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Transverse Nuclear Spin Relaxation Due to Director Fluctuations in Liquid Crystals—A Slow-Motional Theory

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Transverse nuclear spin relaxation measurements, employing the Carr−Purcell−Meiboom−Gill sequence, can provide detailed information on the dynamics of director fluctuations in liquid crystals. In principle, a full characterization of the rate dispersion of the director modes can be derived from such measurements. However, the rigorous analysis of these experiments is generally hampered by the lack of a time-scale separation between the slow director fluctuations and the transverse magnetization decay. Under these conditions, the use of a fast-motion theory (i.e., Redfield theory) is no longer justified and one should resort to a slow-motional approach based on the stochastic Liouville equation for the simultaneous evolution of the stochastic variables (i.e., the director field) and the spin degrees of freedom. In this paper, explicit expressions for transverse deuteron spin relaxation times are derived without invoking any time-scale separation, on condition that (i) the stochastic variables are described as a multidimensional Gaussian process and that (ii) the spin Hamiltonian linearly depends on the stochastic variables. These are precisely the conditions usually adopted for the modeling of director fluctuations and their relaxation effects in the harmonic approximation. Thus, the present theory allows for a rather general analysis of the transverse magnetization decay in different kinds of experiments. In particular, analytical expressions are derived for the transverse relaxation times in Carr−Purcell−Meiboom−Gill sequences and evaluated as a function of the pulse spacing and the number of cycles in the sequence. It is shown that in the limit of an infinite number of pulses, one can interpret the measured asymptotic relaxation time as a superposition of independent contributions evaluated according to the Luz−Meiboom equation (Luz, Z.; Meiboom, S. *J. Chem. Phys.* **1963**, *39*, 366), originally derived within the Redfield limit.

1. Introduction

Two main processes are responsible for the orientational relaxation of an NMR probe in a liquid crystal: (i) the molecular rotational motion with respect to the local system of order,[1,2] i.e., the director for uniaxial phases, and (ii) the fluctuations of the director field.[3−7] The specific role of these two processes in determining the measured relaxation times depends not only on their distinctive features but also on the type of experiment and on the corresponding time window. A variety of experimental observables are accessible by NMR techniques. In the past, longitudinal spin relaxation times were often employed for characterizing both the molecular tumbling and the director fluctuations (see, e.g., the reviews in refs 8−10). More recently, pulse spacing dependent transverse spin relaxation time measurements have also been performed.[11−13] In the following, we shall develop specifically the methods of analysis for the latter type of experiments.

The two dynamical processes are well differentiated in their time scales. The molecular rotations are rather fast, with typical correlation times on the order of hundreds of picoseconds, depending on the size of the probe and on the viscosity of the medium. On the contrary, a wide range of slower motions, usually extending from milliseconds to fractions of a microsecond, is associated with director fluctuations because of their collective character. Consequently, different methods of analysis for the observed relaxation times are generally required. For the probe tumbling, one can safely apply the Redfield theory with a perturbative treatment of the molecular dynamics,[14−16] because the corresponding relaxation rate is much larger than the NMR anisotropies (in frequency units) modulated by the rotational motion. However, the same condition cannot be invoked for director fluctuations because the anisotropies might fall within the broad range of motional rates. In this case, a more general method of analysis is required with a complete treatment of the dynamical coupling between the spin degrees of freedom and the director field.

Such an approach is well-developed for the interpretation of electron paramagnetic resonance (EPR) spectra in the slow-motion regime, where the stochastic Liouville equation is employed for describing the coupled evolution of spin states

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and of stochastic variables.[17] This ensures a rather general description of the magnetization dynamics, with the Redfield limit (or fast-motion limit) recovered as a particular case. However, analytical solutions are in general not available for the stochastic Liouville equation. The calculation of EPR observables usually requires the generation of the matrix representation of the stochastic Liouville equation and its algebraic solution by employing efficient methods for sparse matrices, like the Lanczos algorithm.[18]

In principle, the same methodology has to be employed for the analysis of the effects of director fluctuations on the NMR transverse relaxation times.[19,20] This has been recognized by Heaton et al.,[12] who have selected few director modes and solved numerically the corresponding matrix representation of the stochastic Liouville equation. The main obstacle to a full solution of the problem arises from the fact that the director, being a field, is represented by an infinite set of stochastic variables. Thus, the corresponding stochastic Liouville equation is not reducible to a finite-size matrix to be solved numerically.

A complete analysis is possible only if analytical solutions of the stochastic Liouville equation are available. We shall show that such an analytical solution can be derived when the stochastic variables are described by a generic multidimensional Gaussian process. As a matter of fact, such a representation can be adopted for the director field in the harmonic representation. In this way, one can derive an exact solution of the slow-motion treatment of the transverse magnetization with explicit relations to the corresponding relaxation times.

The feasibility of slow-motional calculations in which the director fluctuations are described as a Gaussian process was already anticipated by Freed,[20] who evaluated the free-induction decay (FID) according to the second cumulant for the independent stochastic modes. Here we shall examine the problem for deuteron (^{2}H) NMR within a more general framework which allows the analysis not only of the FID but also of the time evolution of the transverse magnetization in quadrupolar echo (QE) and Carr−Purcell−Meiboom−Gill (CP) pulse sequences. It will be shown that the Carr−Purcell relaxation time can be represented as independent contributions of the director modes, evaluated according to the Luz−Meiboom equation,[21] originally derived within the Redfield limit. Interestingly, such a representation is valid also under slow-motion conditions if the limit of an infinite number of pulses in the CP sequence is considered. It should be recalled that such an extension to the slow-motion regime was conjectured from the analysis of the dispersion behavior of the experimental transverse relaxation times.[11−13]

The paper is organized as follows. In section two, we introduce the stochastic Liouville equation for the ^{2}H NMR experiments. Formal solutions (in operatorial terms) are derived for the time evolution of the transverse magnetization during the FID and in QE and CP pulse sequences. In section three, we develop explicit expressions for the magnetization observables in the various NMR experiments adopting a generic Gaussian process for the stochastic variables. In section four, the theory is applied to nematic phases and the dispersion behavior of the transverse relaxation times is characterized. The final section contains the conclusions of the work, with a discussion of future developments opened by this new method of analysis.

2. Pulsed Deuteron NMR According to the Stochastic Liouville Equation

Let us consider a ^{2}H nucleus of the molecular probe dissolved in a well-aligned sample of an uniaxial liquid crystal. We assume that the experimental observations refer to a time window such that longitudinal relaxation has negligible effects. Thus, we can employ the secular approximation for the spin Hamiltonian

$$H = H_Z + H_Q$$

$$H_Z = -\hbar\gamma_D B_0 I_z = -\hbar\omega_Z I_z$$

$$H_Q = \frac{3e^2Qq}{4} P_2(\vec{u}_Q\cdot\vec{u}_B)(I_z^2 - {}^2/_3) = \hbar\omega_Q(I_z^2 - {}^2/_3) \qquad (2.1)$$

where ω_Z and ω_Q are the Zeeman and quadrupolar frequencies, respectively, and $P_2(x)$ is the second Legendre Polynomial. The unit vectors $\vec{u}_B$ and $\vec{u}_Q$ denote the direction of the static magnetic field and the symmetry axis of the quadrupolar interaction assumed to be uniaxial. The spin operators are represented in the laboratory frame with the z axis along $\vec{u}_B$.

The magnetic interactions are modulated mainly by two types of processes: (i) the fast rotational motion of the molecule with respect to the local director and (ii) the comparatively slower collective modes of the director fluctuations. We shall assume that all of the director modes are much slower than the orientational relaxation due to the molecular tumbling so that we can treat separately their effects (see ref 7 for a description which includes their dynamical coupling and the corresponding cross-correlation effects). The director field is described through its orientations $\vec{n}(\vec{r}_i)$ at an ensemble of discrete locations $\vec{r}_i$ centered at the smallest domains compatible with the collective nature of such a property. Only two components of the director field are independent, because $|\vec{n}| = 1$. By introducing the director frame (x', y', z') with the z' axis along the average orientation of the director, such that

$$\overline{n_{x'}} = \overline{n_{y'}} = 0 \qquad (2.2)$$

we can select the following ensemble of independent stochastic variables:

$$\mathbf{q} = (..., n_{x'}(\vec{r}_i), n_{y'}(\vec{r}_i), ...) \qquad (2.3)$$

The corresponding variables for the tumbling of the probe are the Euler angles Ω, characterizing its orientation with respect to the local director. Notice that implicitly we assume that the director frame can be oriented independently of the magnetic field, as for example in the case of liquid crystal polymers.[12,13]

Because of the fast time scale of the rotational motion, one can describe the effects of molecular tumbling according to the standard Redfield theory.[14−16] Consequently, the orientational dependence of the quadrupolar Hamiltonian can be specified by the following average with respect to the probe orientation Ω:

$$\langle P_2(\vec{u}_Q\cdot\vec{u}_B)\rangle_\Omega = P_2(\vec{u}_B\cdot\vec{n}(\vec{r}_p))S_Q \qquad (2.4)$$

where $\vec{r}_p$ denotes the position of the probe and

$$S_Q \equiv \langle P_2(\vec{u}_Q\cdot\vec{n}(\vec{r}_p))\rangle_\Omega \qquad (2.5)$$

is the order parameter for the quadrupolar axis. Furthermore, by the retention of only the linear contributions of the orthogonal components of the director, eq 2.4 can be specified as

$$\langle P_2(\vec{u}_Q\cdot\vec{u}_B)\rangle_\Omega \simeq S_Q P_2(\cos(\theta_B)) + S_Q\sqrt{6}\, d^2_{0,1}(\theta_B)\, n_{x'}(\vec{r}_p) \qquad (2.6)$$

where θ_B is the angle between the static field and the average director orientation (i.e., z' axis of the director frame) and $d^j_{l,m}$

denotes a reduced Wigner function.[22] Thus, the following effective Hamiltonian for the quadrupolar interaction is obtained:

$$H_Q/\hbar = [\overline{\omega_Q} + \Delta\omega_Q(\mathbf{q})](I_z^2 - {}^2/_3) \quad (2.7)$$

where $\overline{\omega_Q}$ is the average quadrupolar frequency

$$\overline{\omega_Q} = \frac{3e^2Qq}{4} S_Q P_2(\cos\theta_B) \quad (2.8)$$

and $\Delta\omega_Q$ is the magnitude (in frequency units) of the quadrupolar interactions modulated by director fluctuations

$$\Delta\omega_Q(\mathbf{q}) = \frac{3e^2Qq}{4} S_Q\sqrt{6}\, d^2_{0,1}(\theta_B)\, n_{x'}(\vec{r}_p) \quad (2.9)$$

