Stochastic-molecular theory of spin-relaxation for liquid crystals*

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The theory of spin relaxation for liquid crystals is examined with the objective of properly analyzing the statistical *inter*dependence of the faster rotational reorientation of the individual spin-bearing molecules and the (slower) director or order-parameter fluctuations. The analysis is presented in terms of a composite Markov process including both types of motions. It is shown that one recovers a sum of spectral-density terms which, in lowest order in fluctuations, correspond to (1) reorientation of the molecule relative to the equilibrium potential of mean torque, (2) effects of director fluctuations, and (3) a negative cross-term between these two processes which bears a simple relation to (2). Detailed results are given for the particular models of director fluctuations in the nematic phase, quasicritical order fluctuations on either side of the isotropic–nematic phase transition, and slow fluctuations in the local structure. Effects of localized cooperative modes of molecular reorientation are also included. Explicit expressions for NMR and ESR relaxation and line shapes are given. The results obtained here clearly demonstrate some weaknesses in previous treatments which were presumed to be based on an assumption of the statistical independence of the different motional processes. Discussion is also given on how to formulate director fluctuations as a multidimensional Markov process, and on the applicability of motional narrowing theory in these cases where director fluctuations have very slowly relaxing components.

I. INTRODUCTION

Magnetic resonance relaxation experiments have been very useful in the study of the dynamical properties of liquid crystals.[1,2] The spin–relaxation phenomena differ significantly from what is observed in isotropic fluids as a result of the effects of ordering. The ordering effects manifest themselves in several ways. We focus primarily on spin relaxation by reorientational motions. First of all, relaxation due to molecular tumbling motions is altered by the fact that such motions are no longer isotropic, but rather experience a mean reorienting potential (the potential of mean torque). Secondly, there are long-range cooperative modes, or hydrodynamic modes, associated with the fluctuations in the ordering. They are characterized, in the nematic phase, as being fluctuations in the nematic director (at temperatures removed from phase transitions), and as quasicritical fluctuations in ordering at phase transitions. In this work we will only concern ourselves with nematic phases, although analogous, but more complex, discussions would apply to smectic phases.[1-3] If we regard the effect of ordering on an individual molecule from a mean-field point of view, or more accurately as the potential of mean torque, then fluctuations in the ordering on a hydrodynamic, or slow, time scale would represent fluctuations in this potential of mean torque. The individual molecular reorientation, occurring on a more rapid time scale, is then affected by this fluctuating "mean torque." And, of course, magnetic resonance focuses upon the behavior of the individual molecule as long as the spins on any individual molecule are uncorrelated with those on other molecules, as is usually the case. Thus, it appears that the correct treatment of spin relaxation in ordered fluids would recognize the manner in which the ordering (including its hydrodynamic fluctuations) affects the reorientational motion of the individual molecules. Of course, the overall reorientational motion of an individual molecule in an ordered fluid should still be a complex process involving the short-range cooperative motions of adjacent nonspherical molecules (i.e., nonhydrodynamic effects of range of molecular dimensions). This is a problem that is difficult to treat with any rigor; however, one would hope that a complete statistical-mechanical analysis could cover the range from long-range (and slow) hydrodynamic effects to short-range (and fast) molecular couplings. We do not attempt such an ambitious project here. We will separately consider the effects of the hydrodynamic modes of order fluctuations, taking advantage of the well-developed theories.[1,2] The short-range correlations will be treated very approximately from a point of view developed in a recent statistical-mechanical study of molecular dynamics in liquids.[4] That is, coupled reorientational motion of molecules of similar size is expressed in terms of an appropriate time-dependent rotational diffusion coefficient while, for a small and rapidly reorienting probe molecule in the field of larger solvent molecules, the short-range ordering may perhaps be treated in terms of a fluctuating local orienting potential.

The time-dependent diffusion coefficient is a non-Markovian feature in the approximate model which may be associated with the fact that it is the coupled modes of reorientation of the molecules including inertial effects which define the relaxation process, and the reorientation of one of them is a projection of these modes onto its reorientational degrees of freedom. However, when we deal with the effect of the hydrodynamic modes upon a single molecule, we note that the dissipative character of these modes allows us to treat each normal mode as a simple Markov process. Each such mode leads to fluctuations in the mean orienting potential of the molecule. The combined effect of all these modes may then be treated as a multidimensional Markov process.

Thus, the basic problem we deal with here is spin relaxation for a spin-bearing molecule obeying a rotational diffusion (or jump) equation which includes an orienting potential whose stochastic time dependence is itself treated as a Markov process. It is possible to obtain simple analytic solutions when we utilize the physical requirement we have already noted, that the time dependence of the orienting potential fluctuations is slower than individual molecular reorientations, and when the fluctuating part of the orienting potential is small (relative to kT). This model, while necessarily limited, for the above-noted reasons, is a sounder point of view than the approach of other workers who, for the most part, have arbitrarily assumed that the reorientational motion is *statistically independent* from director fluctuations, etc.[5-7] This approach was recently summarized by Polnaszek and Freed (PF).[6] Our discussion here does indeed emphasize the statistical *dependence* of the reorientational motion upon the director fluctuations. Furthermore, another weakness of the previous treatments, as PF have already pointed out, is that one defines the motion of the molecule with reference to the director frame, which is fluctuating in time. This is physically unsound. In fact, it introduces an *incorrect* statistical dependence of the molecular reorientation on the director fluctuations even while there is a presumed statistical independence. That this is so can be seen as follows. Consider a hypothetical spin probe whose geometry can be changed. Let the probe be partially ordered by a fluctuating director about which it reorients. Now let the probe become more spherical, so its ordering with respect to the director is reduced ultimately to zero. The motion of the spherical probe should now be insensitive to director fluctuations. However, when the calculation is performed relative to a fluctuating coordinate frame, PF point out there are spurious cross-terms which appear and lack the property of going to zero when the probe ordering goes to zero. Thus PF argue such terms should be ignored, since they arise from a physically unsound feature of the usual model. More recently, however, Doane and co-workers[5] have reevaluated the spin–relaxation theory and have chosen to explicitly include these terms. Their cross-terms do indeed have the undesirable feature of remaining finite even as the order parameter goes to zero. We note that our treatment given here completely avoids such physically unsound features, and is thus able to clarify the existence and nature of cross-terms between the molecular reorientation and the orienting potential fluctuations. Cross-terms are indeed to be expected precisely because the reorientation is *statistically dependent* upon the orienting potential fluctuations when, and only when, the molecule of interest is partially ordered.

The formal development of these ideas is presented in Sec. II in terms of stochastic–Markovian processes. The results are then applied in Sec. III to a discussion of fluctuations in the director which are of importance in the nematic phase. We obtain in that section detailed expressions for the spectral densities generated by the motions and needed for spin relaxation. Section IV deals with quasicritical fluctuations in the ordering, which are important near the nematic–isotropic phase transition. The matter of localized structure fluctuations, which is probably most important for small probe molecules, is discussed in Sec. V. The usual expressions which relate magnetic resonance relaxation to the spectral densities are summarized in Sec. VI. A summary and conclusions are given in Sec. VII. In Appendix A we suggest explicit Fokker–Planck equations for the normal modes of director fluctuations and discuss the role of translational diffusion; while in Appendix B we discuss the validity of the use of motional-narrowing relaxation theory for the director fluctuations, since they are characterized by a spectrum of relaxation times with (at least some) very slow components.

II. GENERAL FORMULATION

A. Reorientational relaxation

Our starting point in describing the reorientational relaxation of a liquid-crystal molecule under the effects of an orienting potential is a Smoluchowski equation for the motion of a single molecule[4,6]:

$$\partial P(\Omega, t)/\partial t = -\mathbf{M}\cdot \mathbf{R}(\Omega, t)\cdot \{\mathbf{M} + [\mathbf{M}U(\Omega, t)]/kT\}P(\Omega, t) \ , \tag{2.1}$$

where $P(\Omega, t)$ is the time-dependent probability distribution in orientation of the molecule relative to a *fixed* coordinate frame, where $\Omega \equiv \alpha, \beta, \gamma$ represent the Euler angles specifying the orientation. Here $\mathbf{M}$ is the vector operator which generates an infinitesimal rotation of the molecule:

$$\mathbf{M} = i\mathbf{r} \times (\nabla_r) \ , \tag{2.2}$$

$\mathbf{R}(\Omega, t)$ is the rotational diffusion tensor, and both $\mathbf{R}$ and $\mathbf{M}$ are defined in a molecular coordinate frame (x', y', z'). Then, the operator $\mathbf{M}$ has the properties

$$M^2\phi^L_{KM}(\Omega) = L(L+1)\phi^L_{KM}(\Omega) \ , \tag{2.3a}$$

$$M_\pm\phi^L_{KM}(\Omega) = [(L \mp K)(L \pm K + 1)]^{1/2}\phi^L_{K\pm1,M}(\Omega) \ , \tag{2.3b}$$

$$M_{z'}\phi^L_{KM}(\Omega) = K\phi^L_{KM}(\phi) \ , \tag{2.3c}$$

where $\phi^L_{KM}(\Omega)$ are the eigenfunctions of M^2 and $M_{z'}$, L is the "azimuthal quantum number" and K its component along the z' axis, and

$$M_\pm = M_{x'} \pm iM_{y'} \ . \tag{2.3d}$$

The $\phi^L_{KM}(\Omega)$ are the normalized generalized spherical harmonics:

$$\phi^L_{KM}(\Omega) = [(2L+1)/8\pi^2]^{1/2}\mathfrak{D}^L_{KM}(\Omega) \ . \tag{2.3e}$$

We further assume that it is possible to diagonalize $\mathbf{R}$ in a body-fixed axis system such that it is time independent, an assumption implicit in Brownian-motion models. We choose the (x', y', z') frame to be just these axes. The orienting potential $U(\Omega, t)$ is the potential of mean torque, and the mean orienting torque $\mathcal{T}$ is given by

$$\mathcal{T}(\Omega, t) = i\mathbf{M}U(\Omega, t) \ . \tag{2.4}$$

This orienting potential and its associated torque are allowed to be slowly fluctuating in time. They would include hydrodynamic fluctuations in the director.

