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Magnetic-field induced biaxiality in nematic liquid crystals
Consequences for nuclear spin relaxation

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When a uniaxial nematic liquid crystal is subjected to a magnetic field making a non-zero angle with the C_∞ axis, the uniaxial symmetry is broken. The principal effect is a field-induced biaxiality in the long-wavelength region of the director fluctuation spectrum. Whereas the induced biaxiality has little effect on the mean square director fluctuation amplitudes $\langle n_x^2 \rangle$ and $\langle n_y^2 \rangle$, which are dominated by short-wavelength modes, it can profoundly affect the nuclear spin relaxation behaviour, which is sensitive to long-wavelength modes. Motivated by the increasing number of nuclear spin relaxation studies of director fluctuations in thermotropic, amphiphilic, and polymeric nematic liquid crystals, we present here a theoretical analysis of the effects of field-induced biaxiality on nuclear spin relaxation.

1. Introduction

In the presence of an external electric or magnetic field, the symmetry of a liquid crystal is broken, unless the field direction coincides with a crystal axis. When placed in a magnetic field, a macroscopic sample of a uniaxial nematic liquid crystal adopts an equilibrium configuration with its symmetry axis either parallel or perpendicular to the field, depending on the sign (positive or negative) of the magnetic susceptibility anisotropy, $\Delta\chi$ [1]. In the latter case ($\Delta\chi < 0$), which applies to the majority of discotic amphiphilic nematics [2, 3], the field induces a biaxiality, i.e. the point group symmetry of the nematic liquid crystal is lowered from $D_{\infty h}$ to D_{2h}. While the effect on the microscopic orientational order parameter is negligible, the induced biaxiality in the director fluctuation spectrum [4–6] has observable consequences. Indeed, recent experiments have demonstrated optical biaxiality in nominally uniaxial thermotropic nematics with $\Delta\chi < 0$ in the presence of magnetic [7] or electric [8] fields. Furthermore, an external field with oblique orientation, as can be achieved by boundary effects [1] or sample spinning [9, 10], induces biaxiality in nematic liquid crystals with $\Delta\chi$ of either sign.

In nuclear magnetic resonance studies of nematic liquid crystals, director fluctuations affect the spectral line-shape via the associated orientational order parameter and, more importantly, the spin relaxation rates via the director fluctuation spectral densities. While the order parameter is mainly influenced by short-wavelength director fluctuation modes, the adiabatic relaxation behaviour is dominated by long-wavelength modes. Since the long-wavelength modes are magnetically quenched, one expects field-induced biaxiality to have important consequences for the spin relaxation behaviour. Motivated by the increasing number of nuclear spin relaxation studies of director fluctuations in thermotropic [11–14], amphiphilic

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[15, 16], and polymeric [17, 18] nematic liquid crystals, we present here a theoretical analysis of the effects of field-induced biaxiality on nuclear spin relaxation.

2. Biaxial magnetic quenching of director fluctuations

In a continuum description, the orientational state of a uniaxial nematic liquid crystal is specified by the director field $\mathbf{n}(\mathbf{r})$ [19]. Due to thermal fluctuations, the director $\mathbf{n}(\mathbf{r})$ at a given 'point' $\mathbf{r}$ does not in general coincide with the unit vector $\mathbf{n}_0$ defining the symmetry axis of the uniaxial liquid crystal (or a uniformly aligned part thereof). Our task in this section is to describe how these director fluctuations are affected by a uniform magnetic field $\mathbf{B}$.

The configuration shown in figure 1, with the magnetic field $\mathbf{B}$ at an angle β to the symmetry axis $\mathbf{n}_0$, does not in general correspond to stable equilibrium. The interaction of the magnetic field with the diamagnetic susceptibility anisotropy $\Delta\chi$ of the liquid crystal tends to orient the symmetry axis $\mathbf{n}_0$ parallel (perpendicular) to the field if $\Delta\chi$ is positive (negative). In the absence of external fields, the direction of $\mathbf{n}_0$ is usually dictated by anisotropic surface interactions (strong anchoring boundary conditions). The magnetic torque is then opposed by an elastic torque which tends to minimize the curvature in the director field. The outcome of this competition depends on the sample dimension(s) and on the magnetic coherence length [1]

$$\xi = \left(\frac{\mu_0 K}{|\Delta\chi|}\right)^{1/2} \frac{1}{B}, \tag{1}$$

with K the curvature elastic constant of the liquid crystal [20].

The onset of magnetic realignment, referred to as the Fréedericksz transition [1], can be shown to occur when the sample thickness d and the magnetic coherence length ξ are related by

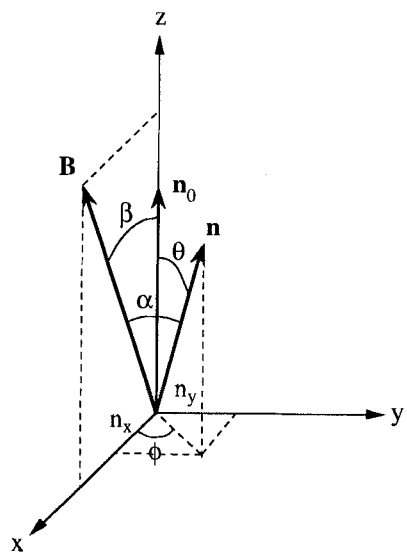

Figure 1. The liquid crystal symmetry axis $\mathbf{n}_0$, the director $\mathbf{n}$, and the magnetic field $\mathbf{B}$.

$$d=2\xi\times\begin{cases}K(\cos^2\beta), & \text{if } \Delta\chi>0,\\ K(\sin^2\beta), & \text{if } \Delta\chi<0,\end{cases} \tag{2}$$

where $K(m)$ is the complete elliptic integral of the first kind with parameter m. For the configurations conventionally used to study the Fréedericksz transition ($\beta=\pi/2$ if $\Delta\chi>0$ and $\beta=0$ if $\Delta\chi<0$), equation (2) reduces to the well-known result $d=\pi\xi$ [1]. If d is smaller than the critical value given by equation (2), the magnetic field has no effect and the sample remains homeotropic with $\mathbf{n}_0$ at an angle β to $\mathbf{B}$. If d is much larger than the critical value, the bulk of the sample undergoes a complete magnetic realignment (to $\beta=0$ if $\Delta\chi>0$ or to $\beta=\pi/2$ if $\Delta\chi<0$), while the director field is non-uniform in a surface layer with a thickness of order ξ.

