Spin-lattice dispersion in nematic and smectic-*A* mesophases in the presence of ultrasonic waves: A theoretical approach

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We present a theoretical study of the Larmor frequency dependence of the nuclear spin-lattice relaxation caused by order director fluctuations for both nematic and smectic-*A* mesophases. The analysis is focused on the case where the molecular system is subjected to sonication during the relaxation process. The departure from the nonsonicated case is discussed for various values of the involved parameters. Two different approaches are discussed for the smectic case.

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I. INTRODUCTION

Fluctuations of the molecular orientational order is shown to be an efficient mechanism for the nuclear magnetic relaxation process in liquid crystal materials. This particularly applies to the nematic phase, where director order fluctuations (DOFs) dominate the spin-lattice relaxation dispersion at low fields [1]. To our knowledge, this result cannot be extended to smectic phases, mainly due to the presence of false dispersions associated with experimental limitations of the field cycling technique. Elucidation of the smectic DOF contribution at low fields is therefore a complex task, because its frequency dependence may be also masked by self-diffusion. It was recently shown that the relaxation dispersion due to nematic DOFs can be enhanced by the application of an ultrasonic field [2,3]. It is hoped that this experiment may be a useful tool for the investigation of the smectic case, provided that the ultrasonic field can be also coupled to smectic order fluctuations.

Since the pioneering work of Pincus [4], many papers have been dedicated to the study of the laboratory frame spin-lattice relaxation time (T_1) Larmor frequency (ν_L) dispersion due to the DOF relaxation mechanism in liquid crystals. Although most of them are mainly experimental reports [1,5–17], some were devoted to the theoretical insights [4,6,18–23]. Summarizing these results, it was widely demonstrated, both theoretically and experimentally, that nematic ODF relaxation gives rise to a $T_1(\nu_L)$ behavior proportional to the square root of the Larmor frequency ν_L (without considering low and high frequency cutoffs).

Relaxation features in the smectic-*A* phase are still unclear, but show an extraordinary richness in the involved physical background. First studies of the proton T_1 relaxation using the field cycling technique were performed in the smectic phases of terephthalibis-butylalinine [6,24]. A linear Larmor frequency dependence was proposed for the case where the nuclear magnetic relaxation is driven by smectic undulation waves, assuming the independence of the coherence length of the fluctuations with the wave vector. In principle, this model was extended, with success, to lamellar systems [25]. In a later, and more refined, treatment, Vilfan, Kogoj, and Blinc [20] calculated the T_1 frequency dispersion for smectic-*A* phases. Although the resulting frequency dependence was very different from a simple linear behavior, most of the later experimental results were interpreted in terms of that simplified model [11,12,15,16]. Though frequently regarded as an accepted and well known result, recent studies strongly suggest that most of the field cycling relaxometry experiments in the smectic-*A* phase are questionable in the low frequency range [26]. In this limit, strong false dispersions related to experimental pitfalls were usually interpreted in terms of a linear-type smectic DOF.

The orienting action of an ultrasonic field in liquid crystals was rarely treated in the literature. Dion was the first person who studied the problem within the picture of minimum entropy production theorem [27]. A new free energy term associated with molecular reorientation was recently proposed on experimental grounds [2]. Almost simultaneously, the same term was used by Selinger *et al.* in a different context, but derived with more rigorous arguments [28]. In the present work, we use this free energy orienting term to examine the $T_1(\nu_L)$ dispersion in the nematic and smectic-*A* phases subjected to ultrasonic irradiation. For the sake of simplicity, two special cases are treated: ultrasonic waves parallel and perpendicular to the director. The main question we have dealt with concerns how relaxation dispersions due to DOFs can change under the influence of sonication. It is still controversial whether this experiment can be used to disentangle the laboratory frame spin-lattice relaxation features in smectic phases.

II. THEORY AND DISCUSSION

A. General case: Anisotropic elastic constants

Order director fluctuations cause dipolar spin-lattice relaxation, essentially by modulating the orientation of the internuclear vector with respect to the external magnetic field. In the limiting situation, where the molecules are, on an average, oriented parallel to the magnetic field, the spectral density $J_1(\omega_L)$ determines almost completely the relaxation time [4]. For a fixed separation distance *r* between two spin-1/2 nuclei, the spin-lattice relaxation time is given by [29,30]

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$$T_1^{OF}(\omega_L)=\beta\left[\mathrm{Re}\left(\int_{-\infty}^{\infty}g_1^{OF}(\tau)\exp(-i\omega\tau)d\tau\right)\right]^{-1},$$

with

$$g_1^{OF}(\tau)=\frac{3}{2}\langle n_x(\vec{r},t)n_x(\vec{r},t+\tau)\rangle+\langle n_y(\vec{r},t)n_y(\vec{r},t+\tau)\rangle,$$

where the magnetic field is assumed to be in the z direction. n_x and n_y stand for the fluctuating part of director $\vec{n}$ ($\vec{n}=n_x\hat{x}+n_y\hat{y}+n_0\hat{z}$). Constant β depends on the gyromagnetic ratio γ, the Planck constant $\hbar$, the interspin distance r, and the molecular order parameter S.

By expanding $n_x(\vec{r})$ and $n_y(\vec{r})$ in Fourier components,

$$g_1^{OF}(\tau)=\frac{3}{2}\frac{1}{V^2}\sum_{\vec{q},\vec{q}'}\langle n_1(\vec{q},t)n_1^*(\vec{q}\,',t+\tau)\rangle$$
$$+\langle n_2(\vec{q},t)n_2^*(\vec{q}\,',t+\tau)\rangle,$$

$$g_1^{OF}(\tau)=\frac{3}{2}\frac{1}{V^2}\sum_{\alpha=1}^{2}\sum_{\vec{q}}\langle|n_\alpha^2(\vec{q},0)|^2\rangle\exp\left[-\frac{\tau}{\tau_\alpha(\vec{q})}\right],\quad(1)$$

where $\vec{q}$ is the wave vector of the mode and $n_1(\vec{q})$ and $n_2(\vec{q})$ are two uncoupled modes: $n_1(\vec{q})$ lies on the $(\widehat{\vec{q},\vec{n}_0})$ plane and $n_2(\vec{q})$ is perpendicular to it. These modes relax with the time constant $\tau_\alpha(\vec{q})$ ($\alpha=1,2$).

