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LINEAR ELECTROOPTIC EFFECT IN THE L_α LIQUID CRYSTALLINE PHASE OF DPPC

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Abstract We report the first observation of a linear electrooptic effect and of two different resonant hydrodynamic modes in the L_α phase of the Dipalmitoyl Phosphatidyl Choline-water system, i.e. the first and second sound. The damping of the resonances, provides some hints concerning the non conventional $1/\omega$ behavior of the viscosities predicted by Mazenko, Ramaswamy and Toner.

INTRODUCTION

Accurate physical studies on the dipalmitoyl phosphatidyl choline (DPPC) - water system, are often considered as a prerequisite to the understanding of at least some of the membrane functions. For instance, linear electric couplings (flexoelectricity) have been invoked in the explanation of processes involving membrane curvature[1] ; similarly the compressional elastic constant (in the L_α e.g. smectic A phase) is a measure of the lateral compressibility[2]. Since the interdigitated electrodes technique has been shown both to be able to evidence flexoelectricity and to provide reliable measurements of the compressional elastic constant in thermotropic smectic A phases[3,4], it seemed natural to adapt it to lyotropic systems.

In the second section of this paper, we give a brief description of the technique, we discuss in particular the hydrodynamic modes which can be excited by an electric field periodic in time and in one direction of space. In principle all three isentropic elastic constants characteristic of a smectic A[5,6] are accessible to experiment ; indeed they govern the locations of resonances corresponding to first and second sound. As usual the damping is controlled by viscosities.

Experimental results are given in the third section. A linear electrooptic effect and two different resonances are indeed observed. For technical reasons, the different curves correspond to different water contents and light polarizations. They illustrate the main features of the system. Eventually we discuss the results in view of the recent theories predicting the divergence of some viscosities in smectics[7,8].

ANALYSIS OF THE EXPERIMENTAL PROCEDURE

A detailed description of the interdigitated electrodes technique has been given in several other places[3,4,9]. Periodic electric field gradients are used to induce, in a monocrystalline sample, an optical phase grating which is detected optically in a conventional scattering set-up. The optical wave vector conservation rules allow to select the linear coupling as previously explained.

One applies in the bulk of an homeotropic sample of thickness D (see Fig. 1 for the definition of the reference frame), an electrostatic potential :

$$\phi\ (x,z,t) = \sum_{n\geq 1} \phi_n \cos(n\, q_x\, x)\, \exp(-nKz) \cos \omega t$$

$0 \leq z \leq D$, $q_x = 2\ \pi/\lambda_e$ where λ_e is the spatial period (200 μm), $K = (\varepsilon^\circ_\perp / \varepsilon^\circ_{/\!/})^{1/2}\ q_x$. $\varepsilon^\circ_\perp$ and $\varepsilon^\circ_{/\!/}$ being the low frequency dielectric constants.

In a smectic A, the electric field gradients are coupled with the hydrodynamic variables u : displacement of the layers and $\theta = -\ \delta\rho/\rho$: dilation, leading to an energy increase[4] :

$$\Delta E = f\ \frac{\partial u}{\partial x}\ \frac{\partial^2 \phi}{\partial x \partial z} + f'\theta\ \frac{\partial^2 \phi}{\partial x^2}$$

f is the flexoelectric constant ∿ some 10^{-4} statvolt[3,10] while f' coupling the density to the electric field is expected to be of the same order[11].

