Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 18 Mar 2009

To cite this article: Diego Frezzato & Giorgio J. Moro (2009): Transverse Nuclear Spin Relaxation in Nematic Liquid Crystals. Angular Dependence of the Relaxation Rate in Pulsed Experiments, Molecular Crystals and Liquid Crystals, 500:1, 91-107

To link to this article: http://dx.doi.org/10.1080/15421400802713744

Mol. Cryst. Liq. Cryst., Vol. 500, pp. 91–107, 2009

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802713744

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Transverse Nuclear Spin Relaxation in Nematic Liquid Crystals. Angular Dependence of the Relaxation Rate in Pulsed Experiments

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The theory underlying the slow-motional description of transverse relaxation in ^{2}H-NMR pulsed experiments, sensitive to order director fluctuations in nematic liquid crystals, is outlined in a comprehensive way in order to highlight the physical parameters which enter the expressions elsewhere derived, to stress the limits of their applicability, and to address those experimental situations which may be more (or less) appealing from the point of view of the extent of information achievable from the analysis of the data. A comparison between fast-motional and slow-motional results is made here, for the first time, in relation to measures performed on samples aligned by the magnetic field.

Keywords: fluctuations, order director, transverse nuclear spin relaxation

1. INTRODUCTION

Fluctuations of the local orientation director in "soft" ordered phases like liquid crystals and biomembranes can be investigated by analizing transverse relaxation in NMR experiments. Here we focus on ^{2}H-NMR performed on deuterated probes in a nematic phase, where the Carr-Purcell-Meiboom-Gill (CP) sequence of radiofrequency pulses is employed to detect the homogeneous transverse relaxation by generating a train of echoes [1]. First, the relaxation rate associated to the decay of the echoes' intensities depends on the angle between the average (macroscopic) director and the magnetic field. Moreover, for a fixed orientation, the relaxation rate may depend on the spacing between the pulses in the CP sequence; such a dependence, if present, is a signature of slow-motional stochastic processes which affect the spin

We thank MIUR for the grants PRIN 2005 and PRIN 2006.

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relaxation. Amogst the slow processes, fluctuations of the local director with respect to the average direction of alignment is the first candidate to be considered [2,3].

Director fluctuations is a collective process having a wide range of characteristic frequencies determined by the viscoelastic parameters of the material (i.e., elastic constants and viscosity coefficients). For a sample of macroscopic extension, the lower frequencies of fluctuation may overlap the range of spreading of the resonance frequencies due to the distribution of the director itself at thermal equilibrium. In this case, the so-called "slow motional analysis" of the NMR experiment has to be done by adopting the Stochastic Liouville Equation to describe how the population of the nuclear spin states is affected by the slow modulation of the spin hamiltonian [4,5].

The formal tools to perform such an analysis have been built and characterized from the theoretical point of view in several works [6–8], and have been applied to rather different situations (different physical systems and spin-probes) like ^{31}P-NMR to study shape's fluctuations in biomembranes [9] and ^{2}H-NMR to investigate fluctuations in nematic polymers [10]. In this paper we outline the main features of the theory with reference to ^{2}H-NMR experiments in nematic liquid crystals, we point out the limits of applicability of the expressions which can be employed directly to fit the experimental data, and discuss about the extent of information that could be extracted from the data if the NMR experiment could be performed on samples at tunable orientation with respect to the magnetic field. Particular emphasis will be given to experiments performed at "canonical orientations", which are the most common situations when the sample is aligned parallel or perpendicular to the magnetic field. Here, for the first time, we point out the differences between the expression up to now adopted to interpret the data [11] on the basis of the fast-motional analysis of linewidhs [12,13], and the slow-motional description of relaxation in the pulsed ^{2}H-NMR experiment.

2. DIRECTOR FLUCTUATIONS IN NEMATICS PROBED BY TRANSVERSE NUCLEAR SPIN RELAXATION

Let us consider a monodeuterated probe molecule (nuclear spin $I = 1$) dissolved in a well aligned nematic phase. Relaxation of the nuclear spin magnetization is driven by stochastic modulation of the spin interactions due to single-molecule and collective motions. Dynamics which may drive the spin relaxation are the fast tumbling motions of the molecule about the local director, and the slower fluctuations of the local director with respect to the average (macroscopic) direction

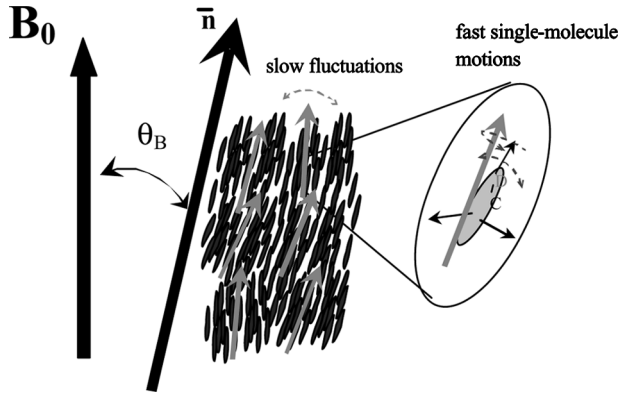

FIGURE 1 Pictorial representation of director fluctuations in a nematic phase.

