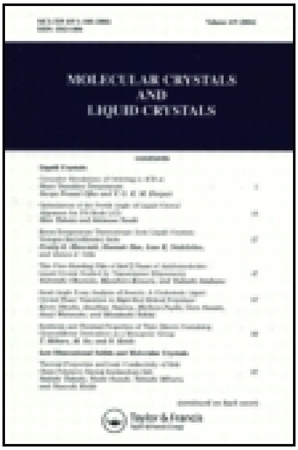

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# Transverse Nuclear Spin Relaxation in Nematic Liquid Crystals. Effect of the Anisotropy of the Viscoelastic Parameters

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# TRANSVERSE NUCLEAR SPIN RELAXATION IN NEMATIC LIQUID CRYSTALS. EFFECT OF THE ANISOTROPY OF THE VISCOELASTIC PARAMETERS

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*Transverse nuclear spin relaxation experiments, employing the Carr-Purcell-Meiboom-Gill (CP) sequence, are analyzed under slow-motional conditions for deuterated probes experiencing order director fluctuations in nematic phases. The pulse-spacing dependent transverse relaxation rate is expressed as a function of all the viscoelastic parameters of the liquid crystal. The theory describes the effects of the anisotropy of the viscoelastic parameters on the dispersion profile beyond the commonly applied one-constant approximation.*

*Keywords*: transverse nuclear spin relaxation; order director fluctuations

## 1. INTRODUCTION

Transverse nuclear spin relaxation experiments, employing the Carr-Purcell-Meiboom-Gill (CP) sequence [1], represent a powerful tool for probing fluctuations of the local orientational director in partially ordered phases [2]. Recently, a slow-motional theory has been presented for the analysis of deuteron ($^2$H) NMR experiments performed on nematic liquid crystals [3]. The use of a slow-motional approach is necessary because of the intrinsic overlap of the magnetic anisotropies, due to the quadrupolar interactions (expressed in angular frequency units), and the slow components

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of the frequency spectrum of the director fluctuations. Thus, the formal description of the experiment requires the solution of the Stochastic Liouville Equation [4,5] for the evolution of the nuclear spin states affected by the order director fluctuations.

An analytical solution of the problem has been obtained for non-canonical director orientations on condition that (i) the amplitude of the fluctuations is small, and (ii) the order director fluctuations constitute a multidimensional Gaussian process [6]. Under these conditions, analytical expressions can be derived for the pulse-spacing dependence of the transverse $^2$H spin relaxation rates in CP sequences [3]. So far, however, analysis of these relaxation rates was performed within a simplified model for nematic director fluctuations, invoking the so-called ***one-constant approximation*** for both the elastic and the viscosity parameters.

In the present work an extension of the theory is presented by introducing a detailed description of director fluctuations on the basis of all the viscoelastic parameters of the medium, i.e. six Leslie viscosity coefficients and three elastic constants for ***splay***, ***twist*** and ***bend*** deformation [12,13]. Consequently, mode-dependent viscosities [7] are considered in the analysis of the fluctuation process. Moreover, we specify the limiting conditions under which the experiments can be described by a reduced set of viscoelastic parameters.

The paper is organized as follows: in Section two, the de Gennes' theory for director fluctuations in nematics is summarized and the viscoelastic parameters are introduced. In Section three, we outline the slow-motional theory for the description of the CP multipulse experiment. In Section four, model calculations are presented by selectively varying the viscosity coefficients of a nematic liquid crystal. Particular reference is given to the nematic phase of 4-methoxybenzylidene-4′-n-butylaniline (MBBA). In Section five, the results are summarized and the appropriate procedures for the analysis of experimental data are presented.