For a nematic liquid crystal of volume V the transverse ($\alpha=x$ or y) director components, $n_\alpha(\mathbf{r})$, may be Fourier expanded as

$$n_\alpha(\mathbf{r})=\sum_{\mathbf{q}}\hat{n}_\alpha(\mathbf{q})\exp(i\mathbf{q}\cdot\mathbf{r}), \tag{3a}$$

with complex-valued mode amplitudes

$$\hat{n}_\alpha(\mathbf{q})=\frac{1}{V}\int_V d\mathbf{r}n_\alpha(\mathbf{r})\exp(-i\mathbf{q}\cdot\mathbf{r}). \tag{3b}$$

We choose the orientation of the x and y axes so that the magnetic field is in the xz plane (cf. figure 1).

The thermal fluctuations of the director components $n_\alpha(\mathbf{r})$ are governed by the free energy of deformation, $F=F_e+F_m$. In the harmonic approximation, where the deviation of the director $\mathbf{n}$ from the symmetry axis $\mathbf{n}_0$ is small throughout the volume V, the curvature-elastic free energy F_e can be Fourier decomposed as [1]

$$F_e=\frac{1}{2}KV\sum_{\mathbf{q}}q^2\{|\hat{n}_x(\mathbf{q})|^2+|\hat{n}_y(\mathbf{q})|^2\}. \tag{4}$$

The magnetic free energy is (apart from a constant term, independent of $\mathbf{n}(\mathbf{r})$)

$$F_m=-\frac{1}{2\mu_0}\int_V d\mathbf{r}\mathbf{B}\cdot\boldsymbol{\chi}\cdot\mathbf{B}. \tag{5}$$

For a locally uniaxial liquid crystal, the irreducible (and traceless) susceptibility tensor can be written on the dyadic form

$$\boldsymbol{\chi}=\chi_\parallel\mathbf{nn}+\chi_\perp(\mathbf{I}-\mathbf{nn}), \tag{6}$$

where $\mathbf{I}$ is the unit tensor and $\chi_\parallel=\chi_{zz}$ and $\chi_\perp=\chi_{xx}=\chi_{yy}$ are the susceptibility components along the director and perpendicular to it. Inserting equation (6) into equation (5), we obtain (after dropping a constant term)

$$F_m=-\frac{\Delta\chi}{2\mu_0}\int_V d\mathbf{r}[\mathbf{B}\cdot\mathbf{n}(\mathbf{r})]^2, \tag{7}$$

where $\Delta\chi=\chi_\parallel-\chi_\perp$ is the susceptibility anisotropy [21], already introduced in equation (1). Evaluating the scalar product in equation (7) in the coordinate system of figure 1 and noting that $B_x=B\sin\beta$, $B_y=0$, and $B_z=B\cos\beta$, we obtain (again dropping a constant term)

$$F_m = \frac{B^2 \Delta\chi}{2\mu_0} \int_V d\mathbf{r}[\cos(2\beta) n_x^2(\mathbf{r}) + \cos^2\beta n_y^2(\mathbf{r}) - \sin(2\beta) n_x(\mathbf{r}) n_z(\mathbf{r})]. \quad (8)$$

Within the harmonic approximation we can set $n_z = 1$ in the last term, which then vanishes since $\int d\mathbf{r} n_x(\mathbf{r}) = 0$ for a homeotropic sample. Using equation (3 *a*) we can then Fourier decompose the magnetic free energy as

$$F_m = \frac{B^2 \Delta\chi}{2\mu_0} V \sum_{\mathbf{q}} \{\cos(2\beta) |\hat{n}_x(\mathbf{q})|^2 + \cos^2\beta |\hat{n}_y(\mathbf{q})|^2\}. \quad (9)$$

Combining equations (4) and (9) and using the definition (1), we obtain for the total free energy of deformation

$$F = \frac{1}{2} KV \sum_{\alpha} \sum_{\mathbf{q}} [q^2 + \sigma \xi^{-2} f_\alpha(\beta)] |\hat{n}_\alpha(\mathbf{q})|^2, \quad (10)$$

with $\sigma = \text{sgn}(\Delta\chi)$ and

$$f_x(\beta) = \cos(2\beta), \quad (11\,a)$$

$$f_y(\beta) = \cos^2\beta. \quad (11\,b)$$

It follows from equation (10) that the x and y modes are statistically *independent*, i.e.

$$\langle \hat{n}_x(\mathbf{q}) \hat{n}_y(\mathbf{q}') \rangle = \langle \hat{n}_x(\mathbf{q}) \rangle \langle \hat{n}_y(\mathbf{q}') \rangle = 0, \quad (12)$$

as are modes of different wavevectors

$$\langle \hat{n}_\alpha(\mathbf{q}) \hat{n}_\alpha(\mathbf{q}') \rangle = \delta_{\mathbf{q}, -\mathbf{q}'} \langle |\hat{n}_\alpha(\mathbf{q})|^2 \rangle. \quad (13)$$

Unless $\beta = 0$, however, the x and y modes are *not* statistically *equivalent*. Indeed, the classical equipartition theorem yields with equation (10)

$$\langle |\hat{n}_\alpha(\mathbf{q})|^2 \rangle = \frac{k_B T}{VK[q^2 + \sigma \xi^{-2} f_\alpha(\beta)]}, \quad (14)$$

showing that while short-wavelength modes ($q\xi \gg 1$) are effectively uniaxial, long-wavelength modes ($q\xi \leq 1$) are biaxial if $\beta \neq 0$.

