

Director Fluctuations and ESR Spectra: A Slow-Motional Treatment[†]

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The analysis of the influence of director fluctuations on the ESR spectra of a spin probe dissolved in oriented phases (liquid crystals, membranes) requires a slow-motional treatment because the director field has always slowly relaxing components. Therefore, under the assumption of fast molecular tumbling of the spin-probe, the stochastic Liouville equation has to be solved for the coupling between the spin degrees of freedom and the fluctuating director field. The condition of small amplitude of director fluctuations is invoked to derive explicit solutions for the line widths in the presence of hyperfine interactions, with distinct contributions from the secular and the pseudosecular terms of the spin Hamiltonian. A perturbational treatment with respect to the nuclear spin states allows one to quantify the pseudosecular contributions, while the secular ones are exactly accounted by employing the methodology developed for the analogous analysis of nuclear spin relaxation due to quadrupolar interactions [Frezzato, D.; Kothe, G.; Moro G. J. *J. Phys. Chem. B* **2001**, *105*, 1281]. Model calculations are reported for a nitroxide spin probe (PD-tempone) in a nematic phase to assess the role of the secular and pseudosecular contributions and to characterize the dependence of the line shapes on the relevant physical parameters. The relative incidence of tumbling dynamics and director fluctuations on the line widths is also investigated.

1. Introduction

Perturbational treatments (i.e., the Redfield theory¹) can be used to analyze ESR spectra only if the anisotropies of the spin Hamiltonian (in frequency units) are much smaller than the rates of their fluctuations due, for instance, to the rotational diffusion of the spin probes. If these anisotropies are comparable or larger than the fluctuation rates, the full analysis of the coupling between the spin degrees of freedom and the stochastic variables is required and one has to solve the corresponding stochastic Liouville equation.^{2,3} The standard procedure is based on a matrix representation of the stochastic Liouville operator, generated by using a suitable basis for both the spin degrees of freedom and the functional dependence on the stochastic variables.³ Then, by employing efficient numerical algorithms,⁴ one can extract the relevant set of eigenvalues and their weights which allow the decomposition of the ESR spectrum into independent (Lorentzian) components. A more complex procedure, involving substantially the same ingredients, is required for the simulation of the pulsed ESR experiments.⁵ Basically, this is the methodology for the interpretation of ESR observables in the slow-motional regime, which has been successfully applied in the past 30 years for a variety of systems such as isotropic fluids,^{6,7} liquid crystals,^{3,8,9} membranes,^{10–13} and biopolymers.¹⁴

In this work we present a slow-motional analysis of the effects of director fluctuations on ESR spectra in partially ordered media such as liquid crystals or membranes. In these systems there are two main sources of fluctuations. First, one has to consider the rotational tumbling of the spin probes with respect to the

local director. In the following, we shall confine our analysis to the case of fast molecular tumbling. Then, after a time interval of the order of the correlation time of the molecular motion, an averaged spin Hamiltonian is acting on the spin degrees of freedom. On a longer time scale this averaged spin Hamiltonian is modulated by fluctuations of the director field. An intrinsic feature of director fluctuations is their broad distribution of relaxation times^{15,16} with components in the range of milliseconds or even slower. It is evident that, to study their effects on the ESR spectra, one has to resort to a slow-motional approach. However, the standard methodology based on a numerical treatment of the matrix representation of the stochastic Liouville operator cannot be employed anymore, since any reasonable discretization of the director field leads to an excessively large number of stochastic variables. Thus, the slow-motional analysis of director fluctuations requires a more analytical approach.

In ref 17, such an analytical procedure has been presented for the transverse nuclear spin relaxation of deuterium nuclei. It has been shown that by employing the secular approximation for the quadrupolar interactions and by restricting the spin Hamiltonian to the linear terms with respect to the director fluctuations, analytical expressions can be derived for the relation between the transverse relaxation times and the correlation function of the director fluctuations. Subsequently, the analysis has been generalized to second-order contributions of the director fluctuations.¹⁸ It should be mentioned that this theory has already been applied to the interpretation of various NMR experiments on membranes¹⁹ and liquid crystal polymers.²⁰

In this paper, we examine how this methodology can be generalized to account for the effects of director fluctuations on the ESR spectra with particular reference to nitroxide spin probes. Compared with the analysis of the quadrupolar interactions in NMR, the main new features of this study are the

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pseudosecular contributions resulting from the hyperfine interactions of the electronic spin with the nuclear spin of the nitrogen atom. Because of these interactions, the methodology presented in ref 17 cannot directly be applied to the present case. Rather, a more general approach is required to account for the effects of director fluctuations on the ESR spectra of nitroxide probes. In particular, the following strategy is employed: (i) we use the linear approximation for the dependence of the spin Hamiltonian on the fluctuating director, (ii) we apply the exact treatment of ref 17 to account for the secular contributions, (iii) we consider the pseudosecular contributions by means of a perturbational treatment with respect to the nuclear spin states. It will be shown that the small amplitudes of director fluctuations justify the latter assumption.

The paper is organized as follows. In the next section, a formal description is presented for a nitroxide probe subject to director fluctuations. In the third section, explicit expressions are derived for the ESR line shapes employing a perturbational analysis for the pseudosecular contributions and the exact treatment for the secular contributions. Model calculations are illustrated in the following section for the specific case of a nematic phase. The general conclusions drawn from this work are reported in the last section.

2. Stochastic Liouville Equation

We shall consider the nitroxide spin probe as a typical free radical with the following spin Hamiltonian²¹

$$H = \beta_e \mathbf{B}_0 \cdot \mathbf{g} \mathbf{S} + \hbar \mathbf{I} \cdot \mathbf{A} \mathbf{S} \quad (1)$$

where \mathbf{S} and \mathbf{I} are the (vector) spin operator for the unpaired electron and the nitrogen nucleus, respectively, and \mathbf{g} and \mathbf{A} represent molecular tensors. By introducing the laboratory frame $LF = (\mathbf{X}, \mathbf{Y}, \mathbf{Z})$ with the Z-axis along the static magnetic field \mathbf{B}_0 , the spin Hamiltonian in the secular approximation can be written as

$$H = [\beta_e B_0 g_{zz} + \hbar (\mathbf{A} \mathbf{I})_Z] S_Z \quad (2)$$

In oriented media two independent types of fluctuations have to be considered: rotational tumbling of the probe and director fluctuations. We suppose that the molecular tumbling is fast enough to be treated according to the Redfield theory,¹ leading to transverse relaxation times $T_{2,M}^{\text{mol}}$ that depend on the quantum number M of the nuclear spin. Then, in a time scale longer than the rotational correlation time, the spin system can be described by the Hamiltonian eq 2 with the following orientationally averaged tensors

$$\begin{aligned} \mathbf{g} &= g_{\perp} \mathbf{1} + (g_{\parallel} - g_{\perp}) \mathbf{n} \otimes \mathbf{n} \\ \mathbf{A} &= A_{\perp} \mathbf{1} + (A_{\parallel} - A_{\perp}) \mathbf{n} \otimes \mathbf{n} \end{aligned} \quad (3)$$

where the unit vector \mathbf{n} denotes the director. The knowledge of the molecular tensors and of the order parameters characterizing the orientational distribution of the spin probe with respect to the director, allows one to evaluate the parallel (g_{\parallel} and A_{\parallel} for $\mathbf{n} \parallel \mathbf{B}_0$) and perpendicular components (g_{\perp} and A_{\perp} for $\mathbf{n} \perp \mathbf{B}_0$) of these averaged tensors.

Let us consider a well aligned sample because of external fields or surface effects, with small amplitude fluctuations of the director field $\mathbf{n}(\mathbf{r}, t)$ relative to its average $\bar{\mathbf{n}}$. Accordingly, we introduce the average director frame $ADF = (\mathbf{x}, \mathbf{y}, \mathbf{z})$ with $\mathbf{z} = \bar{\mathbf{n}}$. Moreover, we choose the transverse axes of the LF such that \mathbf{z} lies in the (\mathbf{X}, \mathbf{Z}) plane. Thus, we can use \mathbf{Y} of the LF as the y-axis of the ADF (see Figure 1), and the Euler angles (α, β, γ)

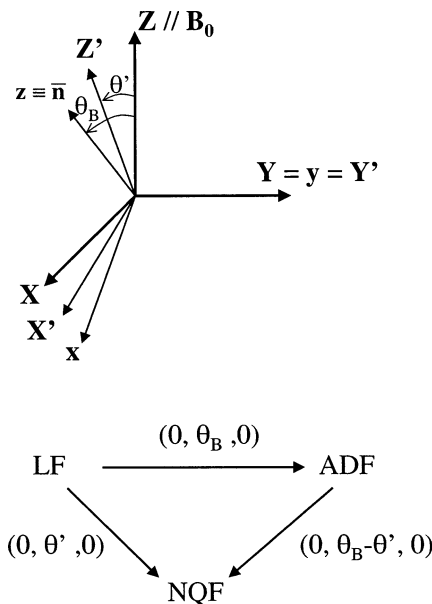


Figure 1. Relative orientations of the laboratory frame LF ($\mathbf{X}, \mathbf{Y}, \mathbf{Z}$), the average director frame ADF ($\mathbf{x}, \mathbf{y}, \mathbf{z}$), and the nuclear spin quantization frame NQF ($\mathbf{X}', \mathbf{Y}', \mathbf{Z}'$), together with the scheme for their transformations and the corresponding sets of Euler angles.