of alignment. A pictorial representation of these dynamics is given in Figure 1. The fast tumbling produces a partial averaging of the spin interactions; such a dynamic averaging is related to an intrinsic "molecular" contribution to the relaxation rate. The residual spin hamiltonian is modulated by slower director fluctuations that provide a further contribution to the relaxation rate. The two processes may be treated independently by invoking a large separation of timescales between single-molecule and collective motions. Moreover, if the rates of the tumbling are much larger compared to the spreading of the resonance frequencies due to the orientational distribution of the molecule about the local director, a "fast motional treatment" (i.e., a perturbative Redfield approach [14,15]) can be applied to estimate the molecular contribution to the relaxation rate. On the contrary, director fluctuations have a range of characteristic rates so wide to include components comparable in magnitude to the spreading of the resonance frequencies due to the orientational distribution of the local director; in such a case the so-called "slow-motional treatment" of the spin relaxation has to be adopted.

Once the NMR experiment is defined in details, and once the residual spin hamiltonian is specified, the slow-motional analysis can be done by solving the corresponding Stochastic Liouville Equation (SLE) [4,5]. The SLE describes the time evolution of the density matrix operator and, in particular, the evolution of the populations of the nuclear spin states as affected by the stochastic modulation of the spin hamiltonian. In the following we shall shortly describe the kind of NMR experiment we are focused on, we specify the residual quadrupolar spin hamiltonian left

by the averaging due to molecular tumbling, and outline the physical processes driving director fluctuations.

Here we focus on the detection of the transverse relaxation process by means of the Carr-Purcell-Meiboom-Gill (CP) sequence of radiofrequency pulses, $(\pi/2)_X - [\tau - (\pi/2)_Y - \tau]_n$, where τ is the pulse-spacing, and the labels X, Y, Z refer to the axes of a Magnetic Rotating Frame (MRF) whose longitudinal axis is parallel to the magnetic field $\mathbf{B_0}$ and the transverse axes spin at one of the average resonance frequencies of the doublet in the NMR spectrum. The first pulse creates the non-equilibrium state by bringing the macroscopic spin magnetization along the Y-axis of MRF, i.e., on the transverse plane with respect to the magnetic field; then one repeats for n times the same pulse scheme including a free evolution for a time τ, followed by a pulse $(\pi/2)_Y$ which reverses the magnetization on the transverse plane to cause the refocusing of the signal (echo) during the subsequent free evolution for the same time interval τ. After the n-th cycle, the maximum intensity of the echo, in the following denoted by $I(2n\tau)$, is detected at time $2n\tau$. Notice that if $n = 1$ the CP reduces to the so-called Quadrupolar Echo experiment.

Let us now introduce the following transverse relaxation rate which quantifies the decrease of the maximum of the n-th echo with respect to that of the previous one:

$$R_{2,n}^{CP}(\tau) = -\frac{1}{2\tau}\ln\frac{I(2n\tau)}{I(2(n-1)\tau)} \tag{1}$$

On the basis of the distinction between fast- and slow-processes in relation to the NMR as qualitatively discussed above, $R_{2,n}^{CP}(\tau)$ can be decomposed as

$$R_{2,n}^{CP}(\tau) = R_2^{mol} + R_{2,n}^{CP,df}(\tau) \tag{2}$$

where R_2^{mol} is the molecular tumbling contribution, while $R_{2,n}^{CP,df}(\tau)$ accounts for director fluctuations. In the presence of fast-motional processes only, the relaxation rate is independent of τ and the echoes' intensities in the CP sequence decay with the same (homogeneous) rate of the Free Induction Decay. On the contrary, if slow motions like director fluctuations are present, a dependence on τ is generally expected. In order to estimate $R_{2,n}^{CP,df}(\tau)$ one has to specify the residual spin hamiltonian, to choose the proper stochastic variables to characterize the actual configuration of the director field, and to model the dynamics of the fluctuations.

Because of the long-range elastic coupling between the director's components at different locations in the sample, one needs to

introduce a collective stochastic variable $\mathbf{q}$ to represent the istantaneous configuration of the director field in a discretized form. To this purpose we adopt an Average Director Frame (ADF) whose longitudinal axis is taken along the macroscopic director of the phase, $\bar{\mathbf{n}}$, while the tranverse axes are arbitrarily chosen; with respect to ADF, the director at each location has two independent transverse components n_x and n_y while $n_z \simeq 1$ is determined by the condition of unitary module of the vector (see Fig. 2). By imaging to divide the sample into small domains of microscopic dimension (but large enough to contain a sufficient number of molecules to allow the definition of the local director as an average ensemble property), $\mathbf{q}$ is taken as the collection of the transverse director components in all the domains labelled by their centers $\mathbf{r}_j$:

$$\mathbf{q} = (\ldots, n_x(\mathbf{r}_j), n_y(\mathbf{r}_j), \ldots) \tag{3}$$

In particular, the spin-probe molecule is assumed to be located in the microdomain centered at $\mathbf{r}_p$ (we neglect here the effect of translational diffusion of the probe across the microdomains). In the small-amplitude limit of director fluctuations, and on the basis of the standard modeling of the free-energy for the nematic phase [16,17], the stochastic fluctuations of $\mathbf{q}$ can be modeled as a Gaussian diffusive process [18]. Correspondingly one can adopt a Smoluchowski operator $\Gamma_{\mathbf{q}}$ for the multidimensional diffusion equation describing the time evolution of the non-equilibrium probability density $p(\mathbf{q}, t)$ whose long-time limit, $p_{eq}(\mathbf{q}) = \lim_{t\to\infty} p(\mathbf{q}, t)$, is the Boltzmann distribution at thermal equilibrium,

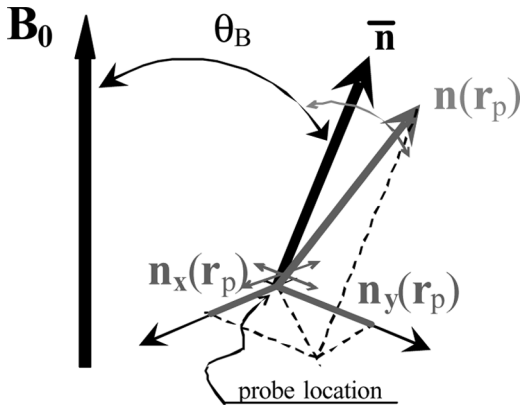

FIGURE 2 Components of the local director at probe's location with reference to the Average Director Frame (ADF).

$$\frac{\partial}{\partial t}p(\mathbf{q},t) = -\Gamma_{\mathbf{q}}p(\mathbf{q},t), \qquad \Gamma_{\mathbf{q}} = -\frac{\partial}{\partial \mathbf{q}}\cdot\mathbf{D}p_{eq}(\mathbf{q})\frac{\partial}{\partial \mathbf{q}}p_{eq}(\mathbf{q})^{-1} \tag{4}$$

D being the multidimensional diffusion matrix. The knowledge of $p_{eq}(\mathbf{q})$ and $p(\mathbf{q},t)$ allows one to evaluate the time-correlation function for the transverse components of the director in the microdomain at $\mathbf{r}_p$; as shown in the following, the relaxation rate $R_{2,n}^{CP,df}(\tau)$ is determined by such a type of correlation function.

Coming back to the spin hamiltonian, for a deuterated probe one has to take into account both the Zeeman contribution, H_{Zeeman}, and the quadrupolar contribution H_Q. By assuming a uniaxial electric field gradient tensor, H_Q depends on the istantaneous orientation of the principal axis of such a tensor (i.e., the direction of the C-D bond) with respect to the magnetic field. First we shall assume that the transverse relaxation (adiabatic spin-spin process) is much faster than the longitudinal (spin-lattice) process. Accordingly, the *Secular Approximation* can be applied by retaining only the longitudinal component I_Z of the nuclear spin operator with reference to the MRF. The fast molecular tumbling with respect to the local director leaves a residual hamiltonian of the form

$$H_Q(\mathbf{q}) = -\hbar\omega_Q(\mathbf{q})(I_Z^2 - 2/3) \tag{5}$$

where the characteristic frequency $\omega_Q(\mathbf{q})$ can be decomposed as

$$\omega_Q(\mathbf{q}) = \omega_Q^0 + \delta\omega_Q(\mathbf{q}) \tag{6}$$

where ω_Q^0 is the average quadrupolar splitting,

$$\omega_Q^0 = \frac{2\Delta}{3}P_2(\cos\theta_B) \tag{7}$$

with $\Delta = (9e^2Qq/8\hbar)S_Q$, $3e^2Qq/4\hbar$ being the quadrupolar constant, while S_Q is the usual second-rank order parameter which quantifies the alignment of the C-D bond of the molecule with respect to the local director, θ_B is the angle between the macroscopic director and the magnetic field, and $P_2(\cos\theta_B)$ is the second-rank Legendre polynomial. In practice, given the spectral splitting $\Delta\upsilon_Q(0^\circ)$ expressed in Hz and measured with the sample oriented at $\theta_B = 0^\circ$, the parameter Δ can be estimated as $\Delta \cong 2\pi \times 3/4\Delta\upsilon_Q(0^\circ)$. The contribution $\delta\omega_Q(\mathbf{q})$ in Eq. (6) is the part of the quadrupolar frequency which is modulated by director fluctuations, and its explicit form in terms of transverse components of the local director field at probe's location is given as [8]

$$\delta\omega_Q(\mathbf{q}) = \Delta\Big\{-P_2(\cos\theta_B)(n_x^2 + n_y^2) + 2\sin\theta_B\cos\theta_B n_x(1 - n_x^2 - n_y^2)^{1/2} + \sin^2\theta_B(n_x^2 - n_y^2)/2\Big\} \tag{8}$$