The fluctuation (or variance) of the transverse director components $n_\alpha(\mathbf{r})$ is obtained from equations (3 *a*) and (13) as

$$\langle n_\alpha^2(\mathbf{r}) \rangle = \sum_{\mathbf{q}} \langle |\hat{n}_\alpha(\mathbf{q})|^2 \rangle = \frac{V}{2\pi^2} \int_{q_-}^{q_+} dq\, q^2 \langle |\hat{n}_\alpha(\mathbf{q})|^2 \rangle, \quad (15)$$

where we have approximated the wavevector sum by an integral with (spherical) cut-offs q_- and q_+. The physical significance of these cut-offs is as follows: $2\pi/q_- = d$, the linear dimension of the liquid crystal sample (or the homeotropically aligned part thereof), and $2\pi/q_+ = a$, the microscopic length (of the order of a molecular or micellar length) below which the continuum description ceases to be valid.

The effect of a magnetic field on the director fluctuations is obtained from equations (14) and (15) as

$$\Delta_\alpha(\beta; \sigma) \equiv \langle n_\alpha^2(\mathbf{r}) \rangle - \langle n_\alpha^2(\mathbf{r}) \rangle_0 = -\sigma f_\alpha(\beta) \frac{k_B T}{2\pi^2 K \xi} \int_{q_- \xi}^{\infty} \frac{du}{u^2 + \sigma f_\alpha(\beta)}, \quad (16)$$

where the subscript zero denotes field-free conditions ($\xi \to \infty$), and we have extended the upper integration limit from $q_+\xi$ to infinity (since invariably $q_+\xi \gg 1$). The integral in equation (16) is standard; depending on the sign of $\sigma f_\alpha(\beta)$ it yields arctan or ln functions.

The magnetic quenching functions $\Delta_\alpha(\beta;\sigma)$ are shown in figures 2 and 3. All curves refer to stable equilibrium configurations, i.e. $q_-\xi > 1$. For $q_-\xi = 1$, equation (16) predicts a divergence of $\langle n_x^2 \rangle$ at $\beta = \pi/2$, if $\Delta\chi > 0$ and of both $\langle n_x^2 \rangle$ and $\langle n_y^2 \rangle$ at $\beta = 0$, if $\Delta\chi < 0$. This divergence is of course unphysical (**n** is a unit vector); it results from the breakdown of the harmonic approximation. Such behaviour is not unexpected: the divergence of the director fluctuations is closely related to the macroscopic Fréedericksz transition [22].

The qualitative behaviour of the curves in figures 2 and 3 may be understood by examining how the magnetic torque $T_m = dF_m/d\alpha \propto \sin(2\alpha)$ varies when the director **n** moves away from $\mathbf{n}_0$, thus changing the angle α between **n** and **B** from β to a slightly

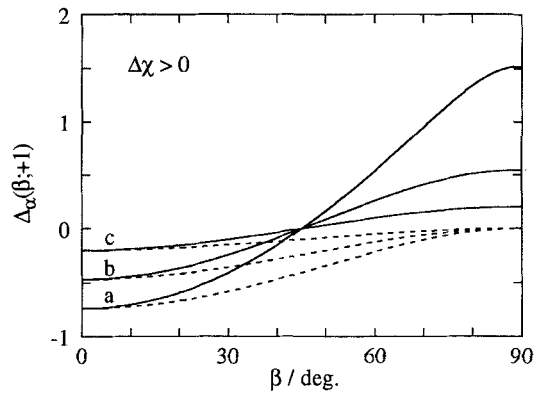

Figure 2. Magnetic quenching of director fluctuations, Δ_x (solid) and Δ_y (dashed) in units of $k_B T/(2\pi^2 K\xi)$, versus the angle β between the magnetic field and the symmetry axis $\mathbf{n}_0$ of a nematic liquid crystal with $\Delta\chi > 0$. The 3 sets of curves refer to (*a*) $q_-\xi = 1{\cdot}1$, (*b*) $q_-\xi = 2$, and (*c*) $q_-\xi = 5$.

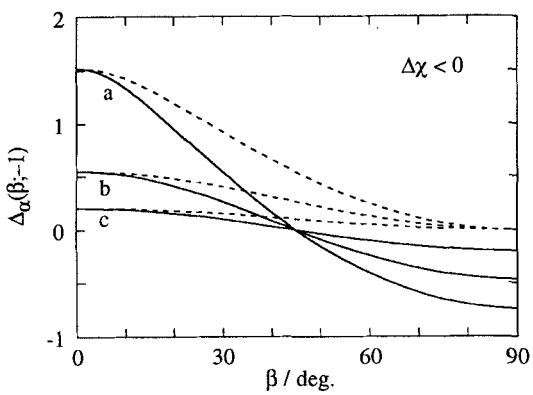

Figure 3. As in figure 2, but for a liquid crystal with $\Delta\chi < 0$.

smaller or larger value (cf. figure 1). Consider first the case $\Delta\chi > 0$ (see figure 2), where the magnetic torque T_m tends to align $\mathbf{n}$ with $\mathbf{B}$ (decrease α). For $\beta < \pi/4$, T_m increases with α and, hence, reduces n_x fluctuations away from $\mathbf{B}$ more than it enhances n_x fluctuations towards $\mathbf{B}$. Consequently $\langle n_x^2 \rangle < \langle n_x^2 \rangle_0$, i.e. director fluctuations in the xz plane are magnetically quenched. For $\beta > \pi/4$, however, T_m decreases with α and, by the same reasoning, $\langle n_x^2 \rangle > \langle n_x^2 \rangle_0$, i.e. the magnetic field *enhances* director fluctuations in the xz plane. Since director fluctuations in the yz plane cannot decrease the angle α between $\mathbf{n}$ and $\mathbf{B}$, we have magnetic quenching, i.e. $\langle n_y^2 \rangle < \langle n_y^2 \rangle_0$, for all $\beta < \pi/2$. The total director fluctuation amplitude $\langle n_x^2 \rangle + \langle n_y^2 \rangle$ is magnetically enhanced for $\beta > \beta_m = \arccos(1/\sqrt{3})$, if $q_- \xi \gg 1$. Analogous considerations apply to the case $\Delta\chi < 0$ (figure 3). In particular, we see from equation (16) that $\Delta_x(\beta; -1) = \Delta_x(\pi/2 - \beta; +1)$.

