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The Goldstone mode in ferroelectric liquid crystals A non-linear dielectric loss process

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The Goldstone mode in ferroelectric liquid crystals

A non-linear dielectric loss process

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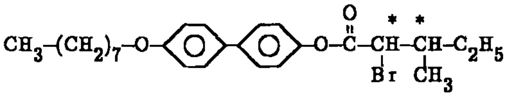
The dielectrically observed Goldstone mode in ferroelectric liquid crystals is shown to have, beside the well-known DC bias field dependence, a strong AC field dependence of the dielectric loss. This non-linearity arises at AC field strengths > 100 V/cm already in the materials which we have studied. It is maximal at the frequency of maximum loss of the Goldstone mode and levels off at frequencies far enough apart. Thus attempts to analyse the Goldstone mode within the framework of the linear response theory are not applicable in general, but are restricted to sufficiently small AC fields.

The dielectrically observed Goldstone mode in ferroelectric liquid crystals is well established [1–11]. It is well known that its dielectric strength can be continuously suppressed by a DC bias field. Despite this fact a possible AC field dependence of the Goldstone mode is not usually considered and has not so far been analysed systematically. In this preliminary communication we present experiments which prove that the Goldstone mode has to be treated as a non-linear dielectric loss process already at oscillator levels higher than 100 V/cm.

For the experiments two different liquid-crystalline samples were used, a pure bromo compound: (4-(3-(*S*)-methyl-2-(*S*)-bromopentanoyloxy)-4′-octyloxy-biphenyl) with two chiral centres, which was synthesized according to known procedures [11, 12]



$$\mathrm{C}\ 293\,\mathrm{K}\ \mathrm{S}_\mathrm{C}^*\ 315\,\mathrm{K}\ \mathrm{S}_\mathrm{A}\ 326\,\mathrm{K}\ \mathrm{I}$$

and a commercial ferroelectric liquid-crystalline mixture (ZLI 3654, Merck Darmstadt) which was used in a previous study [4(*b*)]. Its phase sequence is

$$\mathrm{C}\ 243\,\mathrm{K}\ \mathrm{S}_\mathrm{C}^*\ 335\,\mathrm{K}\ \mathrm{S}_\mathrm{A}\ 349\,\mathrm{K}\ \mathrm{Ch}\ 359\,\mathrm{K}\ \mathrm{I}\ [13].$$

The dielectric measurements [14] covered the frequency range from 10 Hz to 10^7 Hz using an impedance analyser (Hewlett-Packard 4192 A). The AC measuring field varied between 10 V/cm to 1 kV/cm. An additional DC bias field (max 10^4 V/cm) could be superimposed. A nitrogen gas heating system covered the temperature range from 100 K to 450 K having a stability in the temperature adjustment of ±0·02 K (measured over a period of 100 s). The resolution of the temperature measurement was ±0·01 K using a Keithley 195 A multimeter. The liquid-crystalline sample was kept

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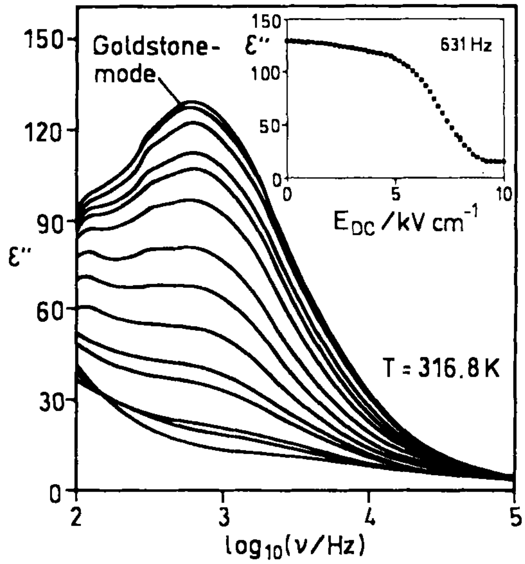
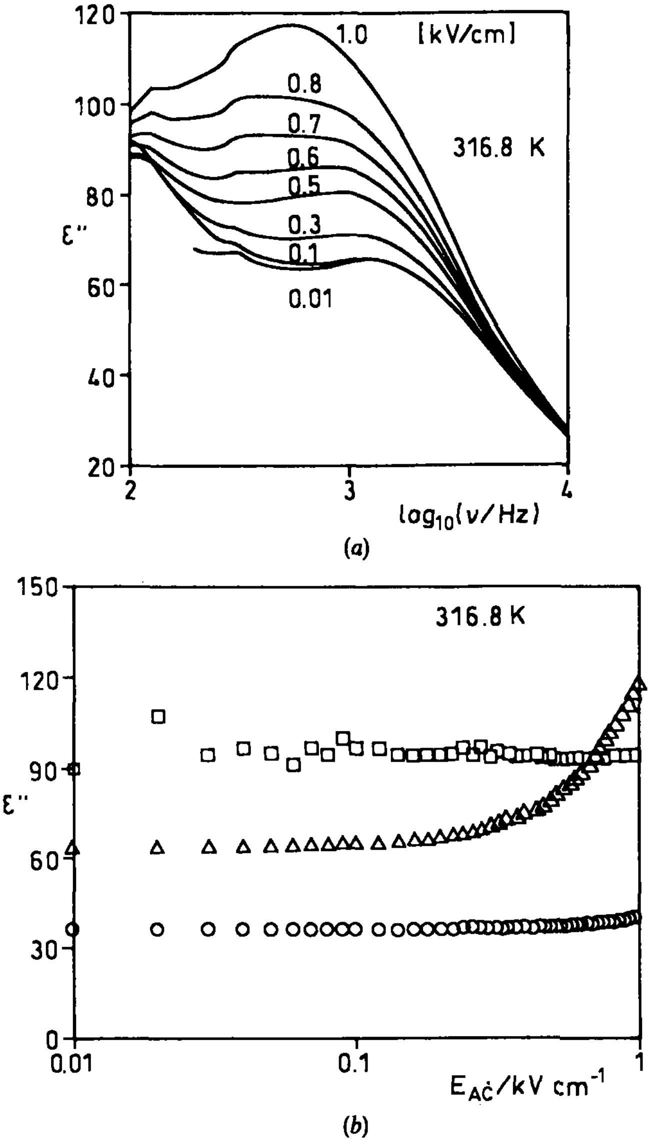