## 2. DIRECTOR FLUCTUATIONS IN NEMATICS

The basic de Gennes' theory of fluctuations in nematics will be employed [7]. First, we introduce the Average Director Frame (ADF), $(\mathbf{x}, \mathbf{y}, \mathbf{z})$, where the z-axis specifies the average direction of molecular alignment, $\vec{n}_0$. By assuming isotropy of the orientational properties about the z-axis, the orthogonal directions are arbitrarily chosen. In the following, the angle between $\vec{n}_0$ and the external magnetic field, $\vec{B}_0$, is denoted by $\theta_B$. With reference to the ADF, the fluctuating director at the location $\vec{r}_p$ of the probe-molecule can be written as $\vec{n}(\vec{r}_p) = (n_x, n_y, n_z)$. In case of small-amplitude fluctuations, the situation $n_x, n_y \approx 0$, $n_z \approx 1$ is realised.

The normal mode analysis of the fluctuation process is obtained by the Fourier expansion of the position dependence of the director field. For a given partition of the sample volume $V$ into elementary cells of volume $V_c$ , the adopted transformation can be written (in discrete form) as

$$n_j(\vec{r}) = V^{-1}\sum_{\mathbf{q}} e^{-i\mathbf{q}\cdot\vec{r}}\tilde{n}_j(\mathbf{q}), \quad \tilde{n}_j(\mathbf{q}) = V_c\sum_{\vec{r}} e^{i\mathbf{q}\cdot\vec{r}}n_j(\vec{r}) \tag{1}$$

where $\tilde{n}_j(\mathbf{q})$ are the transformed components of the director field for $\mathrm{j} = x, y, z$, and $\mathbf{q}$ is the wavevector in the reciprocal space. Following de Gennes [7], we introduce a $\mathbf{q}$-dependent system of axis, qF, identified by the orthogonal unit vectors $qF = (\vec{e}_1(\mathbf{q}), \vec{e}_2(\mathbf{q}), \vec{e}_3(\mathbf{q}) \equiv \vec{n}_0)$, with $\vec{e}_1(\mathbf{q})$ along the wavevector component $\mathbf{q}_\perp$ orthogonal to $\vec{n}_0$ (see Fig. 1). The components in the qF frame of the Fourier-transformed director are denoted as $(\tilde{n}_1(\mathbf{q}), \tilde{n}_2(\mathbf{q}), \tilde{n}_3(\mathbf{q}) = \tilde{n}_z(\mathbf{q}))$.

Under the assumption of small-amplitude fluctuations, the free-energy of the sample can be written as a sum of independent contributions, quadratic in the orthogonal components of the transformed director field, $\tilde{n}_\alpha(\mathbf{q})$ for $\alpha = 1, 2$ [7]:

$$F = (2V)^{-1}\sum_{\mathbf{q}}\sum_{\alpha=1,2} |\tilde{n}_\alpha(\mathbf{q})|^2\{K_3q_z^2 + K_\alpha q_\perp^2\}. \tag{2}$$

Here $\mathbf{q} = q_z\vec{n}_0 + q_\perp\vec{e}_1(\mathbf{q})$, and $K_1, K_2, K_3$ are the *splay*, *twist* and *bend* elastic constant respectively. Notice the mixing between *bend* and *splay* for $\tilde{n}_1$ distortions, and between *bend* and *twist* for $\tilde{n}_2$ distortions.

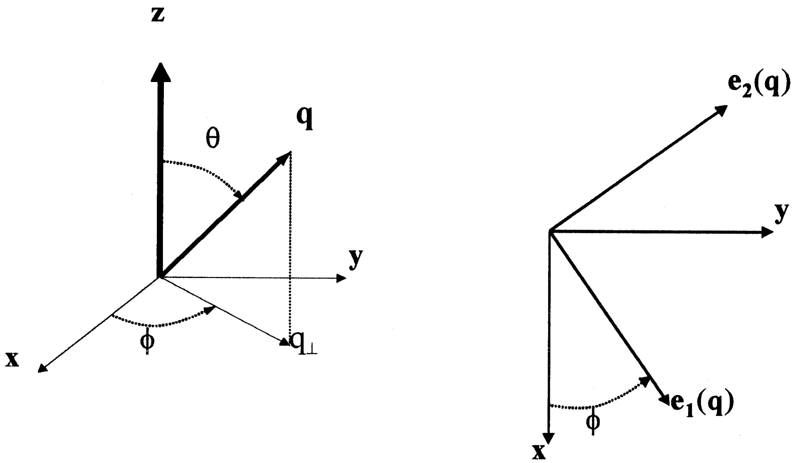

**FIGURE 1** Reference systems of axes: Average Director Frame (ADF), $(\mathbf{x}, \mathbf{y}, \mathbf{z})$, and qF $(\vec{e}_1(\mathbf{q}), \vec{e}_2(\mathbf{q}), \vec{e}_3(\mathbf{q})$.