So far we have only considered fluctuations around stable equilibrium configurations. At the magnetic fields of conventional NMR spectrometers, this means that configurations with $\beta \neq 0$ (for $\Delta\chi > 0$) or $\beta \neq \pi/2$ (for $\Delta\chi < 0$) can be realized only in very thin (typically $d \leq 10\,\mu$m) liquid crystal samples; otherwise a Fréedericksz transition intervenes. Due to the viscous torque exerted by the liquid crystal, however, the Fréedericksz transition is not instantaneous. Sample spinning techniques can therefore be used to achieve steady-state configurations with oblique orientations β even for large samples.

A director fluctuation mode $\hat{n}_\alpha(\mathbf{q})$ of wavevector $\mathbf{q}$ has a characteristic relaxation time [23]

$$\tau(q) = \frac{\eta}{K(q^2 + \xi^{-2})}, \tag{17}$$

with η an effective viscosity coefficient, while the time constant for the Fréedericksz transition is [9, 24]

$$\tau_F = \frac{2\mu_0 \gamma_1}{|\Delta\chi| B^2}, \tag{18}$$

with γ_1 the rotational viscosity. As expected, τ_F is of the same order as the relaxation time of modes of wavevector $1/\xi$. By spinning the liquid crystal sample at an angular frequency $\omega \gg 1/\tau_F$, so that the director does not have time to respond to changes in the angle α (cf. figure 1), one can generate steady-state configurations with oblique orientations β [9, 10, 25]. Thus, for example, if a liquid crystal with $\Delta\chi > 0$ is rapidly spun around the z axis of figure 1, $\mathbf{n}_0$ remains at an angle β to the magnetic field (i.e. there is no Fréedericksz transition) irrespective of the sample size, provided that $\beta < \beta_m = \arccos(1/\sqrt{3})$ [10]. For a liquid crystal with $\Delta\chi < 0$, the same result can be accomplished if $\beta > \beta_m$. For other values of the angle between the spinning axis and the $\mathbf{B}$ field one obtains a two-dimensional isotropic $\mathbf{n}_0$ distribution in the plane normal to the spinning axis [10, 25].

Since only long-wavelength ($q\xi \leq 1$) director fluctuation modes are significantly affected by the magnetic field (cf. equation (14)) and since these modes are effectively static on a time scale $1/\omega \ll \tau_F$ (cf. equation (17)), it follows that director fluctuations in a spinning sample are governed by an effective magnetic free energy $\langle F_m \rangle_s$ which is averaged over one cycle of the spinning motion [10], i.e. equation (7) is replaced by

$$\langle F_m \rangle_s = -\frac{B^2 \Delta\chi}{2\mu_0} \int_V d\mathbf{r} \langle \cos^2 \alpha(\mathbf{r}) \rangle_s. \tag{19}$$

For the case of a homeotropic alignment of $\mathbf{n}_0$ along the spinning axis, equation (19) involves an average over the azimuthal angle ϕ in figure 1, and

$$\langle F_m \rangle_s = \frac{B^2 \Delta\chi}{2\mu_0} P_2(\cos\beta) \int_V d\mathbf{r}[n_x^2(\mathbf{r}) + n_y^2(\mathbf{r})]. \tag{20}$$

A comparison with equation (8) shows that the previous results (equations (10), (14), and (16)) are valid also for the present case if $f_\alpha(\beta)$ is replaced by $P_2(\cos\beta)$. In particular,

$$\Delta_x(\beta) = \Delta_y(\beta) = -\sqrt{[|P_2(\cos\beta)|]} \frac{k_B T}{2\pi^2 K \xi} \left[\frac{\pi}{2} - \arctan \frac{q_- \xi}{\sqrt{[|P_2(\cos\beta)|]}}\right]. \tag{21}$$

This result applies to the case $\Delta\chi > 0$, if $\beta \leq \beta_m$ and to the case $\Delta\chi < 0$, if $\beta \geq \beta_m$. As expected, sample spinning around $\mathbf{n}_0$ eliminates the induced biaxiality ($\Delta_x = \Delta_y$). Figure 4 shows how the magnetic quenching varies with β. The vanishing of the effective magnetic interaction at the magic angle β_m is completely analogous to the well-known technique for elimination of static second-rank spin couplings in solid-state NMR [26].

Another experimentally relevant case is that of a liquid crystal with $\Delta\chi > 0$ which is spun rapidly around an axis orthogonal to the magnetic field (the y axis in figure 1). As noted above, this results in a uniform distribution of β values [10, 25]. The previous results (equations (10), (14), and (16)) are then modified according to

$$f_x(\beta) \rightarrow \langle \cos(2\beta) \rangle_s = 0, \tag{22a}$$

$$f_y(\beta) \rightarrow \langle \cos^2\beta \rangle_s = \frac{1}{2}. \tag{22b}$$

As expected, the n_x fluctuations are unaffected by the magnetic field rotating rapidly in the xz plane. The magnetic quenching of the n_y fluctuations is obtained from equation (16) as

$$\Delta_y = -\frac{k_B T}{2\sqrt{(2)}\pi^2 K \xi} \left[\frac{\pi}{2} - \arctan(\sqrt{(2)} q_- \xi)\right]. \tag{23}$$