One should recognize that $\delta\omega_Q(\mathbf{q})$, which is proportional to the parameter Δ, is strongly affected by the orientation θ_B of the sample. In particular one can devise two situations named the "canonical" orientations (see Fig. 3) for the sample collinear ($\theta_B = 0^\circ$) or perpendicular ($\theta_B = 90^\circ$) with respect to the magnetic field. In these particular cases the expression above reduces to

$$\theta_B = 0^\circ:\ \delta\omega_Q(\mathbf{q}) = -\Delta(n_x^2 + n_y^2) \tag{9}$$

and

$$\theta_B = 90^\circ:\ \delta\omega_Q(\mathbf{q}) = \Delta n_x^2 \tag{10}$$

Therefore, in these situations, the fluctuating part of the quadrupolar frequency depends on the director's components only through second-rank powers. For samples oriented at angles θ_B between 0° and 90° (and sufficiently far from these extremes), in the limit of small amplitude fluctuations of the director, Eq. (8) can be approximated by retaining only the leading first-rank powers of the transverse components so leading to the so-called "linear approximation" for the spin hamiltonian [6]:

$$0^\circ < \theta_B < 90^\circ,\ \overline{n_x^2}, \overline{n_y^2} << 1:\ \delta\omega_Q(\mathbf{q}) \approx 2\Delta\cos\theta_B\sin\theta_B n_x \tag{11}$$

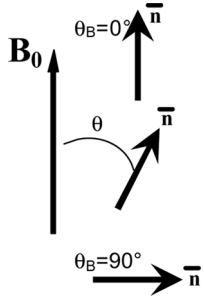

FIGURE 3 Geometries of measure in the ^{2}H-NMR experiments: Canonical orientations with average director parallel or perpendicular to the magnetic field ($\theta_B = 0^\circ$ and $\theta_B = 90^\circ$) and the general case.

Once the stochastic operator and the residual spin hamiltonian have been defined, the evolution of the density matrix operator $\rho(\mathbf{q},t)$ between two pulses in the CP sequence is obtained, in principle, by solving the SLE,

$$\frac{\partial}{\partial t}\rho(\mathbf{q},t) = -\left[iH_Q^{\times}(\mathbf{q})/\hbar + \Gamma_{\mathbf{q}} + R_2^{mol}\right]\rho(\mathbf{q},t) \tag{12}$$

where $H_Q^{\times}(\mathbf{q})$ denotes the spin super-operator (i.e., the commutator) in the Magnetic Rotating Frame (MRF) rotating at the frequency of the Zeeman interaction shifted by ω_Q^0. In order to describe the full CP experiment, one has to account also for the action of the radiofrequency pulses assumed to have duration so short to allow one to transform the density matrix operator under istantaneous rotations about the MRF axes. The signal experimentally detected, which is proportional to the component of the macroscopic magnetization on the transverse plane of MRF, is related to the expectation value of the corresponding I_Y spin operator:

$$I(t) \propto \int d\mathbf{q}\,\mathrm{Tr}\{I_Y\rho(\mathbf{q},t)\} \tag{13}$$

where "Tr" stands for the trace over the nuclear spin states.

By formally solving Eq. (12) with the effect of the istantaneous pulses, starting from the initial condition $\rho(\mathbf{q},0^+) \propto I_Y p_{eq}(\mathbf{q})$ just after the first $(\pi/2)_X$ pulse, and by elaborating Eq. (13), one gets the following compact result

$$I(2n\tau)/I(0) = e^{-2n\tau R_2^{mol}}\,\mathrm{Re}\{G_{CP}(2n\tau)\} \tag{14}$$

where $G_{CP}(2n\tau)$ is a characteristic function to be evaluated by solving the following nested integral structure [6]

$$G_{CP}(2n\tau) = \int d\mathbf{q}\ldots \underbrace{e^{-\Gamma_{-\tau}}e^{-\Gamma_{+\tau}}\underbrace{e^{-\Gamma_{+\tau}}e^{-\Gamma_{-\tau}}\underbrace{e^{-\Gamma_{-\tau}}e^{-\Gamma_{+\tau}}p_{eq}(\mathbf{q})}_{n=1}}_{n=2}}_{n=3} \tag{15}$$