Because $d^2_{0,1}(\theta_B)$ vanishes for $\theta_B = 0$ and π, the Hamiltonian eq 2.7 does not include the coupling to the director when the liquid-crystal sample is aligned along the static magnetic field. In such a case, consideration of the bilinear terms of the director field would be required.[23]

The basis of the analysis of the coupled spin and director dynamics is the stochastic Liouville equation[17,18]

$$\frac{\partial}{\partial t}\rho(\mathbf{q},t) = -[(i/\hbar)(H_Z + H_Q)^\times + \Gamma + R]\rho(\mathbf{q},t) \quad (2.10)$$

which describes the time dependence of the spin density matrix $\rho(\mathbf{q},t)$ under the influence of the Hamiltonian superoperator $(H_Z + H_Q)^\times$ and the evolution operator, Γ, of the stochastic variables

$$\frac{\partial}{\partial t}p(\mathbf{q},t) = -\Gamma p(\mathbf{q},t) \quad (2.11)$$

where $p(\mathbf{q},t)$ is the probability density. Notice that implicitly we neglect the effects of translational diffusion, otherwise the probe position $\vec{r}_p$ has to be included among the stochastic variables. The relaxation times due to the fast rotational motion are taken into account by the Redfield operator R, acting on the spin degrees of freedom only. In agreement with the initial choice of the secular approximation, only the transverse component $1/T_2^0$ will be considered.

The analysis of pulsed experiments is more conveniently performed in the rotating frame.[15] For convenience, we choose the frame rotating clock-wise with the Zeeman frequency ω_Z. This allows a simplification of the problem, because the Zeeman term is eliminated in the corresponding stochastic Liouville equation

$$\frac{\partial}{\partial t}\rho(\mathbf{q},t) = -[iH_Q^\times/\hbar + \Gamma + R]\rho(\mathbf{q},t) \quad (2.12)$$

Its formal solution

$$\rho(\mathbf{q},t) = \exp\{-[iH_Q^\times/\hbar + \Gamma + R]t\}\rho(\mathbf{q},0) \quad (2.13)$$

allows the calculation of the magnetization in the rotating frame

$$M_j(t) = \frac{N}{V}\gamma_D\hbar\int d\mathbf{q}\ \mathrm{Tr}\{I_j\rho(\mathbf{q},t)\} \quad (2.14)$$

where N/V is the spin density and the index j labels the Cartesian components of the magnetization and of the spin operator. It should be emphasized that, because of the secular approximation, the spin degrees of freedom are factorized in the stochastic Liouville equation. Therefore, separate solutions can be written for the elements of the density matrix

$$\langle m_1|\rho(\mathbf{q},t)|m_2\rangle = \exp\{-[i(\overline{\omega_Q} + \Delta\omega_Q(\mathbf{q}))(m_1^2 - m_2^2) + \Gamma + R_{m_1,m_2}]t\}\langle m_1|\rho(\mathbf{q},0)|m_2\rangle \quad (2.15)$$

for m_1 and $m_2 = -1$, 0, and $+1$. The high-temperature approximation will be employed for the equilibrium state:

$$\rho_{eq}(\mathbf{q}) \simeq p_{eq}(\mathbf{q})\frac{\exp(-H_z/k_BT)}{\mathrm{Tr}\{\exp(-H_z/k_BT)\}} \simeq \frac{1}{3}p_{eq}(\mathbf{q})(1 + I_z\hbar\omega_Z/k_BT) \quad (2.16)$$

where $p_{eq}(\mathbf{q})$ is the equilibrium distribution of the stochastic variables. Thus, the equilibrium magnetization results in

$$M_{eq} = \frac{N}{V}\gamma_D\hbar\frac{2\hbar\omega_Z}{3k_BT} \quad (2.17)$$

Free-Induction Decay (FID). We start with the density matrix at equilibrium. Then, after a $(\pi/2)_x$ rotation of the magnetization about the x axis, the density matrix is given by

$$\rho(\mathbf{q},0^+) = \frac{1}{3}p_{eq}(\mathbf{q})(1 + I_y\hbar\omega_Z/k_BT) \quad (2.18)$$

By employing eq 2.18 as the initial condition for solving the stochastic Liouville equation, one can calculate the transverse magnetization $M_y(t)$ according to eq 2.14. It is easily shown that only the part of $\rho(\mathbf{q},0^+)$ proportional to I_y contributes to the transverse magnetization, which can then be written as

$$M_y(t)/M_{eq} = \frac{1}{2}\int d\mathbf{q}\ \mathrm{Tr}\{I_y\exp(-[iH_Q^\times/\hbar + \Gamma + R]t)I_y p_{eq}(\mathbf{q})\} \quad (2.19)$$

Upon the decomposition of the trace according to the required spin components, eq 2.15, the following relation is obtained for the FID:

$$M_y(t)/M_{eq} = \frac{1}{2}\mathrm{Re}\{\exp(i\overline{\omega_Q}t - t/T_2^0)\, G_{FID}(t)^* + \exp(i\overline{\omega_Q}t - t/T_2^0)\, G_{FID}(t)\} \quad (2.20)$$

where the director fluctuations determine the time dependence according to the characteristic function

$$G_{FID}(t) = \int d\mathbf{q}\ U(t)\, p_{eq}(\mathbf{q})$$
$$U(t) \equiv \exp\{-i\Delta\omega_Q(\mathbf{q})t - \Gamma t\} \quad (2.21)$$

Fourier transformation of the FID signal, eq 2.20, yields the absorption spectrum. Its shape depends on the relative weights of the stochastic part (i.e., $|\Gamma|$) and of the Hamiltonian part (i.e., $|\Delta\omega_Q|$) in the evolution operator $U(t)$. The motional narrowing profile in the Redfield limit is recovered only if the relaxation rates of the stochastic variables are much larger than the frequency of the Hamiltonian anisotropy, i.e., if

$$|\Gamma| \gg |\Delta\omega_Q| \quad (2.22)$$

In such a case, the transverse relaxation effects of the stochastic variables can be considered by a perturbation treatment, yielding an exponential decay of the characteristic function

$$G_{FID}(t) = \exp(-t/T_{2,R}) \quad (2.23)$$

where $T_{2,R}$ is the transverse relaxation time of the Redfield limit

$$1/T_{2,R} = \int d\mathbf{q}\, \Delta\omega_Q(\mathbf{q})\Gamma^{-1}\Delta\omega_Q(\mathbf{q})\, p_{eq}(\mathbf{q}) \qquad (2.24)$$

The corresponding absorption spectrum consists of two Lorentzians at frequencies $\omega_Z \pm \overline{\omega_Q}$ with the line width $1/T_2^0 + 1/T_{2,R}$. If the condition in eq 2.22 is violated, the spectrum cannot be reduced to a superposition of two Lorentzians and the full slow-motional calculation should be performed (see section three). In such a case, the Redfield limit expression, eq 2.24, for the transverse relaxation time is not meaningful anymore.

QE Sequence. Starting from the equilibrium state, we now consider the QE sequence $(\pi/2)_x - \tau - (\pi/2)_y - \tau$, in which the transverse magnetization $M_y(2\tau)$ is detected at time 2τ. After the first pulse, the density matrix is given by eq 2.18. However, because only the component proportional to I_y contributes to the final observable, we can write

$$\rho(\mathbf{q},0^+) = \frac{\hbar\omega_Z}{3k_BT} p_{eq}(\mathbf{q}) I_y \qquad (2.25)$$

Immediately before the second pulse, the density matrix can be written as

$$\rho(\mathbf{q},\tau^-) = \exp(-[iH_Q^\times/\hbar + \Gamma + R]\tau)\rho(\mathbf{q},0^+) \qquad (2.26)$$

where the nonvanishing elements are given by

$$\langle 0|\rho(\mathbf{q},\tau^-)|-1\rangle = \langle -1|\rho(\mathbf{q},\tau^-)|0\rangle^* = -\frac{i}{\sqrt{2}} h(\mathbf{q},\tau)$$

$$\langle 1|\rho(\mathbf{q},\tau^-)|0\rangle = \langle 0|\rho(\mathbf{q},\tau^-)|1\rangle^* = -\frac{i}{\sqrt{2}} h(\mathbf{q},\tau)^* \qquad (2.27)$$

and

$$h(\mathbf{q},\tau) = \frac{\hbar\omega_Z \exp(i\overline{\omega_Q}\tau - \tau/T_2^0)}{3k_BT} U(\tau)^*\, p_{eq}(\mathbf{q}) \qquad (2.28)$$

The action of the second pulse is described by a transformation T of the density matrix according to[15,24]

$$\rho(\mathbf{q},\tau^+) = T\rho(\mathbf{q},\tau^-) = \exp(i\pi I_y/2)\rho(\mathbf{q},\tau^-)\exp(-i\pi I_y/2) \qquad (2.29)$$

By taking into account the following relation for the rotation matrix elements[22]

$$\langle n|\exp(-i\pi I_y/2)m\rangle = d^1_{n,m}(\pi/2) \qquad (2.30)$$

one obtains

$$\langle 0|\rho(\mathbf{q},\tau^+)|-1\rangle = \langle -1|\rho(\mathbf{q},\tau^+)|0\rangle^* = -\frac{i}{\sqrt{2}} h(\mathbf{q},\tau)$$

$$\langle 1|\rho(\mathbf{q},\tau^+)|0\rangle = \langle 0|\rho(\mathbf{q},\tau^+)|1\rangle^* = -\frac{i}{\sqrt{2}} h(\mathbf{q},\tau) \qquad (2.31)$$

After the second evolution for a time τ, the relevant elements of the density matrix are given by

$$\langle 0|\rho(\mathbf{q},2\tau)|-1\rangle = \langle -1|\rho(\mathbf{q},2\tau)|0\rangle^* = -\frac{i}{\sqrt{2}} h(\mathbf{q},2\tau)^*$$

$$\langle 1|\rho(\mathbf{q},2\tau)|0\rangle = \langle 0|\rho(\mathbf{q},2\tau)|1\rangle^* = -\frac{i}{\sqrt{2}} h(\mathbf{q},2\tau) \qquad (2.32)$$

where

$$h(\mathbf{q},2\tau) = \frac{\hbar\omega_Z \exp(-2\tau/T_2^0)}{3k_BT} U(\tau)\, U(\tau)^*\, p_{eq}(\mathbf{q}) \qquad (2.33)$$