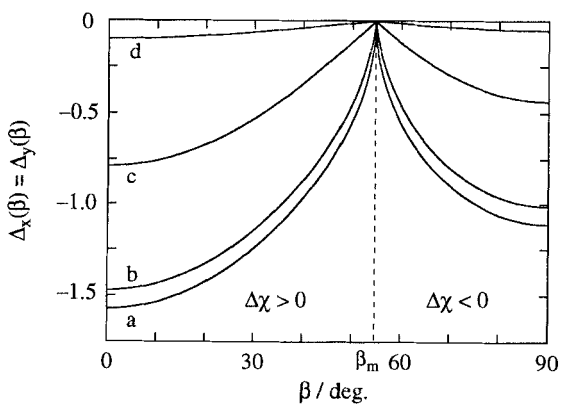

Figure 4. Magnetic quenching of director fluctuations, $\Delta_x = \Delta_y$ in units of $k_B T/(2\pi^2 K\xi)$, versus the angle β between the magnetic field and the spinning axis (which is parallel to $\mathbf{n}_0$). The different curves refer to (*a*) $q_-\xi = 0$, (*b*) $q_-\xi = 0{\cdot}1$, (*c*) $q_-\xi = 1$, and (*d*) $q_-\xi = 10$.

For a large sample ($q_-\xi \ll 1$), the magnetic quenching is thus reduced by a factor $\sqrt{2}$ as compared to the $\beta = 0$ configuration (cf. equation (21)).

3. Orientational order parameters

Most NMR nuclei of interest are coupled to the molecular degrees of freedom via second-rank interaction tensors [27]. The orientational order is then manifested in the static NMR line-shape via the second-rank orientational order parameters $\langle D^2_{m0}(\phi, \theta)\rangle$. When a magnetic field is applied at an angle $\beta \neq 0$ to a uniaxial nematic liquid crystal, the rotational symmetry is lowered from $D_{\infty h}$ to D_{2h} and the non-zero second-rank order parameters are [28, 29]

$$S = \langle P_2(\cos\theta)\rangle = 1 - \frac{3}{2}[\langle n_x^2\rangle + \langle n_y^2\rangle], \tag{24}$$

and

$$P = \mathrm{Re}\,\langle D^2_{20}(\phi, \theta)\rangle = \frac{\sqrt{6}}{4}[\langle n_x^2\rangle - \langle n_y^2\rangle]. \tag{25}$$

In terms of the magnetic quenching functions Δ_α defined in equation (16),

$$S = S_0 - \frac{3}{2}(\Delta_x + \Delta_y), \tag{26}$$

$$P = \frac{\sqrt{6}}{4}(\Delta_x - \Delta_y), \tag{27}$$

with S_0 the uniaxial order parameter in the absence of magnetic field. In static samples, the biaxial order parameter P has the same sign as $\Delta\chi$ (cf. figures 2 and 3). In homeotropically aligned spinning samples, of course, $P = 0$, whereas for a $\Delta\chi > 0$ sample with the spinning axis orthogonal to the field, $P > 0$.

As previously shown [6], $S - S_0$ and P vary as B^2 for sufficiently weak magnetic fields: combination of equations (26), (27), and (16) yields for $B \to 0$

$$S - S_0 = \frac{3\sigma k_B T}{4\pi^2 K q_-\xi^2}[\cos^2\beta + \cos(2\beta)], \tag{28}$$

and

$$P = \frac{\sqrt{6}\sigma k_B T}{8\pi^2 K q_-\xi^2}[\cos^2\beta - \cos(2\beta)]. \tag{29}$$

As seen from figures 2–4, Δ_x and Δ_y are at most of order $k_B T/(2\pi^2 K\xi)$, which is typically of order 10^{-5}. Magnetic quenching of director fluctuations therefore has no significant effect on the static NMR line-shape.

4. Spin relaxation by director fluctuations

Although the relative magnetic quenching $\Delta_\alpha/\langle n_\alpha^2\rangle_0$ of the real-space director fluctuation amplitudes is at most of order $(q_+\xi)^{-1} \ll 1$, the adiabatic (zero-

frequency) spin relaxation behaviour, which mainly reflects long-wavelength director fluctuation modes, can be profoundly affected by magnetic quenching.

Within the regime of the Bloch–Wangsness–Redfield perturbation theory of spin relaxation [27], the observable relaxation behaviour of most spin $I \geq 1$ nuclei is determined by 3 lab-frame spectral density (LFSD) functions $J^{L}_{kk}(k\omega_0)$, evaluated at the multiples $k=0$, 1, 2 of the Larmor frequency ω_0. We focus on the adiabatic spectral density $J^{L}_{00}(0)$, since only this LFSD is significantly affected by field-induced biaxiality.

The LFSD $J^{L}_{00}(0)$ can generally be expressed as an orientation-dependent linear combination of 15 crystal-frame spectral densities (CFSDs) $J^{C}_{\lambda}(0)$, which contain all the available information about the amplitudes and rates of the fluctuations that induce spin relaxation,

$$J^{L}_{00}(0;\beta,\varphi)=\sum_{\lambda}F_{0\lambda}(\beta,\varphi)J^{C}_{\lambda}(0), \tag{30}$$

where β and φ are the polar and azimuthal angles that specify the orientation of the magnetic field with respect to the crystal axes. If the liquid crystal possesses rotational symmetry elements, the number of distinct non-zero CFSDs is reduced. The remaining so-called irrreducible (or symmetry-adapted) CFSDs and the associated angular functions have recently been given in explicit form for all crystallographic point groups [29]. For a uniaxial liquid crystal of point group $D_{\infty h}$ there are only 3 irreducible CFSDs and equation (30) takes the well-known form

$$J^{L}_{00}(0;\beta)=\left(1-\frac{3}{2}s^2\right)^2 J^{C}_{00}(0)+3s^2(1-s^2)J^{C}_{11}(0)+\frac{3}{4}s^4J^{C}_{22}(0), \tag{31}$$

where $s=\sin\beta$ and

$$J^{C}_{np}(0)=\int_0^{\infty}d\tau[\langle D^{2}_{n0}[\phi(0),\theta(0)]D^{2*}_{p0}[\phi(\tau),\theta(\tau)]\rangle-\langle D^{2}_{n0}(\phi,\theta)\rangle\langle D^{2*}_{p0}(\phi,\theta)\rangle]. \tag{32}$$