The free energy for static distortions in liquid crystals is given by [31,32]

$$f_n=\frac{1}{2}\{K_{11}(\nabla\cdot\vec{n})^2+K_{22}(\vec{n}\cdot\nabla\times\vec{n})^2+K_{33}[(\vec{n}\cdot\nabla)\vec{n}]^2\},\quad(2)$$

where K_{11}, K_{22}, and K_{33} are the splay, twist, and bend elastic constants, respectively.

The interaction energy between an acoustic wave and director $\vec{n}$ is given by [2,28]

$$f_a=\frac{1}{2}a^2(\hat{s}\cdot\hat{n}),\quad(3)$$

where a^2 depends on the acoustic intensity, the ultrasound velocity, the average of the sample density, the magnitude of the ultrasound wave vector, and the director-density coupling. In the last equation, $\hat{s}$ represents the ultrasound wave versor and $\hat{n}$ the director. In the last equation, an average over the rapid oscillations of the ultrasound waves was taken [28].

If an ultrasound wave propagates across the liquid crystalline media parallel to the magnetic field, the fluctuations of the local director decrease f_a by

$$\Delta f_a=-\frac{1}{2}a^2(n_x^2+n_y^2).$$

But, if the ultrasound wave consists of two waves of the same intensity, one with $\hat{s}=\hat{x}$ and the other with $\hat{s}=\hat{y}$, fluctuations of the local director increase f_a by

$$\Delta f_a=\frac{1}{2}a^2(n_x^2+n_y^2).$$

From the last equation, and after a Fourier expansion of components $n_x(\vec{r})$ and $n_y(\vec{r})$, the following expression for the free energy in presence of a parallel (perpendicular) ultrasonic wave is obtained:

$$F=\frac{1}{2V}\sum_{\alpha=1}^{2}\sum_{\vec{q}}K_\alpha(\vec{q})|n_\alpha(\vec{q})|^2,$$

with

$$K_\alpha(\vec{q})=K_{\alpha\alpha}q_\perp^2+K_{33}q_z^2-(+)a^2,$$

$$q_\perp^2=q_x^2+q_y^2.$$

Using that $\tau_\alpha(\vec{q})=\eta_\alpha(\vec{q})/K_\alpha(\vec{q})$ [with the typical assumption on viscosities $\eta_\alpha(\vec{q})=\eta_\alpha$], applying the equipartition theorem to obtain $\langle|n_\alpha(\vec{q})|^2\rangle=K_BTV/K_\alpha(\vec{q})$, and extending the sum in Eq. (1) to an integral, we get

$$g_1^{OF}(\tau)=\frac{3}{2}\frac{K_BT}{(2\pi)^3}\sum_{\alpha=1}^{2}\int d^3q\frac{1}{K_\alpha(\vec{q})}\exp\left[-\frac{K_\alpha(\vec{q})\tau}{\eta_\alpha}\right].$$

Then,

$$j_1^{OF+S}\equiv\mathrm{Re}\left(\int_{-\infty}^{\infty}g_1^{OF+S}(\tau)\exp(-i\omega\tau)d\tau\right)$$
$$=\frac{3}{2}\frac{K_BT}{8\pi^3}\sum_{\alpha=1}^{2}\int_q\frac{\eta_\alpha d^3q}{[K_\alpha(\vec{q})]^2+\eta_\alpha^2\omega^2}.$$

Using that $d^3q=q_\perp d\phi dq_\perp dq_z$, integrating over an ellipsoidal volume in the $\vec{q}$ space [21], with high frequency cutoffs given by $q_{\perp c}$ and q_{zc}, defining $q'_{\perp c}=q_{\perp c}[1-(q_z^2/q_{zc})^2]^{1/2}$, and changing the integration variable $q_\perp$ by $s=K_{\alpha\alpha}q_\perp^2+K_{33}q_z^2-(+)a^2$, we get

$$j_1^{OF+S}(\omega)=3\frac{K_BT}{8\pi^2}\sum_{\alpha=1}^{2}\int_0^{q_{zc}}dq_z\int_{K_{33}q_z^2-(+)a^2}^{K_{\alpha\alpha}q'^2_{\perp c}+K_{33}q_z^2-(+)a^2}\frac{ds\,\eta_\alpha}{K_{\alpha\alpha}(s^2+\eta_\alpha^2\omega^2)}$$

$$=\frac{3K_BT}{8\pi^2}\sum_{\alpha=1}^{2}\int_0^{q_{zc}}dq_z\frac{1}{K_{\alpha\alpha}}\frac{1}{\omega}\left[\arctan\left(\frac{K_{\alpha\alpha}q'^2_{\perp c}+K_{33}q_z^2-(+)a^2}{\omega\eta_\alpha}\right)-\arctan\left(\frac{K_{33}q_z^2-(+)a^2}{\omega\eta_\alpha}\right)\right]$$

$$=\frac{3K_BT}{8\pi^2}\sum_{\alpha=1}^{2}\int_0^{q_{zc}}dq_z\frac{1}{K_{\alpha\alpha}}\frac{1}{\omega}\left[\arctan\left(\frac{K_{\alpha\alpha}q^2_{\perp c}\left(1-\frac{q_z^2}{q_{zc}^2}\right)+K_{33}q_z^2-(+)a^2}{\omega\eta_\alpha}\right)-\arctan\left(\frac{K_{33}q_z^2-(+)a^2}{\omega\eta_\alpha}\right)\right].$$

Defining $A_\alpha^2=K_{\alpha\alpha}q_{\perp c}^2/\eta_\alpha\omega$, $B_\alpha^2=K_{33}q_{zc}^2/\eta_\alpha\omega$, $C_\alpha^2=a^2/\eta_\alpha\omega$, and $x=q_z/q_{zc}$, we obtain

$$j_1^{OF+S}(\omega)=I_1+I_2,$$

with

$$I_1=3\frac{K_BT}{8\pi^2\omega}\sum_{\alpha=1}^{2}\frac{q_{zc}}{K_{\alpha\alpha}}\int_0^1dx\,\arctan[x^2(B_\alpha^2-A_\alpha^2)+A_\alpha^2-(+)C_\alpha^2],$$

$$I_2=-3\frac{K_BT}{8\pi^2\omega}\sum_{\alpha=1}^{2}\frac{q_{zc}}{K_{\alpha\alpha}}\int_0^1dx\,\arctan[B_\alpha^2x^2-(+)C_\alpha^2].$$