β, γ) for the transformation from the LF to the ADF can be specified as $(0, \theta_B, 0)$, where θ_B is the angle between the magnetic field \mathbf{B}_0 and the average director $\bar{\mathbf{n}}$. The director \mathbf{n} acting on the spin probe is conveniently represented in the ADF as

$$\mathbf{n} = n_x \mathbf{x} + n_y \mathbf{y} + \sqrt{1 - n_x^2 - n_y^2} \mathbf{z} \quad (4)$$

where n_x and n_y are the two independent fluctuating components.

The g -tensor component in eq 2 can be specified as

$$g_{zz} = g_{\perp} + (g_{\parallel} - g_{\perp})(\mathbf{n} \cdot \mathbf{z})^2 = g_{zz}^0 + \delta g_{zz} \quad (5)$$

where

$$g_{zz}^0 = g_{\perp} + (g_{\parallel} - g_{\perp}) \cos^2 \theta_B \quad (6)$$

is the component in the absence of director fluctuations (i.e., for $\mathbf{n} = \bar{\mathbf{n}}$), and

$$\delta g_{zz} = (g_{\parallel} - g_{\perp}) \sin(2\theta_B) n_x \quad (7)$$

is its fluctuating part in the linear approximation with respect to n_x and n_y . Notice that the average $\overline{\delta g_{zz}}$ vanishes since $\overline{n_x} = 0$.

Let us now examine the hyperfine coupling term which is conveniently specified as

$$(\mathbf{A} \mathbf{I})_Z = \mathbf{a} \cdot \mathbf{I} \quad (8)$$

where the vector \mathbf{a} depends on the local director \mathbf{n}

$$\mathbf{a} = A_{\perp} \mathbf{Z} + (A_{\parallel} - A_{\perp})(\mathbf{n} \cdot \mathbf{Z}) \mathbf{n} \quad (9)$$

In the absence of director fluctuations, such a vector is given as

$$\mathbf{n} = \bar{\mathbf{n}}: \mathbf{a}^0 = A_{\perp} \mathbf{Z} + (A_{\parallel} - A_{\perp}) \cos \theta_B \mathbf{z} \quad (10)$$

which corresponds to a vector in the (\mathbf{X}, \mathbf{Z}) plane of the LF

(see Figure 1) with modulus

$$a^0 \equiv |\mathbf{a}^0| = \sqrt{A_{\perp}^2 + (A_{\parallel}^2 - A_{\perp}^2)\cos^2\theta_B} \quad (11)$$

It is evident that \mathbf{a}^0 represents the most convenient choice for the quantization axis of the nuclear spin since, in the absence of fluctuations, a diagonal representation is readily obtained for the spin Hamiltonian eq 2, with a^0 determining the hyperfine splitting. Thus, we introduce a further reference system, the nuclear spin quantization frame $NQF = (X', Y', Z')$, where the Z' -axis is oriented along \mathbf{a}^0 . Since, according to eq 10, \mathbf{a}^0 lies in the (\mathbf{X}, \mathbf{Z}) plane, we can choose \mathbf{Y}' parallel to the y -axis of the LF (see Figure 1). Then, only the angle θ' between \mathbf{a}^0 and \mathbf{B}^0 (to be calculated according to eq 10) is required to specify the orientation of the NQF with respect to the LF , as shown in Figure 1.

Finally we isolate from the vector \mathbf{a} of eq 9 its fluctuating part $\delta\mathbf{a}$

$$\mathbf{a} = \mathbf{a}^0 + \delta\mathbf{a} \quad (12)$$

In the linear approximation for director fluctuations, $\delta\mathbf{a}$ is given by

$$\delta\mathbf{a} = (A_{\parallel} - A_{\perp})[\cos\theta_B(n_x\mathbf{x} + n_y\mathbf{y}) - \sin\theta_B n_z\mathbf{z}] \quad (13)$$

Then, by specifying the components of the nuclear spin operator in the NQF , the hyperfine interaction term can be written as

$$(\mathbf{AI})_Z = a^0 I_{Z'} + (\delta a_{X'} I_{X'} + \delta a_{Y'} I_{Y'} + \delta a_{Z'} I_{Z'}) \quad (14)$$

where the fluctuating contributions to the hyperfine splitting

$$\begin{aligned} \delta a_{X'} &= (A_{\parallel} - A_{\perp})\cos(2\theta_B - \theta') n_x \\ \delta a_{Y'} &= (A_{\parallel} - A_{\perp})\cos\theta_B n_y \\ \delta a_{Z'} &= -(A_{\parallel} - A_{\perp})\sin(2\theta_B - \theta') n_x \end{aligned} \quad (15)$$

have a vanishing average.

The above analysis provides the spin Hamiltonian in the linear approximation with respect to the local transverse components n_x and n_y of the director. On the other hand, director fluctuations are governed by the viscoelastic behavior of the ordered medium, and therefore can be modeled only by considering the entire sample through the director field $\mathbf{n}(\mathbf{r}, t)$ depending on the time t and the position \mathbf{r} . Of course, the spin Hamiltonian at a given time t feels only the director $\mathbf{n}(\mathbf{r}_p, t)$ at the probe location \mathbf{r}_p . One can model the director fluctuations by identifying the independent stochastic variables $\mathbf{Q}(t)$ with the fluctuating components of the director field, i.e.,

$$\mathbf{Q}(t) = \{\dots, n_x(\mathbf{r}, t), n_y(\mathbf{r}, t), \dots\} \quad (16)$$

at all sample locations \mathbf{r} (in practice by using a discretization procedure^{15,17}). In the Markovian approximation, the time evolution of the stochastic variables is specified according to the Fokker–Planck equation²² for the probability density $p(\mathbf{q}, t)$ with respect to the possible values \mathbf{q} for the stochastic variables $\mathbf{Q}(t)$

$$\frac{\partial}{\partial t} p(\mathbf{q}, t) = -\Gamma p(\mathbf{q}, t) \quad (17)$$

Here Γ denotes the time evolution operator to be modeled according to the specific viscoelastic properties of the ordered

medium, either a liquid crystal phase^{15–17} or a membrane.¹⁹ In the following, the stationary solution of eq 17 (i.e., the equilibrium distribution) will be denoted by $p_{\text{eq}}(\mathbf{q})$. We emphasize, however, that our analysis does not invoke any particular assumption about the dynamics of the director fluctuations.

The full description of the dynamical coupling between the spin degrees of freedom and the director fluctuations requires the solution of the stochastic Liouville equation (SLE)^{2,3}

$$\frac{\partial}{\partial t} \rho(\mathbf{q}, t) = -[iH^{\times}/\hbar + \Gamma + R^{\text{mol}}]\rho(\mathbf{q}, t) \quad (18)$$

for the \mathbf{q} -dependent density matrix $\rho(\mathbf{q}, t)$ with respect to both the electron and the nuclear spin states. In eq 18 we have included the molecular contribution R^{mol} due to the fast tumbling motion with respect to the director. Let us consider the free induction decay (FID) following a $\pi/2$ pulse which rotates the equilibrium magnetization M_{eq} along the Y -axis of the laboratory frame. In this case, the time-dependent magnetization along the same direction can be specified as

$$M_Y(t)/M_{\text{eq}} = \frac{2}{3} \int d\mathbf{q} \text{Tr}\{S_Y \rho(\mathbf{q}, t)\} \quad (19)$$

where the density matrix is evaluated according to the SLE eq 18

$$\rho(\mathbf{q}, t) = \exp\{-[iH^{\times}/\hbar + \Gamma + R^{\text{mol}}]t\} S_Y p_{\text{eq}}(\mathbf{q}) \quad (20)$$

The trace has to be calculated with respect to both the electron spin states, m , and the nuclear spin states, M ,

$$\text{Tr}\{\dots\} = \sum_{m,M} \langle m, M | \dots | m, M \rangle = \sum_{m,M} \langle m | \langle M | \dots | M \rangle | m \rangle \quad (21)$$

The obvious choice for the electron spin states are the eigenstates of S_z , $S_z|m\rangle = m|m\rangle$. Likewise, for the nuclear spin states we employ the eigenstates of $I_{Z'}|M\rangle = M|M\rangle$.