For an intrinsically biaxial liquid crystal of point group D_{2h}, there are 6 irreducible CFSDs [29]. However, for an intrinsically uniaxial nematic phase where the biaxiality is induced by the same external magnetic field that polarizes the nuclear spins, the field direction is always in the plane of two of the crystal axes. Without loss of generality, we can therefore set $\varphi=0$ so that **B** is in the xz plane (as in figure 1). The adiabatic LFSD $J^{L}_{00}(0)$ then depends on only 5 of the 6 irreducible CFSDs according to (cf. table B 2 of [29])

$$\begin{aligned}J^{L}_{00}(0;\beta)=&\left(1-\frac{3}{2}s^2\right)^2 J^{C}_{00}(0)+\sqrt{6}s^2\left(1-\frac{3}{2}s^2\right)\mathrm{Re}\,J^{C}_{20}(0)\\&+\frac{9}{2}s^2(1-s^2)[J^{C}_{11}(0)-\mathrm{Re}\,J^{C}_{1-1}(0)]-\frac{3}{2}s^2(1-s^2)[J^{C}_{11}(0)+\mathrm{Re}\,J^{C}_{1-1}(0)]\\&+\frac{3}{4}s^4[J^{C}_{22}(0)+\mathrm{Re}\,J^{C}_{2-2}(0)].\end{aligned} \tag{33}$$

Expressing the Wigner functions in equation (32) in terms of director components according to

$$D^2_{00}(\phi, \theta) = 1 - \frac{3}{2}(n_x^2 + n_y^2), \tag{34a}$$

$$D^2_{\pm 10}(\phi, \theta) = \mp \frac{\sqrt{6}}{2}(n_x \pm i n_y) n_z, \tag{34b}$$

and

$$D^2_{\pm 20}(\phi, \theta) = \frac{\sqrt{6}}{4}(n_x \mp i n_y)^2, \tag{34c}$$

we can transform equation (33) into

$$J^{\mathrm{L}}_{00}(0; \beta) = \frac{9}{8}[4s^2(1-s^2)(3j_{2x} - j_{2y}) + (2 - 6s^2 + 5s^4)(j_{4x} + j_{4y}) + s^2(3s^2 - 2)(j_{4x} - j_{4y})], \tag{35}$$

with

$$j_{n\alpha} = \int_0^\infty d\tau g_{n\alpha}(\tau), \tag{36}$$

and the time correlation functions (TCFs)

$$g_{2\alpha}(\tau) = \langle n_\alpha(0) n_\alpha(\tau) \rangle, \tag{37}$$

$$g_{4\alpha}(\tau) = \langle n_\alpha^2(0) n_\alpha^2(\tau) \rangle - \langle n_\alpha^2 \rangle^2. \tag{38}$$

To obtain these results we have assumed that the x and y modes are statistically independent at all times (cf. equation (12)). Furthermore, we have neglected contributions to J^{C}_{11} and J^{C}_{1-1} of fourth order in n_α, since they are negligible compared to the second-order contributions. The fourth-order terms in equation (35) correspond (exactly) to the CFSDs J^{C}_{00}, J^{C}_{20}, J^{C}_{22}, and J^{C}_{2-2} in equation (33). These terms are retained in equation (35) since they are the only contributions for $\beta = 0$ and $\beta = \pi/2$. As seen from equation (35), only 3 independent linear combinations of CFSDs can be determined from the angular dependence of the adiabatic LFSD. In fact, this is already apparent in equation (33), which may be expressed as a quadratic polynomial in $\sin^2 \beta$.

5. Second-order spectral densities

Unless β is very close to 0 or $\pi/2$, $J^{\mathrm{L}}_{00}(0; \beta)$ in equation (35) is dominated by the second-order spectral densities $j_{2\alpha}$. Neglecting the fourth-order spectral densities, we then have

$$J^{\mathrm{L}}_{00}(0; \beta) = \frac{9}{2} s^2(1 - s^2)(3j_{2x} - j_{2y}). \tag{39}$$

The second-order TCFs in equation (37) may be expressed as [30]

$$g_{2\alpha}(\tau) = \sum_{\mathbf{q}} \langle |\hat{n}_\alpha(\mathbf{q})|^2 \rangle \exp(-q^2 D_{\mathrm{e}} \tau). \tag{40}$$

Here $D_{\mathrm{e}} = D + K/\eta$, with D the translational diffusion coefficient of the spin-bearing species. Thus

$$j_{2\alpha}=\frac{1}{D_e}\sum_{\mathbf{q}} q^{-2}\langle|\hat{n}_\alpha(\mathbf{q})|^2\rangle=-\frac{1}{\sigma f_\alpha(\beta)}\frac{\xi^2}{D_e}\Delta_\alpha(\beta;\sigma), \tag{41}$$

where we used equations (14)–(16) in the last step.

For thin ($q_-\xi \geq 1$) equilibrium samples, equation (41) yields

$$j_{2\alpha}=j^0_{2\alpha}q_-\int_{q_-}^{\infty}\frac{dq}{q^2+\sigma\xi^{-2}f_\alpha(\beta)}, \tag{42}$$

and, in the absence of a magnetic field ($\xi\to\infty$),

$$j^0_{2x}=j^0_{2y}=\frac{k_BT}{2\pi^2Kq_-D_e}. \tag{43}$$

Since the magnetic quenching depends on the orientation of the liquid crystal with respect to the magnetic field, the CFSDs $j_{2\alpha}$ in (5.4) *depend on* β. As a consequence, the orientation dependence of the LFSD $J^L_{00}(0;\beta)$ in equation (39) deviates from the $\sin^2\beta\cos^2\beta$ dependence characteristic of a uniaxial liquid crystal (cf. equation (31)). This is illustrated in figure 5.