The quadratic form of the free-energy, Eq. (2), allows one to model the real and the imaginary parts of the transformed director field, $\tilde{n}_\alpha = \tilde{n}'_\alpha + i\tilde{n}''_\alpha$, as independent stochastic Gaussian processes [6]. Consequently, the time-autocorrelation function can be expressed as

$$\overline{\tilde{n}'_\alpha(\mathbf{q})_0 \tilde{n}'_\alpha(\mathbf{q})_t} = \overline{\tilde{n}''_\alpha(\mathbf{q})_0 \tilde{n}''_\alpha(\mathbf{q})_t} = \overline{\tilde{n}'_\alpha(\mathbf{q})^2} e^{-t/\tau_\alpha(\mathbf{q})}, \tag{3}$$

where the mean square amplitude and relaxation time for each mode are given by [7,12]

$$\overline{\tilde{n}'_\alpha(\mathbf{q})^2} = \frac{k_B T V}{2(K_3 q_z^2 + K_\alpha q_\perp^2)}, \quad \tau_\alpha(\mathbf{q}) = \left(\frac{K_3 q_z^2 + K_\alpha q_\perp^2}{\eta_\alpha(\mathbf{q})}\right)^{-1}. \tag{4}$$

Here $\eta_\alpha(\mathbf{q})$ are wavevector-dependent viscosities for the mixed distortions $\alpha = 1, 2$. According to de Gennes, these viscosities are related to the six Leslie coefficients, $\alpha_i$, by

$$\begin{aligned} \eta_1(x) &= \gamma_1 - \frac{[\alpha_3(1-\mathrm{x}^2) - \alpha_2 x^2]^2}{\eta_b(1-\mathrm{x}^2)^2 + (\alpha_1+\alpha_3+\alpha_4+\alpha_5)\mathrm{x}^2(1-x^2) + \eta_c x^4}, \\ \eta_2(x) &= \gamma_1 - \frac{\alpha_2^2 x^2}{\eta_a(1-\mathrm{x}^2) + \eta_c x^2}, \end{aligned} \tag{5}$$

where $x = \cos\theta$ (see Fig. 1), $\eta_a, \eta_b, \eta_c$ are the Miesowicz viscosities

$$\begin{aligned} \eta_a &= \alpha_4/2, \\ \eta_b &= (\alpha_3+\alpha_4+\alpha_6)/2, \\ \eta_c &= (-\alpha_2+\alpha_4+\alpha_5)/2, \end{aligned} \tag{6}$$

and $\gamma_1 = \alpha_3 - \alpha_2$ is the ***rotational viscosity***.

The time-autocorrelation function for the transverse components of the local fluctuating director can now be calculated from Eq. (3) by using the Fourier expansion Eq. (1). For convenience, we now adopt the ***continuum limit***, which corresponds to an infinitesimal spacing in the reciprocal space for $V \to \infty$, i.e.

$$V^{-1} \sum_{\mathbf{q}} \to \frac{1}{(2\pi)^3} \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \int_0^{q_c} dq\, q^2. \tag{7}$$

In Eq. (7), $q_c$ is the upper cutoff of the wavevector components associated with the smallest sample size for which a collective property like the director is still meaningful. The resulting autocorrelation function for the $n_x(\vec{r})$ transverse component is finally given by [8]

$$\overline{n_x(\vec{r}(0)) n_x(\vec{r}(t))} = \frac{k_B T}{8\pi^2} \sum_{\alpha=1,2} \int_0^{q_c} dq\, q^2 \int_0^{\pi} d\theta \sin\theta \frac{\tau_\alpha(q,\theta)}{\eta_\alpha(\theta)} e^{-t/\tau_\alpha(q,\theta)}. \tag{8}$$

## 3. TRANSVERSE RELAXATION DUE TO DIRECTOR FLUCTUATIONS

Recently, a slow-motional theory has been presented for the analysis of pulsed $^2$H NMR experiments performed on nematic liquid crystals [3]. In the following, we specifically consider the effect of order director fluctuations on the transverse relaxation rate in CP sequences.