Because of the secular approximation, the dependence on the electron spin states can be eliminated. Let us specify the trace as

$$\begin{aligned} \text{Tr}\{S_Y \rho(\mathbf{q}, t)\} &= \frac{i}{2} \sum_{m,M} \langle m, M | (S_- - S_+) \rho(\mathbf{q}, t) | m, M \rangle \\ &= \frac{i}{2} \sum_M [\langle M | \rho_+(\mathbf{q}, t) | M \rangle - \langle M | \rho_-(\mathbf{q}, t) | M \rangle] \end{aligned} \quad (22)$$

where the coefficients

$$\langle M | \rho_{\pm}(\mathbf{q}, t) | M \rangle \equiv \langle \pm 1/2, M | \rho(\mathbf{q}, t) | \mp 1/2, M \rangle \quad (23)$$

can be interpreted as elements of the density matrices $\rho_{\pm}(\mathbf{q}, t)$ for the nuclear spin states only, with the following initial values:

$$\rho_{\pm}(\mathbf{q}, 0) = \mp i p_{\text{eq}}(\mathbf{q}) \quad (24)$$

From eq 18, two independent evolution equations are derived for ρ_{\pm}

$$\frac{\partial}{\partial t} \rho_{\pm}(\mathbf{q}, t) = -\mathcal{O}_{\pm} \rho_{\pm}(\mathbf{q}, t) \quad (25)$$

where

$$\mathcal{O}_{\pm} = \pm i[\omega^0 + \delta\omega_g + a^0 I_{Z'}^{\pm}/2 + \delta\mathbf{a} \cdot \mathbf{I}^{\pm}/2] + \Gamma + R^{\text{mol}} \quad (26)$$

and $\omega^0 \equiv \beta_e B_0 g_{ZZ}^0 / \hbar$, $\delta\omega_g \equiv \beta_e B_0 \delta g_{ZZ} / \hbar$. I_j^\dagger denotes the anti-commutator of I_j : $I_j^\dagger \rho = I_j \rho + \rho I_j$. Since $\mathcal{O}_+ = \mathcal{O}_-^*$ and $\rho_+(\mathbf{q}, 0) = \rho_-(\mathbf{q}, 0)^*$, the two density matrices are related as

$$\rho_+(\mathbf{q}, t) = \rho_-(\mathbf{q}, t)^* \quad (27)$$

and therefore the FID signal can be specified as

$$M_Y(t) = \frac{M_{eq}}{3} \text{Re}\{G(t)\}$$

$$G(t) = i \int d\mathbf{q} \sum_M \langle M | \rho_+(\mathbf{q}, t) | M \rangle =$$

$$\int d\mathbf{q} \sum_M \langle M | \exp\{-\mathcal{O}t\} p_{eq}(\mathbf{q}) | M \rangle \quad (28)$$

where $\mathcal{O} \equiv \mathcal{O}_+$. Finally, the profile of the absorption spectrum is evaluated from the Fourier–Laplace transform of the FID signal

$$I(\omega) = \int_0^\infty dt \exp(i\omega t) M_Y(t) = \frac{M_{eq}}{3} \text{Re}\{\tilde{G}(\omega)\} \quad (29)$$

where $\tilde{G}(\omega)$ is the spectral density of $G(t)$, i.e.,

$$\tilde{G}(\omega) = \int_0^\infty dt \exp(i\omega t) G(t) \quad (30)$$

3. The ESR Spectrum

Let us introduce the space ϵ with the reduced density matrices $\rho_+(\mathbf{q}, t)$ as elements, i.e., the product space for the functional dependence on the stochastic variables \mathbf{q} and for the matrices of the nuclear spin states. The scalar product $\langle A | B \rangle$ between two elements $A(\mathbf{q})$ and $B(\mathbf{q})$ of ϵ is defined as

$$\langle A | B \rangle \equiv \int d\mathbf{q} \sum_M \langle M | A(\mathbf{q})^\dagger B(\mathbf{q}) | M \rangle =$$

$$\int d\mathbf{q} \sum_{M, M'} \langle M' | A(\mathbf{q}) | M \rangle^* \langle M' | B(\mathbf{q}) | M \rangle \quad (31)$$

Since \mathcal{O} is an operator acting on the elements of such a space, $G(t)$ in eq 28 can be written as a correlation function

$$G(t) = \langle 1 | \exp\{-\mathcal{O}t\} | p_{eq}(\mathbf{q}) \rangle \quad (32)$$

where 1 is the unit matrix of the nuclear spin states

$$1 \equiv \sum_M |M\rangle \langle M| \quad (33)$$

The algebraic manipulations are more conveniently performed by introducing in the correlation function

$$G(t) = \langle p_{eq}(\mathbf{q})^{1/2} | \exp\{-\tilde{\mathcal{O}}t\} | p_{eq}(\mathbf{q})^{1/2} \rangle \quad (34)$$

the symmetrized evolution operator

$$\tilde{\mathcal{O}} \equiv p_{eq}(\mathbf{q})^{-1/2} \mathcal{O} p_{eq}(\mathbf{q})^{1/2} \quad (35)$$

Accordingly, the spectral density is written as

$$\tilde{G}(\omega) = \langle p_{eq}(\mathbf{q})^{1/2} | [\tilde{\mathcal{O}} - i\omega]^{-1} | p_{eq}(\mathbf{q})^{1/2} \rangle \quad (36)$$

TABLE 1: Matrix Representation of the Operator $\tilde{\mathcal{O}}$ (see eq 35)^a

$ 1\rangle\langle 1 $	β_1	$i\alpha$	$i\alpha^*$	0	0	0	0	0	0
$ 1\rangle\langle 0 $	$i\alpha^*$	$\beta_{1/2}$	0	$i\alpha$	$i\alpha^*$	0	0	0	0
$ 0\rangle\langle 1 $	$i\alpha$	0	$\beta_{1/2}$	0	$i\alpha$	$i\alpha^*$	0	0	0
$ 1\rangle\langle -1 $	0	$i\alpha^*$	0	β_0	0	0	0	$i\alpha^*$	0
$ 0\rangle\langle 0 $	0	$i\alpha$	$i\alpha^*$	0	β_0	0	$i\alpha^*$	$i\alpha$	0
$ -1\rangle\langle 1 $	0	0	$i\alpha$	0	0	β_0	$i\alpha$	0	0
$ -1\rangle\langle 0 $	0	0	0	0	$i\alpha$	$i\alpha^*$	$\beta_{-1/2}$	0	$i\alpha$
$ 0\rangle\langle -1 $	0	0	0	$i\alpha$	$i\alpha^*$	0	0	$\beta_{-1/2}$	$i\alpha^*$
$ -1\rangle\langle -1 $	0	0	0	0	0	0	$i\alpha^*$	$i\alpha$	β_{-1}

^a The partition is performed into blocks referred to the basis element products $|M\rangle \langle M'|$ of the nuclear spin states. The ordering of the basis elements is indicated in the left column. The continuous lines separate the blocks having different values of the average nuclear quantum number $\bar{M} = (M + M')/2$.

Given a basis set $\phi_n(\mathbf{q})$ with $n = 0, 1, 2, \dots$ for the functional dependence on the stochastic variables

$$\langle \phi_n(\mathbf{q}) | \phi_{n'}(\mathbf{q}) \rangle \equiv \int d\mathbf{q} \phi_n(\mathbf{q})^* \phi_{n'}(\mathbf{q}) = \delta_{n,n'} \quad (37)$$

where $\phi_0(\mathbf{q}) = p_{eq}(\mathbf{q})^{1/2}$, an orthonormal basis for ϵ is derived in the form

$$||M\rangle \langle M'| \phi_n(\mathbf{q}) \quad (38)$$

Thus, a matrix representation with the structure given in Table 1 is generated for $\tilde{\mathcal{O}}$ by partitioning it into blocks with respect to the basis element products $|M\rangle \langle M'|$ of the nuclear spin states. The continuous lines separate blocks having different values of the average nuclear quantum number

$$\bar{M} = \frac{M + M'}{2} \quad (39)$$

for the product state $|M\rangle \langle M'|$. α and $\beta_{\bar{M}}$ are operators on the stochastic variables only. In particular, α in the off-diagonal blocks is given by

$$\alpha(\mathbf{q}) = \frac{\delta a_{X'} + i\delta a_{Y'}}{\sqrt{8}} \quad (40)$$

where $\delta a_{X'}$ and $\delta a_{Y'}$ are calculated according to eq 15 and the transverse director components n_x and n_y are evaluated at the probe location. Identical diagonal blocks are obtained for a given average nuclear quantum number \bar{M} , and they are represented as

$$\beta_{\bar{M}} \equiv i[\omega^0 + \delta\omega_g + (a^0 + \delta a_Z)\bar{M}] + \tilde{\Gamma} + R_M^{\text{mol}} \quad (41)$$

where $\tilde{\Gamma} \equiv p_{eq}^{-1/2} \Gamma p_{eq}^{1/2}$, and $R_M^{\text{mol}} = 1/T_{2,M}^{\text{mol}}$ is the transverse relaxation rate due to fast molecular tumbling.

In principle, by diagonalizing such a matrix, one can evaluate the ESR spectral profile eq 36. In practice this cannot be done since an infinite number of stochastic variables, and therefore an infinitely large basis set, is required to represent the director field. Solutions of the problem can be obtained only by means of analytical procedures valid under suitable conditions.