For a homeotropically aligned spinning ($\omega\gg 1/\tau_F$) sample, we obtain from equations (41) and (21)

$$j_{2x}=j_{2y}=j^0_{2\alpha}\frac{q_-\xi}{\sqrt{(|P_2(\cos\beta)|)}}\left[\frac{\pi}{2}-\arctan\frac{q_-\xi}{\sqrt{(|P_2(\cos\beta)|)}}\right]. \tag{44}$$

An expansion of the arctan function shows, as expected, that $j_{2\alpha}=j^0_{2\alpha}$ at the magic angle $\beta=\beta_m$. For large samples ($q_-\xi\ll 1$), however, $j_{2\alpha}\ll j^0_{2\alpha}$ for $\beta\neq\beta_m$ and the orientation dependence of the LFSD $J^L_{00}(0;\beta)$ differs qualitatively from the uniaxial case. This is shown in figure 6. Note that magnetic quenching always reduces $J^L_{00}(0;\beta)$ for a liquid crystal aligned by fast sample spinning.

For a liquid crystal with $\Delta\chi>0$ which is spun rapidly around an axis orthogonal to the magnetic field, we obtain from equations (41) and (23)

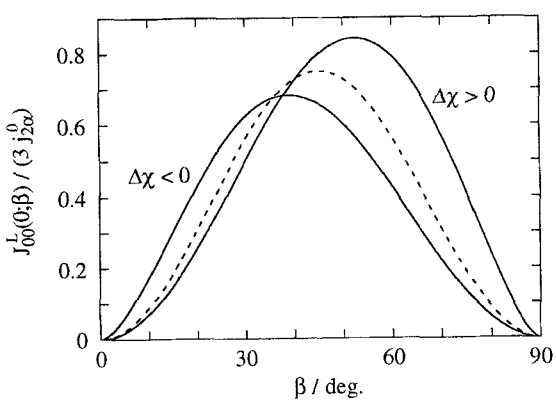

Figure 5. Magnetic quenching effect on the orientation (β) dependence of the lab-frame spectral density $J^L_{00}(0;\beta)$ for thin ($q_-\xi\geq 1$) liquid crystal samples. The dashed curve corresponds to the field-free case ($q_-\xi\gg 1$) and the solid curves to a situation just before the Fréedericksz instability ($q_-\xi=1$).

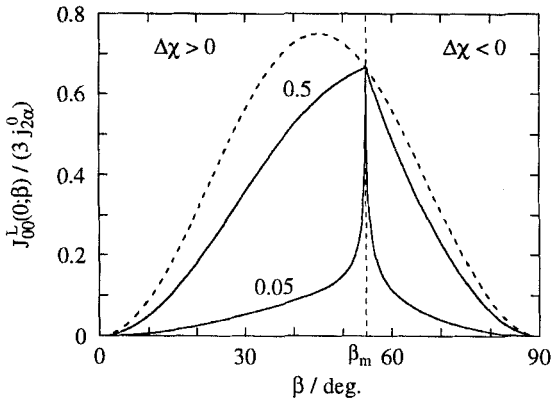

Figure 6. Magnetic quenching effect on the orientation (β) dependence of the lab-frame spectral density $J^L_{00}(0;\beta)$ for a liquid crystal homeotropically aligned by fast sample spinning. The dashed curve corresponds to the field-free case ($q_-\xi \gg 1$) and the solid curves to the $q_-\xi$ values indicated.

$$j_{2y} = j^0_{2\alpha}\sqrt{(2)}q_-\xi\left[\frac{\pi}{2} - \arctan\left(\sqrt{(2)}q_-\xi\right)\right]. \tag{45}$$

Since $j_{2x} = j^0_{2\alpha}$, we can write the LFSD in equation (39) on the uniaxial form (cf. equation (31))

$$J^L_{00}(0;\beta) = 3s^2(1-s^2)J^C_{11}(0), \tag{46}$$

with the CFSD

$$J^C_{11}(0) = \frac{3}{2}(3j_{2x} - j_{2y}) = 3j^0_{2\alpha}\left\{\frac{3}{2} - \frac{q_-\xi}{\sqrt{2}}\left[\frac{\pi}{2} - \arctan\left(\sqrt{(2)}q_-\xi\right)\right]\right\}. \tag{47}$$

In contrast to equation (44), this CFSD is independent of sample orientation (β). For a large sample ($q_-\xi \ll 1$), the contribution j_{2y} from the magnetically quenched y mode is negligible compared to the contribution $j_{2x} = j^0_{2\alpha}$ from the unquenched x mode (cf. equation (45)). Consequently, the CFSD in equation (47), $J^C_{11}(0) = (9/2)j^0_{2\alpha}$, is independent of the magnetic coherence length ξ and a factor 3/2 larger than the result in the absence of magnetic quenching, when $J^C_{11}(0) = 3j^0_{2\alpha}$, since $j_{2x} = j_{2y}$. This factor 3/2 is a direct consequence of the magnetically induced biaxiality.

Since the x modes that are responsible for $J^C_{11}(0)$ are not magnetically quenched, fluctuation modes of very long wavelengths (comparable to the dimension of a homeotropically aligned part of the sample—cf. equation (43)) may contribute to the spin relaxation. Director fluctuation modes of such long wavelengths, however, are so slow (cf. equation (17)) that they can only produce static line-shape effects, but cannot induce spin relaxation [27]. Since the spin relaxation is dominated by the slowest modes that are fast enough to motionally average the spin-lattice coupling, the usual perturbation theory of spin relaxation [27] is not valid. As a consequence, the orientation dependence of $J^L_{00}(0;\beta)$ is no longer of the uniaxial form in equation (46). Such an anomalous orientation dependence was observed recently in [17], where it was also suggested that the discrepancy is due to breakdown of the perturbation theory. Here we have shown explicitly that this breakdown is due to the induced biaxiality, with x modes that are not magnetically quenched.