The sequence of (alternating) pairs of exponential operators in Eq. (15) has to be enlarged up to n times for the specific n-th echo. Each exponential operator, $\exp\{-\Gamma_{+\tau}\}$ or $\exp\{-\Gamma_{-\tau}\}$, depends parametrically on the pulse-spacing τ and acts only on the stochastic variables when applied to a function, since $\Gamma_{\pm} = \pm i\delta\omega_Q(\mathbf{q}) + \Gamma_{\mathbf{q}}$. As we have shown in previous works [6–8], if the fluctuations are

modeled as a Gaussian process, such a characteristic function can be more easily evaluated by turning to the Fourier-transform functional dependence conjugated to variable **q** (in this way the above integral structure is converted into a sequence of deterministic time evolutions for proper functions of the conjugate variable). The complexity of the formal treatment to get $G_{CP}(2n\tau)$ depends dramatically on the specific form of $\delta\omega_Q(\mathbf{q})$. In all situations, the characteristic function can be found in the form

$$G_{CP}(2n\tau) = e^{-a(2n\tau)} \tag{16}$$

but the evaluation of exponent $a(2n\tau)$ requires the use of quite different tools on passing from the case of linear approximation on $\delta\omega_Q(\mathbf{q})$ to the cases of canonical orientations (second order terms only) or to the general case of first and second order terms together.

In the range of validity of the linear approximation for $\delta\omega_Q(\mathbf{q})$, i.e. for the nematic phase oriented at θ_B far enough from canonical angles, the exponent in Eq. (16) can be found by solving an iterative scheme which provides the value of $a(2n\tau)$ once the value of the coefficient at the previous pulse-time, $a(2n\tau - 2\tau)$, is known, and starting from the initial term $a(0) = 0$. For the relaxation rate defined by Eq. (1) one gets the explicit relation [6]

$$R_{2,n}^{CP}(\tau) = R_2^{mol} + \frac{(2\Delta \sin\theta_B \cos\theta_B)^2}{2\tau}\left\{-4\sum_{k=0}^{n-2} g(2k\tau) + \right.$$
$$\left. +(-1)^n[(-1)^k g(2n\tau - 2\tau) - 4g(2n\tau - \tau) + g(2n\tau)]\right\} \tag{17}$$

where the function $g(t)$ contains the features of the specific fluctuation process, and it is given by the following double-time integral of the time-correlation function for the transverse component of the local director at probe's location:

$$g(t) = \int_0^t dt' \int_0^{t'} dt'' \overline{n_x(0)n_x(t'')} \tag{18}$$

As a matter of fact, we have shown that the dependence of $R_{2,n}^{CP}(\tau)$ on the cycle number n is rather weak for $n \geq 5$ [6]. Consequently, the asymptotic rate $R_{2,\infty}^{CP}(\tau)$ for $n \to \infty$ can be adopted. If one expands the time-correlation function as a general weighted sum of exponential decays, i.e.,

$$\overline{n_x(0)n_x(t)} = \sum_l \sigma_l^2 e^{-t/\tau_l} \tag{19}$$

with amplitudes σ_l^2 and characteristic times τ_l to be derived on the basis of the assumed model for director fluctuations, the following asymptotic limit is found

$$R_{2,\infty}^{CP}(\tau) = R_2^{mol} + (2\Delta \sin\theta_B \cos\theta_B)^2 \sum_l \sigma_l^2 \tau_l [1 - (\tau_l/\tau)\tan h(\tau/\tau_l)] \quad (20)$$

Interestingly, this expression for the asymptotic limit of the transverse relaxation rate was derived also by Luz and Meiboom (but in a completely different framework) within the Redfield regime of motion [19] which, however, can not be applied to director fluctuations. This result holds in all generality, and to proceed further one has to specify the correlation function Eq. (19) by parametrizing the ingredients (energetics and dynamic parameters) of the Gaussian fluctuations on the basis of a specific physical model (this will be done in the next section by adopting the basic de Gennes' modeling of fluctuations in nematics).

A rather different scenario emerges when second order terms in $\delta\omega_Q(\mathbf{q})$ have to be taken into account. In this case, the exponent $a(2n\tau)$ cannot be evaluated by means of closed expressions, but it should be calculated by solving convolution-like equations as described in Ref. [7] for the situation of canonical orientations, and in Ref. [8] where both first and second order terms have been accounted to describe the whole angular dependence of the relaxation rate. However, it turns out that the required input information about dyamics is still contained in the time-correlation function $\overline{n_x(0)n_x(t)}$ alone. An important result was that approximate solutions for the relaxation rate can be found for canonical orientations if de Gennes' theory of fluctuations in nematics is adopted under a reasonable parametrization of the system, as outlined in the next section.

3. ANGULAR DEPENDENCE OF THE RELAXATION RATE ACCORDING TO DE GENNES' MODELING OF FLUCTUATIONS IN NEMATIC PHASES

De Gennes' theory of director fluctuations in well aligned nematic phases is based on the modeling of the elastic free-energy density of the sample subject to bend, twist and splay distortions [16,17]. By performing a Fourier transform of the director field, in the limit of small amplitude of fluctuations one finds that the transformed components are independent Gaussian variables, with each component associated to a wavevector $\mathbf{k}$ of the Fourier-transform. The module of $\mathbf{k}$ varies from a minimum value determined by the extension of the sample or by the presence of long-range coherence lengths (and which is usually