Thus, the transverse magnetization at time 2τ, i.e., the intensity of the echo, can be written as

$$M_y(2\tau)/M_{eq} = \exp(-2\tau/T_2^0)\, \mathrm{Re}\{G_{QE}(2\tau)\} \qquad (2.34)$$

where the effects of the director fluctuations on the QE are considered by the following characteristic function

$$G_{QE}(2\tau) = \int d\mathbf{q}\, U(\tau)^*\, U(\tau)\, p_{eq}(\mathbf{q}) \qquad (2.35)$$

CP Sequence. The quadrupolar version of the CP sequence[25-27] consists of a QE sequence followed by a train of $(n-1)$ elementary sequences of the form $\tau - (\pi/2)_y - \tau$. By employing the above method of analysis, one derives the following explicit relation

$$M_y(2n\tau)/M_{eq} = \int d\mathbf{q}\, \mathrm{Tr}\{I_y \exp(-[iH_Q^\times/\hbar + \Gamma + R]\tau) \times [T\exp(-[iH_Q^\times/\hbar + \Gamma + R]2\tau)]^{n-1}\, T\exp(-[iH_Q^\times/\hbar + \Gamma + R]\tau) I_y p_{eq}(\mathbf{q})\} \qquad (2.36)$$

Performing the transformation T like in the previous section, we can eliminate the spin degrees of freedom and obtain

$$My(2n\tau)/M_{eq} = \exp(-2n\tau/T_2^0)\, Re\{G_{CP}(2n\tau)\} \qquad (2.37)$$

where the effects of the director fluctuations on the decay of the CP echo are described by the function

$$G_{CP}(2n\tau) = \int d\mathbf{q} \cdots U(\tau)\, U(\tau)^*\, \mathrm{U}(\tau)^*\, \mathrm{U}(\tau)\, p_{eq}(\mathbf{q}) \qquad (2.38)$$

Notice that the operator U appears $2n$ times. A solution with a similar structure albeit for a quite different dynamical problem, such as the two site exchange, has been derived by Müller et al.[28]

3. Formal Solution for a Gaussian Process

To derive explicit expressions for the magnetization observables, the time evolution for the stochastic variables has to be evaluated. This can be done in a rather general way by supposing that director fluctuations constitute a multidimensional Gaussian process. Accordingly, we assume the following relations for the normalized equilibrium distribution:

$$p_{eq}(\mathbf{q}) = \det(\mathbf{A}/2\pi)^{1/2} \exp(-\mathbf{q}^\dagger\mathbf{A}\mathbf{q}/2) \qquad \int d\mathbf{q}\, p_{eq}(\mathbf{q}) = 1 \qquad (3.1)$$

and for the evolution operator

$$\Gamma - \sum_{i,j} \frac{\partial}{\partial q_i} D_{i,j} p_{eq}(\mathbf{q}) \frac{\partial}{\partial \mathbf{q}_j} p_{eq}(\mathbf{q})^{-1} \equiv -\left(\frac{\partial}{\partial \mathbf{q}}\right)^\dagger \mathbf{D} p_{eq}(\mathbf{q}) \frac{\partial}{\partial \mathbf{q}} p_{eq}(\mathbf{q})^{-1} \qquad (3.2)$$

where $\det(\cdots)$ denotes the determinant of a square matrix and both the curvature matrix $\mathbf{A}$ and the diffusion matrix $\mathbf{D}$ are supposed to be real, symmetric, and positive definite. Notice that the inverse of matrix $\mathbf{A}$ determines the second moments $\overline{q_i q_j} = (\mathbf{A}^{-1})_{i,j}$ in the equilibrium state, whereas the diffusion matrix describes the rates of relaxation to equilibrium and the corresponding dynamical coupling between the stochastic

variables. Because the following analysis does not require specific assumptions about the structure of the matrices **A** and **D**, the final results can be applied to different models of director fluctuations, provided that they are Gaussian processes.

Let us first evaluate the correlation function for the director fluctuations at the probe location

$$\overline{F(t')F(t'')} = \overline{F(0)F(|t''-t'|)} \int \mathrm{d}\mathbf{q}\, F(\mathbf{q}) \exp\{-\Gamma|t''-t'|\}F(\mathbf{q})p_{eq}(\mathbf{q}) \quad (3.3)$$

where

$$F(\mathbf{q}) = n_{x'}(\vec{r}_p) = \mathbf{q}^\dagger \mathbf{v} \quad (3.4)$$

and **v** is an array with null entries except for an unitary value corresponding to the selected director field component $n_{x'}(\vec{r}_p)$.

By taking into account that

$$\Gamma \mathbf{q}^\dagger \mathbf{v} p_{eq}(\mathbf{q}) = \mathbf{q}^\dagger \mathbf{A}\mathbf{D}\mathbf{v} p_{eq}(\mathbf{q}) \exp\{-\Gamma t\}\mathbf{q}^\dagger \mathbf{v} p_{eq}(\mathbf{q}) = \mathbf{q}^\dagger \mathrm{e}^{-\mathbf{A}\mathbf{D}t}\mathbf{v} p_{eq}(\mathbf{q}) \quad (3.5)$$

one can evaluate analytically the average in eq 3.3 to obtain

$$\overline{n_{x'}(0)n_{x'}(t)} = \mathbf{v}^\dagger \mathbf{A}^{-1}\mathrm{e}^{-\mathbf{A}\mathbf{D}t}\mathbf{v} = \mathbf{v}^\dagger \mathrm{e}^{-\mathbf{D}\mathbf{A}t}\mathbf{A}^{-1}\mathbf{v} \quad (3.6)$$

For later use, we introduce also the double time integral of such a correlation function

$$g(t) \equiv {}^1/_2 \int_0^t \mathrm{d}t' \int_0^t \mathrm{d}t'' \overline{n_{x'}(t')n_{x'}(t'')} = \int_0^t \mathrm{d}t' \int_0^{t'} \mathrm{d}t'' \overline{n_{x'}(0)n_{x'}(t'')} = \int_0^t \mathrm{d}t' \int_0^{t'} \mathrm{d}t''\, \mathbf{v}^\dagger \mathrm{e}^{-\mathbf{D}\mathbf{A}t''}\mathbf{A}^{-1}\mathbf{v} = \mathbf{v}^\dagger(\mathbf{D}\mathbf{A})^{-1}[t\mathbf{1} + \mathbf{D}\mathbf{A}^{-1}(\mathrm{e}^{-\mathbf{D}\mathbf{A}t} - \mathbf{1})]\mathbf{A}^{-1}\mathbf{v} \quad (3.7)$$

which corresponds to the second cumulant employed in appendix B of ref 20. The following elaborations require the reduction of the double integral

$$h(\tau, \Delta t) \equiv \int_0^\tau \mathrm{d}\tau' \int_0^\tau \mathrm{d}\tau''\, \mathbf{v}^\dagger \exp(-\mathbf{D}\mathbf{A}(\tau' + \tau'' + \Delta t)\mathbf{A}^{-1}\mathbf{v} = \int_0^\tau \mathrm{d}\tau' \int_{\tau'+\Delta t}^{\tau'+\Delta t+\tau} \mathrm{d}t'' \overline{n_{x'}(0)n_{x'}(t'')} \quad (3.8)$$

to the function $g(t)$, where in the last relation the second integration variable has been changed to $t'' = \tau' + \tau'' + \Delta t$. Such a double integral may be decomposed in

$$h(\tau, \Delta t) = \left(\int_{-\Delta t-\tau}^{\tau} d\tau' - \int_{-\Delta t-\tau}^{0} d\tau'\right) \int_0^{\tau'+\Delta t+\tau} \mathrm{d}t'' \overline{n_{x'}(0)n_{x'}(t'')} - \left(\int_{-\Delta t}^{\tau} \mathrm{d}\tau' - \int_{-\Delta t}^{0} \mathrm{d}\tau'\right) \int_0^{\tau'+\Delta t} \mathrm{d}t'' \overline{n_{x'}(0)n_{x'}(t'')} \quad (3.9)$$

and each term, after a suitable change of the integration variable τ', can then be specified according to the second cumulant eq 3.7. Thus, one finally obtains

$$h(\tau, \Delta t) = g(\Delta t + 2\tau) - 2g(\Delta t + \tau) + g(\Delta t) \quad (3.10)$$

To calculate the observables for the pulsed NMR experiments, it is necessary to evaluate the effects of the transformation $U(t)$, eq 2.21, by solving the following type of equations:

$$f_\pm(\mathbf{q}, t) = \exp\{\mp i\Delta\omega'_Q \mathbf{v}^\dagger \mathbf{q}(t - t_0) - \Gamma(t - t_0)\}\, f_\pm(\mathbf{q}, t_0) \quad (3.11)$$

where **v** is the same array as in eq 3.4 and

$$\Delta\omega'_Q = \frac{\Delta\omega_Q(\mathbf{q})}{n_{x'}(\vec{r}_p)} = \frac{3e^2Qq}{4} S_Q \sqrt{6} d^2_{0,1}(\theta_B) \quad (3.12)$$

A formal solution is easily obtained by means of a Fourier analysis, that is, by introducing the following transformed functions:

$$\tilde{f}_\pm(\mathbf{p}, t) \equiv \int \mathrm{d}\mathbf{q}\, \mathrm{e}^{-i\mathbf{q}^\dagger \mathbf{p}} f_\pm(\mathbf{q}, t) \quad (3.13)$$

which evolve in time according to

$$\frac{\partial}{\partial t}\tilde{f}_\pm(\mathbf{p}, t) = -\tilde{\Gamma}_\pm \tilde{f}_\pm(\mathbf{p}, t) \quad (3.14)$$

where the transformed operators are given by

$$\tilde{\Gamma}_\pm \equiv \mathbf{p}^\dagger \mathbf{D}\mathbf{p} + (\mathbf{p}^\dagger \mathbf{D}\mathbf{A} \pm \Delta\omega'_Q \mathbf{v}^\dagger)\frac{\partial}{\partial \mathbf{p}} \quad (3.15)$$