In a lyotropic system, there is in principle an extra hydrodynamic variable, such as water concentration[12], and extra coefficients[9], but in the frequency range investigated in

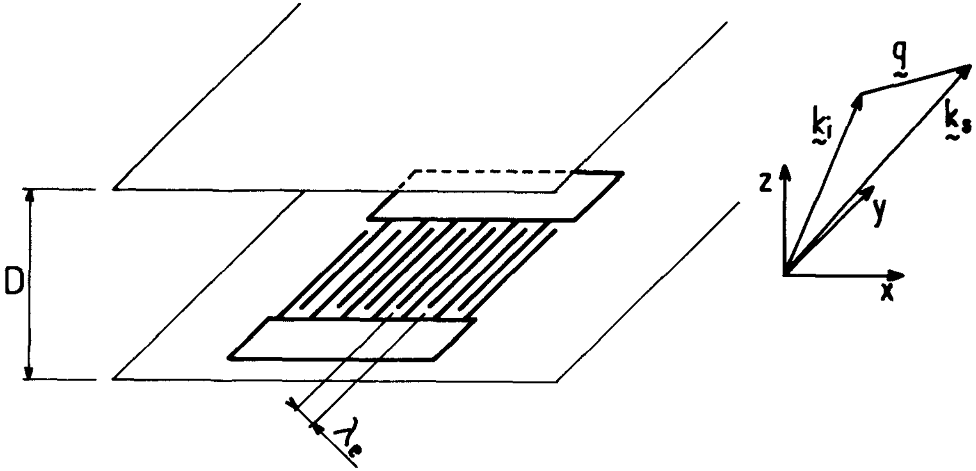

FIGURE 1 Typical geometry used in the experiment. The sample is sandwiched between glass holders in a homeotropic orientation. The interdigitated electrodes have a periodic structure along the direction $\hat{x}$ (period λ_e0 and can be considered as infinite in the $\hat{y}$ direction. $\hat{z}$ is both perpendicular to the layers and the glass holders. The scattering wave vector $\underset{\sim}{q} = \underset{\sim}{k}_s - \underset{\sim}{k}_i$, is such that $q_x = 2\pi/\lambda_e$ and q_z is determined by the incidence angles and the respective polarizations of the beams.

this paper the water slip mode is quenched and for all purposes the usual smectic A equations are valid[13].

The response of the sample is an (u,θ) distortion proportional to the electric potential ϕ, with the same period λ_e in space and the same angular frequency ω. It can be calculated from the general hydrodynamic equations of smectics[5,6]. Neglecting permeation, one finds : (for the Fourier component $e^{jq_x} e^{-j\omega t}$) :

$$u(q_x,z,\omega) = \frac{h}{a+bK^2+cK^4} \left\{ e^{-Kz} + \sum_{i=1}^{4} u_i \, e^{q_i z} \right\}$$

$$\theta(q_x,z,\omega) = \frac{1}{a+bK^2+cK^4} \left\{ \tau \, e^{-Kz} + h \sum_{i=1}^{4} t_i \, u_i \, e^{q_i z} \right\}$$

where a,b,c,h,τ and t are coefficients depending in a rather cumbersome algebraic way on elastic constants, viscosities, frequency and flexoelectric coefficients (for h and τ), the q_i's $(i=1,4)$ are the roots of the characteristic equation $a + bq^2 + cq^4 = 0$, and the u_i coefficients are determined by linear boundary conditions. We give their detailed expression in appendix A.

One may relate the positions and widths of the different predicted resonances of the responses $u(\omega)$ and $\theta(\omega)$ to equations (3) and (4).

The second sound resonances are linked to constructive interferences between the propagating shear waves in the sample $(u \sim \exp[jq_x + q_1 z]$ whenever the "small" root $q_1 = jn\,\pi/D$ $(n \geqslant 1)$ - typical acoustic resonator condition -.

The position n of the nth resonance is given by :

$$\rho\omega^2_{n,2} = \frac{q_x^2 \, (n\,\pi/D)^2 \, A \, \tilde{B}}{q_x^2 \, A + (n\,\pi/D)^2 \, (A+B+2C)}$$

where A,B,C and $\tilde{B} = B - C^2/A$ are the elastic constants of the smectic A or L_α phase. We are using de Gennes' notation[5] : B layers compressional elastic constant, A dilation bulk modulus, C coupling constant between layers and bulk dilation.