Solving the corresponding integrals, we arrive at

$$j_1^{OF+S}(\omega)=3\frac{K_BT}{8\pi\sqrt{2\omega}}\sum_{\alpha=1}^{2}K_{\alpha\alpha}^{-1}\left(\frac{\eta_\alpha}{K_{33}}\right)^{1/2}\left\{\frac{\sqrt{2}B_\alpha}{2\pi\sqrt{2\Delta_\alpha\gamma_\alpha}}\ln\left(\frac{E_\alpha\pm\sqrt{2\Delta_\alpha\gamma_\alpha}+\Delta_\alpha}{E_\alpha\mp\sqrt{2\Delta_\alpha\gamma_\alpha}+\Delta_\alpha}\right)\right.$$
$$-\frac{\sqrt{2}B_\alpha}{2\pi\sqrt{2B_\alpha^2(e_\alpha+(-)C_\alpha^2)}}\ln\left(\frac{e_\alpha+\sqrt{2B_\alpha^2(e_\alpha+(-)C_\alpha^2)}+B_\alpha^2}{e_\alpha-\sqrt{2B_\alpha^2(e_\alpha+(-)C_\alpha^2)}+B_\alpha^2}\right)\mp\frac{\sqrt{2}B_\alpha}{\pi\sqrt{2\Delta_\alpha\tilde{\gamma}_\alpha}}\left[\arctan\left(\frac{\sqrt{2\Delta_\alpha}-\sqrt{\gamma_\alpha}}{\sqrt{\tilde{\gamma}_\alpha}}\right)\right.$$
$$\left.+\arctan\left(\frac{\sqrt{2\Delta_\alpha}+\sqrt{\gamma_\alpha}}{\sqrt{\tilde{\gamma}_\alpha}}\right)\right]+\frac{\sqrt{2}B_\alpha}{\pi\sqrt{2B_\alpha^2(e_\alpha-(+)C_\alpha^2)}}\left[\arctan\left(\frac{\sqrt{2B_\alpha^2}-\sqrt{e_\alpha+(-)C_\alpha^2}}{\sqrt{e_\alpha-(+)C_\alpha^2}}\right)\right.$$
$$\left.\left.+\arctan\left(\frac{\sqrt{2B_\alpha^2}+\sqrt{e_\alpha+(-)C_\alpha^2}}{\sqrt{e_\alpha-(+)C_\alpha^2}}\right)\right]\right\},\qquad(4)$$

where $\Delta_\alpha=|B_\alpha^2-A_\alpha^2|$, $E_\alpha=\sqrt{1+(A_\alpha^2-(+)C_\alpha^2)^2}$, $e_\alpha=\sqrt{1+C_\alpha^4}$, $\gamma_\alpha=E_\alpha\mp(A_\alpha^2-(+)C_\alpha^2)$, and $\tilde{\gamma}_\alpha=E_\alpha\pm[A_\alpha^2-(+)C_\alpha^2]$, and the upper (lower) sign applies if $B_\alpha^2>(<)A_\alpha^2$.

Limiting Cases

Nonsonicated case. In this case, $a=0\Rightarrow C_\alpha=0\Rightarrow e_\alpha=1$. Besides, $E_\alpha=\sqrt{1+A_\alpha^4}$; then,

$$j_1^{OF+S}(\omega)=3\frac{K_BT}{8\pi\sqrt{2\omega}}\sum_{\alpha=1}^{2}K_{\alpha\alpha}^{-1}\left(\frac{\eta_\alpha}{K_{33}}\right)^{1/2}\left\{U(B_\alpha^2)+\frac{\sqrt{2}B_\alpha}{2\pi\sqrt{2\Delta_\alpha(E_\alpha\mp A_\alpha^2)}}\ln\left(\frac{E_\alpha\pm\sqrt{2\Delta_\alpha(E_\alpha\mp A_\alpha^2)}+\Delta_\alpha}{E_\alpha\mp\sqrt{2\Delta_\alpha(E_\alpha\mp A_\alpha^2)}+\Delta_\alpha}\right)\right.$$
$$\left.\mp\frac{\sqrt{2}B_\alpha}{\pi\sqrt{2\Delta_\alpha(E_\alpha\mp A_\alpha^2)}}\left[\arctan\left(\frac{\sqrt{2\Delta_\alpha}-\sqrt{E_\alpha\mp A_\alpha^2}}{\sqrt{E_\alpha\pm A_\alpha^2}}\right)+\arctan\left(\frac{\sqrt{2\Delta_\alpha}+\sqrt{E_\alpha\mp A_\alpha^2}}{\sqrt{E_\alpha\pm A_\alpha^2}}\right)\right]\right\},$$

with $U(B_\alpha^2)=(1/2\pi)\ln[(B_\alpha^2-\sqrt{2}B_\alpha+1)/(B_\alpha^2+\sqrt{2}B_\alpha+1)]+(1/\pi)[\arctan(\sqrt{2}B_\alpha+1)+\arctan(\sqrt{2}B_\alpha-1)]$, according to the expression obtained in Ref. [21].