Thus, the formal solution in the Fourier space can be specified as

$$\tilde{f}_\pm(\mathbf{p}, t) = \exp\{-\tilde{\Gamma}_\pm(t - t_0)\}\, \tilde{f}_\pm(\mathbf{p}, t_0) \quad (3.16)$$

By noting that the Fourier transform of the equilibrium distribution is given by

$$\tilde{p}_{eq}(\mathbf{p}) = (-\mathbf{p}^\dagger \mathbf{A}^{-1}\mathbf{p}/2) \quad (3.17)$$

the characteristic functions, eqs 2.21, 2.35, and 2.38, which have previously been introduced, can be written as

$$G_{FID}(t) = [\mathrm{e}^{-\tilde{\Gamma}_+ t} \exp(-\mathbf{p}^\dagger \mathbf{A}^{-1}\mathbf{p}/2)]_{\mathbf{p}=0}$$
$$G_{QE}(2\tau) = [\mathrm{e}^{-\tilde{\Gamma}_- \tau}\mathrm{e}^{-\tilde{\Gamma}_+ \tau} \exp(-\mathbf{p}^\dagger \mathbf{A}^{-1}\mathbf{p}/2)]_{\mathbf{p}=0}$$
$$G_{CP}(2n\tau) = [\cdots \mathrm{e}^{-\tilde{\Gamma}_+ \tau}\mathrm{e}^{-\tilde{\Gamma}_- \tau}\mathrm{e}^{-\tilde{\Gamma}_- \tau}\mathrm{e}^{-\tilde{\Gamma}_+ \tau} \exp(-\mathbf{p}^\dagger \mathbf{A}^{-1}\mathbf{p}/2)]_{\mathbf{p}=0} \quad (3.18)$$

Given the first-order character of the operators $\tilde{\Gamma}_\pm$, the formal solutions can be obtained using standard procedures for ordinary differential equations. Let us consider the following trial function:

$$\tilde{f}_\pm(\mathbf{p}, t) = \exp\{-a(t) - \mathbf{p}^\dagger \mathbf{b}(t) - \mathbf{p}^\dagger \mathbf{A}^{-1}\mathbf{p}/2\} \quad (3.19)$$

which represents a shifted Gaussian whose width corresponds to that of the equilibrium distribution, eq 3.17. The time-dependent parameters $a(t)$ and $\mathbf{b}(t)$ can be derived by imposing the condition that $\tilde{f}_\pm(\mathbf{p}, t)$ is a solution of the evolution eq 3.14, which after substitution leads to

$$-\frac{\mathrm{d}a}{\mathrm{d}t} - \mathbf{p}^\dagger \frac{\mathrm{d}\mathbf{b}}{\mathrm{d}t} = \pm\Delta\omega'_Q \mathbf{v}^\dagger(\mathbf{b} + \mathbf{A}^{-1}\mathbf{p}) + \mathbf{p}^\dagger \mathbf{D}\mathbf{A}\mathbf{b} \quad (3.20)$$

By equating the terms with the same power of **p**, one obtains a system of ordinary differential equations of the first order:

$$-\frac{\mathrm{d}a}{\mathrm{d}t} = \pm\Delta\omega'_Q \mathbf{v}^\dagger \mathbf{b}$$
$$-\frac{\mathrm{d}\mathbf{b}}{\mathrm{d}t} = \pm\Delta\omega'_Q \mathbf{A}^{-1}\mathbf{v} + \mathbf{D}\mathbf{A}\mathbf{b} \quad (3.21)$$

which have to be solved for a given set of coefficients $a(t_0)$ and $\mathbf{b}(t_0)$ at the initial time t_0. The explicit solution for the vector $\mathbf{b}(t)$ is

$$\mathbf{b}(t) = \mathrm{e}^{-\mathbf{DA}(t-t_0)}\mathbf{b}(t_0) \mp \Delta\omega'_{\mathrm{Q}} \int_0^{t-t_0} \mathrm{d}t'\, \mathrm{e}^{-\mathbf{DA}t'}\mathbf{A}^{-1}\mathbf{v} \qquad (3.22)$$

which after substitution into the equation for da/dt leads to the following relation:

$$a(t) - a(t_0) = \mp\Delta\omega'_{\mathrm{Q}} \int_{t_0}^{t} \mathrm{d}t'\, \mathbf{v}^{\dagger}\mathbf{b}(t') = (\Delta\omega'_{\mathrm{Q}})^2\, g(t-t_0) \mp \Delta\omega'_{\mathrm{Q}} \int_0^{t-t_0} \mathrm{d}t'\, \mathbf{v}^{\dagger}\mathrm{e}^{-\mathbf{DA}t'}\mathbf{b}(t_0) \quad (3.23)$$

where $g(t)$ is given by eq 3.7.

This result can immediately be applied to the calculation of the FID signal by choosing $a(0) = 0$ and $\mathbf{b}(0) = 0$ as initial conditions for $t_0 = 0$. Thus, one obtains

$$G_{\mathrm{FID}}(t) = \exp\{-a(t)\} \qquad a(t) = (\Delta\omega'_{\mathrm{Q}})^2\, g(t) \qquad (3.24)$$

For the calculation of the CP signal, one has to discretize the time axis into equal intervals of length τ, such that the previous relations can be applied iteratively. This means that from the knowledge of $a(n\tau)$ and $\mathbf{b}(n\tau)$ one can calculate both $a(n\tau + \tau)$ and $\mathbf{b}(n\tau + \tau)$. Because only pairs of time intervals need to be considered for the evaluation of the CP signal, it is convenient to eliminate the parameters for odd time intervals. Thus, we finally obtain

$$\mathbf{b}(2n\tau) = \mathrm{e}^{-2\mathbf{DA}\tau}\mathbf{b}(2n\tau - 2\tau) + (-1)^n\Delta\omega'_{\mathrm{Q}}(\mathrm{e}^{-\mathbf{DA}\tau} - \mathbf{1}) \int_0^{\tau} dt'\, \mathrm{e}^{-\mathbf{DA}t'}\mathbf{A}^{-1}\mathbf{v}$$

$$a(2n\tau) = a(2n\tau - 2\tau) + (\Delta\omega'_{\mathrm{Q}})^2[4g(\tau) - g(2\tau)] + (-1)^n\Delta\omega'_{\mathrm{Q}} \int_0^{\tau} \mathrm{d}t'\, \mathbf{v}^{\dagger}e^{-\mathbf{DA}t'}(\mathbf{1} - \mathrm{e}^{-\mathbf{DA}\tau})\mathbf{b}(2n\tau - 2\tau) \quad (3.25)$$

These equations for $n = 1$ allow the direct calculation of the characteristic function

$$G_{\mathrm{QE}}(\tau) = \exp\{-a(2\tau)\}$$
$$a(2\tau) = (\Delta\omega'_{\mathrm{Q}})^2[4g(\tau) - g(2\tau)] \qquad (3.26)$$

With the use of eq 3.26, the QE signal can be specified as

$$M_y(2\tau)/M_{\mathrm{eq}} = \exp\{-2\tau/T_2^{\mathrm{QE}}(\tau)\} \qquad (3.27)$$

where we have introduced the corresponding transverse relaxation time $T_2^{\mathrm{QE}}(\tau)$

$$\frac{1}{T_2^{\mathrm{QE}}(\tau)} = \frac{1}{T_2^0} + (\Delta\omega'_{\mathrm{Q}})^2\frac{4g(\tau) - \mathrm{g}(2\tau)}{2\tau} \qquad (3.28)$$

which in general depends on the pulse spacing τ.

By applying iteratively the first equation of 3.25, one obtains an explicit solution for the coefficients **b**, according to

$$\mathbf{b}(2n\tau) = \Delta\omega'_{\mathrm{Q}}\sum_{k=0}^{n-1}(-1)^{n+k}\mathrm{e}^{-2k\mathbf{DA}\tau}(e^{-\mathbf{DA}\tau} - \mathbf{1}) \times \int_0^{\tau} \mathrm{d}t'\mathrm{e}^{-\mathbf{DA}t'}\mathbf{A}^{-1}\mathbf{v} \quad (3.29)$$

After substitution of this solution into the second equation of 3.25, the increments of the coefficient a result in

$$\frac{a(2n\tau) - a(2n\tau - 2\tau)}{(\Delta\omega'_{\mathrm{Q}})^2} = 4g(\tau) - g(2\tau) + \sum_{k=0}^{n-2}(-1)^k \int_0^{\tau} \mathrm{d}t' \int_0^{\tau} \mathrm{d}t''\, \mathbf{v}^{\dagger}(\mathbf{1} - \mathrm{e}^{-\mathbf{DA}\tau})^2\exp(-\mathbf{DA}(t' + t'' + 2k\tau))\mathbf{A}^{-1}\mathbf{v} \quad (3.30)$$

By the use of property eq 3.8 and by the rearrangement of the summations, the following relation is obtained:

$$\frac{a(2n\tau) - a(2n\tau - 2\tau)}{(\Delta\omega'_{\mathrm{Q}})^2} = -4\sum_{k=0}^{n-1}(-1)^k g(2k\tau) + (-1)^n[g(2n\tau - 2\tau) - 4g(2n\tau - \tau) + g(2n\tau)] \quad (3.31)$$

whose iterative application allows one to evaluate the characteristic function

$$G_{\mathrm{CP}}(2n\tau) = \exp\{-a(2n\tau)\} \qquad (3.32)$$

For the analysis of the CP experiment, we introduce a specific transverse relaxation time, $T_{2,n}^{\mathrm{CP}}(\tau)$, on the basis of the relative decrease of the magnetization during cycle n

$$M_y(2n\tau)/M_y(2n\tau - 2\tau) = \exp\{-2\tau/T_{2,n}^{\mathrm{CP}}(\tau)\} \quad (3.33)$$

where $T_{2,n}^{\mathrm{CP}}(\tau)$ is explicitly given by

$$\frac{1}{T_{2,n}^{\mathrm{CP}}(\tau)} = \frac{1}{\mathrm{T}_2^0} + \frac{2(\Delta\omega'_{\mathrm{Q}})^2 n-1}{\tau}\sum_{k=0}(-1)^k g(2k\tau) - (-1)^n(\Delta\omega'_{\mathrm{Q}})^2\frac{g(2n\tau - 2\tau) - 4g(2n\tau - \tau) + g(2n\tau)}{2\tau} \quad (3.34)$$