The damping is essentially controlled by the viscosities combination : $(\eta_3\ q_x^4 + \tilde{\eta}\ q_n^2\ q_x^2 + \eta_3\ q_n^4)/(q_x^2 + \alpha\ q_n^2)$; $\alpha = 1 + (B + 2C)/A$; $q_n = n\ \pi/D$. According to the MRT theory, η_3 exhibits a regular behavior (or a weak log ω dependence) ; whereas $\tilde{\eta} = (\eta_1 + \eta_2 - 2\eta_3 + \eta_4 - 2\eta_5) + (\eta_2 + \eta_4)\ B/A + 2(\eta_2 - \eta_3 + \eta_4 - \eta_5)\ C/A$ should diverge like $1/\omega$.

The first sound resonances correspond to constructive interferences between the θ waves when, again, $q_1 = n\ \pi/D\ (n \geqslant 0)$.

The position of the (n + 1)th one is given by :

$$\rho\ \omega_{n,1}^2 = q_x{}^2\ A + (q_n)^2\ (A + B + 2C)$$

The damping is controlled by the viscous term :

$$\left[(\eta_2 + \eta_4)\ q_x^4 + \eta_1\ q_n^4 + (2\eta_5 + 4\eta_3)\ q_x^2\ q_n^2\right] / (q_x^2 + \alpha\ q_n^2)$$

For n = 0, this combination is simply $(\eta_2 + \eta_4)\ q_x^2$.

For $n \neq 0$, it depends in a rather sensitive way on the magnitude and sign of η_5, as shown figure 2 and discussed in section III. The reactive part of the $(a + bK^2 + cK^4)$ factor in (3) and (4) vanishes for a frequency ω_c given by :

$$(\rho\omega_c^2)^2 + \rho\omega_c^2 \left\{- q_x^2\ A + K^2(A + B + 2C)\right\} - q_x^2\ K^2\ A\tilde{B} = 0$$

One might thus think that a third resonance could be excited. This would correspond to a surface wave propagating along x, and exponentially decaying along z.

One can show, however, that for any kind of linear boundary conditions this "surface" mode will never be excited. The figure 2 for example, shows a computer simulation assuming "rigid" boundary conditions, i.e. no sound wave propagating in the glass holders. Both first and second sound resonances are seen but no surface mode, due to the cancellation of the e^{-Kz} and $e^{-q_1 z}$ terms in (3) and (4) for $\omega = \omega_c$.

EXPERIMENTAL RESULTS

We have used DPPC (purchased from Calbiochem), aligned homeotropically on glass substrates using the method of

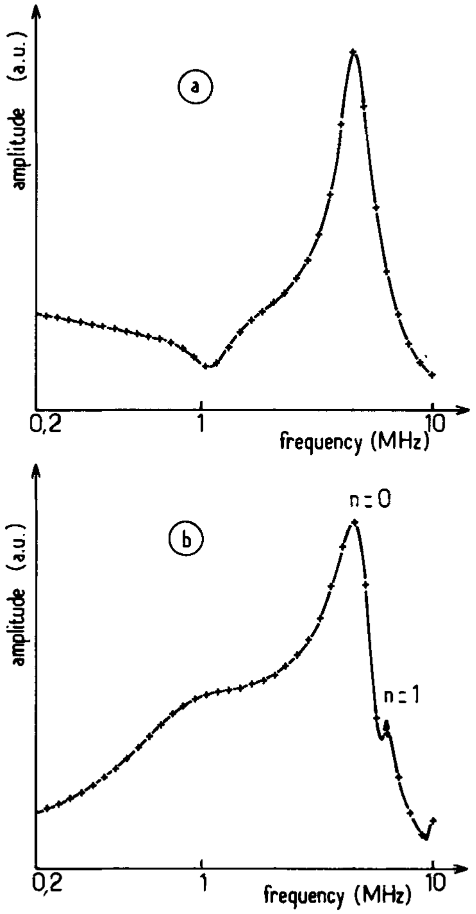

FIGURE 2 Plot of computer calculation showing second sound resonances in the ∿ 9.10^2 kHz regime and first sound in the ∿ 5 MHz one.