Nematic case. In this case, $K_{11}\simeq K_{22}\simeq K_{33}\equiv K$. Then, $\Delta_\alpha\to0$. Using that $\ln(1+x)\simeq x$ and $\arctan(x-a)+\arctan(x+a)\simeq2x/(1+a^2)$, for small values of x variable,

$$j_1^{OF+S}(\omega)=3\frac{K_BT\eta^{1/2}}{4\pi K^{3/2}\sqrt{2\omega}}\Bigg\{-\frac{\sqrt{2}B}{2\pi\sqrt{2B^2(e+(-)C^2)}}\ln\left(\frac{e+\sqrt{2B^2(e+(-)C^2)}+B^2}{e-\sqrt{2B_\alpha^2(e+(-)C^2)}+B^2}\right)+\frac{\sqrt{2}B}{\pi\sqrt{2B^2(e-(+)C^2)}}\left[\arctan\left(\frac{\sqrt{2B^2}-\sqrt{e+(-)C^2}}{\sqrt{e-(+)C^2}}\right)+\arctan\left(\frac{\sqrt{2B^2}+\sqrt{e+(-)C^2}}{\sqrt{e-(+)C_\alpha^2}}\right)\right]\Bigg\}.$$

If $B\to\infty$ [equivalent to considering $\omega\ll\omega_c$, with $\omega_c=(K/\eta)q_c^2$] and using that $C_\alpha^2=1/\omega\tau_0$, with $\tau_0\equiv\eta/a^2$,

$$\begin{aligned}j_1^{OF+S}(\omega)&=\frac{3K_BT\eta^{1/2}}{4\pi K^{3/2}\sqrt{2\omega}}\frac{1}{\sqrt{e-(+)C^2}}\\&=\frac{3K_BT\eta^{1/2}}{4\sqrt{2}\pi K^{3/2}\sqrt{\omega}}\frac{1}{\sqrt{\sqrt{1+\frac{1}{(\omega\tau_0)^2}}-(+)\frac{1}{\omega\tau_0}}}\\&=\frac{3K_BT\eta^{1/2}}{4\sqrt{2}\pi K^{3/2}\sqrt{\omega}}\frac{\sqrt{\omega}\sqrt{\tau_0}}{\sqrt{\sqrt{1+(\omega\tau_0)^2}-(+)1}}\\&=\frac{3K_BT\eta^{1/2}}{4\sqrt{2}\pi K^{3/2}}\frac{\sqrt{\tau_0}}{\sqrt{\sqrt{1+(\omega\tau_0)^2}-(+)1}}.\end{aligned}$$

This expression is the same as derived in Ref. [2]. The corresponding expression for T_1 will be

$$\begin{aligned}T_1^{OF+S}(\omega)&=\beta[j_1^{OF+S}(\omega)]^{-1}\\&=\beta\frac{4\sqrt{2}\pi K^{3/2}}{3K_BT\eta^{1/2}}\frac{\sqrt{\sqrt{1+(\omega\tau_0)^2}-(+)1}}{\sqrt{\tau_0}}.\end{aligned}$$

It is important to note that in the absence of sound ($\tau_0\to\infty$), the typical $\omega^{1/2}$ behavior is obtained. Another important limit arises when in the presence of perpendicular audio waves (the sign between parentheses applies), constant a (proportional to the sound intensity and the coupling between the ultrasound wave and the director) tends to infinity. In this case, ($\tau_0\to 0$) and $T_1^{OF+S}(\omega)\to\infty$, i.e., there is no relaxation induced by the DOF mechanism. This situation corresponds to a complete sound induced quenching of the DOFs.

The angular amplitudes of director fluctuations increase with the ultrasonic power when the sonic waves are parallel to the director. In this case, the assumption on small angle director fluctuations may not be satisfied [Eq. (4)]. In this limit, application of the previous equation lacks sense.

In a $\log_{10}(T_1^{OF+S})$ versus $\log_{10}(\omega)$ plot, the slope of the curve will be between 0 and 1/2 (perpendicular), and between 1/2 and 1 (parallel). This assertion will be shown in the following:

$$\begin{aligned}\frac{d\log_{10}(T_1^{OF+S})}{d\log_{10}(\omega)}&=\frac{d\ln(T_1^{OF+S})}{d\ln(\omega)}=\omega\frac{d\ln(T_1^{OF+S})}{d\omega}\\&=\frac{1}{2}\left[\frac{1}{1+\sqrt{1+(\omega\tau_0)^2}}\frac{\omega^2\tau_0^2}{\sqrt{1+(\omega\tau_0)^2}}\right]\leq\frac{1}{2},\end{aligned}$$

for perpendicular sound waves, and

$$\begin{aligned}\frac{d\log_{10}(T_1^{OF+S})}{d\log_{10}(\omega)}&=\frac{1}{2}\left[\frac{(\omega\tau_0)^2}{1+(\omega\tau_0)^2-\sqrt{1+\omega^2\tau_0^2}}\right]\\&=\frac{1}{2}\left(\frac{x^2}{1+x^2-\sqrt{1+x^2}}\right),\end{aligned}$$

with $x\equiv\omega\tau_0$, for sound waves parallel to the director. It can be easily shown that

$$1\leq\frac{x^2}{1+x^2-\sqrt{1+x^2}}\leq 2.$$

Figure 1 contains $\log_{10}(T_1^{OF+S})$ versus $\log_{10}(\nu)$ plots for different values of a (equivalent to considering different audio intensities). Typical values of $\tau_0=2\times10^{-5}$ s and $\tau_0=1\times10^{-5}$ s [2] and $\eta=0.1$ Ns/m^2 were used in both of them (equivalent to considering $a^2=10^4$ N/m^2 and $a^2=2\times10^4$ N/m^2, respectively). Concerning these plots, it is important to observe that parallel waves makes the DOF relaxation mechanism more effective, and an opposite effect is produced by perpendicular waves. An arbitrary value of constant $\beta[(4\sqrt{2}\pi K^{3/2})/(3K_BT\eta^{1/2})]$ was used in all of these graphs.

Figure 2 shows the slope behavior in a $\log_{10}(T_1^{OF+S})$ versus $\log_{10}(\nu)$ plot for both perpendicular and parallel sound waves.

Smectic case. In this case, $K_{33}\ll K_{11}=K_{22}$, then limits $B_\alpha\ll 1$, $A_\alpha\gg 1$ should be taken and the lower sign in Eq. (4) must be used. Thus, $\Delta_\alpha=A_\alpha^2(1-y)$, $E_\alpha\approx A_\alpha^2[1+(x/2)]$, with $y=B_\alpha^2/A_\alpha^2$, $x=(1-2C_\alpha^2A_\alpha^2+C_\alpha^4)/A_\alpha^4$ considered as small parameters.