Let us assume that the experimental observations refer to a time window such that longitudinal relaxation has negligible effects. Thus, we employ the ***Secular Approximation*** for the spin hamiltonian of the probe-molecule experiencing the fluctuations of the local director. The train of radiofrequency pulses in the CP sequence can be represented as $(\pi/2)_x - [\tau - (\pi/2)_y - \tau]_n$, where $\tau$ is the pulse-spacing. For convenience, we now introduce the specific transverse relaxation rate, $R_{2,n}^{CP}(\tau)$, characterizing the decrease of the echo intensity, $I(2n\tau)$, during cycle $n$:

$$I(2n\tau)/I(2(n-1)\tau) = \exp\{-2n\tau R_{2,n}^{CP}(\tau)\}. \tag{9}$$

The analysis of this experiment under slow-motional conditions requires the solution of the Stochastic Liouville Equation [4,5] for the time evolution of the density matrix describing the nuclear spin-states coupled to the fluctuating director. An analytical expression for the CP transverse relaxation rate $R_{2,n}^{CP}(\tau)$ can be derived if (i) the order director fluctuations constitute a (multidimensional) Gaussian process, as discussed in Section 2, and (ii) if the amplitudes of the fluctuations are small, i.e. $n_z(\vec{r}_p) \approx 1$. The second condition allows one to consider in the modulated part of quadrupolar spin-hamiltonian only those contributions which linearly depend on the transverse components of the local fluctuating director. Notably, such an approximation strictly holds only for non-canonical director orientations, i.e. $\theta_B \neq 0°, 90°$ [3]. Using the above approximations, the transverse relaxation rates $R_{2,n}^{CP}(\tau)$ can be specified as [3]:

$$\begin{aligned} R_{2,n}^{CP}(\tau) = R_2^0 + \frac{(\Delta\omega'_Q)^2}{2\tau}\Bigg\{ & -4\sum_{k=0}^{n-2} g(2k\tau) \\ & + (-1)^n[(-1)^k g(2n\tau - 2\tau) \\ & - 4g(2n\tau - \tau) + g(2n\tau)]\Bigg\} \end{aligned} \tag{10}$$

where $R_2^0$ is the contribution from the fast molecular motions, and the function

$$g(t) = \int_0^t dt' \int_0^{t'} dt'' \overline{n_x(0)n_x(t'')} \tag{11}$$

has to be evaluated from the autocorrelation function, Eq. (8), of the transverse component of the fluctuating director. In Eq. (10), the frequency-factor $\Delta\omega'_Q$ is given by [3]

$$\Delta\omega'_Q = 3\left(\frac{3e^2Qq}{4\hbar}\right)S_{MOL}\sin\theta_B\cos\theta_B, \tag{12}$$

where $3e^2Qq/4\hbar$ is the quadrupolar coupling constant, and $S_{MOL}$ is the second-rank orientational order parameter for the long-molecular axis of the probe-molecule with respect to the instantaneous local director. An expression similar to Eq. (10) has been derived for the transverse relaxation rate of $I = 1/2$ nuclei, such as $^{31}$P in the head groups of lipid molecules forming membrane vesicles [10]. In this case, the hamiltonian is modulated via the orientational-dependence of the chemical shift tensor.