Such a relaxation time depends on both the pulse spacing, τ, and the number of cycles of the pulse train, n, with the obvious equivalence

$$T_{2,1}^{\mathrm{CP}}(\tau) \equiv T_2^{\mathrm{QE}}(\tau) \qquad (3.35)$$

It will be shown in the next section that the dependence of $T_{2,n}^{\mathrm{CP}}(\tau)$ on the number of cycles is rather weak, so that one can interpret the experimental data in terms of an asymptotic relaxation time for an infinite sequence

$$T_{2,\infty}^{\mathrm{CP}}(\tau) \equiv \lim_{n\to\infty} T_{2,n}^{\mathrm{CP}}(\tau) \qquad (3.36)$$

For such an asymptotic relaxation time, one can derive a useful relation by extending the summation in eq 3.30 to infinity and by noting that

$$\sum_{k=0}^{\infty}(-1)^k\mathrm{e}^{-2k\mathbf{DA}\tau} = (\mathbf{1} + \mathrm{e}^{-2\,\mathbf{DA}\tau})^{-1} \qquad (3.37)$$

Using the explicit form of the second cumulant, eq 3.7, the following compact result is obtained:

$$1/T_{2,\infty}^{\mathrm{CP}}(\tau) = 1/\,T_2^0 + (\Delta\omega'_{\mathrm{Q}})^2 g_{\mathrm{LM}}(\tau)$$
$$g_{\mathrm{LM}}(\tau) = \mathbf{v}^{\dagger}(\mathbf{DA})^{-1}[\mathbf{1} - (\tau\mathbf{DA})^{-1}\tanh(\tau\mathbf{DA})]\mathbf{A}^{-1}\mathbf{v} \qquad (3.38)$$

where tanh denotes the hyperbolic tangent

$$\tanh(\tau\mathbf{DA}) \equiv (e^{\tau\mathbf{DA}} - e^{-\tau\mathbf{DA}})(e^{\tau\mathbf{DA}} + e^{-\tau\mathbf{DA}})^{-1} \quad (3.39)$$

Let us consider the particular case of a one-dimensional Gaussian process, i.e., $\boldsymbol{q} = q_1$, such that the matrix **DA** can be substituted by the motional rate $1/\tau_1$ of the stochastic variable q_1, whereas $\mathbf{vA}^{-1}\mathbf{v}$ can be identified with the average $\overline{q_1^2}$. Then, the relaxation rate can be specified as

$$1/T_{2,\infty}^{CP}(\tau) = 1/T_2^0 + \overline{\Delta\omega_Q^2}\tau_1[1 - (\tau_1/\tau)\tanh(\tau/\tau_1)] \quad (3.40)$$

which is just the same result as that obtained by Luz and Meiboom[21] and later by Blicharski[29] from the analysis of the CP experiment in the Redfield limit. To check its range of validity, slow-motional calculations have been performed for the two-site exchange by Allerhand and Gutowsky[30] and by Vega et al.[31] It turned out that for such a process the Luz−Meiboom equation is valid only on specific conditions. A completely different result is obtained in the case of Gaussian processes. As is shown by our analysis, eq 3.40 is the exact solution in one dimension on all dynamical conditions. For a multidimensional Gaussian process, such as director fluctuations, eq 3.38 represents the exact solution, where $g_{LM}(\tau)$ considers the contributions of all independent director modes (see the Appendix). It should be mentioned that such an extension of the Luz−Meiboom equation to the slow-motion regime of director fluctuations was conjectured in the past.[11−13] The above derivation provides a proof of the conjecture.

In the following, the main features of the present analysis will be applied to the specific case of a nematic phase. It should be emphasized, however, that the theory is rather general and can be applied to director fluctuations in other systems such as smectic phases[6,32] or bilayer membranes,[33] provided that they fulfill the requirement of a Gaussian process.

4. Application to Nematic Phases

In the Appendix, the relevant time-dependent functions for the director fluctuations in nematics are reported. The most important one for the analysis of transverse relaxation times is the second cumulant, eq A17, which can be rewritten in a scaled form as

$$g(t) = \overline{n_{x'}^2}\tau_c h(t/\tau_c) \quad (4.1)$$

where the characteristic function $h(x)$ depends on the time $x = t/\tau_c$ scaled by the fastest relaxation time τ_c of the director fluctuations:

$$h(x) = \frac{1}{3}[2\sqrt{\pi x}\,\mathrm{erf}(\sqrt{x}) + 2e^{-x} - 3 + (1 - e^{-x})/x] \quad (4.2)$$

Here erf(z) denotes the error function. Asymptotic expansions of $h(x)$ at short and long times are easily derived, yielding

$$x \ll 1: \quad h(x) = \frac{x}{2} - \frac{x^2}{18}$$

$$x \gg 1: \quad h(x) = \frac{2}{3}\sqrt{\pi x} \quad (4.3)$$

It is convenient to scale also the transverse relaxation time according to

$$\tilde{T}_2 \equiv \omega_\sigma^2\tau_c T_2 \quad (4.4)$$

where ω_σ can be identified as the root-mean-square amplitude of the modulated quadrupolar interactions eq 2.9:

$$\omega_\sigma = (\overline{n_{x'}^2})^{1/2}\Delta\omega'_Q \quad (4.5)$$

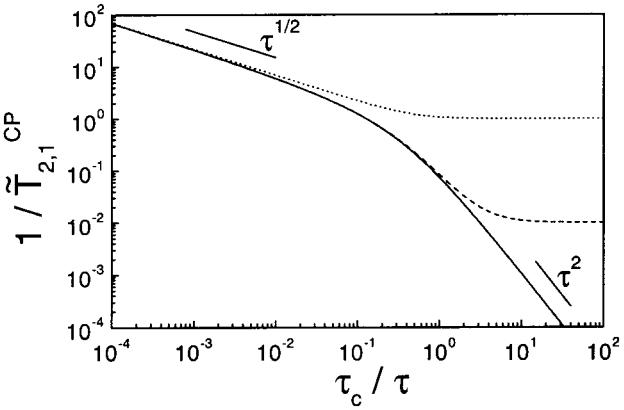

Figure 1. Scaled initial Carr−Purcell relaxation rate $1/\tilde{T}_{2,1}^{CP}(\tau)$ as a function of the scaled pulse frequency τ_c/τ for nematic director fluctuations and three different molecular contributions: $1/\tilde{T}_2^0 = 0.0$ (full line), $1/\tilde{T}_2^0 = 0.01$ (dashed line), and $1/\tilde{T}_2^0 = 1.0$ (dotted line). $\tilde{T}_{2,1}^{CP}(\tau)$ characterizes the decay of the transverse magnetization during the first cycle of a CP sequence. The straight lines with the slopes $-1/2$ and -2 indicate different dispersion regimes. $\tilde{T}_2 \equiv \omega_\sigma^2\tau_c T_2$; ω_σ = root-mean-square amplitude of the modulated quadrupolar interactions; τ_c = fastest relaxation time of the director modes.

Let us first consider the initial CP relaxation time, eq 3.35, whose scaled form can be specified as

$$\frac{1}{\tilde{T}_{2,1}^{CP}(\tau)} = \frac{1}{\tilde{T}_2^0} + 2h(\tau/\tau_c) - h(2\tau/\tau_c) \quad (4.6)$$

Note that this relaxation time characterizes the decay of the magnetization during the first cycle of a CP sequence. It is evident that the evaluation of $\tilde{T}_{2,1}^{CP}(\tau)$ requires a choice for the molecular contribution T_2^0, which can be estimated as

$$1/T_2^0 \sim (\Delta\omega'_Q)^2\tau_p \quad (4.7)$$

where τ_p is the correlation time for the rotational motion of the probe. Then, consideration of eq 4.4 yields

$$\frac{1}{\tilde{T}_2^0} \sim \frac{1}{\overline{n_{x'}^2}}\frac{\tau_p}{\tau_c} \quad (4.8)$$

Because $\overline{n_{x'}^2}$ should not be exceedingly small, whereas the molecular correlation time τ_p might be some orders of magnitude smaller than the fastest time τ_c of the director fluctuations, it is reasonable to confine $1/\tilde{T}_2^0$ within a range having an upper limit of the order of unity. In Figure 1 we represent the pulse spacing dependence of the scaled initial CP relaxation rate for $1/\tilde{T}_2^0 = 0.0$ (solid line), 0.01 (dashed line), and 1.0 (dotted line). The first example is considered just for showing in a clear form the limiting behavior of $1/\tilde{T}_{2,1}^{CP}(\tau)$

$$\tau \ll \tau_c: \quad \frac{1}{\tilde{T}_{2,1}^{CP}(\tau)} - \frac{1}{\tilde{T}_2^0} = \frac{(\tau/\tau_c)^2}{9}$$

$$\tau \gg \tau_c: \quad \frac{1}{\tilde{T}_{2,1}^{CP}(\tau)} - \frac{1}{\tilde{T}_2^0} = \frac{4 - 2\sqrt{2}}{3}\sqrt{\pi\tau/\tau_c} \quad (4.9)$$

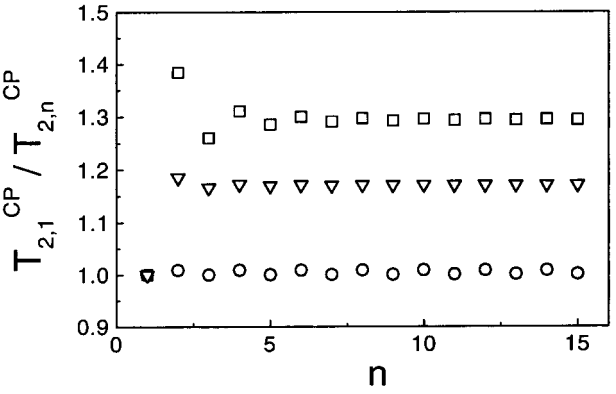

Figure 2. Dependence of the ratio $T_{2,1}^{CP}(\tau)/T_{2,n}^{CP}(\tau)$ between the initial and the *n*th Carr−Purcell relaxation time on the number of cycles *n* in a CP sequence for nematic director fluctuations and three different scaled pulse spacings: $\tau/\tau_c = 0.01$ (circles), 1.0 (squares), and 100 (triangles). $\tilde{T}_{2,n}^{CP}(\tau)$ characterizes the decay of the transverse magnetization during the *n*th cycle of the multipulse sequence. The calculations have been performed for the case of a vanishing molecular contribution $1/T_2^0 = 0$. τ_c = fastest relaxation time of the director modes.