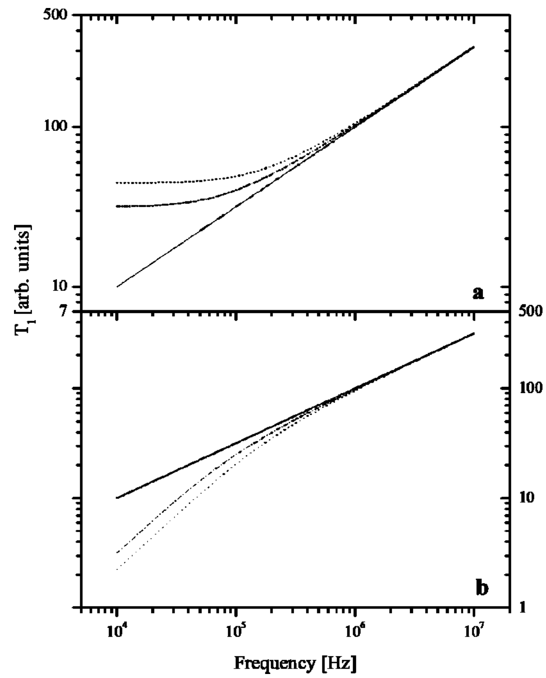

FIG. 1. Frequency dependence of T_1 in nematics in the presence of different intensities of (a) perpendicular and (b) parallel ultrasonic waves. Dotted and dashed lines correspond to the higher and lower sound intensities, respectively. The nonsonicated case is also included (solid line).

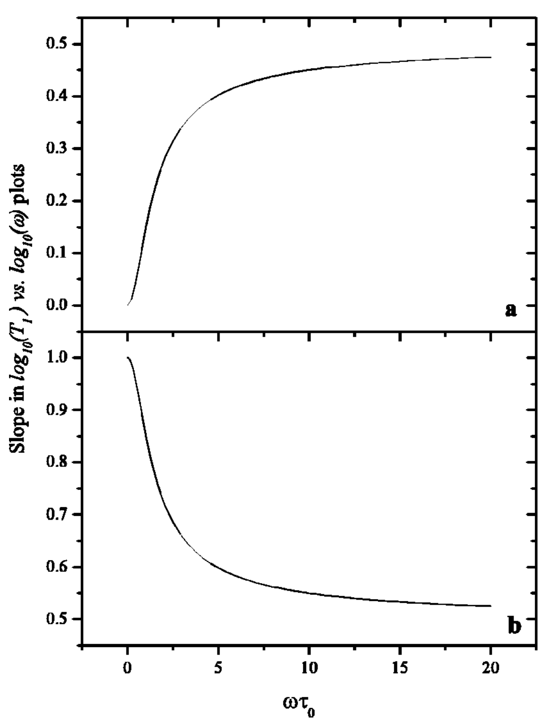

FIG. 2. Dependence of the slope in a $\log_{10}(T_1^{OF+S})$ vs $\log_{10}(\omega)$ plot with magnitude $\omega\tau_0$ for nematic liquid crystals in the presence of (a) perpendicular and (b) parallel ultrasonic waves.

Expanding $j_1^{OF+S}(\omega)$ in power series of parameters y and x, the following result is found:

$$I_1=\frac{3K_BT}{4\pi\sqrt{2\omega}}\left(\frac{\eta}{K_{33}}\right)^{1/2}\frac{1}{K_{11}}\frac{\sqrt{2}}{2\pi}\frac{B_\alpha}{\sqrt{1+C_\alpha^4}}\times\left[+(-)2\arctan\left(\frac{C_\alpha^2}{\sqrt{1+C_\alpha^4}}\right)+\pi\right]+O\left(\frac{B_\alpha}{A_\alpha}\right),$$

$$I_2=O(B_\alpha^2).$$

Then,

$$j_1^{OF+S}(\omega)=\frac{3K_BT}{2\pi\sqrt{2\omega}}\left(\frac{\eta}{K_{33}}\right)^{1/2}\frac{1}{K_{11}}\frac{\sqrt{2}}{2\pi}\frac{B_\alpha}{\sqrt{1+C_\alpha^4}}\times\left[+(-)2\arctan\left(\frac{C_\alpha^2}{\sqrt{1+C_\alpha^4}}\right)+\pi\right]$$
$$=\frac{3K_BT}{4\pi^2\omega}\frac{q_{zc}}{K_{11}}\frac{1}{\sqrt{1+\frac{1}{(\omega\tau_0)^2}}}\times\left[+(-)2\arctan\left(\frac{\frac{1}{\omega\tau_0}}{\sqrt{1+\frac{1}{(\omega\tau_0)^2}}}\right)+\pi\right].$$

It is important to note that in the complete absence of ultrasound waves, $\tau_0\rightarrow\infty$, and the linear expression

$$j_1^{OF+S}(\omega)=(3K_BT/4\pi)(q_{zc}/K_{11})\omega^{-1}=(3K_BT/2K_{11})(1/\xi)\omega^{-1}$$

is reobtained. Besides, in the presence of perpendicular sound waves, in limit $\tau_0\rightarrow 0$, a null value for $j_1^{OF+S}(\omega)$ is obtained, as expected, because of the complete quenching of order fluctuations produced by the ultrasound waves. As was previously established, the analog case for sound waves parallel to the director lacks sense.

In a $\log_{10}(T_1^{OF+S})$ versus $\log_{10}(\omega)$ plot, the slope of the curve is given by

$$\frac{d\ \log_{10}(T_1^{OF+S})}{d\ \log_{10}(\omega)}=\frac{x^2}{1+x^2}+(-)\times\frac{2x^2}{\sqrt{1+x^2}(2+x^2)\left[2\arctan\left(\frac{1}{\sqrt{1+x^2}}\right)+\pi\right]}.$$

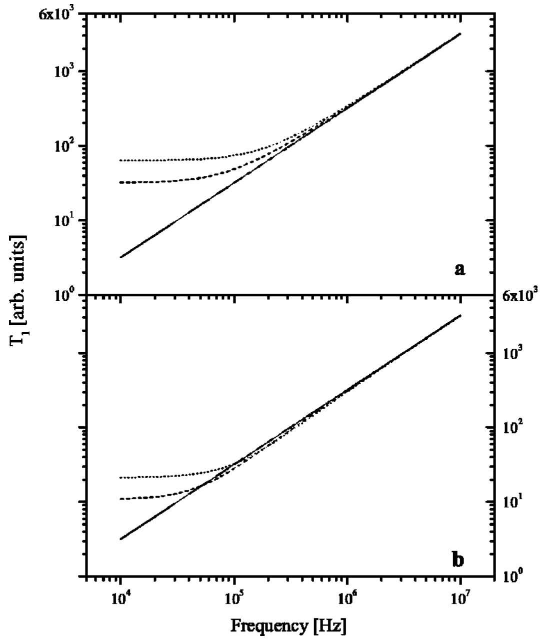

FIG. 3. Frequency dependence of T_1 in smectics (simplified model) in the presence of different intensities of (a) perpendicular and (b) parallel ultrasonic waves. Again, the dotted line corresponds to the higher intensity and the nonsonicated case to the solid line.