Figure 1. Dielectric loss ϵ'' versus frequency at 316·8 ± 0·02 K with different DC bias fields ranging from 0 to 10 kV/cm, AC field: 1 kV/cm, sample thickness: 10 μm, sample: the bromo compound. Inset: DC bias field dependence of the dielectric loss at 631 Hz and 316·8 K.

between two glass plates coated with polyimid and separated by about 10 μm (EHC-cell, Japan). The parallel rubbing direction led to the desired uniform bookshelf geometry. The electric field was applied via two evaporated indium–tin oxide electrodes with an area of $4 \times 4\,\mathrm{mm}^2$. The temperature gradient across the sample is estimated to be less than 0·04 K.

The Goldstone mode exhibits in its dielectric strength a pronounced DC bias field dependence (see figure 1), which is sinusoidal in shape (see inset in figure 1). A similar dependence was observed for a variety of different (low molar mass and polymeric) ferroelectric liquid crystals. On measuring the AC field dependence of the Goldstone mode we also find a strong influence on the dielectric strength (see figure 2 (*a*)). Varying the field strength of the AC field from 10 V/cm up to 1 kV/cm results, for the frequency of the Goldstone mode at maximum loss of about 630 Hz, in a nearly twofold increase of the dielectric loss (see figure 2 (*b*)). At frequencies far enough apart (e.g. 63 Hz and 6300 Hz in figure 2 (*b*)) a linear relationship is observed.