[hydrodynamic parameters (c.g.S units) $A = 10^{10}$, $B = 1.510^9$, $C = 10^8$, $\eta_i \simeq 30$ p, $q_x = 2\pi/\lambda_e = 314\ \mathrm{cm}^{-1}$, $qz = 21\ \mathrm{cm}^{-1}$

a) Note the absence of the n = 1 mode in the first sound resonance.

b) Note the existence of the n = 1 mode in the first sound resonance linked to the equality:

$$\eta_5 = - \sqrt{\eta_1\ \eta_4}.$$

L. Powers et al.[14]. This method allows the alignment of monocrystalline samples of thicknesses of about 200 μm, but as it uses an annealing of the compound at temperatures up to 120°C, one is left with a somewhat degraded material (formation of lysolecithin due to hydrolysis, up to 30% in worst cases). Thus the results reported here apply to a material which is a mixture of lecithin, lysolecithin and fatty acid (after all perhaps not so far from a biological material !..).

The experimental set-up is an adaptation of the one already described[3,4,10], with an oven allowing to adjust the water content with a controlled vapor pressure (± 10^{-3} bar), and the temperature between 30°C and 150°C with a 10 mK accuracy.

In a first experiment, in the "annealing" region ($T \sim 115°C$, $C_{H_2O} < 4$ ωt.%) we have evidenced a linear electrooptic effect and isolated a resonance in the extraordinary-ordinary geometry which we identify to be the second sound (n=1) mode. The fitting of the curve leads to a compressional elastic constant $\tilde{B} \sim 1.6\ 10^9$ dyne cm^{-2} which is in close agreement with those found for genuine bilayer smectic A[15], but is lower by a factor of ten than that measured by Le Pesant et al. at a lower temperature on the same compound with a Brillouin scattering technique[16]. The same kind of dispersion exists in thermotropic liquid crystals[4] ; Brillouin resonances are obtained outside the hydrodynamic regime. The apparent viscosity is anomalously large. We find $\eta_3 + \tilde{\eta}/4 \simeq$ 50 poises. Such high viscosities could arise from a strong structuration of water[14], or from the Mazenko, Ramaswamy, Toner divergence of viscosities, in the case of a small K_1 elastic constant (a K_1 value of a few 10^{-7} dyne is necessary, which is not unrealistic ; note that in that case η_3 would be regular and $\tilde{\eta}$ only diverging).

A second experiment (fig. 4), with an hydrated sample ($T = 47°C$, $C_{H_2O} \sim 25$ ωt.%), in the extraordinary-extraordinary geometry, shows two successive resonances at 4.5 and 5.3 Mhz that we identify as the first sound propagating parallel to the layers (n=0 in (6)) and obliquely (n=1). This yields an order of magnitude for the elastic constant $A \sim 10^{10}$ dyne cm^{-2} essentially coherent with the literature[16,17]. The factor of two difference between Brillouin datas and this one can again be attributed to a dispersion quite frequent in thermotropic liquid crystals.

The width of the resonances implies again a fairly large viscosity : $\eta_2 + \eta_4 \simeq 130$ poises, and the observation of

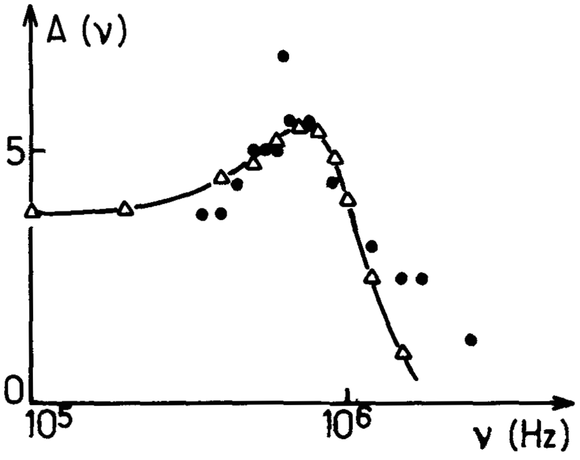

FIGURE 3 Second sound resonance in the Lecithin - water system (Extraordinary - ordinary teometry): T = 115°C; C_{H_2O} < 4 wt %. The solid line corresponds to a fit, according to formulae (3) and (4).