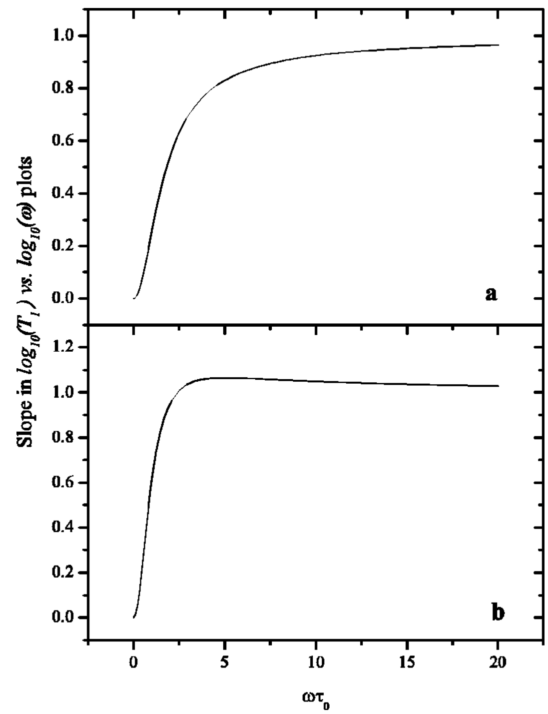

FIG. 4. Dependence of the slope in a $\log_{10}(T_1^{OF+S})$ vs $\log_{10}(\omega)$ plot with magnitude $\omega\tau_0$ for smectic liquid crystals (simplified model) in the presence of (a) perpendicular and (b) parallel ultrasonic waves.

Figure 3 shows $\log_{10}(T_1^{OF+S})$ versus $\log_{10}(\omega)$ plot for different values of a^2. They are compared with the typical linear behavior obtained for smectics. Again, an arbitrary value of constant $\beta[(4\pi^2/3K_BT)(K_{11}/q_{zc})]$ was used in all of these graphs, and the values of τ_0, η, and a^2 parameters are the same as in the previous case.

Figure 4 shows the slope behavior in a $\log_{10}(T_1^{OF+S})$ versus $\log_{10}(\omega)$ plot for both parallel and perpendicular sound waves in smectics.

B. Smectic-*A* phase: Coupling of smectic order with DOFs

A more refined model for the smectic-*A* phase can be obtained by considering the coupling between smectic order with director fluctuations. In this picture, smectic f_s and the nematic-smectic interaction f_I free energy terms are added [32], while also keeping the acoustic and nematic elastic free energy density [Eqs. (3) (2)]:

$$f_s=\varepsilon(T)|\psi|^2+\lambda(T)|\psi|^4+\cdots,$$

$$f_I=(\vec{\nabla}+iq_s\hat{\delta}n)\psi^*\frac{1}{2M}(\vec{\nabla}-iq_s\vec{\delta}n)\psi,$$

where ε and λ are coefficients in the expansion of f_s in powers of ψ, M is a mass tensor with components $M_\parallel$ and $M_\perp$, along the normal to the layers and perpendicular to them, respectively, and $q_s=2\pi/d$, d being the distance between smectic layers and ψ, the smectic order parameter [$\psi=|\psi|\exp(i\phi)$].

Using that $f=f_n+f_s+f_I+f_a$, with a similar analysis like the one previously presented, it is possible to arrive at [33,34]

$$\langle|n_1(\vec{q})|^2\rangle = \frac{K_BTV}{K_{11}q_\perp^2+K_{33}q_z^2-(+)a^2+B\left(\frac{q_z}{q_\perp}\right)^2\frac{1}{1+\frac{B}{D}\left(\frac{q_z}{q_\perp}\right)^2}},$$

$$\langle|n_2(\vec{q})|^2\rangle=\frac{K_BTV}{K_{22}q_\perp^2+K_{33}q_z^2+D-(+)a^2}, \qquad (5)$$

where $B=\psi_0^2q_s^2/M_\parallel$ and $D=\psi_0^2q_s^2/M_\perp$. Here, B and D are the restoring forces related with fluctuations in the layer thickness and fluctuations of the director orientation away from the normal to the layers, respectively, and ψ_0 is the equilibrium value of the smectic order parameter.

The corresponding decay times are given by

$$\tau_1(\vec{q}) = \frac{\eta_1}{K_{11}q_\perp^2 + K_{33}q_z^2 - (+)a^2 + B\left(\frac{q_z}{q_\perp}\right)^2 \dfrac{1}{1+\dfrac{B}{D}\left(\dfrac{q_z}{q_\perp}\right)^2}},$$

$$\tau_2(\vec{q}) = \frac{\eta_2}{K_{11}q_\perp^2 + K_{33}q_z^2 + D - (+)a^2}.$$

In the last two equations, an independence of viscosities η_1 and η_2 with $\vec{q}$ was assumed, and they stand for parallel (perpendicular) sound waves.

In this way,

$$j_1^{OF+S}(\omega) = \frac{3}{2\pi^2 V}\sum_{\alpha=1}^{2}\int_0^\infty dq_z \int_0^\infty \langle |n_\alpha^2(\vec{q})|^2\rangle \times \frac{\tau_\alpha(q)}{1+[\tau_\alpha(q)\omega]^2} q_\perp dq_\perp = j_{1,1}^{OF+S}(\omega) + j_{1,2}^{OF+S}(\omega),$$

where $j_{1,1}^{OF+S}(\omega)$ and $j_{1,2}^{OF+S}(\omega)$ correspond to the terms for $\alpha=1$ and $\alpha=2$, respectively.