We shall analyze the case where the off-diagonal blocks have only a perturbational effect. Since they couple diagonal blocks with a different average nuclear quantum number \bar{M} , such a situation is realized if

$$|\alpha| \ll |\beta_{\bar{M}} - \beta_{\bar{M} \pm 1/2}| \quad (42)$$

or, by taking into account that the difference between diagonal blocks is mainly due to the hyperfine splitting a^0 , if

$$|A_{||} - A_{\perp}|(n_x^2)^{1/2} \ll |a^0| \quad (43)$$

where the magnitude of α has been evaluated according to its squared average. We expect that this condition is always satisfied as long as the director fluctuations have small amplitudes, $n_x^2 \ll 1$, while $|A_{||} - A_{\perp}|$ and a^0 are of comparable magnitude. If the off-diagonal blocks have a perturbational effect, then the spectral density can be decomposed into three contributions corresponding to the diagonal pair of nuclear spin states $|M\rangle\langle M|$ for $M = -1, 0, 1$:

$$\tilde{G}(\omega) \approx \sum_M \tilde{G}_M(\omega - \omega^0 - Ma^0) \quad (44)$$

where

$$\tilde{G}_M(\Delta\omega) = (|M\rangle\langle M|\phi_0|[\tilde{\mathcal{O}} - i(\Delta\omega + \omega^0 + Ma^0)]^{-1}|\phi_0\rangle\langle M|) \quad (45)$$

In this way the ESR spectrum is described by three independent contributions, which can be identified as the line shapes at the reference frequencies $\omega^0 + Ma^0$.

Given the structure of the resolvent in eq 45 for a given M , we decompose the space $\epsilon = \epsilon_0 \oplus \epsilon_1$ into the one-dimensional subspace ϵ_0 along the vector $|\phi_0\rangle\langle M|$ and its complement subspace ϵ_1 . Then, by organizing the matrix representation of $\tilde{\mathcal{O}}$ in blocks $A_{p,q}$ for $p, q = 0, 1$ in correspondence to the subspaces ϵ_0 and ϵ_1 , respectively, and by applying the theorem of inverse matrix partitioning,²³ each spectral component can be specified as

$$1/\tilde{G}_M(\Delta\omega) = A_{0,0} - i(\Delta\omega + \omega^0 + Ma^0) - A_{0,1}[A_{1,1} - i(\Delta\omega + \omega^0 + Ma^0)]^{-1}A_{1,0} \quad (46)$$

By neglecting in $A_{1,1}$ the off-diagonal blocks specified by α or α^* (see eq 42), the last term at the right hand side of eq 46 can be decomposed into independent contributions of diagonal blocks $\beta_{\bar{M}}$. Let us consider the specific case of $M = 1$, whose contributions result from the diagonal blocks for (i) $|1\rangle\langle 1|$, for (ii) $|1\rangle\langle 0|$, and for (iii) $|0\rangle\langle 1|$. The contribution (ii) to $1/\tilde{G}_1(\Delta\omega)$, once the reference to the no more relevant basis elements of nuclear spin states is eliminated, can be specified as

$$\sum_{n,n'} \langle \phi_0 | \alpha | \phi_n \rangle \langle \phi_n | [i(\delta\omega_g - a^0/2 + \delta a_z/2 - \Delta\omega) + R_{1/2}^{\text{mol}} + \tilde{\Gamma}]^{-1} | \phi_{n'} \rangle \langle \phi_{n'} | \alpha^* | \phi_0 \rangle \quad (47)$$

By taking into account eq 43 and by introducing the further assumption

$$|\Delta\omega|, |\delta\omega_g|, R_M^{\text{mol}} \ll |a^0/2| \quad (48)$$

which is justified as long as there is no superposition between

the three line shapes of the ESR spectrum, the operator for the diagonal block can be simplified to $[-ia^0/2 - \tilde{\Gamma}]$, and eq 47 results in

$$\langle \phi_0 | \alpha^* | [-ia^0/2 + \tilde{\Gamma}]^{-1} | \alpha^* | \phi_0 \rangle = \int_0^\infty dt e^{ia^0 t/2} h(t) \quad (49)$$

where $h(t)$ is the correlation function

$$h(t) \equiv \overline{\alpha(0)\alpha(t)^*} = \langle p_{\text{eq}}^{1/2} \alpha^* | \exp\{-\tilde{\Gamma}t\} | \alpha^* p_{\text{eq}}^{1/2} \rangle \quad (50)$$

Therefore, by introducing the spectral density of such a correlation function

$$\tilde{h}(\omega) \equiv \int_0^\infty dt e^{i\omega t} h(t) \quad (51)$$

the contribution eq 49 can be written as $\tilde{h}(a^0/2)$. By inserting the explicit form eq 40 for α , and by taking into account the relations eq 15, the function $h(t)$ can be reduced to the correlation function of the director fluctuations

$$h(t) = \frac{(A_{||} - A_{\perp})^2}{8} [\cos^2(2\theta_B - \theta') + \cos^2\theta_B] \overline{n_x(0)n_x(t)} \quad (52)$$

Since the function $h(t)$ is real, the corresponding spectral density has the property $\tilde{h}(-\omega) = \tilde{h}(\omega)^*$.

By using the same procedure for the term (iii), an identical contribution $\tilde{h}(a^0/2)$ is obtained. Then, the line shape for $M = 1$ can be written as

$$1/\tilde{G}_1(\Delta\omega) = 2\tilde{h}(a^0/2) + \langle \phi_0 | \Delta\beta_1 | \phi_0 \rangle - \sum_{n,n' \neq 0} \langle \phi_0 | \Delta\beta_1 | \phi_n \rangle \langle \phi_n | \Delta\beta_1^{-1} | \phi_{n'} \rangle \langle \phi_{n'} | \Delta\beta_1 | \phi_0 \rangle \quad (53)$$

where

$$\Delta\beta_M \equiv \beta_M - i(\Delta\omega + \omega^0 + Ma^0) = i(\delta\omega_g + M\delta a_z - \Delta\omega) + \tilde{\Gamma} + R_M^{\text{mol}} \quad (54)$$

Let us introduce the functions

$$f_M(t) \equiv \langle p_{\text{eq}}^{1/2} | \exp\{-[i(\delta\omega_g + M\delta a_z) + \tilde{\Gamma} + R_M^{\text{mol}}]t\} | p_{\text{eq}}^{1/2} \rangle \quad (55)$$

as well as their spectral densities

$$\tilde{f}_M(\Delta\omega) \equiv \int_0^\infty dt e^{i\Delta\omega t} f_M(t) = \langle \phi_0 | \Delta\beta_M^{-1} | \phi_0 \rangle \quad (56)$$

By applying the theorem of inverse matrix partitioning²³ to the matrix representation of $\Delta\beta_M$, subdivided into blocks corresponding to the one-dimensional subspace along ϕ_0 and its complementary subspace, eq 56 can be rewritten as

$$1/\tilde{f}_M(\Delta\omega) = \langle \phi_0 | \Delta\beta_M | \phi_0 \rangle - \sum_{n,n' \neq 0} \langle \phi_0 | \Delta\beta_M | \phi_n \rangle \langle \phi_n | \Delta\beta_M^{-1} | \phi_{n'} \rangle \langle \phi_{n'} | \Delta\beta_M | \phi_0 \rangle \quad (57)$$

which, for $M = 1$, corresponds to the last two terms at the right hand side of eq 53.

The same procedure can be applied to the line shapes of the other hyperfine components to obtain

$$\begin{aligned} 1/\tilde{G}_{-1}(\Delta\omega) &= 2\tilde{h}(a^0/2)^* + 1/\tilde{f}_{-1}(\Delta\omega) \\ 1/\tilde{G}_0(\Delta\omega) &= 4\text{Re}\{\tilde{h}(a^0/2)\} + 1/\tilde{f}_0(\Delta\omega) \\ 1/\tilde{G}_1(\Delta\omega) &= 2\tilde{h}(a^0/2) + 1/\tilde{f}_1(\Delta\omega) \end{aligned} \quad (58)$$

To analyze the consequences of these results, let us consider the simpler situation when $\delta\omega_g = \delta a_Z = 0$, which is realized at canonical orientations between average director and magnetic field (i.e., for $\theta_B = 0$ or $\theta_B = \pi/2$). In this case, a purely exponential decay is obtained for the function eq 55, i.e., $f_M(t) = \exp(-R_M^{\text{mol}}t)$, where $R_M^{\text{mol}} = 1/T_{2,M}^{\text{mol}}$ is the transverse relaxation rate due to fast molecular tumbling. The corresponding spectral density is given by

$$\tilde{f}_M(\Delta\omega) = \frac{1}{R_M^{\text{mol}} - i\Delta\omega} \quad (59)$$

Then, a Lorentzian profile is obtained for the three contributions to the ESR spectrum

$$\begin{aligned} G_{-1}(\Delta\omega) &= \frac{1}{1/T_{2,-1}^R + 2\tilde{h}(a^0/2)^* - i\Delta\omega} \\ G_0(\Delta\omega) &= \frac{1}{1/T_{2,0}^R + 4\text{Re}\{\tilde{h}(a^0/2)\} - i\Delta\omega} \\ G_1(\Delta\omega) &= \frac{1}{1/T_{2,1}^R + 2\tilde{h}(a^0/2) - i\Delta\omega} \end{aligned} \quad (60)$$

where $\tilde{h}(a^0/2)$ determines the pseudosecular contributions of the director fluctuations to the line shapes. In particular, its real part contributes to the line width, while its imaginary part generates a shift of the outer lines. The pseudosecular contributions produce the same broadening of the two outer hyperfine lines, and a two-fold larger broadening of the central line.