taken as vanishing in the limit of macroscopic dimension of the domain), and a maximum value $k_c = 2\pi/\lambda_c$ where λ_c is the so-called short-wavelength cutoff identified as the smallest linear extension of the microdomains into which the nematic sample can be partitioned (λ_c is usually taken of the order of some molecular lengths, even if a well established definition of such a cutoff is still missing). On the top of this normal-modes decomposition from energetics, a diffusive bahaviour with a single relaxation time per mode, $\tau(\mathbf{k})$, is invoked. Such a characteristc time depends on the viscoelastic parameters of the material, that is, on the three elastic constants for splay, twist and bend distortions, and on the six Leslie's viscosity coefficients [16]. For nematic samples constituted by low-molecular weight mesogens, one usually invokes the so-called "one constant approximation" which consists on adopting an average elastic constant $\mathbf{K}$ and an-effective viscosity η_{eff}. Within such an approximation one gets $\tau(\mathbf{k}) = \eta_{eff}/(Kk^2)$ where $\mathbf{k}$ is the module of the wavevector. Coming back from Fourier-transformed director field to the n_x and n_y components at probe's location (which are statistically independent and equivalent due to the axial symmetry of the phase), one finds that the time-correlation function Eq. (19) that we need to incorporate in the description of the NMR experiment, has a multiexponential decay given by

$$\overline{n_x(0)n_x(t)} = \overline{n_x^2}\frac{1}{k_c}\int_0^{k_c} dk\, e^{-t/\tau(\mathbf{k})} = \overline{n_x^2}\frac{\sqrt{\pi}}{2}\frac{\mathrm{erf}\left(\sqrt{t/\tau_c}\right)}{\sqrt{t/\tau_c}} \tag{21}$$

where $\overline{n_x^2} = (k_B T/2\pi^2)k_c$ is the amplitude of fluctuations, $\tau_c = \eta_{eff}/(Kk_c^2)$, and $\mathrm{erf}(\cdot)$ is the Error Function.

By using this model for the correlation function entering Eq. (20), the following asymptotic limit of the relaxation rate for non-canonical orientations has been obtained [6]

$$R_{2,\infty}^{CP}(\tau) = R_2^{mol} + c(2\sin\theta_B\cos\theta_B)^2\frac{k_B T}{2\pi^2}\Delta^2(\eta_{eff}/K^3)^{1/2}\sqrt{\tau} \tag{22}$$

where $c = 0.7933$. The generalization beyond the "one constant approximation" has been presented in refs [10,20], by obtaining an expression like Eq. (22) but with, in place of η_{eff}/K^3, a different factor depending on all viscoelastic parameters. We stress that Eq. (22) does not include the cutoff k_c; this represents a positive feature of the present theory as long as such a parameter cannot be estimated without ambiguities but, on the other hand, the lack of dependence on k_c prevents the possibility to estimate it from data fitting. Moreover,

one should notice the dependence on $\sqrt{\tau}$ which is a signature of director fluctuations in a three-dimensional sample (while a linear dependence on τ is found for bidimensional systems like biomembranes [9]). Let us suppose to be able to perform an experiment with the sample oriented at a fixed angle θ_B with respect to the magnetic field; once the parameter Δ is estimated from the splitting of the quadrupolar doublet in the spectrum at canonical orientation, and if R_2^{mol} is not exceedingly large, the fit of the experimental dispersion profile of $R_{2,\infty}^{CP}(\tau)$ versus τ by using Eq. (22) allows one to get the ratio η_{eff}/K^3. Then, if one of the parameters η_{eff} or K is known from an independent experiment, the other can be determined. However, common low-molecular weight nematics are oriented at canonical angles $\theta_B = 0^\circ$ or $\theta_B = 90^\circ$ by the magnetic field, depending on the sign of the anisotropy of the diamagnetic susceptibility. Thus, unless special techniques to pin the sample at fixed angles are employed (like application of competitive strong electric fields), the canonical cases are the most common experimental situations.

By adopting the standard modeling of fluctuations in nematic phases, we have performed model calculations for canonical orientations solving numerically the convolution-like equations derived in ref. [7]. It turned out that the transverse relaxation is strictly controlled by the magnitude of the dimensionless parameter $\bar{\varepsilon} = \Delta\overline{n_x^2}\tau_c$. By adopting $e^2Qq/4h = 170\,\text{kHz}$ and an order parameter of $S_Q = 0.7$ for the C-D bond, $\overline{n_x^2} \simeq 0.01$ corresponding to an angular amplitude of fluctuations less than ten degrees, and by adopting $\tau_c \simeq 10^{-8}\,\text{s}$ which lays close to the characteristic times of single-molecule reorientations, the estimate $\bar{\varepsilon} \simeq 10^{-4}$ is expected to be a reasonable guess for common nematics. In this limit we found that the transverse relaxation rate of the echoes' intensities in the CP sequence is essentially independent of τ (and it is the same of homogenous relaxation rate of the Free Induction Decay). Moreover, the following approximation has been derived [7]