The term for $\alpha=2$ is easily solved to give

$$j_{1,2}^{OF+S}(\omega) = \begin{cases} \dfrac{3K_B T\eta_2}{4\sqrt{2}\pi K_{22}K_{33}^{1/2}\sqrt{|D-a^2|}} \dfrac{1}{\sqrt{\sqrt{1+\left(\dfrac{\omega}{\omega_{s2}}\right)^2}-1}} & \text{if } D<a^2 \text{ for parallel waves,} \\[2ex] \dfrac{3K_B T\eta_2}{4\sqrt{2}\pi K_{22}K_{33}^{1/2}\sqrt{|D-(+)a^2|}} \dfrac{1}{\sqrt{\sqrt{1+\left(\dfrac{\omega}{\omega_{s2}}\right)^2}+1}} & \text{otherwise,} \end{cases}$$

with $\omega_{s2} = [D-(+)a^2]/\eta_2$.

The term for $\alpha=1$ is

$$j_{1,1}^{OF+S}(\omega) = \frac{3K_B T\eta_1}{2\pi^2}\int_0^\infty dq_z \int_0^\infty \frac{q_\perp dq_\perp}{\left(K_{11}q_\perp^2 + K_{33}q_z^2 + a + B\left(\dfrac{q_z}{q_\perp}\right)^2 \dfrac{1}{1+\dfrac{B}{D}\left(\dfrac{q_z}{q_\perp}\right)^2}\right)^2 + \eta_1^2\omega^2}.$$

Changing variables, and after lengthy but straightforward algebra, the following expression is obtained:

$$j_{1,1}^{OF+S}(\omega) = \frac{3K_B T\eta_1}{4\sqrt{2}\pi\sqrt{D}K_{11}^{3/2}} \frac{B}{D}\int_0^1 \frac{dx}{\left[\dfrac{B}{D}(1-x^2) + \dfrac{K_{33}}{K_{11}}x^2\right]^{3/2}\sqrt{x^2-(+)\dfrac{a^2}{D} + \sqrt{\left(x^2-(+)\dfrac{a^2}{D}\right)^2 + \left(\dfrac{\omega}{\omega_{s1}}\right)^2}}},$$

with $\omega_{s1} = D/\eta_1$. Therefore, the expression obtained for the spin-lattice relaxation due to ODF in presence of parallel (perpendicular) sound waves will be

$$T_1^{OF+S}(\omega) = \beta[j_{1,1}^{OF+S}(\omega) + j_{1,2}^{OF+S}(\omega)]^{-1} = \beta\left\{\frac{3K_B T}{4\sqrt{2}\pi}\left[\frac{1}{\sqrt{D}}\eta_1 K_{11}^{-3/2} Y + \frac{4\sqrt{2}\pi}{3K_B T} j_{1,2}^{OF+S}(\omega)\right]\right\}^{-1},$$

with

$$Y = \frac{B}{D}\int_0^1 \frac{dx}{\left(\dfrac{B}{D}(1-x^2) + \dfrac{K_{33}}{K_{11}}x^2\right)^{3/2}\sqrt{x^2-(+)\dfrac{a^2}{D} + \sqrt{\left(x^2-(+)\dfrac{a^2}{D}\right)^2 + \left(\dfrac{\omega}{\omega_{s1}}\right)^2}}}.$$

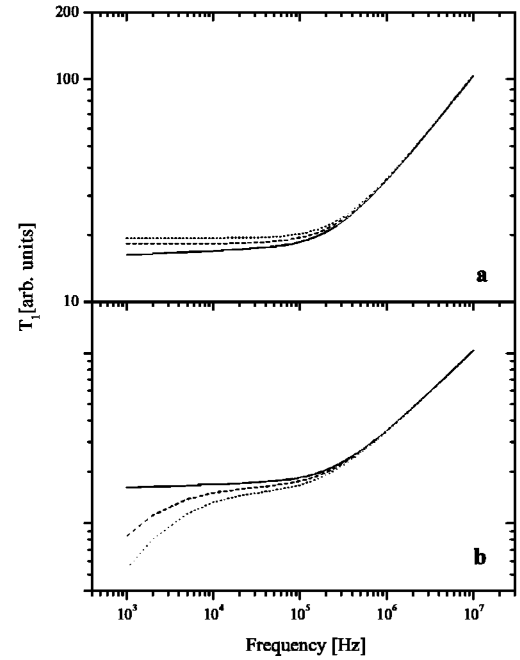

FIG. 5. Frequency dependence of T_1 in smectics in the presence of different intensities of (a) perpendicular and (b) parallel ultrasonic waves. Dotted, dashed, and solid lines correspond to the higher, lower, and zero sound intensities, respectively.

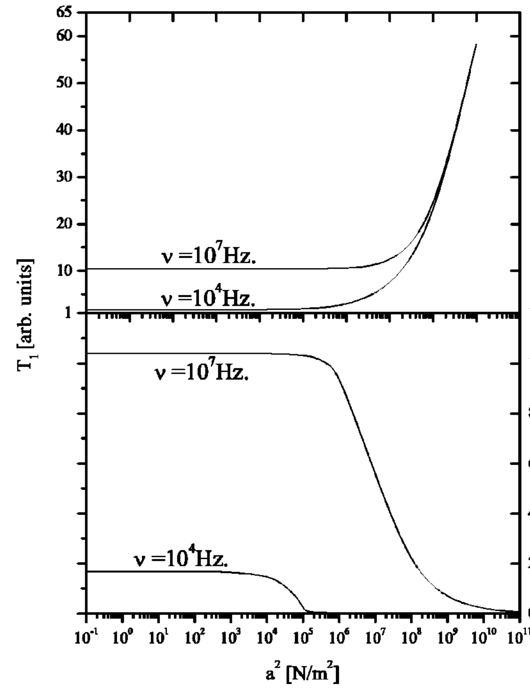

FIG. 6. Dependence of T_1 with the parameter $\log_{10}(a^2)$ on different Larmor frequencies corresponding to (a) perpendicular and (b) parallel ultrasonic waves. The nonsonicated case could be obtained taking limit $a \rightarrow 0$ in any of the plots.