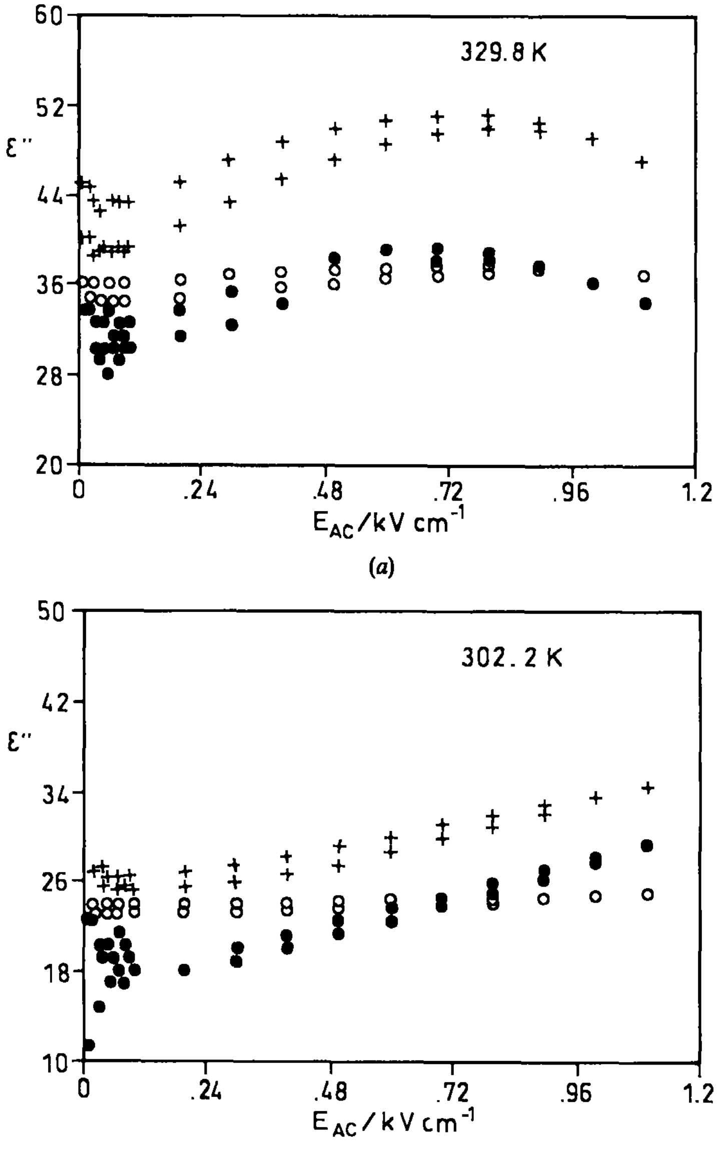
To prove if this effect is just a peculiarity of our pure ferroelectric liquid crystal we have studied the AC field dependence of the dielectric loss for a commercial ferroelectric mixture (ZLI 3654, Merck, Darmstadt), which has been studied with dielectric spectroscopy by Biradar *et al.* [4 (a)]. (Unfortunately the applied AC field strength is not reported in this paper.) The AC field dependence was measured at two different temperatures: 302 K and 329·8 K where the spontaneous polarization changes from 18 nC/cm^2 to 5 nC/cm^2 [13]. At the temperature of 329·8 K (close to the $S_C^* \rightarrow S_A$ transition) the non-linearity of the dielectric loss is small (see figure 3 (*a*)). With decreasing temperature and hence increasing spontaneous polarization the AC field dependence of the Goldstone mode becomes stronger. As for the bromo compound the non-linearity is strong at the frequency (250 Hz) of maximum loss of the Goldstone



(*a*)

(*b*)

Figure 2. (*a*) Dielectric loss ε'' versus frequency at 316·8 K and at oscillator fields varying between 0·01 kV/cm and 1·0 kV/cm. DC bias field: 0 V/cm, sample thickness: 10 μm, sample: the bromo compound. The experimental uncertainty is estimated to be less than ±5 per cent. Presumably due to alignment effects in the sample cell the curve in figure 1, with DC field 0 V/cm and AC field 1 kV/cm and that in figure 2 (*a*), do not fully coincide. (*b*) Dielectric loss ε'' versus oscillator level at 316·8 K and at three different frequencies: □, 63 Hz; △, 630 Hz; and ○, 6300 Hz. Otherwise as in figure 2 (*a*).



(a)

(b)

Figure 3. (a) Dielectric loss ϵ'' versus oscillator level at 329·8 K and at three different frequencies: +, 100 Hz; ●, 250 Hz; ○, 1000 Hz. DC bias field 0 V/cm, sample thickness: 10 μm, sample: ferroelectric mixture ZLI 3654. The experimental uncertainty is estimated to be less than ± 5 per cent. (b) Dielectric loss ϵ'' versus oscillator level at 302·2 K. Otherwise as for figure 3 (a). The experimental uncertainty is estimated to be less than 5 per cent.

mode and levels off at frequencies far enough apart (see figure 3 (*b*)). The question as to why at a frequency of 100 Hz an AC field dependence is observed and why the pure bromo compound shows a stronger and qualitatively different non-linearity in comparison to the ferroelectric mixture remains open. For that the detailed composition of the ferroelectric mixture would have to be known.

In summary we have to conclude that the dielectrically observed Goldstone mode in ferroelectric liquid crystals has to be treated as a non-linear loss process for electrical fields > 100 V/cm. Besides the well established DC bias field dependence it shows a strong AC field dependence as well. The dielectrically observed Goldstone mode has a negligible temperature dependence within the ferroelectric mesophase. This can be clearly seen in measurements on ferroelectric combined main chain side group liquid-crystalline polymers, where the S_C^* phase has a broad temperature range [9 (a), (b)]. As discussed in [7] the 'relaxation' time distribution of the Goldstone mode has its long wings on the low frequency side in contrast to all empirical relaxation functions such as Cole–Davidson, Havriliak–Negami, Fuoss–Kirkwood, etc. [15]. The observed non-linearity is also reflected in the studies with our molecular gyroscope based on the Goldstone mode [16]. By driving in a four electrode microstructure the smectic layers with phase locked, 90° shifted, rotating electrical fields we find, at frequencies close to the Goldstone mode frequency, a strong non-linear response which levels off at frequencies far enough apart.