For $\delta\omega_g \neq 0$ and/or $\delta a_Z \neq 0$ (i.e., for sample orientations different from the canonical ones) there is also a secular contribution to the line widths in relation to the functions $f_M(t)$. According to eqs 7 and 15, the relevant frequency factors are linearly dependent on the transverse component n_x of the director at the probe location. Therefore, the functions $f_M(t)$ can be specified as

$$f_M(t) = \int d\mathbf{q} p_{eq}(\mathbf{q})^{1/2} \exp\{-[ic_M n_x + R_M^{\text{mol}} + \tilde{\Gamma}]t\} p_{eq}(\mathbf{q})^{1/2} \quad (61)$$

where

$$c_M = (\beta_e B_0 / \hbar)(g_{\parallel} - g_{\perp})\sin(2\theta_B) - M(A_{\parallel} - A_{\perp})\sin(2\theta_B - \theta') \quad (62)$$

The stochastic Liouville operator in eq 61 has the same structure as the operator used in ref 17 for the analysis of transverse nuclear spin relaxation due to quadrupolar interactions in NMR. Thus, by adapting to the present case the same analysis of director fluctuations represented as a multidimensional Gaussian process, the following exact relation is obtained

$$f_M(t) = \exp\{-c_M^2 g(t) - R_M^{\text{mol}} t\} \quad (63)$$

where $g(t)$ is the double time integral of the correlation function

of the director fluctuations¹⁷

$$g(t) = \int_0^t dt' \int_0^{t'} dt'' \overline{n_x(0)n_x(t'')} \quad (64)$$

It should be noted that according to eq 63 the decay of the transverse magnetization is not described by a simple exponential, and therefore Lorentzian profiles are not in general expected for the ESR line shapes because of the secular contributions.

In conclusion, all the ingredients for the evaluation of director fluctuation effects on the ESR spectra are now well specified. Explicit calculations require (i) the correlation function $n_x(0)n_x(t)$ of the director fluctuations to be modeled according to the viscoelastic properties of a given ordered phase, and (ii) the molecular tensors as well as the orientational order parameters of the spin probe in order to specify the magnetic properties.

4. Application to Nematic Phases

In this section, model calculations are reported for a spin probe in a nematic phase in order to describe the effect of director fluctuations on the ESR line shape. Particular emphasis is given to the contributions of secular and pseudosecular terms of the spin Hamiltonian. First, a specific spin probe in a given nematic phase is chosen in order to evaluate the relevant hyperfine frequencies and their angular dependence. Second, we summarize the standard model of order director fluctuations in nematics to provide explicit relations for the required correlation functions. On the basis of these results, we shall first analyze the line shapes from the secular terms alone. This allows the characterization of their specific features and a parametrization of their widths. Then, the pseudosecular contributions are evaluated. Finally, we discuss the effect of the angular dependence and the magnitude of director fluctuation contributions to the ESR spectra. Notably, for a complete characterization of these spectra also the molecular contributions are required given by the relaxation rates R_M^{mol} . Although these rates can be evaluated according to the Redfield theory by applying a diffusion model for the fast tumbling motion of the spin probe in the presence of an orienting potential,^{21,24} they will simply be parametrized in order to avoid a too cumbersome presentation and to focus the attention on the contributions of the director fluctuations.

The Magnetic Parameters. To carry out calculations pertinent to a realistic situation, we choose the perdeuterated 2,2,6,6-tetramethyl-4-piperidone *N*-oxide (PD-Tempone) as spin probe molecule dissolved in the nematic phase of 8CB. The ESR spectra of this nitroxide radical have been analyzed in detail by Lin and Freed.²⁵ The spectra have been recorded with a static magnetic field $B_0 = 3300$ G. The authors report the principal values for the molecular g -tensor, $g_{xx} = 2.0099$, $g_{yy} = 2.0062$, $g_{zz} = 2.00215$, for the hyperfine tensor, $A_{xx} = 5.52$ G, $A_{yy} = 4.94$ G, $A_{zz} = 33.1$ G, as well as for the Saupe ordering matrix, $S_{xx} = -0.006$, $S_{yy} = 0.069$, $S_{zz} = -0.063$, at the temperature of 37.6 °C. The latter parameters quantify the alignment of the molecular axes with respect to the director. By assuming that all of these tensors have the same system of principal axes, the parallel and perpendicular components of the averaged g -tensor result in

$$g_{\parallel} = \sum_j g_{jj}(2S_{jj} + 1)/3 \quad g_{\perp} = \sum_j g_{jj}(1 - S_{jj})/3 \quad (65)$$

and similar expressions hold for the averaged components A_{\parallel} and A_{\perp} of the hyperfine tensor. From the data reported in ref

25, we obtain the following averaged components of these tensors: $g_{\parallel} = 2.0062$, $g_{\perp} = 2.0060$, and $A_{\parallel} = 13.33$ G, $A_{\perp} = 15.11$ G. They allow the calculation of the angular-dependent coefficients $c_M(\theta_B)$, eq 62, whose squares determine the strength of the secular contributions according to eq 63. For the specific system under investigation, these squared coefficients are represented in Figure 2 as a function of the angle θ_B between average director and magnetic field. Notice that for each θ_B the value of θ' in eq 62 is calculated as the angle between the magnetic field and \mathbf{a}^0 according to eq 10 (see Figure 1). Relatively small values are obtained for the coefficient c_0^2 since the anisotropy of the g -tensor is smaller than that of the hyperfine tensor. On the basis of these data we expect that the largest effect of the secular contributions is observed at $\theta_B \approx 45^\circ$ corresponding to the maximum of these coefficients. On the other hand, the secular contributions have no effect on the ESR line shape at canonical orientations, $\theta_B = 0^\circ$ or $\theta_B = 90^\circ$, since the coefficients $c_M(\theta_B)$ vanish at these orientations.

Correlation Functions for Director Fluctuations. To evaluate the characteristic functions $h(t)$ eq 52 and $g(t)$ eq 64, which determine the contribution of the director fluctuations to spin relaxation, we need to specify the time-correlation function for the transverse components of the local director. We shall employ the standard theory of elasticity and hydrodynamics for well-aligned nematics.^{15,16} By introducing a normal-mode decomposition, the required correlation function of the transverse component $n_x(\mathbf{r}, t)$ at an arbitrary location r can be written in the following form

$$\overline{n_x(0)n_x(t)} = \overline{n_x^2} \frac{1}{k_c} \int_0^{k_c} dk e^{-t/\tau(k)} \quad (66)$$

where k is the module of the wavevector associated with the generic normal mode of the fluctuating director field, and $\tau(k) = (Kk^2/\eta)^{-1}$ is the corresponding relaxation time. The parameters K and η are the average elastic constant and the effective viscosity, respectively, in the so-called *one constant approximation*. The wavevector modules have an upper limit of $k_c = 2\pi/\lambda_c$, where λ_c is the short-wavelength cutoff. Accordingly, $\tau_c \equiv \tau(k_c)$ is the lower boundary of the relaxation times, i.e., the fastest relaxation time of the director fluctuations. Moreover, $\overline{n_x^2} = k_B T k_c / (2\pi^2 K)$ is the mean square amplitude of the fluctuations. The integral eq 66 can be solved analytically yielding¹⁷

$$\overline{n_x(0)n_x(t)} = \overline{n_x^2} \frac{\sqrt{\pi}}{2} \frac{\text{erf}(\sqrt{t/\tau_c})}{\sqrt{t/\tau_c}} \quad (67)$$

where $\text{erf}(\cdot)$ denotes the Error Function.