This form of the Smoluchowski equation requires the following assumptions[4]:

(1) Angular momentum relaxation occurs very rapidly, and it is possible to introduce a coarse-graining in a time interval such that the angular momentum is at equilibrium while the molecule has not appreciably reoriented. This also implies that the orienting potential is not too large.

(2) The rapidly fluctuating components of the torque, which induce the reorientation of the molecule, are averaging to zero in times short compared to the molecular reorientational relaxation times. This assumption does not allow for localized coupled modes of reorientation of molecules such as a simultaneous flip of two neighboring molecules. The latter type effects can be introduced into the Smoluchowski equation (2.1) to a reasonable approximation by the introduction of an **R** with "memory" such that

$$\frac{\partial P(\Omega,t)}{\partial t} = -\mathbf{M}\cdot\int_0^t d\tau\,\mathbf{R}(t-\tau)\cdot[\mathbf{M}-i\mathcal{T}/kT]P(\Omega,\tau)\,, \tag{2.5}$$

where the Fourier–Laplace transform of $\mathbf{R}(t)$ is

$$\mathbf{R}[s]=(kT)^2\mathbf{K}^{-1}[s] \tag{2.6}$$

and $\mathbf{K}(t)$ is a torque correlation function:

$$\mathbf{K}(t)\equiv\langle\Delta\mathbf{N}(t=0)\Delta\mathbf{N}(t)\rangle\,, \tag{2.7a}$$

where

$$\Delta\mathbf{N}(t)=\mathbf{N}(t)-\mathcal{T} \tag{2.7b}$$

That is, $\Delta\mathbf{N}$ is the rapidly fluctuating part of the total time-dependent torque $\mathbf{N}(t)$. This separation of torque components into parts that are fluctuating at rates faster than (or comparable to) molecular reorientation rates (i.e., $\Delta\mathbf{N}$) and those that fluctuate more slowly (i.e., the time-dependent part of $\mathcal{T}$) is a simplifying approximation.[4] When we use exponential decay with relaxation time τ_M for $\mathbf{K}(t)$, we obtain $(s\rightarrow i\omega)$

$$R(\omega)=R(0)[1-i\omega\tau_M]$$

with

$$R(0)\equiv(kT)^2/\langle|\Delta N|^2\rangle\tau_M\,.$$

We shall proceed with the simpler Smoluchowski equation (2.1) to obtain our results, but we will later comment about the effects on our results of including the "memory" in **R**. An examination of Eq. (2.1) makes it clear that if there are director fluctuations yielding fluctuations in $U(\Omega,t)$, then the reorientational motion of the molecule expressed by $P(\Omega,t)$ may not be assumed to be independent of these director fluctuations. We have already noted this fact in the introduction.

B. Fluctuations in the orienting potential

Now the fluctuations causing the time dependence in $U(\Omega,t)$ may be regarded as a random-stochastic process. That is, Eqs. (2.5) or (2.1) may be shown to be useful approximations to the 1-particle orientational distribution function involving averaging the N-particle Liouville equation over the other $N-1$ particles. The dynamical effects of the other $N-1$ particles on the Nth then take on a random nature which may be analyzed by stochastic methods. Thus, under the assumption that the time dependence of $U(\Omega,t)$ derives from its dependence on a set of variables Ξ (e.g., the instantaneous orientation of the director relative to a fixed lab axis), and the stochastic behavior of Ξ is governed by a stationary Markov process, we may write

$$\partial f(\Xi,t)/\partial t=-\Gamma_\Xi f(\Xi,t)\,, \tag{2.8}$$

where Γ_Ξ is the appropriate Markov operator for the distribution function $f(\Xi,t)$. We show in Appendix A that the well-known hydrodynamic theory of director fluctuations[1,2] may be expressed in the form of Eq. (2.8).

C. The composite process

We now have from Eqs. (2.1) and (2.8) that the combined distribution function in Ω and Ξ may be regarded as a multidimensional Markov process. That is, we may combine Eqs. (2.1) and (2.8) into

$$\partial P(\Omega,\Xi,t)/\partial t=-(\Gamma_\Omega+\Gamma_\Xi)P(\Omega,\Xi,t) \tag{2.9}$$

with

$$\Gamma_\Omega=\mathbf{M}\cdot\mathbf{R}\cdot[\mathbf{M}+\mathbf{M}U(\Xi)/kT] \tag{2.9a}$$

[or, if Eq. (2.5) is used, one uses the Fourier–Laplace transform of Γ_Ω, or $\Gamma_\Omega[s]$, which is given by Eq. (2.9a) but with **R** replaced by the $\mathbf{R}[s]$ of Eq. (2.6)]. Here $P(\Omega,\Xi,t)$ is the joint probability distribution function in both Ω and Ξ and is Markovian. The general validity of this "stochastic Liouville" approach has been discussed by Kac[8] and by Kubo,[9] and ample examples of its use are found elsewhere.[6,10-12] Thus, the general problem we face is the solution of Eq. (2.9) for appropriate choices of Γ_Ξ.

Actually, because of the assumption that Ξ is fluctuating at rates significantly more slowly than is Ω (i.e., the molecular reorientation), it is possible to simplify the solution of Eq. (2.9). Let τ_q be a typical relaxation time of Ξ and τ_R of Ω. Then, since $\tau_R^{-1}\gg\tau_q^{-1}$, we may assume that a molecule reorients in a time $t\sim\tau_R$ which is short compared to τ_q, so that Ξ appears essentially static or fixed. Then, on longer time scales $t\sim\tau_q$ the variable Ξ "relaxes." Thus, we may solve for the distribution function $P_\Xi(\Omega,t)$ which is the solution to Eqs. (2.1) or (2.9) with an arbitrary value of Ξ [i.e., the solution of Eq. (2.9) with $\Gamma_\Xi=0$], and then solve Eq. (2.8) for $f(\Xi,t)$ separately. Then we may approximate:

$$P(\Omega,\Xi,t)\cong P_\Xi(\Omega,t)f(\Xi,t)\,. \tag{2.10}$$

This approach in solving the "diffusion" equation (2.9) is closely analogous to the Born–Oppenheimer approximation in molecular quantum mechanics. [Note, however, we are assuming by the use of Eq. (2.9) that $f(\Xi,t)$ is independent of the distribution in the orientation of the molecule.] This analogy is perhaps clearer when we recognize that the Markovian operator Γ_Ω (written for arbitrary Ξ) will have eigenfunctions u_m and eigenvalues E_m such that

$$\Gamma_\Omega|u_m(\Omega,\Xi)\rangle=E_m(\Xi)|u_m(\Omega,\Xi)\rangle\,. \tag{2.11a}$$

Then the general solution to Eq. (2.1) for fixed Ξ is given by

$$P_{\Xi}(\Omega, t) = \sum_m c_m \,|\, u_m(\Omega, \Xi)\rangle\, e^{-E_m t} \qquad (2.11b)$$

with the c_m the expansion coefficients. Similarly

$$f(\Xi, t) = \sum_q d_q \,|\, v(\Xi)\rangle\, e^{-\epsilon_q t} \qquad (2.12a)$$

with

$$\Gamma_{\Xi} \,|\, v_q(\Xi)\rangle = \epsilon_q \,|\, v_q(\Xi)\rangle \; . \qquad (2.12b)$$

Thus

$$P(\Omega, \Xi, t) \cong \sum_{m,q} a_{m,q} \,|\, u_m(\Omega, \Xi)\rangle \,|\, v_q(\Xi)\rangle\, e^{-(E_m + \epsilon_q)t} \; . \qquad (2.13)$$

The actual forms of these eigenfunctions and eigenvalues may be obtained from previous work[6,13,14] and are discussed further below. Then our separability approximation is based upon having $\epsilon_q \ll E_m$ for q and $m \neq 0$ where $\epsilon_q \equiv \tau_q^{-1}$, $E_m \equiv \tau_m^{-1} \propto \tau_R^{-1}$ (by analogy with the Born–Oppenheimer method).

Note that we shall be interested in the unique equilibrium distributions $P_{\mathrm{eq},\Xi}(\Omega)$ and $f_{\mathrm{eq}}(\Xi)$. They are associated with the zero eigenvalue solutions in Eqs. (2.11b) and (2.12b), respectively. That is,

$$P_{\mathrm{eq},\Xi}(\Omega) = |\, u_0\rangle, \quad E_0 = 0 \qquad (2.14a)$$

$$f_{\mathrm{eq}}(\Xi) = |\, v_0\rangle, \qquad \epsilon_0 = 0 \; . \qquad (2.14b)$$

Also

$$P_{\mathrm{eq}}(\Omega, \Xi) \cong P_{\mathrm{eq},\Xi}(\Omega) f_{\mathrm{eq}}(\Xi) \; . \qquad (2.14c)$$

It follows from the form of the Smoluchowski equation (2.1) for fixed Ξ that

$$P_{\mathrm{eq},\Xi}(\Omega) = \exp[-U(\Omega, \Xi)/kT] \Big/ \int d\Omega \exp[-U(\Omega, \Xi)/kT] \; . \qquad (2.14d)$$

Also, we shall need the conditional probability distribution subject to the initial conditions that

$$\Omega = \Omega_0, \quad \Xi = \Xi_0 \text{ at } t = 0 \qquad (2.15a)$$

or

$$P(\Omega, \Xi, t = 0) = \delta(\Omega - \Omega_0)\delta(\Xi - \Xi_0) \; . \qquad (2.15b)$$

Now we may use the eigenfunction representation of the Dirac delta function (e.g.,

$$\delta(\Omega - \Omega_0) = \sum_m |\, u_m(\Omega, \Xi)\rangle \langle u_m(\Omega_0, \Xi) \,| \; , \qquad (2.16)$$

written in standard bra–ket notation), to obtain the conditional probability distribution functions:

$$P_{\Xi}(\Omega_0 \,|\, \Omega, t) = \sum_m |\, u_m(\Omega, \Xi)\rangle\, e^{-E_m t} \langle u_m(\Omega_0, \Xi) \,| \; , \qquad (2.17)$$

$$f(\Xi_0 \,|\, \Xi, t) = \sum_q |\, v_q(\Xi)\rangle\, e^{-\epsilon_q t} \langle v_q(\Xi) \,| \; , \qquad (2.18)$$

and

$$P(\Omega_0, \Xi_0 \,|\, \Omega, \Xi, t) \cong f_{\Xi}(\Omega_0 \,|\, \Omega, t) P(\Xi_0 \,|\, \Xi, t) \; , \qquad (2.19)$$

by Eq. (2.13). Note that only Ξ appears throughout Eq. (2.17) as required by the delta function representation of Eq. (2.16), but the dependence upon Ξ_0 properly appears in Eq. (2.19).