It can be observed that in the absence of ultrasound waves $(a=0)$, the calculated expression in Ref. [20] is reobtained (even though the expression obtained here in the absence of ultrasound seems to be different from the one obtained by Vilfan Kogof, and Blinc [20], it can be verified that they are the same). It is also important to notice that only one (ω_{s2}) of the important frequencies in the determination of T_1 depends on the presence of ultrasound waves.

Another important limit is obtained when B and D tend to zero (but ratio B/D is constant). In this limit, only the audio and nematic elastic free energy are involved, and the result [Eq. (4)] is reobtained, as can be demonstrated.

Finally, it is possible to show that in case of perpendicular waves, in limit $a \rightarrow \infty$, both $j_{1,1}^{OF+S}(\omega)$ and $j_{1,2}^{OF+S}(\omega)$ tend to zero, producing in this way, a complete quenching of DOFs.

Figure 5 shows $\log_{10}(T_1^{OF+S})$ versus $\log_{10}(\omega)$ plot for different values of a^2 ($a^2=10^4$ N/m^2 in dashed line and $a^2 \simeq 2\times10^4$ N/m^2 in dotted line). They are compared with the nonsonicated case $(a=0)$. Here, typical values of the constants were used [20]: $B=10^6$ N/m^2, $D=10^5$ N/m^2, $K_{11}=10^{-11}$ N, $K_{22}=0.7\times10^{-11}$ N, $K_{33}=10^{-12}$ N, and $\eta=0.1$ Ns/m^2. It can be numerically shown that $T_1^{OF+S} \leqslant T_1^{OF}$ $(T_1^{OF+S} \geqslant T_1^{OF})$ for parallel (perpendicular) waves. This fact is related with the enhancement (diminution) of DOF relaxation mechanism produced by the sound waves.

Figure 6 shows the a^2 dependence of T_1 for two different Larmor frequencies. As T_1 is a growing function with frequency, all the curves that correspond to frequencies in the range 10^4–10^7Hz will be in between the plots presented in the figure.

III. COMMENTS AND CONCLUSIONS

We are primarily concerned with the spin-lattice relaxation of spin systems linked to ordered calamitic settlements subjected to an ultrasonic irradiation. We show for the first time to the best of our knowledge, how ultrasound wave affects the relaxation dispersion in nematic and smectic-*A* phases. For the sake of simplicity, two kinds of ultrasonic waves were treated: parallel and perpendicular, with respect to the order director. In the latter case, a particular wave was assumed to preserve the symmetry in the x-y plane.

It is worth noting that the magnetic free energy was never considered in the previous analysis. However, it is assumed that the magnetic field induces a preferential macroscopic orientational order (nonzero spatial average director $\widehat{n_0}$) along the magnetic field. Therefore, the magnetic field amplitude should be strong enough to induce a partial (or total) orientational order in the sample, while being sufficiently weak in order to keep the magnetic free energy term negligible compared to the acoustic and elastic free energies. These conditions determine the magnetic intensity range (different for nematic and smectic-*A* phases) where the model can be applied. Anyway, the validity of the model is strictly valid within a local spatial domain, where a well defined director exits. However, in experiments, usually a complete uniformity of director alignment is not achieved, but the model is still valid via averaging the director over the sample. This statement is a consequence of the fact that the measured time T_1 is the result of the "averaged T_1" over the sample.

Another important observation concerns the ultrasonic frequency. In the whole calculus presented, the information about the ultrasonic frequency is not on the scene due to the assumption of rapid oscillations of the density [time averaging in Eq. (3)]. This approximation is clearly valid when the ultrasonic frequency is in the megahertz region, because ODF are dominant at frequencies lower than 1 MHz. However, in our previous experiments, using an ultrasound frequency of 30 kHz [2,3], we observed that the acoustic energy was distributed in the whole observed frequency interval. This experimental fact implies that even in this case, it is correct to average over fast density oscillations. Perhaps, since both order fluctuations and DOF-ultrasound coupling are due to different physical phenomena (thermal fluctuations and density oscillations, respectively), it is not correct to compare both the time scales. This topic deserves a deeper analysis, which will be avoided in the present work.

Results obtained here for the nematic phase have been already successfully contrasted with experimental data in different compounds [2,3]. It is prominent how the remarkable changes in the dispersion curves tend to manifest at low frequencies (at fixed ultrasound intensity). This feature certainly makes the field cycling technique highly convenient to observe them. Herein we did not pursue technical limitations of the technique, instead, we examined at qualitative level the expected behavior of the relaxation dispersion at different limiting situations. For instance, we showed here that parallel sound waves enhance the relaxation by DOFs while the opposite behavior is observed for normal incidence.

We reported here two different results for the smectic phase. In the simplified model sketched above, results are similar to those observed in nematics, except in the case of parallel incidence at low frequencies. In this case, the relaxation becomes less efficient, in a clear contradiction with the expected behavior. This feature could be attributed to the simplifications of the model and/or a departure from the small angle approximation discussed herein. In the other model for smectic-*A*, this point does not appear to be relevant, while logical and intuitive results are obtained. It is important to observe that within this picture, more appreciable effects are observed for parallel incidence. This result may be useful to disentangle the relative contribution of the DOF mechanism to the relaxation dispersion in the smectic-*A* phase.

A final word concerns the particular case of parallel incidence, where $a^2=D$. In this situation, the second normal mode [Eq. (5), n_2] becomes the same as the corresponding one for a nematic liquid crystal without acoustic excitation. This feature can be interpreted as a kind of sound induced break down of the smectic order. In turn, this result suggests that molecular order may be switched by the application of an adequate ultrasonic field.

The findings presented here for the smectic case will be tested in forthcoming experiments. Hopefully, it might be an interesting point for future work to investigate the kinky processes underlying the mentioned ultrasonic induced smectic symmetry breaking. A still open question concerns the relative contribution of the DOF mechanism to the low field regime smectic relaxation dispersion.

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