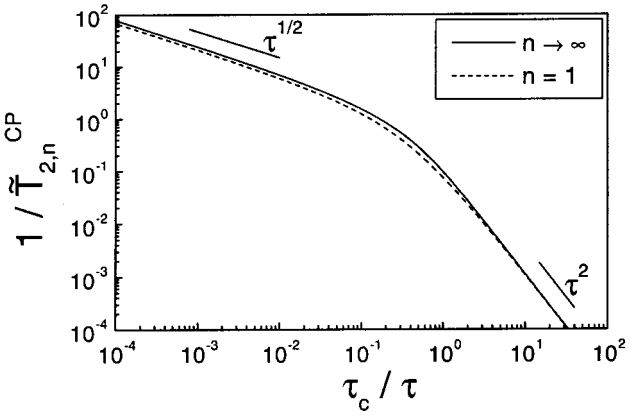

Figure 3. Comparison of the dispersion profiles of the scaled initial $\tilde{T}_{2,1}^{CP}(\tau)$ (dashed line) and the scaled asymptotic Carr−Purcell relaxation rate $1/\tilde{T}_{2,\infty}^{CP}(\tau)$ (solid line) for nematic director fluctuations in case of a vanishing molecular contribution $1/\tilde{T}_2^0 = 0.0$. $\tilde{T}_{2,\infty}^{CP}(\tau)$ characterizes the decay of the transverse magnetization in a CP sequence in the limit of an infinite number of pulses. The straight lines with the slopes $-1/2$ and -2 indicate different dispersion regimes. $\tilde{T}_{2,n}^{CP}(\tau) \equiv \omega_\sigma^2 \tau_c T_{2,n}^{CP}(\tau)$; ω_σ = root-mean-square amplitude of the modulated quadrupolar interactions; τ_c = fastest relaxation time of the director modes.

derived from the asymptotic expansions, eq 4.3. Apparently, two different dispersion regimes can be distinguished. For short pulse spacings, the transverse relaxation rate exhibits a quadratic dependence on τ. In contrast, for long pulse spacings, a square root dispersion law, $1/\tilde{T}_{2,1}^{CP}(\tau) \sim \tau^{1/2}$, is predicted. It is evident, however, that with realistic values of $1/\tilde{T}_2{}^0$ (dashed and dotted lines) one can observe the dispersion of $1/\tilde{T}_{2,1}^{CP}(\tau)$ only with pulse spacings longer than τ_c with an associated square root dependence, whereas for shorter pulse spacings, the molecular contribution prevails, leading to a substantially constant transverse relaxation rate. It should be mentioned that the dispersion of the transverse relaxation time because of director fluctuations can be detected in other pulsed experiments, such as two-dimensional Fourier transform EPR.[34]

In a similar way, one can analyze the *n*th CP relaxation time, $\tilde{T}_{2,n}^{CP}(\tau)$, defined in eq 3.34, whose scaled form can be written as

$$\frac{1}{\tilde{T}_{2,n}^{CP}(\tau)} = \frac{1}{\tilde{T}_2{}^0} - 4\sum_{k=0}^{n-1} k(-1)^k h(2k\tau/\tau_c) + (-1)^n[(n-1)h((2n-2)\tau/\tau_c) - 2(2n-1)h((2n-1)\tau/\tau_c) + nh(2n\tau/\tau_c)] \quad (4.10)$$

Obviously, this relaxation time depends on the number of cycles in the CP sequence. Figure 2 shows such a dependence of the ratio $\tilde{T}_{2,1}^{CP}(\tau)/\tilde{T}_{2,n}^{CP}(\tau)$ in the absence of the molecular term, $1/T_2^0 = 0.0$, for three different pulse spacings, $\tau/\tau_c = 0.01$ (circles), 1.0 (squares), and 100 (triangles). It is evident that the asymptotic behavior described by $\tilde{T}_{2,\infty}^{CP}(\tau)$ is reached after a few cycles. For short pulse spacings ($\tau/\tau_c = 0.01$, circles), one observes a weak alternating behavior with respect to *n*, which disappears if τ decreases further. As a matter of fact, in the limit of a vanishing ratio τ/τ_c, the CP relaxation time tends to become independent of the number of cycles

$$\tau \ll \tau_c: \qquad T_{2,1}^{CP}(\tau) = T_{2,n}^{CP}(\tau) = T_{2,\infty}^{CP}(\tau) \qquad (4.11)$$

This can easily be explained by considering that the integrals in eq 3.30 provide a leading contribution of the order of τ^4 for $\tau \to 0$ and that they are negligible with respect to $4g(\tau) - g(2\tau)$, which is proportional to τ^3 according to the first asymptotic expansion of eq 4.3. Thus, for $\tau/\tau_c \to 0$, the contributions of the integrals can be neglected, leading to a transverse relaxation time which is independent of the number of cycles.

On the contrary, a marked difference arises for $\tau \gtrsim \tau_c$. In particular, the largest difference of the order of 40% is found for $\tau \sim \tau_c$ (squares). In the limit of long pulse spacings, $\tau \gg \tau_c$, the same power law as for the initial CP relaxation time is also found for $\tilde{T}_{2,\infty}^{CP}(\tau)$, which is easily verified by inserting the second asymptotic expansion of eq 4.3 into eq 4.10

$$\tau \gg \tau_c: \qquad \frac{1}{\tilde{T}_{2,\infty}^{CP}(\tau)} = \frac{1}{\tilde{T}_2^0} + c\sqrt{\pi\tau/\tau_c} \qquad (4.12)$$

where *c* is a numerical constant given by $c = 0.4476$. In Figure 3, we compare the dispersion profiles of $1/\tilde{T}_{2,1}^{CP}(\tau)$ (dashed line) and $1/\tilde{T}_{2,\infty}^{CT}(\tau)$ (solid line) for the particular case of $1/\tilde{T}_2^0 = 0.0$. Because of the relatively small differences between the two relaxation times, one can apply to $\tilde{T}_{2,\infty}^{CP}(\tau)$ the same arguments about the effects of the molecular contribution, $\tilde{T}_2^0$, as employed in the case of $\tilde{T}_{2,1}^{CP}(\tau)$ (see Figure 1).

The theoretical predictions for the CP experiment are illustrated in Figure 4, depicting the echo intensity $I(n, \tau) = M_y(2n\tau)/M_{eq}$ as a function of the number *n* of cycles for some choices of the scaled pulse spacing, τ/τ_c, on condition that the dispersion of the transverse relaxation times can effectively be detected, i.e., $\tau \gg \tau_c$. The dashed line represents the intensity of the QE signal, calculated according to eqs 3.26 and 4.3

$$I(1, \tau) = \exp\{-a(2\tau)\}$$
$$a(2\tau) = \omega_\sigma{}^2 \tau_c{}^2 \left\{\frac{4}{3}(2-\sqrt{2})\sqrt{\pi}\right\}(\tau/\tau_c)^{3/2} \quad (4.13)$$

It is evident that the decay of the QE signal cannot be characterized by a single exponential. Consequently, the concept of a uniform transverse relaxation time, T_2^{QE}, associated with the QE sequence, is inadequate. Rather, the pulse spacing dependence of $T_2^{QE}(\tau)$, according to eq 3.28, has to be considered.

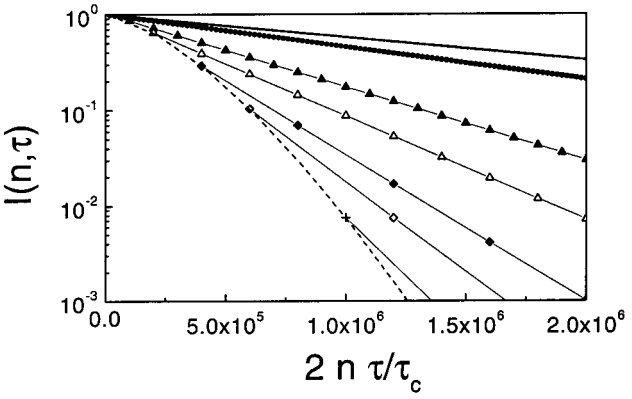

Figure 4. Echo intensity $I(n, \tau)$ as a function of the number n of pulses in the CP sequence for nematic director fluctuations and seven different values of the scaled pulse spacing: $\tau/\tau_c = 5 \times 10^3$ (small filled circles), 10^4 (large filled circles), 5×10^4 (filled triangles), 10^5 (open triangles), 2×10^5 (filled diamonds), 3×10^5 (open diamonds), and 5×10^5 (crosses). The dashed line indicates the decay of the QE signal. The calculations have been performed for the case of a vanishing molecular contribution, $1/\tilde{T}_2^0 = 0.0$, and for $\omega_\sigma \tau_c = 10^{-4}$. ω_σ = root-mean-square amplitude of the modulated quadrupolar interactions; τ_c = fastest relaxation time of the director modes.

Let us now examine the FID signal, which can be evaluated according to eqs 2.20, 3.24, and 4.1

$$M_y(t)/M_{eq} = \cos(\overline{\omega_Q} t)\, \exp\{-t/T_2^0 - (\Delta\omega'_Q)^2 \overline{n_{x'}^2} \tau_c th(t/\tau_c)\} \tag{4.14}$$

The analysis becomes simpler by considering the corresponding absorption spectrum:

$$\int_0^\infty dt \cos(\omega t)\, M_y(t) = \frac{\pi M_{eq}}{2} I(\omega - \overline{\omega_Q}) + \frac{\pi M_{eq}}{2} I(\omega + \overline{\omega_Q}) \tag{4.15}$$

which consists of two lines centered at the average resonance frequencies $\pm\overline{\omega_Q}$. Here $I(\omega)$ describes the line shape function

$$I(\omega) = \frac{1}{\pi}\int_0^\infty dt \cos(\omega t)\, \exp\{-t/T_2^0 - (\Delta\omega'_Q)^2 \overline{n_{x'}^2} \tau_c th(t/\tau_c)\} \tag{4.16}$$

normalized to unity

$$\int_{-\infty}^{+\infty} d\omega\, I(\omega) = 1 \tag{4.17}$$

Notice that eq 4.15 is written in the rotating frame, where ω denotes the frequency shift with respect to the Zeeman resonance frequency ω_Z.