The time evolution of Eq. (2.19) based upon our model is that for short times

$$P(\Xi_0 \,|\, \Xi, t) \sim \delta(\Xi - \Xi_0) \; ,$$

so that

$$P(\Omega_0, \Xi_0 \,|\, \Omega, \Xi, t) \cong P_{\Xi_0}(\Omega_0 \,|\, \Omega, t)\delta(\Xi - \Xi_0) \, , \quad t \lesssim \tau_R \; . \qquad (2.19a)$$

Then, over the longer time scale, $t > \tau_R$, when $P_{\Xi}(\Omega_0 \,|\, \Omega, t)$ has relaxed to $P_{\mathrm{eq},\Xi}(\Omega)$, Eq. (2.19) takes on the form

$$P(\Omega_0, \Xi_0 \,|\, \Omega, \Xi, t) \cong P_{\mathrm{eq},\Xi}(\Omega) f(\Xi_0 \,|\, \Xi, t), \quad t \gg \tau_R \; . \qquad (2.19b)$$

We might note also that the operators Γ_Ω and Γ_Ξ are typically not Hermitian. However, as shown elsewhere, one can convert Γ_Ω to the Hermitian form $\tilde{\Gamma}_\Omega$ by the simple "symmetrizing" transformation:

$$\tilde{\Gamma}_\Omega \equiv [P_{\mathrm{eq},\Xi}(\Omega)]^{-1/2}\, \Gamma_\Omega [P_{\mathrm{eq},\Xi}(\Omega)]^{1/2} \qquad (2.20)$$

with Hermitian eigenfunctions

$$|\, G_m(\Omega, \Xi)\rangle = [P_{\mathrm{eq},\Xi}(\Omega)]^{-1/2} \,|\, u_m(\Omega, \Xi)\rangle \qquad (2.21a)$$

and

$$\langle G_m(\Omega, \Xi) \,| = \langle u_m(\Omega, \Xi) \,|\, [P_{\mathrm{eq},\Xi}(\Omega)]^{1/2} \; . \qquad (2.21b)$$

The operator Γ_Ξ may be dealt with in a similar manner. One may conveniently work with the original or "symmetrized" forms in developing the general expressions; we are using the original forms here for compactness. The $|\, G_m\rangle$ are not only a complete orthogonal basis set (as are the $|\, u_m\rangle$), they are also normalized. They may be expressed as linear combinations of the $\phi^L_{KM}(\Omega)$ of Eqs. (2.3).[13]

Finally, we note that for these Markovian probability functions we can write

$$P(\Omega_0, \Xi_0, \Omega, \Xi, t) = P_{\mathrm{eq}}(\Omega_0, \Xi_0) P(\Omega_0, \Xi_0 \,|\, \Omega, \Xi, t) \; , \qquad (2.22)$$

where $P(\Omega_0, \Xi_0, \Omega, \Xi, t)$ is the joint probability distribution in Ξ, Ξ_0, Ω, and Ω_0.

D. Spin-Hamiltonian and correlation functions

The orientation-dependent part of the spin-Hamiltonian, $\mathcal{H}_1(\Omega)$ may be written as:

$$\mathcal{H}_1(\Omega) = \sum_{L,K,M} (-1)^K \mathcal{D}^L_{-KM}(\Omega) F'^{(L,K)}_\mu A^{(L,M)}_\mu \; , \qquad (2.23)$$

where the $F'^{(L,K)}_\mu$ and $A^{(L,M)}_\mu$ are irreducible tensor components of rank L, with F' in molecule-fixed coordinates, while A is a spin operator in the laboratory axes (whose z axis coincides with the applied dc field). The subscript μ refers to the type of perturbation and the particular nuclei involved. Here, the Euler angles $\Omega = (\alpha, \beta, \gamma)$ refer to the rotation of the coordinate system from the molecular (x', y', z') axis system into the stationary laboratory (x, y, z) coordinate system. The orientation of the director axis system (x'', y'', z'') relative to the laboratory frame can be specified by

Euler angles Ψ which can be related to the two polar angles θ and ϕ such that $\Psi=(0,\theta,\phi)$.

The typical perturbation terms in Eq. (2.23) require $L=2$. As a result of the reorientational motion relative to the fluctuating director, $\mathcal{H}_1(\Omega)$ will be partially averaged, and its average value is given by

$$\langle\mathcal{H}_1(\Omega)\rangle=\sum_{L,K,M,\mu}(-1)^K\langle\mathcal{D}^{(2)}_{-KM}(\Omega)\rangle F'^{(2,K)}_{\mu}A^{(2,M)}_{\mu}\ , \qquad (2.24)$$

where

$$\langle\mathcal{D}^L_{KM}(\Omega)\rangle=\int d\Xi\int d\Omega\, P_{\rm eq}(\Omega,\Xi)\mathcal{D}^L_{KM}(\Omega)$$

$$\cong\int f_{\rm eq}(\Xi)\,d\Xi\int d\Omega\, P_{{\rm eq},\Xi}(\Omega)\mathcal{D}^L_{KM}(\Omega)\ , \qquad (2.25)$$

where Eq. (2.14c) is used for the approximate equality. The spin relaxation in the motional-narrowing region is determined by the correlation function $\langle\mathcal{H}_1(\Omega,t)\mathcal{H}^*_1(\Omega_0,t=0)\rangle-\langle\mathcal{H}_1(\Omega)\rangle\langle\mathcal{H}^*_1(\Omega_0)\rangle$. Since the only time dependence in $\mathcal{H}_1(\Omega)$ occurs in the $\mathcal{D}^L_{-KM}(\Omega)$ due to their dependence on Ω, it is sufficient to study the correlation functions:

$$C_{-KM,-K'M'}(t)\equiv\langle\mathcal{D}^{(2)}_{+KM}(\Omega)\mathcal{D}^{(2)*}_{+K',M'}(\Omega_0)\rangle-\langle\mathcal{D}^{(2)}_{+KM}(\Omega)\rangle\langle\mathcal{D}^{(2)*}_{K'M'}(\Omega_0)\rangle\ , \qquad (2.26)$$

where Eq. (2.25) is used and

$$\langle\mathcal{D}^L_{KM}(\Omega)\mathcal{D}^{L'*}_{K'M'}(\Omega_0)\rangle=\int d\Xi_0\int d\Omega_0\mathcal{D}^{L'*}_{K'M'}(\Omega_0)P_{\rm eq}(\Omega_0,\Xi_0)\int d\Xi\int d\Omega\,\mathcal{D}^L_{KM}(\Omega)P(\Omega_0,\Xi_0|\Omega,\Xi,t)$$

$$\cong\int d\Xi_0 f_{\rm eq}(\Xi_0)\int d\Omega_0\, P_{{\rm eq},\Xi}(\Omega)\mathcal{D}^{L'*}_{K'M'}(\Omega_0)\int d\Xi f(\Xi_0|\Xi,t)\int d\Omega\, P_\Xi(\Omega_0|\Omega,t)\mathcal{D}^L_{KM}(\Omega)\ . \qquad (2.27)$$

It is useful to introduce the modified conditional probability functions $\overline{P}_\Xi(\Omega_0|\Omega,t)$ and $\overline{f}(\Xi_0|\Xi,t)$ by

$$\overline{P}_\Xi(\Omega_0|\Omega,t)=P_\Xi(\Omega_0|\Omega,t)-P_{{\rm eq},\Xi}(\Omega)\ , \qquad (2.28a)$$

$$\overline{f}(\Xi_0|\Xi,t)=f(\Xi_0|\Xi,t)-f_{\rm eq}(\Xi)\ . \qquad (2.28b)$$

These forms have the property of going to zero as $t\to\infty$. We then let

$$\Delta(\Xi,\Omega)\equiv P_{{\rm eq},\Xi}(\Omega)-P_{{\rm eq},\Xi_{\rm eq}}(\Omega) \qquad (2.29a)$$

and

$$\epsilon_\Xi(\Omega_0|\Omega,t)\equiv\overline{P}_\Xi(\Omega_0|\Omega,t)-\overline{P}_{\Xi_{\rm eq}}(\Omega_0|\Omega,t)\ . \qquad (2.29b)$$

Thus Δ and ϵ measure the deviations of the respective distribution functions associated with arbitrary but fixed Ξ from their values for the equilibrium value $\Xi_{\rm eq}$.