It has been shown that the dependence of $R^{CP}_{2,n}(\tau)$ on the cycle number $n$ is rather weak for $n \geq 5$ [3]. Consequently, it is convenient to characterize the experimental data in terms of an asymptotic rate $R^{CP}_{2,\infty}(\tau)$, i.e. $n \to \infty$, which can be specified according to [3]:

$$R^{CP}_{2,\infty}(\tau) = R^0_2 + (\Delta\omega'_Q)^2 g_{LM}(\tau), \tag{13}$$

where the characteristic function $g_{LM}(\tau)$ is given by

$$g_{LM}(\tau) = \frac{k_BT}{8\pi^2}\sum_{\alpha=1,2}\int_0^{q_c} dq \int_0^{\pi} d\theta \sin\theta \frac{\tau_\alpha(q,\theta)}{K_3\cos^2\theta + K_\alpha\sin^2\theta} \left[1 - \frac{\tau_\alpha(q,\theta)}{\tau}\tanh\frac{\tau}{\tau_\alpha(q,\theta)}\right] \tag{14}$$

and the label "LM" has been introduced to recall the similarity with the Luz-Meiboom equation, derived for a *random-walk* stochastic process [11].

In order to evaluate the integral in Eq. (14), the change of variable $q \to z = \sqrt{\tau_\alpha(q,\theta)/\tau}$ is performed, yielding

$$g_{LM}(\tau) = \frac{k_BT}{8\pi^2}\tau^{1/2}\sum_{\alpha=1,2}\int_0^{\pi} d\theta \sin\theta \frac{\eta_\alpha(\theta)^{1/2}}{\left(K_3\cos^2\theta + K_\alpha\sin^2\theta\right)^{3/2}} \int_{\sqrt{\tau_\alpha(q_c,\theta)/\tau}}^{\infty} dz\left[1 - z^2\tanh z^{-2}\right] \tag{15}$$

where we have taken into account that for $q \to 0$ $\tau_\alpha(q,\theta)$ increases to infinity (see Eq. (4)). Since the accessible pulse spacing $\tau$ is generally much longer than the fastest relaxation time of the director fluctuations, we can safely assume that

$$\tau >> \tau_\alpha(q_c, \theta) \tag{16}$$

for both distortions $\alpha = 1, 2$ and for all angles $\theta$ in the range of the integration. Then, the lower integration boundary for $z$ in Eq. (15) can be extended to zero. Moreover, by changing the other integration variable from $\theta$ to $x = \cos\theta$, the following relation is obtained for $g_{LM}(\tau)$:

$$g_{LM}(\tau) = c\frac{k_B T}{4\pi^2} Q_{LM}\tau^{1/2}, \tag{17}$$

where the factor $Q_{LM}$is given by

$$Q_{LM} = \sum_{\alpha=1,2} \int_0^1 dx \frac{\eta_\alpha(x)^{1/2}}{\left[K_3 x^2 + K_\alpha(1 - \mathrm{x}^2)\right]^{3/2}}, \tag{18}$$

the functions $\eta_\alpha(x)$ are defined in Eq. (5), and the numerical constant results in

$$c = \int_0^\infty dz\left[1 - z^2 \tanh z^{-2}\right] = 0.7933. \tag{19}$$

Inserting Eq. (17) into Eq. (13) yields the following dispersion relation for the pulse spacing dependence of the transverse relaxation rate

$$R_{2,\infty}^{CP}(\tau) \propto \tau^{1/2} \tag{20}$$

if the molecular tumbling contribution $R_2^0$ is neglected. It should be mentioned that a square root dependence on $\tau$ was derived in ref. [3] within the one constant approximation for both the elastic constants and the viscosities. The previous analysis demonstrates that, if the condition Eq. (16) is satisfied, such a behavior is quite general and Eq. (18) should be employed in order to evaluate the proportionality factor $Q_{LM}$. Indeed, this square root dependence of the transverse relaxation rate on the pulse spacing has been observed experimentally for viscous nematics such as liquid crystal polymers [8,9]. Thus, by evaluating the proportionality factor $Q_{LM}$, this type of experiments can in principle supply accurate information on the director fluctuation process. Unfortunately, the integration in Eq. (18) cannot be performed analytically. This prevents the establishment of an explicit relation between $Q_{LM}$ and the different elastic and viscosity parameters. If, however, the $x$-dependence of the viscosities $\eta_\alpha(x)$ is neglected, i.e. if some (constant) *effective viscosities* $\bar{\eta}_1$ and $\bar{\eta}_2$ can be identified on the basis of suitable conditions for the Leslie coefficients, the integration in Eq. (18) is easily performed, yielding

$$Q_{LM} = \left(\frac{\bar{\eta}_1}{K_3 K_1^2}\right)^{1/2} + \left(\frac{\bar{\eta}_2}{K_3 K_2^2}\right)^{1/2}. \tag{21}$$