It is also of interest to investigate the effect of field-induced biaxiality on the frequency-dependent second-order spectral densities

$$j_{2\alpha}(\omega)=\int_0^\infty d\tau\,\cos(\omega\tau)g_{2\alpha}(\tau), \tag{48}$$

which may be studied, for example, by field-cycling or echo-train techniques. Combination of equations (14), (40), and (48) yields for the case with $\Delta\chi<0$ and $\beta=\pi/2$,

$$j_{2x}(\omega)=\frac{k_BT}{2\pi^2KD_e}\int_{q_-}^{q_+}dq\,\frac{q^4}{(q^2+\xi^{-2})[q^4+(\omega/D_e)^2]}, \tag{49a}$$

and

$$j_{2y}(\omega)=\frac{k_BT}{2\pi^2KD_e}\int_{q_-}^{q_+}dq\frac{q^2}{q^4+(\omega/D_e)^2}. \tag{49b}$$

The integrals are standard and we obtain for $\omega\gg\omega_-=q_-^2D_e$ (which is always the case for a macroscopic sample if $\omega\neq0$),

$$j_{2x}(\omega)=\frac{k_BT}{4\pi K\sqrt{(2D_e\omega)}}\left\{\frac{U_-(\omega)-(\omega_m/\omega)U_+(\omega)}{1+(\omega_m/\omega)^2}+\frac{4\sqrt{(2\omega/\omega_m)}}{2\pi[1+(\omega/\omega_m)^2]}[\arctan(\xi q_+)-\arctan(\xi q_-)]\right\}, \tag{50a}$$

and

$$j_{2y}(\omega)=\frac{k_BT}{4\pi K\sqrt{(2D_e\omega)}}U_-(\omega), \tag{50b}$$

with

$$U_\pm(\omega)=\frac{1}{\pi}\left[\arctan(\sqrt{(2\omega_+/\omega)}-1)+\arctan(\sqrt{(2\omega_+/\omega)}+1)\pm\operatorname{arctanh}\left(\frac{\sqrt{(2\omega_+/\omega)}}{1+\omega_+/\omega}\right)\right], \tag{51}$$

and with the characteristic frequencies $\omega_+=q_+^2D_e$ and $\omega_m=\xi^{-2}D_e$.

The result in equation (50*b*) for the spectral density $j_{2y}(\omega)$, which is not magnetically quenched in the configuration considered, agrees with the traditional result [31, 32]. In practice, one always has $\omega_m\ll\omega$, $\xi q_+\gg1$, and $\xi q_-\ll1$, in which case

$$j_{2x}(\omega)=j_{2y}(\omega), \tag{52}$$

i.e. magnetic quenching plays no role at non-zero frequencies.

6. Fourth-order spectral densities

In the absence of boundary effects (thin samples) and non-equilibrium effects (spinning samples), a nematic liquid crystal placed in a magnetic field will be magnetically aligned with $\beta=0$, if $\Delta\chi>0$ or $\beta=\pi/2$, if $\Delta\chi<0$. According to equation (35), at these orientations the second-order spectral densities $j_{2\alpha}$ do not contribute to the observable adiabatic LFSD $J_{00}^L(0;\beta)$, which thus becomes dominated by the fourth-order spectral densities $j_{4\alpha}$ [12, 13, 15].

In the case $\Delta\chi > 0$, the uniaxial symmetry of the liquid crystal is not broken by the magnetic field and equation (35) reduces to

$$J^{L}_{00}(0;\,0) = J^{C}_{00}(0) = \frac{9}{4}(j_{4x} + j_{4y}) = \frac{9}{2} j_{4x}, \tag{53}$$

since $j_{4x} = j_{4y}$. In the case $\Delta\chi < 0$, on the other hand, the uniaxial symmetry *is* broken and $j_{4x} \neq j_{4y}$. In the $\beta = \pi/2$ configuration, however, the y modes do not contribute to the adiabatic LFSD $J^{L}_{00}(0;\beta)$ since they do not modulate the angle (α) between the director and the magnetic field (cf. figure 1). Indeed, with $\beta = \pi/2$ in equation (35), we have

$$J^{L}_{00}(0;\,\pi/2) = \frac{9}{4} j_{4x}. \tag{54}$$

Since $\sigma f_{\alpha}(\beta) = 1$ for $\Delta\chi > 0$, $\beta = 0$ as well as for $\Delta\chi < 0$, $\beta = \pi/2$, j_{4x} has the same form in the two cases [33]. For example, if translational diffusion of the spin-bearing species through the spatially inhomogeneous director field is much faster than the viscous damping of the fluctuation modes ($D \gg K/\eta$), we have [15]

$$j_{4x} = \left(\frac{k_B T}{\pi K}\right)^2 \frac{1}{8D} [\ln(q_+ \xi) - 1{\cdot}119], \tag{55}$$

where terms of order $(q_+\xi)^{-1}$ and smaller have been neglected.

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[19] The director **n** is a unit vector along the major principal axis of the second-rank orientational order tensor, averaged over a microscopic volume at **r**.
[20] Throughout this work we adopt the one-constant approximation, i.e. we assume that the curvature elastic constants associated with splay, twist, and bend deformations are equal.
[21] Macroscopic susceptibility measurements average over director fluctuations and hence yield the quantity $S\Delta\chi$, with S the uniaxial order parameter defined in § 3.
[22] For the classical configurations ($\beta=\pi/2$ and $\Delta\chi>0$, or $\beta=0$ and $\Delta\chi<0$), equation (2) predicts a Fréedericksz transition at $q_{-}\xi=2$, whereas the director fluctuations in equation (16) diverge at $q_{-}\xi=1$. The difference is presumably due to the use of a spherical cut-off in our treatment of director fluctuations.
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