One may then use the general stationary Markovian properties:

$$\int P(x_0|x,t)\,dx=1\ , \qquad (2.30a)$$

so

$$\int \overline{P}(x_0|x,t)\,dx=0 \qquad (2.30b)$$

and

$$\int P_{\rm eq}(x_0)P(x_0|x,t)\,dx_0=\int P(x_0,x,t)\,dx_0=P_{\rm eq}(x)\ , \qquad (2.31a)$$

so

$$\int P_{\rm eq}(x_0)\overline{P}(x_0|x,t)=0\ , \qquad (2.31b)$$

to show that the correlation function equation (2.26) may be rewritten as

$$C^{LL'}_{-KM,-K'M'}(t)=C^{(1)LL'}_{-KM,-K'M'}+C^{(2)LL'}_{-KM,-K'M'}+C^{(3)LL'}_{-KM,-K'M'}\ , \qquad (2.32)$$

where

$$C^{(1)LL'}_{-KM,-K'M'}(t)=\int d\Omega_0\mathcal{D}^{L'*}_{K'M'}(\Omega_0)\left[\int d\Xi_0 f_{\rm eq}(\Xi_0)P_{{\rm eq},\Xi_0}(\Omega_0)\right]$$

$$\times\int d\Omega\mathcal{D}^L_{KM}(\Omega)\left[\int d\Xi f_{\rm eq}(\Xi)\overline{P}_\Xi(\Omega_0|\Omega,t)\right]\ , \qquad (2.33a)$$

$$C^{(2)LL'}_{-KM,-K'M'}(t)=\int d\Xi_0\, f_{\rm eq}(\Xi_0)\int d\Xi\,\overline{f}(\Xi_0|\Xi,t)$$

$$\times\left[\int d\Omega_0\mathcal{D}^{L'*}_{K'M'}(\Omega_0)\cdot\Delta(\Xi_0,\Omega_0)\right]\left[\int d\Omega\,\mathcal{D}^L_{KM}(\Omega)\Delta(\Xi,\Omega)\right]\ , \qquad (2.33b)$$

$$C^{(3)LL'}_{-KM,-K'M'}(t)=\int d\Xi_0\, f_{\rm eq}(\Xi_0)\int d\Xi\,\overline{f}(\Xi_0|\Xi,t)$$

$$\times\int d\Omega_0\mathcal{D}^{L'*}_{K'M'}(\Omega_0)\Delta(\Xi_0,\Omega_0)\int d\Omega\,\epsilon_\Xi(\Omega_0|\Omega,t)\mathcal{D}^L_{KM}(\Omega)\ . \qquad (2.33c)$$

Note that in the limit of no ordering, since $P_{{\rm eq},\Xi}(\Omega)$ and $P_\Xi(\Omega_0|\Omega,t)$ become independent of Ξ, it follows from Eqs. (2.29) that $\Delta(\Xi,\Omega)$ and $\epsilon_\Xi(\Omega_0|\Omega,t)$ both go to zero. One then sees that $C^{(2)}(t)$ and $C^{(3)}(t)$ given by Eqs. (2.33b and c) must be zero. Then, in this case, we are left with the simple isotropic result

$$C^{LL'}_{-KM,-K'M'}(t)=C^{(1)LL'}_{-KM,-K'M'}(t)=\int d\Omega_0\mathcal{D}^{L'*}_{K'M'}(\Omega_0)P_{\rm eq}(\Omega_0)$$

$$\times\int d\Omega\,\mathcal{D}^L_{KM}(\Omega)\overline{P}(\Omega_0|\Omega,t)\ . \qquad (2.34)$$

Equation (2.33a) is closely related to the correlation function appropriate for just the molecular reorientational motion under the potential $U(\Omega)$. It just involves first averaging the distribution functions in Ω over the equilibrium distribution in Ξ. In fact, when the fluctuations in Ξ are small enough, then we may expand $\Delta(\Xi,\Omega)$ and $\epsilon_\Xi(\Omega_0|\Omega,t)$ in power series in Ξ:

$$\Delta(\Xi,\Omega)=\Xi\Delta^{(1)}(\Omega)+\Xi^2\Delta^{(2)}(\Omega)+\cdots\ , \qquad (2.35a)$$

$$\epsilon_\Xi(\Omega_0|\Omega,t)=\Xi\epsilon^{(1)}(\Omega_0|\Omega,t)+\Xi^2\epsilon^{(2)}(\Omega_0|\Omega,t)+\cdots\ . \qquad (2.35b)$$

Then, since we may define Ξ relative to its mean taken as zero, it follows that

$$\int d\Xi\, f_{\rm eq}(\Xi)\Xi=0 \qquad (2.36)$$

so that

$$C^{(1)}_{-KM,-K'M'}(t)$$

$$=\int d\Omega_0 \int d\Omega\, \mathfrak{D}^{L'*}_{K'M'}(\Omega_0)P_{\mathrm{eq},\Xi_{\mathrm{eq}}}(\Omega_0)\bar{P}_{\Xi_{\mathrm{eq}}}(\Omega_0|\Omega,t)\mathfrak{D}^L_{KM}(\Omega)$$

$$+\text{terms in} \int \Xi^2 f_{\mathrm{eq}}(\Xi)\, d\Xi+\cdots \ . \tag{2.37}$$

For the case of small fluctuations in Ξ we will find it convenient to keep only lowest order terms in Ξ. The leading term in Eq. (2.37) is just the correlation function for molecular reorientation for a static value of $\Xi = \Xi_{\mathrm{eq}}$. The next order terms are proportional to the mean square fluctuations in Ξ (see below).

Equation (2.33b) can be related to the relaxation term which arises from fluctuations in Ξ (e.g., from director fluctuations). In order to obtain correspondence with the previous theories of relaxation from e.g., director fluctuations,[5,6] it would be necessary to replace the two terms in braces in Eq. (2.33b) by $\Xi \times \Xi_0 \langle \mathfrak{D}^{L'*}_{K'M'}(\Omega_0)\rangle \langle \mathfrak{D}^L_{KM}(\Omega)\rangle$, i.e., the $\Delta(\Xi,\Omega)$ would have to be replaced by $\Xi P_{\mathrm{eq},\Xi_{\mathrm{eq}}}(\Omega)$. This, first of all, corresponds to keeping only the term linear in Ξ in Eq. (2.34a). Secondly, we have to study the character of $\Delta^{(1)}(\Omega)$ in some detail.

We have, so far, not specified the nature of Ξ corresponding to a specific model. In order to proceed further it is convenient to select a specific model.

III. FLUCTUATIONS IN DIRECTOR ORIENTATION

We now study the simplest useful form for $P_{\mathrm{eq},\Xi}(\Omega)$ by choosing a simple, one-parameter functional form for $U(\Omega,\Xi)$. Further, we explicitly define Ξ to correspond to the hydrodynamic model of director fluctuations in which the director **n** fluctuates about its mean position, but the *magnitude* of the ordering potential is unchanged. That is, we use Eq. (2.14d) for $P_{\mathrm{eq},\Xi}(\Omega)$, while we let

$$U=\epsilon_0^{(2)}\mathfrak{D}^2_{00}(\Omega-\Psi)=\epsilon_0^{(2)}\tfrac{1}{2}[3\cos^2(\beta-\theta)-1]\ . \tag{3.1}$$

Here $\Xi \to \Psi$, the Euler angles for the director relative to the lab frame (see above). More precisely the value of Ψ at the molecule of interest is a function of all the hydrodynamic modes which, taken together, constitute the Markov process in Ξ, (cf. Appendix A). While this form is similar to, it should not be confused with the Maier–Saupe form; the latter is a mean field approximation, while in Eq. (3.1) we retain the leading term in the expansion of the "potential of mean torque" in a series in $\mathfrak{D}^L_{K0}(\Omega-\Psi)$.[6] Equation (3.1) represents the feature that the molecule reorients toward the instantaneous direction of **n**. One uses the properties of the generalized spherical harmonics[16] to obtain

$$U=\epsilon_0^{(2)}\sum_N \mathfrak{D}^{(2)}_{0N}(\Omega)\mathfrak{D}^{(2)}_{N0}(-\Psi)\ . \tag{3.2}$$

Then, for small fluctuations in the angle θ we may approximate $\mathfrak{D}^{(2)}_{N0}(-\Psi)$ to terms linear in θ by[6,13]

$$\mathfrak{D}^{(2)}_{N0}(-\Psi)=(-)^N\mathfrak{D}^{(2)}_{0,-N}(\Psi)=(-)^N\mathfrak{D}^{(2)}_{0,-N}(0,\theta,\phi)$$

$$\cong[\delta_{0,N}+\tfrac{1}{2}\sqrt{6}\theta(\delta_{N,-1}\,e^{i\phi}-\delta_{N,+1}\,e^{-i\phi})] \tag{3.3}$$

(with the terms quadratic in θ also given by PF). Then we have

$$U/kT\cong-\bar{\lambda}\{\mathfrak{D}^2_{00}(\Omega)+\tfrac{1}{2}\sqrt{6}\theta[\mathfrak{D}^2_{0,-1}(\Omega)\,e^{i\phi}-e^{-i\phi}\mathfrak{D}^2_{0,1}(\Omega)]\} \tag{3.4}$$

with $\bar{\lambda}=-\epsilon_0^{(2)}/kT$. Then to lowest order in θ we write, using Eqs. (2.29a) and (2.35a):

$$P_{\mathrm{eq},\Psi_{\mathrm{eq}}}(\Omega)=\exp[\bar{\lambda}\mathfrak{D}^2_{00}(\Omega)]\Big/\int d\Omega\,\exp[\bar{\lambda}\mathfrak{D}^2_{00}(\Omega)] \tag{3.5}$$

while

$$\Xi\Delta^{(1)}(\Omega)=\tfrac{1}{2}\sqrt{6}\theta\bar{\lambda}[\mathfrak{D}^{(2)}_{0,-1}(\Omega)\,e^{i\phi}-\mathfrak{D}^{(2)}_{0,1}(\Omega)\,e^{-i\phi}]P_{\mathrm{eq},\Psi_{\mathrm{eq}}}(\Omega)\ , \tag{3.6}$$

where in Eq. (3.5) we have let $\Psi_{\mathrm{eq}}=(0,0,0)$. It then follows from (1) the orthogonality properties of the $\mathfrak{D}^L_{KM}(\Omega)$ and (2) the fact that the expansion of $P_{\mathrm{eq},\Psi_{\mathrm{eq}}}(\Omega)$ in terms of the C.O.N. set $[(2L+1)/8\pi^2]^{1/2}\mathfrak{D}^L_{KM}(\Omega)$ only involves $\mathfrak{D}^L_{00}(\Omega)$ terms by symmetry, that

$$\int \Xi\Delta^{(1)}(\Omega)\,d\Omega=0\ . \tag{3.7}$$

Note also that for the same reasons the conventional order parameter S, defined by

$$S\equiv\int d\Psi\int d\Omega\,\mathfrak{D}^2_{00}(\Omega)P_{\mathrm{eq},\Psi}(\Omega)f_{\mathrm{eq}}(\Psi) \tag{3.8}$$

is, to terms first order in Ξ (or θ), simply given by

$$S\cong\langle\mathfrak{D}^2_{00}\rangle_\Omega\equiv\int d\Omega\,\mathfrak{D}^2_{00}(\Omega)P_{\mathrm{eq},\Psi_{\mathrm{eq}}}(\Omega) \tag{3.9}$$

and is unaffected by the director fluctuations to this order. This establishes one aspect of the correspondence between our model and the requirements of the usual hydrodynamic model of director fluctuations.