In Section 4, the conditions to use these effective viscosities $\bar{\eta}_1$ and $\bar{\eta}_2$ are discussed, and a comparison between the exact value of the factor $Q_{LM}$ (Eq. (18)) and its approximate form (Eq. (21)) is presented.

## 4. MODEL CALCULATIONS

The model calculations have been performed on the basis of the known viscoelastic parameters of MBBA (4-methoxybenzylidene-4′-n-butylaniline) in the nematic phase 10 K below the clearing point. The values for these parameters are listed in Table 1.

The parameter set in Table 1 has been considered as a starting set for subsequent selective variations of the magnitude of the coefficients. Any change of the Leslie coefficients must satisfy the following consistency conditions [13]:

$$\begin{aligned}
&(a)\ \alpha_2 < \alpha_3\\
&(b)\ \alpha_6 - \alpha_3 = \alpha_2 + \alpha_5\\
&(c)\ \alpha_4 \geq 0\\
&(d)\ 2\alpha_1 + 3\alpha_4 + 2\alpha_5 + 2\alpha_6 \geq 0\\
&(e)\ 2\alpha_4 + \alpha_5 + \alpha_6 \geq 0\\
&(f)\ 4(\alpha_3 - \alpha_2)(2\alpha_4 + \alpha_5 + \alpha_6) \geq (\alpha_2 + \alpha_3 - \alpha_5 + \alpha_6)^2
\end{aligned} \tag{22}$$

In particular, relation (a) is a consequence of $\gamma_1 = \alpha_3 - \alpha_2 > 0$, and relation (b) is the Onsager-Parodi relation which reduces the number of independent Leslie coefficients from 6 to 5 [12,13].

First, the dependence of $\eta_1(\theta)$ and $\eta_2(\theta)$ on the angle $\theta$ has been considered. In Figure 2a, the profiles refer to the set of coefficients listed in Table 1. Notice that for $\theta = 0, \pi$ both viscosities converge to the value of $\eta_{bend} = \gamma_1 - \alpha_2^2/\eta_c$, while for $\theta = \pi/2$ one finds $\eta_1(\pi/2) = \eta_{splay} =$

**TABLE 1** Viscoelastic Parameters of MBBA [12]

| $\alpha_1/10^{-3}$ Pa s | $\alpha_2/10^{-3}$ Pa s | $\alpha_3/10^{-3}$ Pa s | $\alpha_4/10^{-3}$ Pa s | $\alpha_5/10^{-3}$ Pa s |
|---|---|---|---|---|
| $6.5 \pm 4$ | $-77.5 \pm 1.6$ | $-1.2 \pm 0.1$ | $83.2 \pm 1.4$ | $46.3 \pm 4.5$ |
| $\alpha_6/10^{-3}$ Pa s | $\gamma_1/10^{-3}$ Pa s | $K_1/10^{-12}$N | $K_2/10^{-12}$N | $K_3/10^{-12}$N |
| $-34.4 \pm 2.2$ | $76.3 \pm 1.7$ | $5.3 \pm 0.5$ | $2.2 \pm 0.7$ | $7.45 \pm 1.1$ |