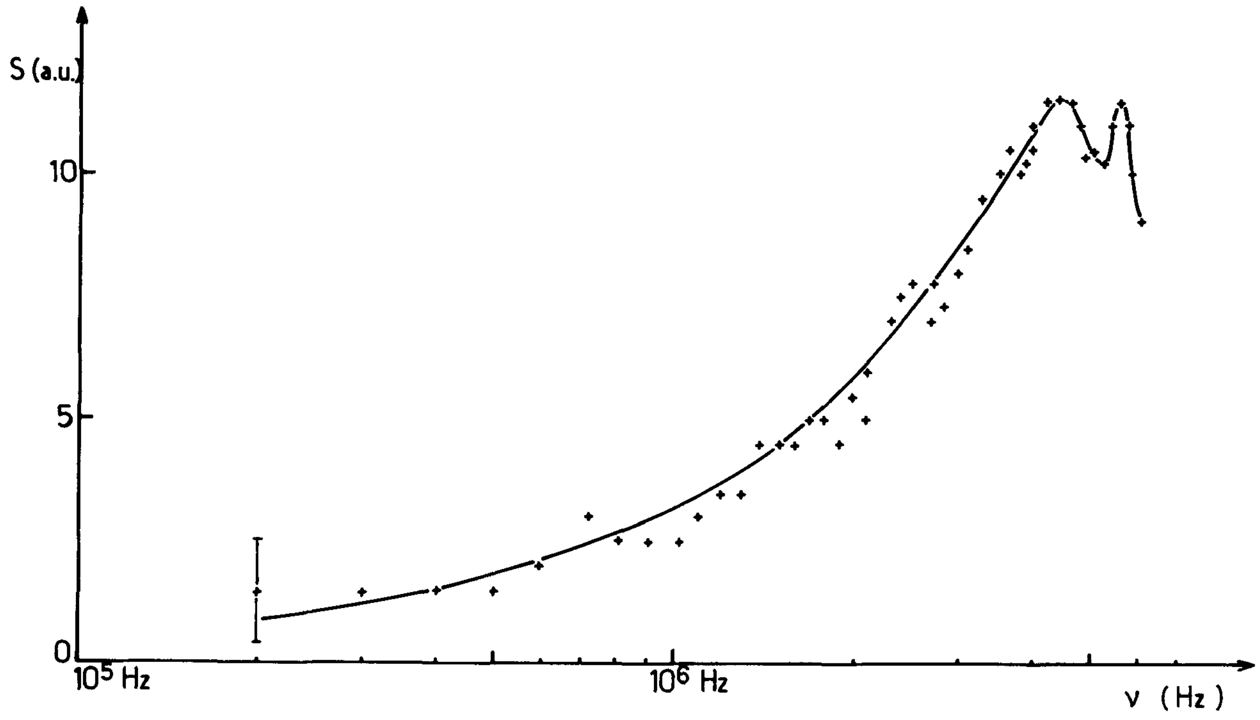

FIGURE 4 First sound resonance in the Lecithin - water system (Extraordinary - Extraordinary geometry): T = 47°C, C_{H_2O} ∿ 25 wt %. The solid line is a guide for the eye. A perfect fit cannot be obtained with formulae (3) and (4).