We may now evaluate Eq. (2.33b) by substituting Eq. (3.6) for $\Delta(\Xi,\Omega)$. Then, with the aid of the contraction form[16]

$$\mathfrak{D}^L_{KM}(\Omega)\mathfrak{D}^{L'}_{K'M'}(\Omega)=\sum_{j,m,m'}(2j+1)\begin{pmatrix}LL'j\\KK'm'\end{pmatrix}\begin{pmatrix}LL'j\\MM'm\end{pmatrix}\mathfrak{D}^j_{m'm}(\Omega)\ , \tag{3.10}$$

where

$$\begin{pmatrix}LL'j\\KK'm'\end{pmatrix}$$

is a $3-j$ symbol, one obtains the result

$$C^{(2)}_{-K,M,-K'M'}(t)$$

$$=\tfrac{2}{3}\lambda^2[\kappa(0,1)]^2\langle\theta_0\theta\,e^{\mp i(\phi_0-\phi)}\rangle\,\delta_{K,K'}\delta_{M,M'}\delta_{K,0}\,\delta_{M,\pm1} \tag{3.11}$$

with $\lambda\equiv\frac{3}{2}\bar{\lambda}$, where the correlation function in Eq. (3.11) is

$$\langle\theta_0\theta e^{\mp i(\phi_0-\phi)}\rangle\equiv\int d\Psi_0\int d\Psi\,P_{\mathrm{eq}}(\Psi_0)\bar{P}(\Psi_0|\Psi,t)\theta_0\theta e^{\mp i(\phi_0-\phi)} \tag{3.12}$$

and $\kappa(0,1)$ is given in Table I with the averaging of the $\mathfrak{D}^L_{00}(\Omega)$ as given by Eq. (3.9).

TABLE I. Mean square values of the rotation-matrix elements: $\mathcal{D}^L_{KM}(\Omega)$.[a]

$\kappa(K,M)^{b,c}$		Function of $\langle\mathcal{D}^2_{00}\rangle_\Omega$ and $\langle\mathcal{D}^4_{00}\rangle_\Omega{}^{b,d}$	Function of $\langle\mathcal{D}^2_{00}\rangle_\Omega$ and $\lambda^{b,d}$
K	M		
0	0	$\frac{1}{5}+\frac{2}{7}\langle\mathcal{D}^2_{00}\rangle_\Omega+\frac{18}{35}\langle\mathcal{D}^4_{00}\rangle_\Omega-\langle\mathcal{D}^2_{00}\rangle^2_\Omega$	$\frac{1}{2}+\left(\frac{1}{2}-\frac{9}{4\lambda}\right)\langle\mathcal{D}^2_{00}\rangle_\Omega-\langle\mathcal{D}^2_{00}\rangle^2_{r\,\Omega}$
0	1	$\frac{1}{5}+\frac{1}{7}\langle\mathcal{D}^2_{00}\rangle_\Omega-\frac{12}{35}\langle\mathcal{D}^4_{00}\rangle_\Omega$	$\frac{3}{2\lambda}\langle\mathcal{D}^2_{00}\rangle_\Omega$
0	2	$\frac{1}{5}-\frac{2}{7}\langle\mathcal{D}^2_{00}\rangle_\Omega+\frac{3}{35}\langle\mathcal{D}^4_{00}\rangle_\Omega$	$\frac{1}{4}-\left(\frac{1}{4}+\frac{3}{8\lambda}\right)\langle\mathcal{D}^2_{00}\rangle_\Omega$
1,	1	$\frac{1}{5}+\frac{1}{14}\langle\mathcal{D}^2_{00}\rangle_\Omega+\frac{8}{35}\langle\mathcal{D}^4_{00}\rangle_\Omega$	$\frac{1}{3}+\left(\frac{1}{6}-\frac{1}{\lambda}\right)\langle\mathcal{D}^2_{00}\rangle_\Omega$
1,	2	$\frac{1}{5}-\frac{1}{7}\langle\mathcal{D}^2_{00}\rangle_\Omega-\frac{2}{35}\langle\mathcal{D}^4_{00}\rangle_\Omega$	$\frac{1}{6}+\left(-\frac{1}{6}+\frac{1}{4\lambda}\right)\langle\mathcal{D}^2_{00}\rangle_\Omega$
2,	2	$\frac{1}{5}+\frac{2}{7}\langle\mathcal{D}^2_{00}\rangle_\Omega+\frac{1}{70}\langle\mathcal{D}^4_{00}\rangle_\Omega$	$\frac{5}{24}+\left(\frac{7}{24}-\frac{1}{16\lambda}\right)\langle\mathcal{D}^2_{00}\rangle_\Omega$

[a] Cf. Ref. 17.

[b] $\kappa(K,M)\equiv\int P_{eq}(\Omega)\left(|\mathcal{D}^2_{KM}|^2-\langle\mathcal{D}^2_{00}(\Omega)\rangle^2_\Omega\,\delta_{K,0}\delta_{M,0}\right)d\Omega$, with $P_{eq}(\Omega)$ given by Eq. (3.5) and the angular brackets with subscript Ω imply averaging as in Eq. (3.9).

[c] $\kappa(K,M)=\kappa(-K,-M)=\kappa(-K,M)=\kappa(M,K)$.

[d] $\langle\mathcal{D}^2_{00}\rangle_\Omega=(1/3\lambda)\{e^\lambda/z_0-[1+(2/3\lambda)]\}$, $\langle\mathcal{D}^4_{00}\rangle_\Omega=(7/12)\{5[\frac{1}{7}-(3/2\lambda)]\times\langle\mathcal{D}^2_{00}\rangle_\Omega+1\}$, and $z_0=\int_0^1\exp(\lambda x^2)\,dx$.

It is easy to see that for small director fluctuations $\delta\mathbf{n}(\mathbf{r})$ which are orthogonal to $\mathbf{n}(\mathbf{r})$, that we have the relation

$$\langle\mathbf{n}(\mathbf{r}_0)^*_\pm\,\mathbf{n}(\mathbf{r})_\pm\rangle=\langle\theta_0\theta e^{\mp i(\Phi_0-\Phi)}\rangle\ , \tag{3.13}$$

where $n_\pm=n_x\pm in_y$, and n_x and n_y are the x and y component of $\delta\mathbf{n}(\mathbf{r})$. We may thus employ the hydrodynamic theory wherein the fluctuation $\delta\mathbf{n}(\mathbf{r})$ is a superposition of plane-wave disturbances given by Fourier components:

$$\delta\mathbf{n}(\mathbf{q})\equiv\frac{1}{V}\int\delta\mathbf{n}(\mathbf{r})\,e^{-i\mathbf{q}\cdot\mathbf{r}}\,dV\ , \tag{3.14}$$

where V is the sample volume.[1,2] The usual analysis leads to purely viscous type of relaxation for the qth mode given by

$$(\partial/\partial t)\delta\mathbf{n}_\alpha(\mathbf{q})=-[1/\tau_\alpha(\mathbf{q})]\,\delta\mathbf{n}_\alpha(\mathbf{q}) \tag{3.15}$$

with $\alpha=1$ or 2 corresponding to distortions in the x-y plane but with $\mathbf{n}_1(\mathbf{q})$ parallel to the projection of $\mathbf{q}$ in the x-y plane and $\mathbf{n}_2(\mathbf{q})$ normal to $\mathbf{n}_1(\mathbf{q})$.[1,2] For simplicity in presentation, however, we shall use the "one constant approximation" so that we may write[1,2]

$$(\partial/\partial t)\,\delta\mathbf{n}_i(\mathbf{q})=-(1/\tau_q)\,\delta\mathbf{n}_i(\mathbf{q}) \tag{3.16}$$

with $i=x$ or y, and $\tau_q^{-1}=Kq^2/\eta$, where K is the average elastic constant of the liquid crystal with η an average viscosity. Furthermore, the mean-square values in the one constant approximation are

$$\langle|n_-(\mathbf{q})|^2\rangle=\langle|n_+(\mathbf{q})|^2\rangle=\langle|\theta(\mathbf{q})|^2\rangle=2kT/Kq^2V\ . \tag{3.17}$$

Equations (3.15) or (3.16) with Eqs. (3.17) may equivalently be characterized by Markov probability distributions (or equivalently, diffusion equations with diffusion operator Γ_Ψ). This is shown in Appendix A. However, once the identification of Eq. (3.13) is made, we may simply use the result from previous work that[5,6]

$$\langle n(\mathbf{r}_0)^*_\pm n(\mathbf{r})_\pm\rangle=\frac{V}{(2\pi)^3}\int_0^{q_c}\frac{kT}{Kq^2V}\exp\left\{-\frac{Kq^2t}{\eta}\right\}4\pi q^2\,dq$$

$$=\mathfrak{a}t^{-1/2}\Phi[(\omega_ct)^{1/2}]\ , \tag{3.18}$$

where $\omega_c=Kq_c^2/\eta$ is the cutoff frequency, which is introduced since the hydrodynamic theory should break down for wavelengths $\lambda_c=2\pi/\omega_c$ comparable to molecular dimensions. Also $\Phi[\chi]$ is the error function, and

$$\mathfrak{a}=kT\eta^{1/2}/2\pi^{3/2}K^{3/2} \tag{3.19}$$

[Eq. (3.19) is corrected for the effects of finite translational diffusion in Appendix A]. Thus, Eq. (3.11) becomes

$$C^{(2)}_{0,\pm1}(t)=\tfrac{3}{2}S^2\mathfrak{a}t^{-1/2}\Phi[(\omega_ct)^{1/2}]\ , \tag{3.20}$$

which is the usual result.[4,5] It arises, however, because of the simple form of $\kappa(0,1)$ given in Table I. This simple form would not persist if we were to include higher order terms in the expansion equation (3.3). Recall also that the result Eq. (3.21) is based on the one parameter potential of Eq. (3.1). It will necessarily be modified if further terms $\epsilon_0^{(L)}\mathcal{D}^L_{00}(\Omega-\Psi)$ for Leven are included in the expansion of U. (These are the only terms required when the distribution of molecular orientations is axially symmetric with respect to the director orientation).