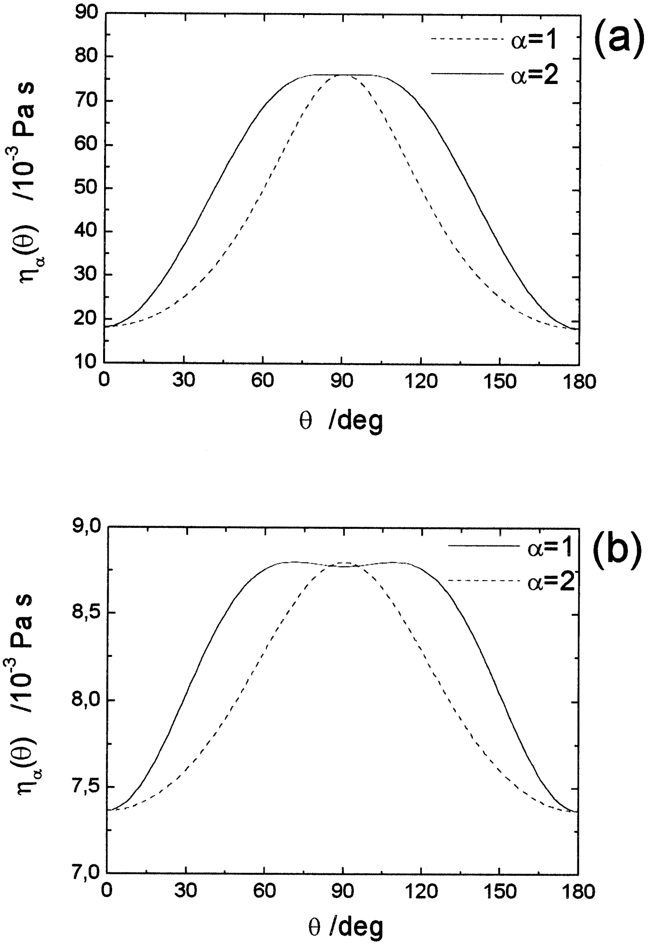

**FIGURE 2** Angular dependence of the viscosities $\eta_1(\theta)$ and $\eta_2(\theta)$. In (a), the viscoelastic parameters of MBBA have been used as listed in Table 1; in (b), $\alpha_2 = -10.0 \times 10^{-3}$Pa s has been assumed.

$\gamma_1 - \alpha_3^2/\eta_b$ and $\eta_2(\pi/2) = \eta_{twist} = \gamma_1$, where the Miesowicz viscosities $\eta_b$ and $\eta_c$ are given in Eqs. (6). The viscosity coefficients $\eta_{bend}$, $\eta_{twist}$, $\eta_{splay}$ refer to measurements under special shearing geometries [12,13]. In the present case, $\eta_{bend} = 18.3 \times 10^{-3}$ Pa s. It should be evident from the profiles shown in Figure 2a that, because of the strong angular dependence, it is impossible to identify unambiguosly the effective viscosities $\bar{\eta}_1$ and $\bar{\eta}_2$. Similar calculations have been performed for a smaller coefficient $\alpha_2$; the value $\alpha_2 = -10.0 \times 10^{-3}$ Pa s has been chosen. Consequently, the rotational viscosity $\gamma_1 = \alpha_3 - \alpha_2$ has been recalculated, as well as the coefficient $\alpha_6 = \alpha_2 + \alpha_3 + \alpha_5$ according to relation (b) of Eqs (22), while the coefficients $\alpha_1, \alpha_3, \alpha_4, \alpha_5$ have been kept unchanged with respect to the ones listed in Table 1. The new profiles are shown in Figure 2b. Notably, the angular dependence of $\eta_1(\theta)$ and of $\eta_2(\theta)$ is now strongly reduced, and this allows one to identify some constant effective viscosities $\bar{\eta}_1$ and $\bar{\eta}_2$. In particular, the approximation $\bar{\eta}_1 = \bar{\eta}_2 = \eta_{bend}$ turns out to be acceptable when $|\alpha_2| << \alpha_5$.