The Fourier transform of this correlation function allows one to evaluate the spectral density eq 51 for the pseudosecular contributions. It is conveniently calculated by integrating first over the time variable, and then over the wavevector modules. With a suitable change of variables, the final result for $\tilde{h}(\omega)$ is

$$\tilde{h}(\omega) = \frac{(A_{\parallel} - A_{\perp})^2}{8} [\cos^2(2\theta_B - \theta') + \cos^2\theta_B] \overline{n_x^2} \tau_c \int_0^1 dx \frac{x^2 + i\omega\tau_c}{x^4 + (\omega\tau_c)^2} \quad (68)$$

The evaluation of the characteristic function $g(t)$ eq 64 requires the double time integral of eq 67, which can be

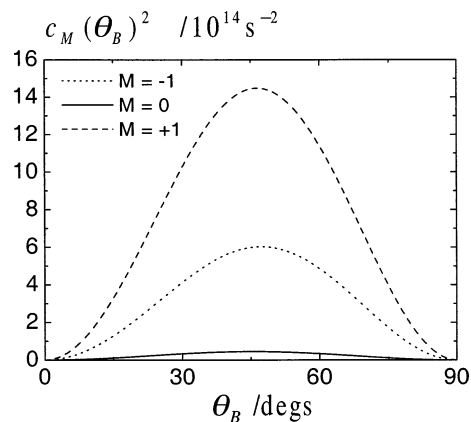


Figure 2. Angular dependence of the coefficients $c_M^2(\theta_B)$ characterizing the strength of the secular contributions for the examined nitroxide spin probe.

performed analytically to yield¹⁷

$$g(t) = \frac{\overline{n_x^2} \tau_c^2}{3} [2\sqrt{\pi}(t/\tau_c)^{3/2} \text{erf}\sqrt{t/\tau_c} + (t/\tau_c)(2e^{-t/\tau_c} - 3) + 1 - e^{-t/\tau_c}] \quad (69)$$

In summary, the only parameters necessary to specify the director fluctuations within the one constant approximation are the amplitude $\overline{n_x^2}$ and the fastest relaxation time τ_c . In all the calculations presented in the following, we set $\overline{n_x^2} = 0.01$ which corresponds to typical values for the viscoelastic parameters²⁶ and to a short-wavelength cutoff of the order of a molecular length.

Secular Contributions. First, we analyze the secular contributions to the ESR spectrum as described by the spectral densities $\tilde{f}_M(\Delta\omega)$ defined in eq 56. According to eq 58, these spectral densities represent the line shapes, $\tilde{G}_M(\Delta\omega) = \tilde{f}_M(\Delta\omega)$, in the absence of pseudosecular contributions, i.e., in the hypothetical case where $\tilde{h}(a^0/2) = 0$. From eq 63 it follows that the spectral densities depend on the magnetic parameters only through the coefficient c_M^2 whose angular dependence is reported in Figure 2 for the examined spin probe. One can easily figure out the effects of changing the coefficient c_M^2 for a given model of director fluctuations as specified by the function $g(t)$. Clearly, an increase of c_M^2 leads to a faster relaxation of the magnetization component described by $f_M(t)$, and correspondingly to a broader line shape $\tilde{f}_M(\Delta\omega)$ in the ESR spectrum. For these reasons, we shall concentrate the analysis of the line shape for a fixed coefficient c_M^2 . In particular, we choose the value $c_M^2 = 4 \times 10^{14} \text{ s}^{-2}$, which is within the range of values displayed in Figure 2. With this choice, the line shape $\tilde{f}_M(\Delta\omega)$, and its time dependent counterpart $f_M(t)$, depend only on two parameters: the molecular relaxation rate R_M^{mol} and the fastest relaxation time τ_c of director fluctuations (the amplitude of the director fluctuations being fixed to $\overline{n_x^2} = 0.01$).

In Figure 3, the time dependence of $f_M(t)$ is displayed for two different values of τ_c . The corresponding line shapes, obtained from the real part of $\tilde{f}_M(\Delta\omega)$, are depicted in Figure 4 (continuous lines). Both model calculations refer to a vanishing molecular contribution, $R_M^{\text{mol}} = 0$, to display the effects of secular contributions only. Because of the logarithmic scale employed in Figure 3, it should be evident that $f_M(t)$ cannot be represented as a simple exponential decay and, therefore, significant deviations from the Lorentzian line shape are

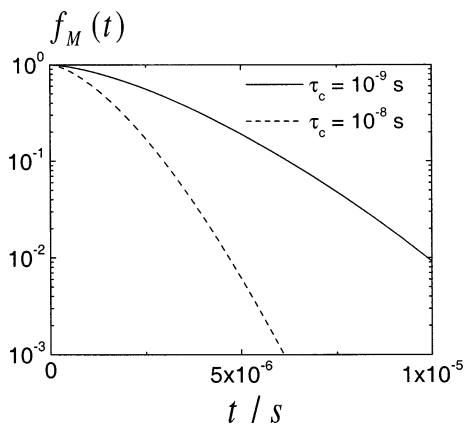


Figure 3. Time dependence of the function $f_M(t)$ describing the secular contributions for a nitroxide spin probe subject to director fluctuations in a nematic phase. The time profiles refer to two different values for the shortest relaxation time τ_c of the director fluctuations: $\tau_c = 10^{-9}$ s (continuous line), $\tau_c = 10^{-8}$ s (dashed line). Fixed parameters are $c_M^2 = 4 \times 10^{14} \text{ s}^{-2}$, $R_M^{\text{mol}} = 0$, and $n_x^2 = 0.01$.

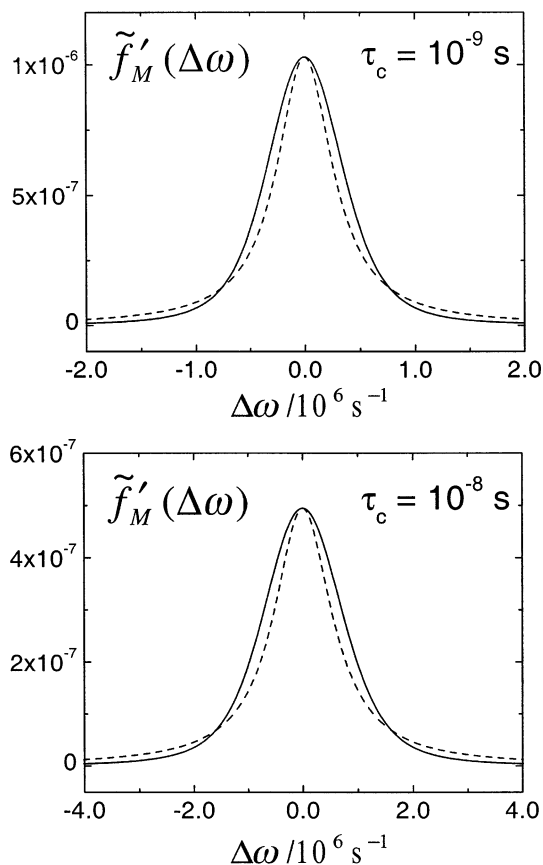


Figure 4. Line shapes of the secular contributions (continuous lines) for a nitroxide spin probe subject to director fluctuations in a nematic phase. The profiles are calculated as the real part of $\tilde{f}_M(\Delta\omega)$ for the same parameters used in Figure 3. For comparison, also Lorentzian profiles (dashed lines) are depicted. The line widths of these Lorentzians have been evaluated according to eq 73.

expected for $\tilde{f}_M(\Delta\omega)$. To quantify these deviations, a relation has been established between the line shape function $\tilde{f}_M(\Delta\omega)$ and the Lorentzian profile parametrized according to its width R , i.e.,

$$L_R(\Delta\omega) = \frac{R}{\Delta\omega^2 + R^2} \quad (70)$$

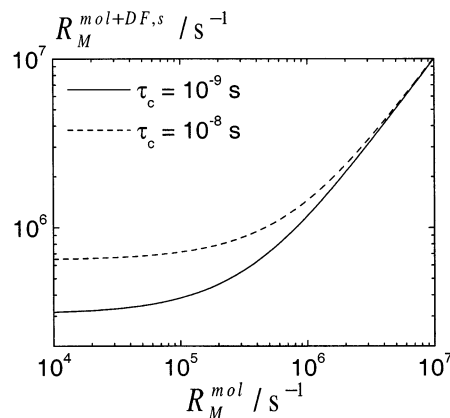


Figure 5. Dependence of the cumulative width of the line shape function $\tilde{f}_M(\Delta\omega)$ on the molecular tumbling contribution R_M^{mol} . The line widths have been calculated for two different values for the shortest relaxation time τ_c of director fluctuations: $\tau_c = 10^{-9}$ s (continuous line), $\tau_c = 10^{-8}$ s (dashed line). The parameters $c_M^2 = 4 \times 10^{14} \text{ s}^{-2}$ and $n_x^2 = 0.01$ have been employed as in Figure 3.