We first analyze the limiting case, in which the director fluctuations are frozen on the NMR time scale, corresponding to $\tau_c \rightarrow \infty$. In this case (and assuming $1/T_2^0 = 0$), the first asymptotic expansion of eq 4.3, truncated at the linear term $h(x) = x/2$, yields a Gaussian line profile

$$I(\omega) = \frac{1}{\pi}\int_0^\infty dt \cos(\omega t)\, \exp(-\omega_\sigma^2 t^2/2) = \frac{\exp(-\omega^2/2\omega_\sigma^2)}{\omega_\sigma\sqrt{2\pi}} \tag{4.18}$$

whose width is determined by the root-mean-square amplitude of the modulated quadrupolar interactions ω_σ introduced in eq 4.5. Obviously, such a line profile describes the powder spectrum in the limiting case of frozen director fluctuations.

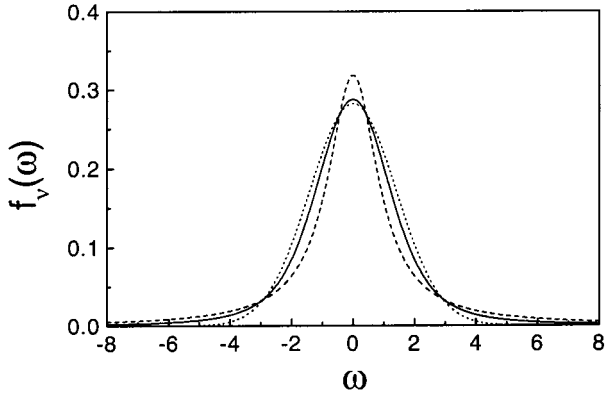

Figure 5. Normalized line shape function, $f\nu(\omega)$, calculated as Fourier transform of a stretched exponential $\exp(-t_\nu)$ for different power law coefficients ν. The line profiles for $\nu = 1$ (dashed line) and 2 (dotted line) correspond to a Lorentzian and a Gaussian, respectively. The line profile with $\nu = 3/2$ (solid line) has been obtained for nematic director fluctuations in the $\tau_c \rightarrow 0$ limit in the absence of a low-frequency cutoff of the director modes.

Let us now consider the opposite limit, i.e., $\tau_c \rightarrow 0$, which corresponds to the regime where the frequency ω_σ for the magnetic anisotropies is much smaller than the fastest director fluctuation rate $1/\tau_c$. When the second asymptotic expansion of eq 4.3 is employed, the following line shape function is derived:

$$I(\omega) = \frac{1}{\pi}\int_0^\infty dt \cos(\omega t)\, \exp(-2\omega_\sigma^2 \sqrt{\pi\tau_c} t^{3/2}/3) = \frac{f_{3/2}[\omega/(4\pi\omega_\sigma^4\tau_c/9)^{1/3}]}{(4\pi\omega_\sigma^4\tau_c/9)^{1/3}} \tag{4.19}$$

where the normalized function

$$f_\nu(\omega) = \frac{1}{\pi}\int_0^\infty dt \cos \omega t\, \exp(-t^\nu) \tag{4.20}$$

is the Fourier transform of a stretched exponential, characterized by the power law coefficient ν. Clearly, for ν= 1 or 2, a pure Lorentzian or Gaussian line shape is recovered. Thus, in the limit of fast director fluctuations (and assuming $1/T_2^0 = 0$), one obtains a peculiar line profile characterized by a power law coefficient of $\nu = 3/2$, which is intrinsically different from a Gaussian or a Lorentzian. This is demonstrated in Figure 5, where the three line shapes are compared. We emphasize that for $\tau_c \rightarrow 0$ the Redfield limit, which predicts a Lorentzian profile, is not recovered. On the other hand, the absence of such a limit for the contribution of director fluctuations should be expected, as long as the director modes are characterized by relaxation rates without a lower bound. It should be recalled that a fast-motion description according to the Redfield limit rigorously holds only if the motional rates of the stochastic variables are much larger than the anisotropy (in frequency units) of the spin Hamiltonian, a condition which is never reached for director fluctuations in the absence of a low-frequency cutoff. It has been shown, however, that consideration of magnetic field effects on the elastic free energy eq (A5) leads to a lower bound for the director fluctuation rates.[6,7] Nevertheless, to avoid a too cumbersome exposition by introducing a further parameter (the magnetic coherence length), depending on the magnetic field intensity, we prefer here to restrict ourselves to the standard director fluctuation model summarized in the Appendix.

To characterize the absorption spectrum in the entire dynamic range, it is convenient to scale the frequency and the time

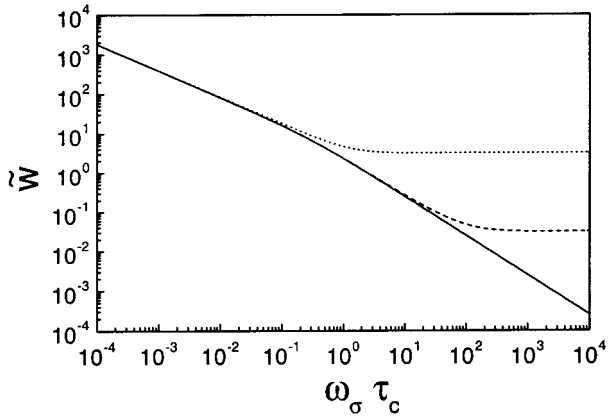

Figure 6. Scaled line width, $\tilde{w}$, as a function of the parameter $\omega_\sigma\tau_c$ for nematic director fluctuations and three different molecular contributions: $1/\tilde{T}_2^0 = 0.0$ (full line), 0.01 (dashed line), and 1.0 (dotted line). $\tilde{w} \equiv w/\omega_\sigma^2\tau_c$; $\tilde{T}_2^0 \equiv \omega_\sigma^2\tau_c T_2^0$; ω_σ = root-mean-square amplitude of the modulated quadrupolar interactions; τ_c = fastest relaxation time of the director modes.

according to eq 4.4

$$\tilde{\omega} \equiv \omega/\omega_\sigma^2\tau_c \qquad \tilde{t} \equiv \omega_\sigma^2\tau_c t \tag{4.21}$$

Consequently, the line shape function, eq 4.16, has to be transformed to

$$I(\omega) = \frac{1}{\omega_\sigma^2\tau_c}\tilde{I}(\tilde{\omega})$$
$$\tilde{I}(\tilde{\omega}) = \frac{1}{\pi}\int_0^\infty d\tilde{t}\, \cos(\tilde{\omega}\tilde{t})\, \exp\{-\tilde{t}/\tilde{T}_2^0 - \tilde{t}h(\tilde{t}/\omega_\sigma^2\tau_c^2)\} \tag{4.22}$$

where $\tilde{I}(\tilde{\omega})$ is normalized by an integration over the scaled frequency $\tilde{\omega}$. Then, one can employ the inverse of the scaled intensity at zero frequency as a measure of the scaled width $\tilde{w}$ of the NMR line

$$\tilde{w} \equiv 1/\tilde{I}(0) \tag{4.23}$$

Such scaled line widths are represented in Figure 6 as a function of $\omega_\sigma\tau_c$ for $1/\tilde{T}_2^0 = 0.0$ (solid line), 0.01 (dashed line), and 1.0 (dotted line). Values for $\tilde{w}$ in the limit $1/\omega_\sigma\tau_c \ll 1$ can be obtained by inserting the first asymptotic expansion of eq 4.3, truncated at the linear term, $h(x) = x/2$, into eq 4.22

$1/\omega_\sigma\tau_c \ll 1$:

$$1/\tilde{w} = \frac{1}{\pi}\int_0^\infty d\tilde{t}\, \exp(-\tilde{t}/\tilde{T}_2^0 - \tilde{t}^2/2\omega_\sigma^2\tau_c^2) \tag{4.24}$$

which, for $1/\tilde{T}_2^0 = 0$, leads to the relation

$$\tilde{w} = \sqrt{2\pi}/\omega_\sigma\tau_c \tag{4.25}$$

whereas, for $1/\omega_\sigma\tau_c \ll 1/\tilde{T}_2^0$, the molecular tumbling contribution prevails, leading to a substantially constant width of $\pi/\tilde{T}_2^0$. For the opposite limit, one can use the second asymptotic expansion of eq 4.3, yielding

$1/\omega_\sigma\tau_c \gg 1$:

$$1/\tilde{w} = \frac{1}{\pi}\int_0^\infty d\tilde{t}\, \exp(-\tilde{t}/\tilde{T}_2^0 - 2\sqrt{\pi\tilde{t}}^{3/2}/3\omega_\sigma\tau_c) \tag{4.26}$$

On condition that $1/\omega_\sigma\tau_c \gg (1/\tilde{T}_2^0)^{3/2}$, the following explicit relation is obtained:

$$\tilde{w} = \frac{(3\pi^4/2)^{1/3}}{\Gamma(^2/_3)}\frac{1}{(\omega_\sigma\tau_c)^{2/3}} \tag{4.27}$$

where $\Gamma(z)$ denotes the gamma function.

5. Conclusions

A slow-motional approach to the analysis of transverse spin relaxation experiments in liquid crystals has been presented for systems in which director fluctuations constitute the dominant relaxation process. It has been shown that an analytical solution of the stochastic Liouville equation[17,18] is obtained if the director fluctuations are modeled as a multidimensional Gaussian process.

The theory has been employed to describe transverse deuteron spin relaxation experiments, including the FID and the time evolution of the transverse magnetization in QE and CP[25−27] pulse sequences. An important result is the representation of the Carr−Purcell relation time as independent contributions of the director modes, evaluated according to the Luz−Meiboom equation,[21] originally derived within the Redfield limit.[14] It turns out that such a representation is valid also under slow-motion conditions, provided an infinite number of pulses in the CP sequence are considered.

Generally, the methodology developed in this paper can be applied to characterize the dynamics of director fluctuations in a wide class of nematic liquid crystals, including mesomorphic polymers.[12,35] Analysis of the transverse spin relaxation experiments on the basis of the new approach will give reliable information on the elastic constants of these systems, which are difficult to determine by any other technique.

So far, the main features of the new theory have been demonstrated for the specific case of nematic phases. It should be emphasized, however, that the theory is rather general and can be applied to director fluctuations in other systems such as smectic phases[6,32] or bilayer membranes,[33] provided they fulfill the requirement of a Gaussian process.