$$\theta_B = 0^\circ\colon\ R_{2,\infty}^{CP} = R_2^{mol} + 2\Delta^2\left(\frac{k_BT}{2\pi^2}\right)^2\frac{\eta_{eff}}{K^3}\ln\left[\frac{2\pi^2}{k_BT}\frac{B_\infty}{\Delta}\frac{K^2k_c}{\eta_{eff}}\right] \tag{23}$$

where $B_\infty = 0.0944$; the relaxation rate for $\theta_B = 90^\circ$ has the same expression, but without the factor 2 in the contribution of director fluctuations; the relaxation rate for $\theta_B = 90^\circ$ has the same expression, but without the factor 2 for the contribution of director fluctuations. When θ_B approaches the canonical orientations, the contribution to $R_{2,\infty}^{CP}$ due to director fluctuations does not vanish as it would be erroneously obtained by means of Eq. (22). Of course, when θ_B is close enough to

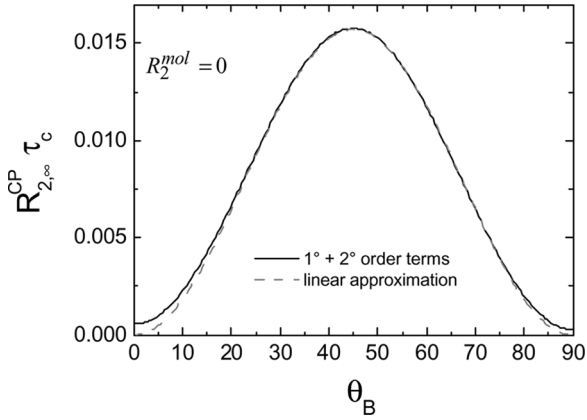

FIGURE 4 Angular dependence of the contribution of director fluctuations to the transverse relaxation rate $R_{2,\infty}^{CP}$. The calculation has been performed for $\tau/\tau_c = 10$ where τ_c is the shortest relaxation time of director fluctuations (taken as scaling factor), for the large value $\bar{\varepsilon} = 0.01$ of the control-parameter, and for $\overline{n_x^2} = 0.01$.

0° or 90°, both first and second order terms in $\delta\omega_Q(\mathbf{q})$ have to be considered. In this general case, full calculations of the whole angular profile of $R_{2,\infty}^{CP}$ (for a fixed τ) have been presented in ref. [8]. A representative profile is shown in Figure 4.

Notice that, in the case of canonical orientations, the cutoff parameter k_c explicitly enters the expression of $R_{2,\infty}^{CP}$. In principle, if η_{eff} and K are determined by independent experiments, or if the measures at canonical orientations were integrated with experiments at non-canonical angles, k_c could be estimated from experimental data, hence the short-wavelength cutoff λ_c could be determined unambiguously and this might provide useful information in the modeling of such a "vague" parameter.

It should be stressed here the important point that the full information about the physical parameters controlling amplitude and rates of director fluctuations can be obtained only if $R_{2,\infty}^{CP,df}$ dominates over R_2^{mol}. As a matter of fact, the presence of a relevant molecular contribution R_2^{mol} may spoil such an analysis. If Eq. (23) is rewritten to highlight the factor $\overline{n_x^2}$, one sees that $R_{2,\infty}^{CP}$ depends linearly on $\overline{n_x^2}$ for non-canonical angles while it depends quadratically on $\overline{n_x^2}$ at canonical orientations. Thus, the contribution of director fluctuations to the relaxation rate may drop strongly right in the cases which are more common from the point of view of the experimental

setup, and where the information about the cutoff k_c could be recovered. When θ_B tends to 0° or to 90°, the molecular contribution may become dominant and the measured τ-independent relaxation rate could be nothing but R_2^{mol}. Both the contributions from director fluctuations and molecular tumbling depend quadratically on the splitting parameter Δ. In order to minimize the molecular contribution, one has to take care of the choice of the proper probe molecule. The probe should be well aligned with respect to the local director (so to leave a relevant residual quadrupolar spin hamiltonian) and have fast tumbling; in fact one expects that $R_2^{mol} \sim \Delta^2 \tau_p$ where τ_p is the average relaxation time of the tumbling motions [21]. By keeping the average elastic constant within the typical range of variability (say, of the order of pN), the relevant parameter which determines the magnitude of the contribution from director fluctuations is the effective viscosity. Indeed, effects of director fluctuations on the transverse relaxation rate has been observed without ambiguities in nematic polymers [10], where the effective viscosity was estimated of the order of 5×10^3 Pa s, that is, much larger than typical viscosity coefficients in low-molecular weight nematics.