One can easily verify that the two line shape functions $\tilde{f}_M(\Delta\omega)$ and $L_R(\Delta\omega)$ have the same normalization evaluated as the integral in the frequency domain

$$\int_{-\infty}^{+\infty} d\Delta\omega \tilde{f}_M(\Delta\omega) = \int_{-\infty}^{+\infty} d\Delta\omega L_R(\Delta\omega) = \pi \quad (71)$$

To choose the Lorentzian line shape which exhibits the optimized superposition with a given profile $\tilde{f}_M(\Delta\omega)$, we impose the constraint of identical values at zero frequency

$$\tilde{f}_M'(0) = L_R(0) = 1/R \quad (72)$$

and this allows one to determine the width parameter R of the Lorentzian profile. Such a parameter will be identified with the cumulative width due to both molecular tumbling and secular contributions modulated by director fluctuations

$$R_M^{\text{mol+DF,s}} \equiv 1/\tilde{f}_M'(0) \quad (73)$$

In the absence of molecular contributions, i.e., for $R_M^{\text{mol}} = 0$, this parameter is denoted by $R_M^{\text{DF,s}}$. For the parametrization used in Figure 4, $R_M^{\text{DF,s}}$ assumes values of $R_M^{\text{DF,s}} = 6.4 \times 10^5 \text{ s}^{-1}$ ($\tau_c = 10^{-8}$ s) and $R_M^{\text{DF,s}} = 3.1 \times 10^5 \text{ s}^{-1}$ ($\tau_c = 10^{-9}$ s), which correspond to a few tenths of one Gauss when converted to magnetic field units. The shortening of the fastest relaxation time of the director fluctuations induces a narrowing of the line shape due to secular contributions. Indeed, the lowering of τ_c , for a given amplitude n_x^2 of the director fluctuations, leads to a decrease of the weight of the slower fluctuation modes that are more effective in producing the line broadening.

The dashed lines in Figure 4 indicate Lorentzian profiles evaluated according to the effective width $R_M^{\text{DF,s}}$. The comparison with the spectral density $\tilde{f}_M'(\Delta\omega)$ (continuous lines) reveals the peculiarities of the line shape due to the secular contributions modulated by director fluctuations. In principle, specific effects of director fluctuations could be detected from the deviations in the line shapes of the ESR spectrum from the Lorentzian profile. However, these effects on the line shapes tend to disappear by increasing the molecular tumbling contribution, R_M^{mol} .

To quantify the molecular contribution to the cumulative width, we have represented in Figure 5 the parameter $R_M^{\text{mol+DF,s}}$ as a function of R_M^{mol} for the same parameter set used in Figure

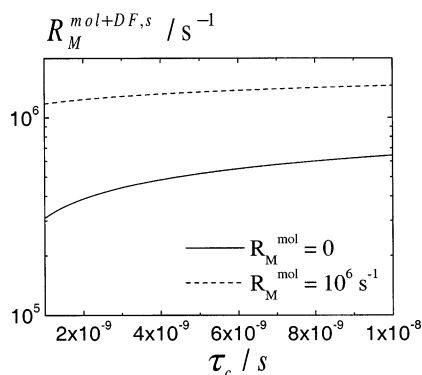


Figure 6. Dependence of the cumulative width of the line shape function $\tilde{f}_M(\Delta\omega)$ on the shortest relaxation time τ_c of the director fluctuations. The calculations refer to two different values for the molecular tumbling contributions: $R_M^{\text{mol}} = 0$ (continuous line), $R_M^{\text{mol}} = 10^6 \text{ s}^{-1}$ (dashed line). The fixed parameters are $c_M^2 = 4 \times 10^{14} \text{ s}^{-2}$ and $n_x^2 = 0.01$.

3. Of course, for $R_M^{\text{mol}} \ll R_M^{\text{DF},s}$ the line width is determined by the secular contributions: $R_M^{\text{mol}+\text{DF},s} \approx R_M^{\text{DF},s}$. In the opposite situation, $R_M^{\text{mol}} \gg R_M^{\text{DF},s}$, the secular contributions are negligible and the width is controlled by the molecular tumbling: $R_M^{\text{mol}+\text{DF},s} \approx R_M^{\text{mol}}$. Correspondingly, the Lorentzian profile is recovered for the line shape.

Let us now examine the effect of the fastest relaxation time τ_c of the director fluctuations on the cumulative line width. Figure 6 shows the dependence of $R_M^{\text{mol}+\text{DF},s}$ on τ_c for two different values of the molecular contribution R_M^{mol} . A significant dependence on τ_c is detected if R_M^{mol} is negligible, with a nearly 3-fold decrease of the width for a reduction of τ_c by one decade. On the contrary, this dependence becomes much weaker if the molecular contribution prevails, i.e., if R_M^{mol} is large enough to wash out the secular contributions.

Finally, one could examine also the dependence of the line shape on the amplitude n_x^2 of the director fluctuations. However, this parameter enters as a factor in the characteristic function $g(t)$ eq 69 describing the effects of the director fluctuations on the modulation of secular contributions. Thus, the modification of n_x^2 and the change of the coefficient c_M^2 have similar effects on the function $f_M(t)$ eq 63. Therefore, the above considerations about the influence of the coefficients c_M^2 can be applied also to the change of the director fluctuation amplitude.

Pseudosecular Contributions. The pseudosecular contributions are described by the spectral density $\tilde{h}(\omega)$, eq 68, at half of the hyperfine splitting a^0 . According to eq 60, the real part of $\tilde{h}(a^0/2)$ determines the contribution to the line widths, while the imaginary part gives rise to a shift of the outer hyperfine lines. In Figure 7, $\tilde{h}'(a^0/2)$ (continuous line) and $\tilde{h}''(a^0/2)$ (dashed line) are plotted as a function of the fastest relaxation time τ_c of the director fluctuations. Both curves refer to a director orientation of $\theta_B = 45^\circ$. Notably, the values of $\tilde{h}'(a^0/2)$ and $\tilde{h}''(a^0/2)$ are orders of magnitude smaller than the secular contributions $R_M^{\text{DF},s}$ to the line width under similar conditions (see Figure 6). This suggests that pseudosecular contributions can be neglected in the analysis of the ESR line shape. However, one should take into account that the secular contributions strongly depend on the magnitude of the coefficients $c_M(\theta_B)^2$, and the results of Figures 3–6 refer to a particular choice of these coefficients. To provide a more precise comparison, we have evaluated the secular contributions, $R_M^{\text{DF},s}$, and the

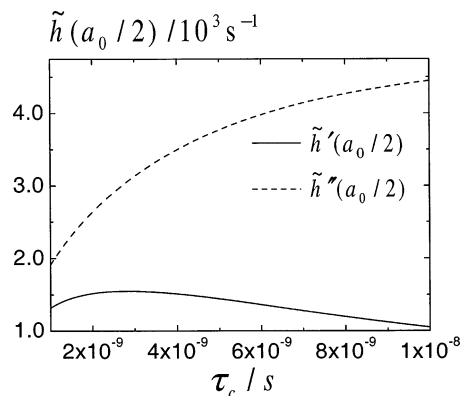


Figure 7. Real (continuous line) and imaginary part (dashed line) of the spectral density function $\tilde{h}(a^0/2)$ describing the pseudosecular contributions as a function of the shortest correlation time τ_c of the director fluctuations. The spectral densities refer to the examined nitroxide spin probe in a nematic phase and a director orientation of $\theta_B = 45^\circ$.

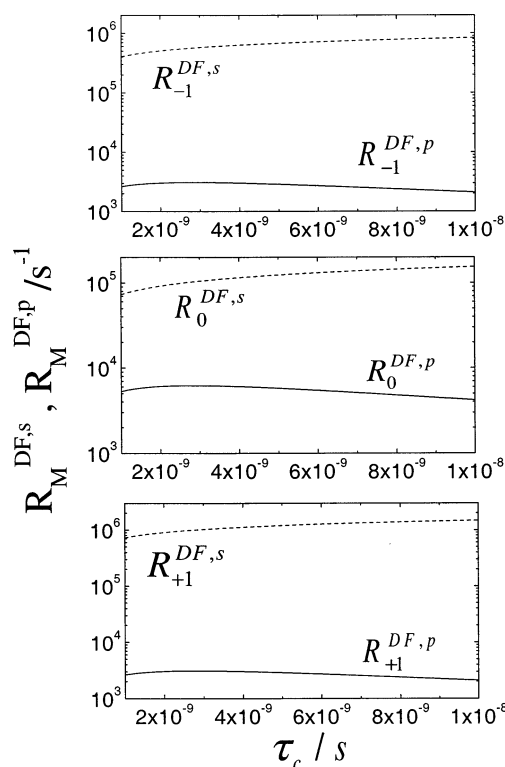


Figure 8. Secular and pseudosecular contributions to the line width, $R_M^{\text{DF},s}$ and $R_M^{\text{DF},p}$, for the three hyperfine lines of the examined nitroxide spin probe in a nematic phase. The line widths are calculated as functions of the shortest relaxation time τ_c of the director fluctuations. The angle between the magnetic field and the average director is $\theta_B = 45^\circ$.

pseudosecular contributions, $R_M^{\text{DF},p}$, to the line widths for the same physical situations of the examined spin probe, i.e., for $\theta_B = 45^\circ$ and $R_m^{\text{mol}} = 0$. According to eq 60, the pseudosecular line widths are given by

$$R_{\pm 1}^{\text{DF},p} = 2\tilde{h}'(a^0/2) \quad R_0^{\text{DF},p} = 4\tilde{h}'(a^0/2) \quad (74)$$