In the present model, only linear contributions of the orthogonal components of the director have been employed. Consequently, the theory cannot account for sample orientations, in which the director is aligned either parallel or perpendicular to the magnetic field. In such cases, consideration of the bilinear terms of the director field would be required. Studies along these lines are currently in progress.

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Appendix

In this appendix, we shall review the standard model of director fluctuations for nematic phases,[3−7] in order to specify the correlation function and the associated functions which are required in the evaluation of transverse relaxation times.

Let us examine a macroscopic sample of size L^d (L = macroscopic length, $d = 3$ = dimensionality), represented by an ensemble of elementary cells of identical size L_c^d at positions $\vec{r}_j$, in which the orthogonal director components $n_{x'}(\vec{r}_j)$ and $n_{y'}(\vec{r}_j)$ constitute the stochastic variables **q**, eq 2.3, of the problem. The length L_c is the shortest dimension compatible with a discrete representation of the director field $\vec{n}(\vec{r})$. The normal modes of the director fluctuations are obtained from

the Fourier transform of the director field according to the kernel $\exp(i\vec{k}\cdot\vec{r})$, where the wavevector $\vec{k}$ spans the d-dimensional Euclidean space. The use of periodic boundary conditions is the most convenient way of taking into account the finite size of the sample. Thus, we discretize the wavevector $\vec{k}$ for each component according to

$$\Delta k = 2\pi/\mathrm{L} \tag{A1}$$

Such a discrete representation of the nematic field limits the upper values of the wavevector components to

$$|k_\alpha|_{\max} = \pi/L_c \tag{A2}$$

Then, for the allowed values $\vec{k}_m$ of the wavevector, the transformed director field components $\tilde{n}_\alpha(\vec{k}_m)$, $\alpha = x', y'$, can be calculated as

$$\tilde{n}_\alpha(\vec{k}_m) = L_c^d \sum_j \exp(i\vec{k}_m\cdot\vec{r}_j) n_\alpha(\vec{r}_j) = \tilde{n}_\alpha(-\vec{k}_m)^* \tag{A3}$$

Because of the latter symmetry relation, only half of the space of the wavevector (say, for $k_{x'} > 0$) has to be considered in the representation of the independent components of the transformed field. The antitransform is given by

$$n(\vec{r}_j) = (1/L^d)\sum_m \exp(-i\vec{k}_m\cdot\vec{r}_j)\tilde{n}_\alpha(\vec{k}_m) = (2/L^d)\sum_m{}' \mathrm{Re}\{\exp(-i\vec{k}_m\cdot\vec{r}_j)\tilde{n}_\alpha(\vec{k}_m)\} \tag{A4}$$

where the primed summation symbol denotes the sum over independent components of the transformed field.

Using the harmonic approximation[6] and the one constant K representation, the elastic free energy can be written as

$$F(\tilde{\mathbf{q}}) = (K/L^d)\sum_{\alpha=x',y'}\sum_m{}' |\vec{k}_m|^2 |\tilde{n}_\alpha(\vec{k}_m)|^2 \tag{A5}$$

Because of the linear relation, eq A4, the independent components of the transformed field

$$\tilde{\mathbf{q}} = (..., \tilde{n}'_{x'}(\vec{k}_m), \tilde{n}''_{x'}(\vec{k}_m), \tilde{n}'_{y'}(\vec{k}_m), \tilde{n}''_{y'}(\vec{k}_m), ...) \tag{A6}$$

can be employed as stochastic variables instead of the local values $\mathbf{q}$, eq 2.3. Consequently, it is now possible to factorize the equilibrium distribution $p_{eq}(\tilde{\mathbf{q}}) \propto \exp\{-F(\tilde{\mathbf{q}})/k_B T\}$ according to

$$p_{eq}(\tilde{\mathbf{q}}) = \prod_{\alpha=x',y'}\prod_m{}' p_{eq}(\tilde{n}'_\alpha(\vec{k}_m), \tilde{n}''_\alpha(\vec{k}_m)) \tag{A7}$$

where each factor represents a Gaussian distribution

$$p_{eq}(\tilde{n}'_\alpha(\vec{k}_m), \tilde{n}''_\alpha(\vec{k}_m)) = \frac{\exp\{-|\tilde{n}_\alpha(\vec{k}_m)|^2/2\sigma(k_m)^2\}}{2\pi\sigma(k_m)^2}$$

$$\sigma(k_m)^2 = k_B T L^d/2K k_m{}^2 = \overline{|\tilde{n}_\alpha(\vec{k}_m)|^2}/2 \tag{A8}$$

and $k_m \equiv |\vec{k}_m|$. With this factorization, standard models for director fluctuations[4-7] can be represented as a multidimensional Markov process, with an independent Fokker−Planck operator for each component

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

$$\Gamma(\tilde{\mathbf{q}}) = \sum_{\alpha=x',y'}\sum_m{}' \Gamma(\tilde{n}_\alpha(\vec{k}_m))$$

$$\Gamma(\tilde{n}_\alpha) = -D\frac{\partial}{\partial \tilde{n}'_\alpha} p_{eq}(\tilde{\mathbf{q}}) \frac{\partial}{\partial \tilde{n}'_\alpha} p_{eq}(\tilde{\mathbf{q}})^{-1} - D\frac{\partial}{\partial \tilde{n}''_\alpha} p_{eq}(\tilde{\mathbf{q}}) \frac{\partial}{\partial \tilde{n}''_\alpha} p_{eq}(\tilde{\mathbf{q}})^{-1} \tag{A9}$$

where

$$D = k_B T L^d/2\eta \tag{A10}$$

is a constant diffusion coefficient and η is an effective viscosity. Clearly, the time evolution of the probability for the transformed variables $\tilde{\mathbf{q}}$ is governed by independent Gaussian processes. Because of the linear relation between the transformed component, eq A3, and the director field $n_\alpha(\vec{r})$, also the probability $p(\mathbf{q}, t)$ for the latter variables is represented by a Fokker−Planck equation for a Gaussian process. This justifies the use of a Gaussian model, eqs 3.1 and 3.2, for the evaluation of the NMR observables, as performed in section 3. On the other hand, the time correlation function of the director fluctuations, eq 3.6, is more conveniently evaluated by employing the transformed field, because in this case each component contributes independently as

$$\overline{\tilde{n}'_\alpha(\vec{k}_m)_t \tilde{n}'_\alpha(\vec{k}_m)_{t=0}} = \overline{\tilde{n}''_\alpha(\vec{k}_m)_t \tilde{n}''_\alpha(\vec{k}_m)_{t=0}} = \frac{\overline{|\tilde{n}_\alpha(\vec{k}_m)|^2}}{2}\exp\{-t/\tau(k_m)\} \tag{A11}$$

where

$$1/\tau(k_m) = D/\sigma(k_m)^2 = K k_m{}^2/\eta \tag{A12}$$

is a wavevector-dependent mode relaxation time. The time-dependent functions eqs 3.6, 3.7, and 3.38, describing transverse relaxation effects of director fluctuations, are easily evaluated in the $\tilde{\mathbf{q}}$ representation, where both matrices $\mathbf{A}$ and $\mathbf{DA}$ are diagonal with elements $1/\sigma(k_m)^2$ and $1/\tau(k_m)$, respectively. The components of the array $\mathbf{v}$ in the same representation are readily obtained from eq A4 according to eq 3.4. Thus, one derives the following equation for the time correlation function, eq 3.6, of the director fluctuations:

$$\overline{n_{x'}(0)n_{x'}(t)} = \frac{2k_B T}{L^d \eta}\sum_m{}' \tau(k_m)\exp\{-t/\tau(k_m)\} \tag{A13}$$

Let us now consider an infinite nematic sample, by imposing the limit $L \to \infty$ which corresponds to vanishing increments Δk of eq A1. Then, the summation over the allowed values of the wavevector in eq A13 can be replaced by an integral

$$\overline{n_{x'}(0)n_{x'}(t)} = \frac{k_B T}{\eta}\frac{1}{(2\pi)^3}\int_{|\vec{k}|\le k_c} \mathrm{d}\vec{k}\ \tau(k)\mathrm{e}^{-t/\tau(k)} = \frac{k_B T}{2\pi^2 K}\int_0^{k_c} \mathrm{d}k\ \mathrm{e}^{-t/\tau(k)} \tag{A14}$$

where the cutoff k_c is estimated from the upper limit in eq A2. The integral can be solved analytically to yield an explicit form

of the director fluctuation correlation function

$$\overline{n_{x'}(0)n_{x'}(t)} = \overline{n_{x'}^2}\frac{\sqrt{\pi}}{2}\frac{\mathrm{erf}(\sqrt{t/\tau_c})}{\sqrt{t/\tau_c}} \qquad \overline{n_{x'}^2} = \frac{k_B T k_c}{2\pi^2 K} \tag{A15}$$

which has often been employed in the interpretation of longitudinal spin relaxation times, T_1.[7,15,16] Here erf(z) denotes the error function and $\tau_c \equiv \tau/(k_c) = \eta/Kk_c^2$ is the relaxation time associated with the cutoff k_c. The same general methodology can be applied to the second cumulant, eq 3.7, yielding

$$g(t) = \overline{n_{x'}^2}\int_0^{k_c}\frac{dk}{k_c}\tau(k)[t + \tau(k)(e^{-t/\tau(k)} - 1)] \tag{A16}$$

By changing the integration variable to $z = t/\tau(k) = Kk^2t/\eta$, and after integration by parts, the following explicit relation is obtained

$$g(t) = \frac{\overline{n_{x'}^2}\tau_c^2}{3}[2\sqrt{\pi}(t/\tau_c)^{3/2}\,\mathrm{erf}(\sqrt{t/\tau_c}) + (t/\tau_c)(2e^{-t/\tau_c} - 3) + 1 - e^{-t/\tau_c}] \tag{A17}$$

The function $g_{LM}(\tau)$, eq 3.38, can be evaluated in a similar way to yield the following decomposition with respect to the independent director modes:

$$g_{LM}(t) = \overline{n_{x'}^2}\int_0^{k_c}\frac{dk}{k_c}\tau(k)\{1 - [\tau(k)/t]\tanh[t/\tau(k)]\} \tag{A18}$$

Note that for a given k the same time dependence is obtained as that derived by Luz and Meiboom for the CP relaxation rate in the Redfield limit.[21] Exact closed form solutions to eq A18 are not available, and therefore, a numerical evaluation of the integral is generally required.

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