac{(a\eta_0)^2 \bar{T} \chi_\eta^0}{C^E(\bar{T})} \times \sum_{j=0}^{\infty} \frac{1}{q_j^2} \frac{i\omega\tau_j(\bar{T})}{1-i\omega\tau_j(\bar{T})} \right). \quad (8)$$

III. DISCUSSION

To clarify the message of Eq. (8) and to provide a possibility of comparing it with the analogous result of Chaves *et al.*,² we rewrite it in the abbreviated form

$$\chi_\eta(\omega, \bar{T}) = \chi^T - (\chi^T - \chi^S) \mathcal{E}(\omega), \quad (9a)$$

where $\mathcal{E}(\omega)$ is the crossover function between the adiabatic and isothermal limits. The derivation $(\partial\eta_0/\partial T) = p(T)$ is the pyroelectric coefficient, which reads

$$p(T) = -a\eta_0\chi_\eta^0. \quad (9b)$$

Hence

$$\chi^T = \chi_\eta^0. \quad (9c)$$

$$\chi^T - \chi^S = -\frac{p(\bar{T})^2 \bar{T}}{C^E(\bar{T})}, \quad (9d)$$

$$\begin{aligned} \mathcal{E}(\omega) &= \frac{8}{L^2} \sum_{j=0}^{\infty} \frac{1}{q_j^2} \frac{i\omega\tau_j(\bar{T})}{1-i\omega\tau_j(\bar{T})} \\ &= \frac{8}{\pi^2} \sum_{j=0}^{\infty} \frac{1}{(2j+1)^2} \frac{1}{1-i\omega\tau_j(\bar{T})} - 1. \end{aligned} \quad (9e)$$

In a more elegant form, the crossover function can be written in terms of the digamma function $\Psi(z) = [d\Gamma(z)/dz] \times [1/\Gamma(z)]$ with $z \in \mathcal{C}$,

$$\mathcal{E}(\omega) = \frac{1-i}{\pi\sqrt{\xi}} [\Psi^+(\xi) - \Psi^-(\xi)] - 1, \quad (10a)$$

with the abbreviation $\xi = (\omega L^2)/(2D)$ and

$$\Psi^\pm(\xi) = \Psi\left[\frac{1}{2} \left(1 \pm \frac{1+i}{\pi} \sqrt{\xi} \right)\right]. \quad (10b)$$

Chaves *et al.*² presented a theory and measurements concerning the problem of the heat-diffusion central peak in macroscopic susceptibilities. Equation (9) in Ref. 2 gives the following crossover function for the same problem:

$$\mathcal{E}_{\text{Chaves}}(\omega) = \frac{1 - \exp(-[1-i]\sqrt{\xi})}{(1-i)\sqrt{\xi}} - 1, \quad (11)$$

and the temperature profile can be calculated from Eq. (2) of Chaves *et al.*'s work by Fourier transformation.

Figure 2 shows the ξ dependence of the crossover function according to Eq. (10a) and compares it to Eq. (11) and to the usual Debye relaxator (only one relaxation time). It can easily be seen that for low frequencies the Debye function and our model coincide, whereas for high frequencies our model is very similar to that of Chaves *et al.* It should be emphasized that the crossover function depends on one parameter ξ only. This means that decreasing the thickness L or increasing the thermal diffusivity (by changing the temperature) leads to the same effect: the relaxation frequency shifts to higher values.

There are some important differences between the work and that of Chaves *et al.*² Here everything is derived straightforwardly from the equations of motion. Chaves *et al.* on the other hand, assume a temperature step (we do not assume it, the coupling $\eta^2 T$ provides it in the framework of our model) and treats the Fourier transform of the temperature response function as a dielectric constant which cannot be justified. In addition, Chaves *et al.* deal with free boundary conditions that lead to wrong results at low frequencies, as they pointed out themselves. In their work they assume the thermal bath simply as a continuation of the crystal where no heating due to the electric field takes place. As a consequence the temperature profile always gives $\delta T \neq 0$. For $\omega \rightarrow 0$ there occurs an unphysical divergence. The temperature profile for our ansatz is shown in Fig. 1 using Eq. (7). One sees that as a consequence of our boundary conditions $\delta T(z = \pm L/2) = 0$ the temperature fluctuations δT vanish for $\omega = 0$, as expected from a realistic system.