In Figure 8 the various contributions to the line width are plotted as a function of the fastest relaxation time τ_c of the director fluctuations. Continuous lines denote pseudosecular contributions, while dashed lines indicate secular contributions. One sees that in the case of the outer lines $M = \pm 1$, the secular line

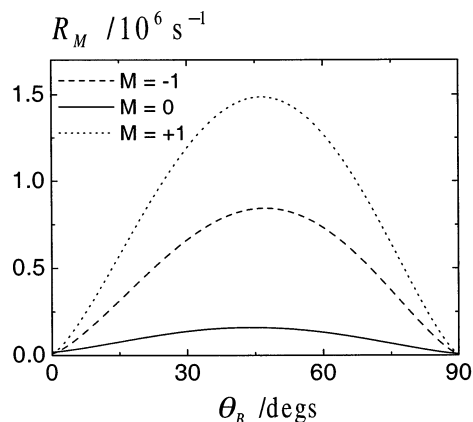


Figure 9. Dependence of the widths of the three hyperfine lines of the examined nitroxide spin probe in a nematic phase, as function of the angle θ_B between magnetic field and average director. The line widths are calculated for the fixed parameters $\tau_c = 10^{-8}$, $R_M^{\text{mol}} = 0$, and $\overline{n_x^2} = 0.01$.

widths are larger by more than 2 orders of magnitude, while a somewhat smaller difference is obtained for the central line $M = 0$ because of the low value of the coefficient c_0^2 (see Figure 2). These results confirm that pseudosecular line widths can be neglected in the analysis of ESR line shapes. A similar consideration applies to the shift induced by pseudosecular contributions since, according to Figure 7, these shifts are much smaller than the secular line widths.

Angular Dependence of the Line Widths. On the basis of the previously analyzed properties, the overall line widths of the hyperfine lines can be evaluated as

$$R_M = R_M^{\text{mol+DF,s}} + R_M^{\text{DF,p}} \quad (75)$$

In Figure 9 the angular dependence of these line widths is depicted for $\tau_c = 10^{-8}$ s and a vanishing molecular contribution, i.e., for $R_M^{\text{mol}} = 0$. The profiles roughly follow the behavior of the coefficients c_M^2 shown in Figure 2, because of the predominance of the secular contributions. This implies that director fluctuations have a small effect at the canonical orientations ($\theta_B = 0^\circ, 90^\circ$) where only pseudosecular terms contribute. Of course, for a realistic representation of the line widths in the ESR spectrum, also the angular dependent contributions R_M^{mol} due to the molecular tumbling motion have to be considered, and this would change the angular dependence of the overall line widths, as well as their dependence on the nuclear spin quantum number M .

An important issue to raise is the relative role of director fluctuations and molecular tumbling in determining the ESR profile. A quantitative estimate is extremely difficult, mainly because the director fluctuation effects are weighted by the fluctuation amplitude $\overline{n_x^2}$, a parameter for which precise estimates or experimental values do not exist. Moreover, also the other parameter τ_c , determining the fastest relaxation time of director fluctuations, is not easily accessible. Therefore, we can only highlight the situations where director fluctuations exhibit the largest effect. The angular dependence displayed in Figure 9 clearly points to sample orientations different from the canonical ones, with a maximum contribution at $\theta_B \approx 45^\circ$. Because of the difficulties of imposing arbitrary orientations to nematic samples, this suggests to study the effects of director fluctuations in smectics or membranes, where the alignment can more easily be controlled by surface effects. Also the choice of the spin probe molecule could be optimized for this purpose.

Since the secular contributions are weighted by the square of the coefficients c_M , eq 62, which are linearly dependent on the anisotropy of the averaged tensors, i.e., $(g_{\parallel} - g_{\perp})$ and $(A_{\parallel} - A_{\perp})$, director fluctuation effects would be enhanced for highly ordered probes. In principle, this can be realized by increasing the anisotropy of the shape or the size of the spin probe.²⁷ In the latter case, however, a slower tumbling motion would result with a large competing effect of the molecular contribution R_M^{mol} . Therefore, the optimal probe should have a very anisotropic shape but still a small size.

5. Conclusions

To the best of our knowledge, this work represents the first slow-motional analysis of director fluctuation effects on ESR spectra. By employing the methodology introduced in ref 17, and by generalizing it to pseudosecular contributions, explicit relations have been derived for the line shapes in the ESR spectrum, under the assumption that the lines are well separated, i.e., for fast molecular tumbling. It should be recalled that the full solution of the stochastic Liouville equation is required to treat the fluctuations of the director field, which has always components whose relaxation rates are smaller than the anisotropies of the spin Hamiltonian.

In the final expressions for the ESR line shapes, the director fluctuations are accounted for by the correlation function of the transverse components of the director. Thus, although we have reported specific results for the nematic phase in the so-called one constant approximation,¹⁵ the theory can easily be combined with more detailed representations of director fluctuations in nematics,²⁰ or with models for director fluctuations in smectic phases²⁸ or membranes.¹⁹ The only requirement is the knowledge of the correlation function of the transverse director components.

On the application side, we have examined in detail the shape of ESR spectra of a typical spin probe (PD-tempone) in a nematic phase. Even if a truly quantitative prediction of the effects of director fluctuations on the line widths is impossible because of the uncertainty in the amplitude $\overline{n_x^2}$ of the fluctuations and in its shortest relaxation time τ_c , the theory allows a separate treatment of the secular and the pseudosecular contributions with a clear identification of the physical parameters controlling them. In particular, the secular terms of the spin Hamiltonian provide the largest contribution to the line width for a director alignment different from the canonical orientations, i.e. $\theta_B \neq 0^\circ, 90^\circ$.

An important control parameter is the ordering of the spin probe, since the magnitude of the effects of director fluctuations is determined by the anisotropy of the magnetic tensors averaged with respect to the molecular orientational distribution. Thus, director fluctuations exhibit a stronger effect in the case of highly ordered spin probes. However, the molecular tumbling has a competing effect on the relaxation rates of the transverse magnetization. Generally, the contribution of the molecular motion increases with the size of the spin probe because of the slowing down of the rotational diffusion. Therefore, the ideal situation for detecting the effects of director fluctuations on the ESR spectra is that of small sized but highly ordered spin probes. Moreover, the line widths should be measured at orientations different from the canonical ones (i.e., $\theta_B \neq 0^\circ, 90^\circ$). On the other hand, the magnitude of director fluctuation effects strongly depends on the values of their amplitude ($\overline{n_x^2}$) and their shortest relaxation time (τ_c). As an example we consider the case of PD-tempone in the nematic phase of 8CB. From the

data of ref 25 for a macroscopically aligned sample at $\theta_B = 0^\circ$, i.e., in conditions where the director fluctuations contribute only through negligible pseudosecular terms, we estimate an average molecular contribution to the line widths of $R^{\text{mol}} \simeq 5 \times 10^{-6} \text{ s}^{-1}$. Calculations of $R^{\text{mol+DF,s}}$ versus τ_c have been performed like in Figure 6 by using such an estimate of R^{mol} and the parameter $c_M^2 = 4 \times 10^{14} \text{ s}^{-1}$ attainable at noncanonical orientations (see Figure 2), but with n_x^2 ranging from 0.01 up to 0.03. For the case $n_x^2 = 0.01$ (which corresponds to an average angular fluctuation of $\sim 6^\circ$), if τ_c is varied within the meaningful range 10^{-9} – 10^{-8} s , the director fluctuations would contribute to the line shape (mainly through the secular terms) with an amount between 2 ÷ 5%. For $n_x^2 = 0.03$ (corresponding to a larger but still reasonable fluctuation amplitude of $\sim 10^\circ$), the contribution is enhanced to 5 ÷ 15%. Therefore, with PD-tempone in 8CB one expects a nonnegligible contribution to the line shape due to director fluctuations (of the order of $\sim 10\%$) if the spectra are detected at noncanonical orientations.

Since the ESR line widths include contributions from both molecular tumbling and director fluctuations, it is difficult to separate them in the experimental spectra. Therefore, CW detection of ESR spectra does not provide enough information for a complete characterization of director fluctuations in ordered fluids. On the other hand, the previous work on deuterium NMR^{17–20} demonstrates that the dispersion of the transverse relaxation rates with respect to the pulse-spacing in multipulse experiments provides a more efficient tool for recognizing specifically the director fluctuation effects. We expect that a similar procedure can be applied to pulsed ESR experiments analyzed through two-dimensional Fourier transforms, such as the two-dimensional electron–electron double resonance (2D-ELDOR²⁹) experiments. Also in this case one can probe the dependence of the transverse relaxation phenomena on the pulse separation time (i.e., the *mixing time*) corresponding to the time scale of the slow relaxing modes of the director fluctuations.^{13,30} However, the theoretical interpretation of the director fluctuation effects on the 2D-ELDOR experiments requires the generalization of the theory developed for the ESR line width, and this will represent the natural continuation of the present work.

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