the second mode necessitates imperatively $\eta_5^2 \simeq \eta_1 \eta_4$ or more precisely $\eta_5 \simeq -\sqrt{\eta_1 \eta_4}$. All theoretical plots which do not respect this equality are unable to reveal the second resonance (mode n=1) together with the first one (n=0). Figure 2 shows the difference between computer plots respecting this equality, and others with similar order of magnitudes of the "mean" viscosity but $\eta_5 \neq -\sqrt{\eta_1 \eta_4}$. Thus the anomalously large viscosities on one hand, the relation $\eta_5 \simeq -\sqrt{\eta_1 \eta_4}$ on the other are clues supporting the Mazenko Ramaswamy Toner theory. The lower frequency range ($\sim$ 1 MHz) reveals the existence of a second sound resonance hidden by the tail of the first sound one. It corresponds to a compressional elastic constant $\tilde{B} \simeq 10^9$, and $\eta_3 \simeq 30$ poises. One must however point out that it is very hard to get a fully satisfactory fit of the experimental curve over the whole frequency range. This may be due to a dispersion in the definition of the optical phase of the local oscillator used in our heterodyne detection.

In any case, the proof of the existence of a linear electro mechanical coupling in the Lecithin water system is of importance since it has been invoked in many biologically relevant processes. Furthermore the order of magnitude of the elastic constants that we obtain, are lower than those measured in Brillouin scattering experiments : this is exactly the situation known with conventional thermotropic liquid crystals[18]. Eventually, the anomalously large viscosities that we find, could be interpreted either as reflecting a high structuration of water between the planes, as was commonly done before, or as revealing the $1/\omega$ divergence of viscosities according to the MRT theory. The $\eta_5 \simeq -\sqrt{\eta_1 \eta_4}$ equality pleads in favor of the last hypothesis. A more detailed investigation is clearly called for ; a systematic study on a thermotropic compound is currently underway in our laboratory[19].

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APPENDIX A

Summary of the hydrodynamic coefficients used in the calculations (in M.P.P.[6] notations) :

$$a = (\rho\omega^2 + j\omega\eta_3\, q_x^2)\ (j\rho\omega^2 - jq_x^2\, A - (\eta_2 + \eta_4)\ \omega q_x^2)$$

$$\begin{aligned} b = {} & j\rho\omega^2\ (A + B + 2C) - jq_x^2\ A\ \tilde{B} + \tilde{\eta}\,\omega\, q_x^2\ A \\ & + j\omega^2\ q_x^2\ \left[\eta_1\ (\eta_2 + \eta_4) - \eta_5\ (2\eta_3 + \eta_5)\right] + \rho\omega^3\ (\eta_1 + \eta_3) \end{aligned}$$

$$c = \eta_3\ \omega\ (A + B + 2C - j\ \eta_1\ \omega)$$

$$\begin{aligned} h = {} & - j\, q_x^4 K\, \phi_1\ (fA + f'C) + j\rho\omega^2\ (f - f')\ q_x^2 K\, \phi_1 + \omega q_x^2 K\, \phi_1 \\ & \left[- f q_x^2\ (\eta_2 + \eta_4) + f' q_x^2\ (\eta_2 - \eta_3 + \eta_4 - \eta_5) + (f - f') K^2 \eta_3\right] \end{aligned}$$

$$\begin{aligned} \tau = {} & - j q_x^4 K^2\, \phi_1\ (fC + f'B) + j\, \rho\omega^2\, q_x^2\, \phi_1\ \left[(f' - f)\ K^2 - f' q_x^2\right] \\ & + \omega\, q_x^2\, \phi_1\ \left[f' q_x^4\ \eta_3 + (f' - f)\, K^4\, \eta_3\right. \\ & \qquad \left. + \left\{- f'\ (\eta_1 + \eta_2 - 2\eta_3 + \eta_4 - 2\eta_5) + f(\eta_2 - \eta_3 + \eta_4 - \eta_5)\right\}\right] \end{aligned}$$

$$t_i = q_i\ \frac{\left[j q_x^2 C + j\rho\omega^2 - (\eta_2 - \eta_3 + \eta_4 - \eta_5)\ \omega\, q_x^2\right] + \eta_3\ \omega\, q_i^2}{\left[- j q_x^2 A + j\rho\omega^2 - (\eta_2 + \eta_4)\, \omega\, q_x^2\right] + \eta_3\ \omega\, q_i^2}$$

(i=1,4)

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