Our model also predicts a thickness dependence of the relaxation times scaling with L^2 . Although there is no possibility to give an analytic expression for the dependence of the mean relaxation time $\bar{\tau}$, it is clear that the thinner the sample the higher the maximum's frequency. As the first mode $j=0$ in Eq. (8) by far makes the largest contribution to $\chi''_{\text{Max}}(\omega)$, the dependence is nearly

$$\omega_{\text{Max}} \propto \left(\frac{1}{L}\right)^2 \quad \text{or} \quad \bar{\tau} \propto (L)^2.$$

IV. CONCLUSION

In Fig. 3 the calculated frequency dependence of the dielectric constant of KDP using the values for the thermal conductivity κ and the specific heat from Ref. 6 is depicted taking into account the HD-CP. As low-frequency phenomena occur in many measurements but could not be ascribed satisfactorily to an origin, this may be an important step in the right direction. Also a comparison with the data published by Chaves *et al.*² shows that the model presented might be helpful to explain them properly.

We have presented a model for calculating the crossover function between the isothermal and adiabatic limits of a macroscopic susceptibility deduced from the Landau free energy and the heat-diffusion equation. Choosing the appropriate boundary conditions we derived a crossover function which has the following main characteristics: (i) a distribution of relaxation times; (ii) a thickness dependence of the relaxation times, scaling with L^2 ; (iii) a very long high-frequency tail of the dispersion; and (iv) a Debye-like low-frequency behavior. This very long high-frequency tail provides the possibility of observing the heat-diffusion phenomenon even up to 10 kHz using a typical sample thickness of about 1 mm. In several works (e.g., Refs. 7 and 8) low-frequency dispersions with a non-Debye behavior are

mentioned, but are mostly interpreted as defect-induced phenomena. We believe that for some of these experiments an explanation of the data with our model would be satisfactory.

ACKNOWLEDGMENT

This work was supported by the Österreichischen Fonds zur Förderung der wissenschaftlichen Forschung P 9793.

APPENDIX

The general solution of the partial differential equation (5) reads

$$\delta T(z, t) = \sum_{j=0}^{\infty} \left(a_j \exp\{-\lambda_j t\} + \int_0^t c_j(s) \exp\{-\lambda_j(t-s)\} ds \right) b_j(z),$$

where

$$a_j = \left(\frac{2}{L}\right)^{1/2} \delta T_0 \int_{-L/2}^{L/2} \cos(q_j z) dz = \delta T_0 \left(\frac{2}{L}\right)^{1/2} \frac{2}{q_j} \sin\left(q_j \frac{L}{2}\right),$$

$$b_j(z) = \left(\frac{2}{L}\right)^{1/2} \cos(q_j z),$$

$$c_j(s) = \int_{-L/2}^{L/2} h(\bar{T}, t) b_j(z) dz,$$

and λ_j are the eigenvalues fulfilling

$$-D(\bar{T}) \frac{d^2 b_k}{dz^2} = \lambda_k b_k,$$

which (after taking the limit $t \rightarrow \infty$) leads directly to Eq. (7).

¹W. Schranz and D. Havlik, Phys. Rev. Lett. **73**, 2575 (1994).

²A. S. Chaves, F. V. Letelier, J. F. Sampaio, and R. Gazzinelli, Phys. Rev. B **47**, 4480 (1993).

³E. Courtens and R. Gammon, Ferroelectrics **24**, 19 (1980).

⁴*Taschenbuch der Mathematik*, edited by I. N. Bronshtein and K. A. Semendyayev (Verlag H. Deutsch, Frankfurt, 1985).

⁵J. R. Cannon, in *The One-Dimensional Heat Equation*, edited by G. C. Rota, Encyclopedia of Mathematics and Its applications

Vol. 23 (Addison-Wesley, Reading, MA, 1984), Chap. 19.

⁶*Ferroelectrics: Non oxides*, edited by T. Mitsui and E. Nakamura, Landolt-Börnstein, New Series, Group III, Vol. 28b (Springer-Verlag, Berlin, 1990), p. 69ff.

⁷P. Kubinec, M. Fally, A. Fuith, H. Kabelka, and C. Filipič, J. Phys. Condens. Matter **7**, 2205 (1995).

⁸E. Nakamura, K. Deguchi, K. Kuramoto, I. Hirata, T. Ozaki, and J. Ogami, Ferroelectrics **140**, 157 (1993).