We are now left with the term $C^{(3)}$ of Eq. (2.33c). It involves the combined time dependences of Ξ (or Ψ) and Ω, and thus has the property of being a cross term. This cross-term arises because of the statistical *dependence* of $\Omega(t)$ on Ξ. An evaluation of Eq. (2.33c) depends on the properties of $\epsilon_\Xi(\Omega_0|\Omega,t)$, which derives from $P_\Xi(\Omega_0|\Omega,t)$ by Eq. (2.31b). Now $P_\Xi(\Omega_0|\Omega,t)$ is the solution to Eq. (2.1) given by Eq. (2.18). It is first necessary to diagonalize $\tilde{\Gamma}_\Omega$ given by Eq. (2.20) to obtain eigenvalues E_m and eigenfunctions $|G_m(\Omega,\Xi)\rangle$. Such solutions are discussed in several places. Because of the complicated form of these solutions, the basic physical features of Eq. (2.33c) will be masked by detail. Thus, for clarity in presentation, we shall use a rotational diffusion model which yields a very simple form for $P_\Xi(\Omega_0|\Omega,t)$: viz, a strong collision model. In this model, a molecule reorients by a strong collision which destroys all memory of its previous orientation. The new orientation is weighted by the distribution function $P_{eq,\Psi}(\Omega)$. In this case, one has[13]

$$P_\Psi(\Omega_0|\Omega_0;t)=P_{eq,\Psi}(\Omega)+[\delta(\Omega-\Omega_0)-P_{eq,\Psi}(\Omega)]\exp(-t/\tau_R)\ , \tag{3.21}$$

where τ_R is the mean time between collisions and $\tau_R^{-1}=R$ of Eq. (2.8). It then follows using Eqs. (2.29) that

$$\epsilon_\Psi(\Omega_0|\Omega,t)=-\Delta(\Psi,\Omega)\exp(-t/\tau_R)\ . \tag{3.22}$$

Substitution of Eq. (3.22) into (2.38c) then yields

$$C^{(3)}_{-KM,-K'M'}(t)=-\exp(-t/\tau_R)C^{(2)}_{-KM,-K'M'}(t)\ . \tag{3.23}$$

Also, for this model, when we neglect terms quadratic in Ξ, we have from Eq. (2.37)

$$C^{(1)}_{-KM,K'M'}(t)=\int d\Omega_0 \mathfrak{D}^{L'*}_{K'M'}(\Omega_0)P_{\mathrm{eq},\Psi_{\mathrm{eq}}}(\Omega_0)\Big[\mathfrak{D}^{L}_{KM}(\Omega_0) - \int d\Omega\, P_{\mathrm{eq},\Psi_{\mathrm{eq}}}(\Omega)\mathfrak{D}^{L}_{KM}(\Omega)\Big]\exp(-t/\tau_R)\ . \tag{3.24}$$

When a potential U, appropriate for cylindrical symmetry in the ordering tensor of the molecules, is used [e.g., Eq. (3.1)], then we have for the strong-collision model

$$C^{(1)}_{KM,K'M'}(t)=C^{(1)}_{KM}(t)\delta_{KK'}\delta_{MM'}=\kappa(K,M)\,e^{-t/\tau_R}\,\delta_{KK'}\delta_{MM'}\ , \tag{3.25}$$

where the $\kappa(K,M)$ are given in Table I. The solutions for $\kappa(K,M)$ have also been obtained numerically for the Brownian diffusion model, and are given in Table II. Actually, since this is a more complicated solution we, for simplicity only, give the κ_{KM} defined in terms of the zero-frequency Fourier transforms of Eq. (3.24), so their meanings are not identical to those defined in Table I.

Our results may now be summarized by

$$C_{KM}(t)=C^{(1)}_{KM}+C^{(2)}_{KM}+C^{(3)}_{KM}=\kappa(K,M)\,e^{-t/\tau_R}+\delta_{K,0}\delta_{M,\pm1}\times\tfrac{3}{2}S^2\mathfrak{a}\,t^{-1/2}\phi(\omega_c)^{1/2}(1-e^{-t/\tau_R}). \tag{3.26}$$

Since we have in our model that

$$\tau_R^{-1}\gg\omega_c\geq\tau_q^{-1}\ , \tag{3.26$'$}$$

it follows from Eq. (3.26) that initially

$$C_{KM}(0)=C^{(1)}_{KM}(0)\ ,$$

i.e., it just depends on the mean square distribution in molecular orientations; but for $t>\tau_R$, this initial correlation function decays to zero and is replaced by

$$C_{KM}(t)\cong C^{(2)}_{KM}(t),\quad t\gg\tau_R^{-1}$$

representing the slower director fluctuations. Of course, when $\lambda\to0$ corresponding to no ordering of the molecule, $C_{KM}(t)\to C^{(1)}_{KM}(t)$ for all times, independent of director fluctuations, as it should.

TABLE II. Zero-frequency spectral densities $J^{(1)}_{KM}(0)$ for the isotropic Brownian reorientation of a molecule experiencing a reorienting potential $U(\beta)/kT=-\lambda\cos^2\beta$. The table lists $5\kappa_{K,M}\equiv5J^{(1)}_{KM}(0)/\tau_R$ expanded according to $5\kappa_{K,M}=(a_0+a_1S+a_2S^2+a_3S^3)$ with $S=\langle\mathfrak{D}^2_{00}(0,\beta,0)\rangle_\Omega$.[a,b,c,d]

	K	M	a_0	a_1	a_2	a_3
$S>0$	0	0	1.000	3.008	−9.704	5.654
	0	1	1.000	1.169	−3.157	0.786
	0	2	0.992	−1.998	0.824	0.191
	1	2	0.993	−0.981	−0.537	0.459
	2	2	1.003	2.111	0.784	−0.133
	1	1	0.992	1.116	−1.077	10.716
$S<0$	0	0	1.000	2.118	−5.112	−10.703
	0	1	0.998	0.797	−5.234	−5.046
	0	2	1.000	−2.165	0.944	−3.956
	1	2	0.998	−1.278	−1.891	−2.666
	2	2	0.999	2.032	−0.253	−2.508
	1	1	1.000	−0.601	−8.405	−22.900

[a] Cf. Ref. 6, 13, 17. We thank Dr. C. F. Polnaszek for computing these results.

[b] $\kappa(K,M)=\kappa(M,K)=\kappa(K,-M)=\kappa(-K,-M)$.

[c] For $S>0$, valid for $S<0.85$; For $S<0$, valid for $S>-0.42$.

[d] These results for $\kappa_{K,M}$ may also be used for $J^{(1)}_{KM}(\omega)$ when $\omega^2\tau_R^2\ll1$, so that $J^{(1)}_{KM}(\omega)=J^{(1)}_{KM}(0)$; but they become only approximate, when $\omega^2\tau_R^2\gtrsim1$, (cf. Refs. 6, 13, 17 for the general case). Also, *anisotropic* diffusion is properly discussed in Refs. 6, 13, 17. For the limit of very anisotropic rotation, such that the parallel and perpendicular components of **R** [cf. Eq. (2.1)] obey: $R_\parallel\gg R_\perp$ (and $R_\parallel\gg|\lambda|R_\perp$), then $\kappa_{0,M}$ is obtained from the table with $\tau_R=(6R_\perp)^{-1}$, while $5\kappa_{K,M}\approx(K^2R_\parallel)^{-1}$ for $K\neq0$. [The result for $\kappa_{0,M}$ is correct for all degrees of anisotropy.]

We are usually interested in the Fourier transforms of the $C_{KM}(t)$ given by

$$J_{KM}\equiv\mathrm{Re}K_{KM}(\omega)=\mathrm{Re}\int_0^\infty C_{KM}(t)\,e^{-i\omega t}\,dt \tag{3.27a}$$

and

$$J^{(i)}_{KM}\equiv\mathrm{Re}K^{(i)}_{KM}(\omega)=\mathrm{Re}\int_0^\infty C^{(i)}_{KM}(t)\,e^{-i\omega t}\,dt\ . \tag{3.27b}$$

Thus, one obtains from Eq. (3.26)

$$J_{KM}(\omega)=\kappa(K,M)\tau_R/(1+\omega^2\tau_R^2)+\tfrac{3}{2}S^2\mathfrak{a}\,\delta_{K,0}\delta_{M,\pm1}\times\left[\sqrt{\frac{\pi}{2}}\,\frac{u(\omega/\omega_c)}{\sqrt{\omega}}-\left(\frac{\tau_R}{1+\omega^2\tau_R^2}\right)\frac{2}{\sqrt{\pi}}\,\omega_c^{1/2}\right]\ , \tag{3.28}$$

where[5,6]

$$u(\omega/\omega_c)=1-\frac{1}{2\pi}\ln\left|\frac{1+\sqrt{2\omega/\omega_c}+\omega/\omega_c}{1-\sqrt{2\omega/\omega_c}+\omega/\omega_c}\right|-\frac{1}{\pi}\tan^{-1}\left(\frac{\sqrt{2\omega/\omega_c}}{1-\omega/\omega_c}+\rho\right)\ , \tag{3.29}$$

$$\rho=0\ \text{if}\ \omega/\omega_c<1;\ \rho=1\ \text{if}\ \omega/\omega_c>1\ .$$

Thus, for small ω/ω_c, $u\approx1-(2\sqrt{2}/\pi)(\omega/\omega_c)^{1/2}$; while for large ω/ω_c $u\to0$. The effect of ω_c is to suppress the high-frequency spectral densities.

When we consider the memory in $R(t-\tau)$ of Eq. (2.5), then one has that $\tau_R/[1+\omega^2\tau_R^2]$ in Eq. (3.28) is to be replaced by $\tau_R(0)/[1+\epsilon\omega^2\tau_R(0)^2]$ for the exponential memory [cf. discussion of Eq. (2.5)], where $\tau_R(0)^{-1}=R(0)$ for the strong collision model, and $\epsilon\equiv[1+\tau_M/\tau_R(0)]^2$. Modifications for Brownian diffusion and anisotropic diffusion tensors **R** are discussed by PF.