We now compare the exact factor $Q_{LM}$ as evaluated from Eq. (18), with its approximate form derived from Eq. (21) using the condition $\bar{\eta}_1 = \bar{\eta}_2 = \eta_{bend}$. The calculations have been performed by increasing the value of $\alpha_2$ from $-77.5 \times 10^{-3}$ Pa s (see Table 1) up to its maximum allowed value, $-1.2 \times 10^{-3}$ Pa s, imposed by relation (a) of Eqs. (22). Correspondingly, the rotational viscosity has been recalculated and the coefficient $\alpha_6$ has been varied in order to satisfy the relation (b) of Eqs. (22). The remaining Leslie coefficients, i.e. $\alpha_1, \alpha_3, \alpha_4, \alpha_5$, have been kept unchanged. Notably, by decreasing $|\alpha_2|$ the value of $\alpha_6$ remains negative up to $\alpha_2 = -45.1 \times 10^{-3}$Pa s, and then becomes positive. A positive coefficient $\alpha_6$ appears to be peculiar, since such a coefficient is negative for common nematics. By looking at the profiles in Figure 3, one sees that if $|\alpha_2| << \alpha_5$ the exact and the approximate values of $Q_{LM}$ tend to converge. This means that the use of effective viscosities with the assignment $\bar{\eta}_1 = \bar{\eta}_2 = \eta_{bend}$ are good approximations in the quantitative description of the dispersion

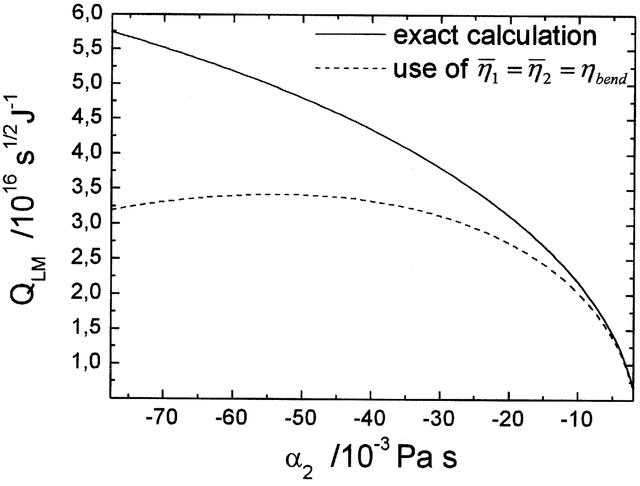

**FIGURE 3** The factor $Q_{LM}$ in Eq. (17); the exact calculation is referred to Eq. (18), the approximated one is referred to Eq. (21).

profile of the transverse relaxation rate, $R_{2,\infty}^{CP}(\tau)$, at least in case of particular relations between the values of the Leslie coefficients.

## 5. DISCUSSION AND CONCLUSIONS

A comprehensive slow-motional description of the pulsed NMR experiment performed in nematics has been considered, and the effects of the anisotropy of the viscoelastic parameters on the dispersion profile of the transverse relaxation rate have been explored.

The anisotropy of the elastic constants and viscosity parameters (the Leslie coefficients) has been introduced in the modelling of the order director fluctuations and in the expression of the experimentally accessible transverse relaxation rate, i.e. Eq. (13) together with Eq. (17). For the proportionality factor $Q_{LM}$ we have analysed the possibility of substituting the wavevector-dependent viscosities $\eta_1(\theta)$ and $\eta_2(\theta)$, referring to the mixed ***bend-splay*** and ***bend-twist*** distortions by some constant effective viscosities $\bar{\eta}_1$ and $\bar{\eta}_2$. The condition $|\alpha_2| << \alpha_5$ supports the assignment $\bar{\eta}_1 = \bar{\eta}_2 = \eta_{bend}$, as well as the use of Eq. (21) for the proportionality factor $Q_{LM}$. In such a case one can analyse the experimental dispersion profile of the transverse relaxation rate by considering four parameters, that is $\eta_{bend}$ and the three elastic constants, while the general expression Eq. (18) needs the specification of all five independent Leslie coefficients and the three elastic constants. In particular, for high molecular weight nematics whose viscosity coefficient $\eta_{bend}$ can be independently measured with rheo-NMR experiments employing the ***step-rotation*** technique [14], one can determine the following ***average*** elastic constant

$$\bar{K} = K_3\left[\left(\frac{K_3}{K_1}\right)^2 + \left(\frac{K_3}{K_2}\right)^2\right]^{-1/3} \tag{23}$$

from the analysis of the CP relaxation times according to the proportionality factor written as $Q_{LM} = (\eta_{bend}/\bar{K}^3)^{1/2}$.

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