Now we shall compare the expression Eq. (23), deriving from the slow-motional description of the experiment, with the relation normally employed and based on a fast-motional approach [11]. By using standard Redfield theory to get the transverse relaxation rate (i.e., the homogeneous contribution of spin-spin relaxation to the spectral linewidths) one has to evaluate spectral densities of time-correlation functions for second-order powers of the transverse components of the local director, $\overline{n_x(0)^2 n_x(t)^2}$. Such a formal problem has been tackled by Vold and Vold who have exploited the formal properties of Gaussian fluctuations which allow one to reduce these correlation functions to square powers of $\overline{n_x(0) n_x(t)}$ [12]. However, the resulting relaxation rate is diverging at low frequencies, and this is strictly a consequence of employing the Redfield theory outside its region of validity. As we have emphasized from the beginning, director fluctuations have always slow components which dictate the use of a more general methodology like the slow-motional theory. In this way, as shown in Eq. (23), one naturally derives a relaxation rate devoid of any divergence.

However, the authors of ref. [12], in order to recover a well defined result from the Redfield theory, have modified *a posteriori* the relation for the transverse relaxation rate by inserting a damping term based on the parameter $\omega_l = (K/\eta_{eff}) k_l^2$, where k_l is the wavevector associated to *some* linear extension of the nematic domain. For a macroscopic sample, k_l is taken as $k_l = \xi(B_0)^{-1}$, where $\xi(B_0) = (K\mu_0/\Delta\chi)^{1/2}/B_0$ is

the magnetic coherence length [15], $\Delta\chi = \chi_{||} - \chi_{\perp}$ being the anisotropy of the magnetic susceptivity tensor, and $\mu_0 = 4\pi \times 10^{-7}\mathrm{NA}^{-2}$ the magnetic permeability in vacuum. The final expression for the relaxation rate, taken from Ref. [11] and adapted to our notation, is

$$\theta_B = 0^\circ\colon R_2 = R_2^{mol} + \frac{\pi}{6} \times 2\Delta^2 \left(\frac{k_B T}{2\pi^2}\right)^2 \frac{\eta_{eff}}{K^3} \ln\left[\frac{\omega_c}{\omega_l}\right] \qquad (24)$$

(fast motional analysis)

where $\omega_c = 1/\tau_c = (K/\eta_{eff})k_c^2$ is the so-called high-frequency cutoff of director fluctuations.

To compare such an expression with the outcome from the slow-motional analysis, we rewrite Eq. (23) as follows,

$$\theta_B = 0^\circ\colon R_2 = R_2^{mol} + 2\Delta^2 \left(\frac{k_B T}{2\pi^2}\right)^2 \frac{\eta_{eff}}{K^3} \ln\left[\frac{\omega_c}{\omega_\Delta}\right] \qquad (25)$$

(slow motional analysis)

where

$$\omega_\Delta = \frac{k_B T}{2\pi^2} \frac{\Delta}{B_\infty} \frac{k_c}{K} \qquad (26)$$

Notice that, in this way, Eqs. (24) and (25) appear, qualitatively, very similar. The main difference lays in the argument of the logarithm for the presence of two characteristic frequencies, ω_l and ω_Δ, which may differ by orders of magnitude. In fact, for magnetic fields of the order if 7 Tesla, by taking the reasonable values of $\Delta\chi \simeq 10^{-7}$ (c.g.s. units), $K \simeq 10\,\mathrm{pN}$, and $\eta_{eff} \simeq 0.5$ Pa s for low-molecular-weight nematics, one gets that ω_l is of the order of $10^3 - 10^4\,\mathrm{s}^{-1}$. On the contrary, with the parameters previously fixed one finds that $\omega_\Delta \simeq \Delta$, that is, ω_Δ should be in the range $10^5 - 10^6\,\mathrm{s}^{-1}$. Furthermore, even if the two frequencies were comparable, $\omega_l \simeq \omega_\Delta$, a completely different relaxation rate would result because of the extra numerical factor $\pi/6 \simeq 0.5$ in Eq. (24).

CONCLUSIONS

In this paper, starting from a review of our previous works concerning the slow-motional treatment of director fluctuations effects in NMR, we have addressed the analysis towards the transverse relaxation rate detected at canonical orientations ($\theta_B = 0^\circ$ or 90°) which represent the normal conditions of alignment of a nematic sample with respect to the magnetic field. We have provided the formal expressions to be

employed for the analysis of the experimental results, and discussed the relative contribution of director fluctuations and molecular tumbling on approaching the canonical orientations where the former contributions becomes negligible since it is proportional to the square of the amplitude of the fluctuations. Then we have discussed in details about the differences of the outcome from the present slow-motional approach with respect to the normally employed relation derived according to the Redfield theory. By taking the most relevant case from the point of view of the experimental setup, $\theta_B = 0^\circ$, we have shown that the two approaches provide expressions for the transverse relaxation rate which can be put in forms qualitatively similar (Eqs. (24) and (25)). However, an extra numerical factor appears in the expression from the Redfield-like treatment. Morevor, in the fast-motional treatment a low-frequency cutoff has to be introduced ad hoc in order to avoid a divergence on the relaxation rate, while in the slow-motional approach this cutoff is naturally replaced by a scaling frequency (ω_Δ in Eq. (26)) which derives naturally from the mathematical elaboration of the stochastic Liouville equation in the regime of slow motions.

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