The effect of the cutoff on the contribution from $C^{(3)}_{KM}(t)$ is crucial. Thus, if we had let $\omega_c\to\infty$ in evaluating its contribution to Eq. (3.28), we would have obtained, instead of $[\tau_R/(1+\omega^2\tau_R^2)](2/\pi)\omega_c^{1/2}$, the quantity $\sqrt{\pi}(\tau_R/\sqrt{2})\sqrt{(1+\sqrt{1+x^2})/(1+x^2)}$, where $x^2\equiv\omega^2\tau_R^2$, which is very different behavior, because of the incorrect inclusion of modes $q>q_c$.[18] The form given in Eq. (3.28) results from the more general expression

$$J^{(3)}_{0\pm1}(\omega)=-\tfrac{3}{2}S^2[kT\eta/4\pi^2K^2][\alpha^{-1/2}\tan^{-1}(q_c/\sqrt{\alpha})+\alpha^{*-1/2}\tan^{-1}(q_c/\sqrt{\alpha^*})]\ , \tag{3.30}$$

where $\alpha\equiv(\tau_R^{-1}-i\omega)\eta/K$ and α^* is its complex conjugate. Now using the inequality of Eq. (3.27) we have

$$|q_c/\sqrt{\alpha}|^2=q_c^2/|\alpha|\leq(Kq_c^2/\eta)\tau_R=\omega_c\tau_R\ll1. \tag{3.31}$$

Thus, only the lowest order terms in $q_c/\sqrt{\alpha}$ are retained in Eq. (3.28). For typical values of $K/\eta\sim10^{-6}$ cm^2/

sec, $q_c = 2\pi/\lambda$ with $\lambda \sim 20$ Å, and $\tau_R \sim 10^{-10}$ sec, one has $\omega_c \sim 10^9$ sec^{-1} and

$$J^{(3)}(\omega)/J^{(2)}(\omega) = [\tau_R/(1+\omega^2\tau_R^2)](2\sqrt{2}/\pi) \times(\omega_c\omega)^{1/2}u(\omega)^{-1} \xrightarrow[\omega\sim 3\times 10^8]{} 0.1 \ . \quad (3.32)$$

In concluding this section we remind the reader that the cross term in Eq. (3.28) is not the only one. There are corrections to the leading term in Eq. (3.28) that appear in lowest order as mean squares of the director fluctuations [cf. Eq. (2.37)], but are not dependent on the τ_q, and these could well be comparable to the cross term of Eq. (3.28) in some cases.

Also, we note that an expression like Eq. (3.28) may require that, e.g., the first term be corrected for anisotropic diffusion as outlined by PF and/or for more complex ordering (cf. PF).

IV. ORDER FLUCTUATIONS NEAR THE PHASE TRANSITION

The analysis of the quasicritical fluctuations near the isotropic–nematic phase transition begins in an analogous manner to that for director fluctuations. Thus, we choose the one-parameter functional form for $U(\Omega,\Psi)$ given by Eq. (3.1), and expand it according to Eq. (3.2). However, here we assume that the fluctuations are in the magnitude as well as the orientation of the potential, and $\bar{\lambda}_{eq} = 0$ for the isotropic phase, so that

$$P_{eq,\Xi_{eq}}(\Omega) = 1/8\pi^2 \quad (4.1)$$

while

$$P_{eq,\Xi}(\Omega) = \exp[\bar{\lambda}\mathcal{D}^2_{00}(\Omega-\Psi)] \Big/ \left[\int d\Omega \exp[\bar{\lambda}\mathcal{D}^2_{00}(\Omega-\psi)]\right] , \quad (4.2)$$

where Ξ includes both $\bar{\lambda}$ and Ψ (or again more precisely the complete set of hydrodynamic modes, cf. Appendix A). For small fluctuations in $\bar{\lambda}$, we have

$$\Xi\Delta^{(1)} = (\bar{\lambda}/8\pi^2)\sum_N \mathcal{D}^2_{0N}(\Omega)\mathcal{D}^2_{N0}(-\Psi) \quad (4.3)$$

with the use of Eqs. (2.29) and (2.35) and Eq. (3.7) again applies. One may then use Eq. (4.3) to evaluate the correlation function equation (2.33b). One easily finds

$$C^{(2)}_{-K,M,-K'M'}(t) = \tfrac{1}{25}\langle\bar{\lambda}(t=0)\mathcal{D}^{2*}_{0,M'}(\Psi_0)\,\bar{\lambda}(t)\mathcal{D}^2_{0,M}(\Psi)\rangle\,\delta_{K,0}\delta_{K',0} \ . \quad (4.4)$$

Let us now consider some arbitrary instantaneous value of $\bar{\lambda}$, while $\Psi = (0,0,0)$. Then for this instantaneous set we can associate an order parameter in accord with Eq. (3.8) [with $P_{eq,\Psi}(\Omega)$ given here by Eq. (4.2)]. Since $\bar{\lambda}$ is small, one may expand the exponents in Eq. (4.2), and obtain

$$S \cong \tfrac{1}{5}\bar{\lambda} \ . \quad (4.5)$$

More generally we introduce the order tensor $Q_{\alpha\beta}$ by[19,1,2]

$$Q_{\alpha\beta} \equiv \tfrac{1}{2}S(3n_\alpha n_\beta - \delta_{\alpha\beta}) , \quad (4.6a)$$

where $\mathbf{n}$ is the instantaneous director whose components n_α, n_β are referred to the lab z axis. Or alternatively in irreducible tensor notation:

$$Q_M = S\mathcal{D}^2_{0,M}(\Psi) \cong (\bar{\lambda}/5)\mathcal{D}^2_{0,M}(\Psi) \ . \quad (4.6b)$$

Then Eq. (4.4) becomes

$$C^{(2)}_{-K,M,-K',M'}(t) \cong \langle (Q^*_{M'})_0(Q_M)_t\rangle\,\delta_{K,0}\,\delta_{K',0} \ . \quad (4.7)$$

It is precisely the fluctuations in the $Q_{\alpha\beta}$ which are described by the Landau–de Gennes mean-field theory.[21,22] Our approximate result, Eq. (4.7), which permits us to employ this theory to evaluate the correlation function, required we assume that these fluctuations are small in the sense that $\bar{\lambda} \ll 1$. When one is dealing with a small probe molecule, then Eq. (4.5) become $S^{(p)} \cong \frac{1}{5}\bar{\lambda}^{(p)}$, and Eqs. (4.6) do not apply, since $Q_{\alpha,\beta}$ is defined in terms of the liquid-crystal molecules. However, since we have $\bar{\lambda}^{(p)} \approx \bar{\lambda}S^{(p)}/S$, it seems reasonable to rewrite Eq. (4.7) for the probe as

$$C^{(2)}_{-K,M,-K',M'}(t) \cong (S^{(p)}_{\mathrm{T.P.}}/S_{\mathrm{T.P.}})^2\langle (Q^*_{M'})_0(Q_M)_t\rangle\delta_{K,0}\delta_{K',0} , \quad (4.7')$$

where the ratio $S^{(p)}_{\mathrm{T.P.}}/S_{\mathrm{T.P.}}$ may be evaluated from the actual measured values just below the phase transition. This assumes that the ratio is constant over a range of S. Since, in a mean field theory, we may write $\bar{\lambda}^{(p)} \propto S$ for dilute solutions of probe,[22] it follows from Eqs. (4.2) and (3.8) that as long as $\bar{\lambda}^{(p)}$ is small, such a constancy is quite reasonable, without even requiring that $\bar{\lambda}$ be small. [Thus, for a mean-field theory we can let $\bar{\lambda}^{(p)} \equiv u^{(ps)}S/kT$ (with $u^{(ps)}$ independent of S) directly in Eq. (4.4).]

Recently, observations of order fluctuations on the nematic side of the phase transition have been reported and explained in terms of an extension of Landau–de Gennes mean-field theory.[23] In this case Eq. (4.2) becomes

$$P_{eq,\Xi}(\Omega) = e^{y(\Omega)} \Big/ \int d\Omega\, e^{y(\Omega)} \quad (4.8a)$$

with

$$y(\Omega) = \bar{\lambda}_0\mathcal{D}^2_{00}(\Omega) + \bar{\lambda}_1\mathcal{D}^1_{00}(\Omega-\Psi) , \quad (4.8b)$$

where $\bar{\lambda}_0$ is the equilibrium value of the potential in the nematic phase, while $\bar{\lambda}_1$ now refers to the fluctuating component, with Ψ specifying the Euler angles between its principal axes and those of the dominant component (viz. $\bar{\lambda}_0$). Thus, $P_{eq,\Xi_{eq}}(\Omega)$ is obtained from Eqs. (4.8) by letting $\bar{\lambda}_1 = 0$.[24] The analysis to lowest order in $\bar{\lambda}_1$ is straightforward, and one obtains in place of Eq. (4.4)

$$C^{(2)}_{-K,M,-K'M'}(t) = \kappa(0,M)\kappa(0,M') \times\langle\bar{\lambda}_1(t=0)\mathcal{D}^{2*}_{0M'}(\Psi_0)\bar{\lambda}_1(t)\mathcal{D}^2_{0,M}(\Psi)\rangle\,\delta_{K,0}\delta_{K',0} , \quad (4.9)$$

where the $\kappa(0,M)$ are given in Table I, and the $\langle\mathcal{D}^L_{00}(\Omega)\rangle_\Omega$ in that table refer to averaging with $P_{eq,\Xi_{eq}}(\Omega)$. The effect of these $\kappa(0,M)$ coefficients is to reduce the importance of the order fluctuations as the ordering becomes greater. We now must define

$$S_1 \cong \tfrac{1}{5}\bar{\lambda}_1 \quad (4.10)$$

in terms of the change in order tensor $\Delta Q_{\alpha\beta}$ from its mean values in the nematic, i.e., in terms of Eqs. (4.6) with $\Delta Q_{\alpha\beta}$ replacing $Q_{\alpha,\beta}$ and Q_{0M} replacing Q_M. Then Eqs. (4.7) become

$$C^{(2)}_{-K,M,-K'M'}(t) \cong 25\kappa(0,M)\kappa(0,M')\langle (Q^*_{M'})_0(\Delta Q_M)_t\rangle\,\delta_{K,0}\delta_{K',0} \quad (4.11)$$

and for a probe molecule we multiply this by $(S^{(p)}_{\mathrm{T.P.}}/$

$S_{\mathrm{T.P.}})^2$. Also, in the case of a probe, the $\kappa(0,M)$ refer to the ordering of the probe.