The observed non-linearity of the dielectrically measured Goldstone mode requires a word of caution. The conventional AC bridges (like the HP 4192 A) are based on the autobalance of sinusoidal signals. They are, in principle, not capable of analysing higher harmonics of non-sinusoidal signals caused by non-linear materials. Thus the measured non-linearity in the dielectric loss is no more than a *qualitative* feature. A detailed analysis requires a frequency–response analysis (for instance with a Solartron Schlumberger FRA 1254).

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References

[1] Martinot-Lagarde, Ph., and Durand, G., 1981, *J. Phys.*, Paris, **42**, 269.

[2] (a) Cava, R. J., Patel, J. S., and Rietman, E. A., 1986, *J. appl. Phys.*, **60**, 3093. (b) Cava, R. J., Patel, J. S., Collen, K. R., Goodby, J. W., and Rietman, E. A., 1987, *Phys. Rev.* A, **35**, 4378.

[3] (a) Levstik, A., Carlsson, T., Filipič, C., Levstik, I., and Žekš, B., 1987, *Phys. Rev.* A, **35**, 3527. (b) Levstik, A., Carlsson, T., Filipič, C., Levstik, I., and Žekš, B., 1988, *Molec. Crystals liq. Crystals*, **154**, 259. (c) Filipič, C., Carlsson, T., Levstick, A., Žekš, B., Blinc, R., Gouda, F., Lagerwall, S. T., and Skarp, K., 1988, *Phys. Rev.* A, **38**, 5833.

[4] (a) Biradar, A. M., Wrobel, S., and Haase, W., 1989, *Phys. Rev.* A, **39**, 2693. (b) Biradar, A. M., Wrobel, S., and Haase, W., 1989, *Liq. Crystals*, **5**, 1227.

[5] (a) Gouda, F., Andersson, G., Carlsson, T., Lagerwall, S. T., Skarp, K. Stebler, B., Filipič, C., Žekš, B., and Levstik, A., 1989, *Molec. Crystals liq. Crystals Lett.*, **6**, 151. (b) Gouda, F., Andersson, G., Carlsson, T., Lagerwall, S. T., Skarp, K. Stebler, B., Filipič, C., Žekš, B., and Levstik, A., 1989, *Liq. Crystals*, **6**, 219.

[6] Ozaki, M., Nakoa, K., Hatai, T., and Yoshino, K., 1989, *Liq. Crystals*, **5**, 1219.

[7] Vallerien, S. U., Kremer, F., Kapitza, H., Zentel, R., and Frank, W., 1989, *Physics Lett.* A, **138**, 219.

[8] Glogorova, M., and Pavel, J., 1989, *Liq. Crystals*, **6**, 325.

[9] (a) Vallerien, S. U., Zentel, R., Kremer, F., Kapitza, H., and Fischer, E. W., 1989, *Makromolek. Chem. rap. Commun.*, **10**, 333. (b) Vallerien, S. U., Zentel, R., Kremer, F., Kapitza, H., and Fischer, E. W., 1989, *Proceedings of the Second Ferroelectric Liquid Crystals Conference*, Göteborg, Sweden, *Ferroelectrics* (in the press). (c) Vallerien, S. U., Kremer, F., Kapitza, H., Zentel, R., and Fischer, E. W., 1989, *Proceedings of the Seventh International Meeting on Ferroelectricity* (IMF-7), Saarbrücken, F.R. Germany, *Ferroelectrics*, **109**, 273.

[10] Vallerien, S. U., Kremer, F., Scherowsky, G., Schliwa, A., Kühnpast, K., and Fischer, E. W., 1990, *Liq. Crystals*, **8**, 719.

[11] Vallerien, S. U., 1990, Dissertation, University of Mainz (in preparation).

[12] Yoshino, K., Ozaki, M., Kishio, S., Sakurai, T., Mikami, N., Higuchi, R., and Humoa, M., 1987, *Molec. Crystals liq. Crystals*, **144**, 87.

[13] Geelhaar, Th., Merck AG Darmstadt (private communication).

[14] Kremer, F., Boese, D., Meier, G., and Fisher, E. W., 1989, *Prog. Colloid Polym. Sci.*, **80**, 129.

[15] Böttcher, C. J. T., and Bordewijk, P., 1978, *Theory of Electric Polarization*, Vol. II (Elsevier).

[16] Kremer, F., Vallerien, S. U., Kapitza, H., and Zentel, R., 1990, *Physics Lett.* A, **146**, 273.