When the Landau–de Gennes approach outlined in Appendix C is used, one obtains

$$C^{(2)}_{-K,M,-K',M'}(t) \cong \left(\frac{S^{(i)}_{\mathrm{T.P.}}}{S_{\mathrm{T.P.}}}\right)^2 \frac{1}{4\pi^{3/2}} \frac{kT\nu^{1/2}}{L^{3/2}} e^{-a^2 t} \times [t^{-1/2} - \sqrt{\pi}\, a e^{a^2 t} \operatorname{erfc}(a t^{1/2})] \delta_{K,0}\delta_{K',0}\delta_{M,M'} \qquad (4.12a)$$

from Eq. (4.7), so that

$$J^{(2)}_{-K,M,-K',M'}(\omega) \cong \left(\frac{S^{(i)}_{\mathrm{T.P.}}}{S_{\mathrm{T.P.}}}\right)^2 \frac{1}{4\sqrt{2}\pi} \frac{kT\nu^{1/2}}{L^{3/2}\omega_\xi^{1/2}} \times \left(\frac{1}{1+\sqrt{1+(\omega/\omega_\xi)^2}}\right)^{1/2} \delta_{K,0}\delta_{K',0}\delta_{M,M'} \qquad (4.12b)$$

with $\omega_\xi = L/\nu\xi^2$. We have not, in Eq. (4.12b), included the effect of a finite q_c. The expressions resulting from Eq. (4.11) are obtained from Eqs. (4.12) by multiplying them by $[\kappa(0,M)]^2$ and letting $\nu \to \nu_N$, $L \to L_N$, and $\xi \to \xi$.

By an analysis similar to that used for obtaining Eq. (3.26) and (3.28) wherein Eq. (3.26′) is used, we again have Eq. (3.23) and we obtain

$$J_{KM}(\omega) = \frac{\kappa(K,M)\tau_R}{1+\omega^2\tau_R^2} + \left(\frac{S^{(i)}_{\mathrm{T.P.}}}{S_{\mathrm{T.P.}}}\right)^2 \frac{kT\nu^{1/2}}{4\pi^{3/2}L^{3/2}} \delta_{K,0} \times \left\{\sqrt{\frac{\pi}{2}}\, \omega_\xi^{-1/2} / [1+\sqrt{1+(\omega/\omega_\xi)^2}]^{1/2} - \left(\frac{\tau_R \omega_c^{+1/2}}{1+\omega^2\tau_R^2}\right)\frac{2}{\sqrt{\pi}} \times \left[1 - \left(\frac{\omega_\xi}{\omega_c}\right)^{1/2} \tan^{-1}\left(\frac{\omega_c}{\omega_\xi}\right)^{1/2}\right]\right\}, \qquad (4.13)$$

where again $\omega_c = Lq_c^2/\nu$, and below the phase transition the modifications noted for Eq. (4.12b) are appropriate; but since q_c^{-1} is of the order of a molecular dimension, while ξ is of the order of many molecular dimensions near the phase transition, $(\omega_\xi/\omega_c)^{1/2} \ll 1$, and we can neglect the term in $(\omega_\xi/\omega_c)^{1/2}$ in Eq. (4.13). For $T - T^* \sim 1°$ and typical values ($L_1 \sim 10^{-6}$ dyn, $a \sim 6\times10^5$ erg/cm^3 °C, and $\nu \sim 0.3$ P)[19] one has $\omega_\xi \sim 2\times10^6$ sec^{-1}; while for $q_c = 2\pi/\lambda_c$ and $\lambda_c \sim 2\times10^{-7}$ cm, one has $\omega_c \sim 3\times10^9$ sec^{-1}. Finally, we note for these values and $\tau_R \sim 10^{-10}$ sec,

$$\left|\frac{J^{(3)}(0)}{J^{(2)}(0)}\right| = \tau_R \frac{2\sqrt{2}}{\pi} (\omega_\xi - \omega_c)^{1/2} \sim 7\times10^{-3}, \text{ while for } \omega \gg \omega_\xi$$

$$\left|\frac{J^{(3)}(\omega)}{J^{(2)}(\omega)}\right| \cong \frac{\tau_R}{1+\omega^2\tau_R^2} \frac{2\sqrt{2}}{\pi} (\omega\omega_c)^{1/2} \xrightarrow{\omega\sim3\times10^8} 8.5\times10^{-2},$$

i.e., a negligible contribution to $J(0)$ and a small but possibly nonnegligible contribution to $J(\omega)$.[25]

The results, Eqs. (4.12), do not include the effects from finite translational diffusion, but if a procedure, analogous to that of Appendix A is used, one has that these equations are to be replaced by equations of the form of Eqs. (B3) and (B4) (cf. Appendix B), e.g.,

$$J^{(2)}_{KM}(\omega) \cong \left(\frac{S^{(i)}_{\mathrm{T.P.}}}{S_{\mathrm{T.P.}}}\right)^2 \frac{1}{4\pi} \frac{kT\xi}{L} \times \left[\frac{D[1-\sqrt{x^2+(\omega/\omega_\xi)^2}] + (\omega\xi^2/\sqrt{2})\sqrt{\sqrt{x^2+(\omega/\omega_\xi)^2}-x}}{\omega^2\xi^4+D^2}\right], \qquad (4.14)$$

with $\omega_\xi' \equiv L'/\nu\xi^2$, $L' \equiv L + \nu D$, $x = L/L'$.

V. LOCAL STRUCTURE FLUCTUATIONS

PF have suggested, in explaining some observed spin relaxation anomalies from spin probes in nematics, that the local viscous motions of the larger solvent molecules are likely to be slower than the reorientation rate of the probe. Thus, the surrounding solvent molecules may be regarded as providing a local structure which relaxes on a slower time scale than the probe.

We may use the formulation of the previous sections to deal with such a physical model. In particular if we assume an otherwise isotropic liquid with local order-parameter fluctuations, then by analogy to Eqs. (4.1)–(4.6) we have

$$C^{(2)}_{-K,M,-K',M'}(t) = \langle S_{lM'}(\Psi_0) S_{l,M}(\Psi)\rangle \delta_{K,0}\delta_{K',0}, \qquad (5.1)$$

where

$$S_{l,M} = S_l \mathfrak{D}^{(2)}_{0,M}(\Psi) \cong (\bar{\lambda}/5)\mathfrak{D}^{(2)}_{0,M}(\Psi) \qquad (5.2)$$

and S_l is the local order parameter. The PF derivation is based on S_l being constant and only the $\mathfrak{D}^{(2)}_{0,M}(\Psi)$ fluctuate in time but isotropically. Furthermore, a single decay time τ_x with activation energy characteristic of the viscous modes was assumed for simplicity (although it was also allowed to have anisotropic properties). In this case then, one obtains

$$C^{(2)}_{-K,M,-K',M'}(t) = \tfrac{1}{5} S_l^2 e^{-t/\tau_x} \delta_{M,M'}\delta_{K,0}\delta_{K',0}. \qquad (5.3)$$

If we do not assume S_l remains constant, then S_l^2 in Eq. (5.3) is replaced by the mean square value $\langle |S_l|^2\rangle$, and is analogous to the results in Sec. IV for a single q mode. Similarly, we can include the effects of a static orienting potential by analogy to Eqs. (4.9)–(4.11). In this case one has

$$C^{(2)}_{-K,M,-K',M'}(t) = [5\kappa(0,M)]^2 \tfrac{1}{5} \langle |S_l|^2\rangle e^{-t/\tau_x} \delta_{M,M'}\delta_{K,0}\delta_{K',0}. \qquad (5.4)$$

We then obtain

$$J_{KM}(\omega) = \frac{\kappa(K,M)\tau_R}{1+\omega^2\tau_R^2} + \tfrac{1}{5}[5\kappa(0,M)]^2 \delta_{K,0}\langle |S_l|^2\rangle \times \left[\frac{\tau_x}{1+\omega^2\tau_x^2} - \frac{\tau_R'}{1+\omega^2\tau_R'^2}\right], \qquad (5.5)$$

where $\tau_R'^{-1} \equiv \tau_R^{-1} + \tau_x^{-1} \cong \tau_R^{-1}$ by our requirement that $\tau_R^{-1} \gg \tau_x^{-1}$. This result is similar to that of PF, but differs from it in several respects: (1) the local structure contribution includes the correction for the static ordering in Eq. (5.5); (2) the cross-term involving τ_R' was not obtained in the approximate PF treatment, but it is always small compared to the sum of the other terms provided $\langle |S_l|^2\rangle$ is small as required by our analysis utilizing Eqs. (2.35); (3) the PF treatment yielded the corrections to the leading term of Eq. (5.5) (for isotropic reorientation) due to the local structure, which according to Eq. (2.37) come in, in lowest order as

$\langle |S_l|^2 \rangle$, and could in principle be calculated from Eq. (2.33a).[26]

One can also, by analogy with Sec. III, treat a model of local structure fluctuations as fluctuations in orientation of a "local director," although it does not appear likely to be of physical importance. This model is discussed by PF.[27]

We have not explicitly included in our analysis the effects of translational diffusion by which means the probe can sample different local structures. To do this properly would require a more detailed model of the local structure than we have provided, including some specification of its correlation range. At the level of simplicity of our results we can simply regard τ_x^{-1} as the combined rate for relaxation of a given local structure and for molecular translational diffusion leading to a sampling of spatially displaced local structures. Evidence from pressure-dependent studies[22] indicates that a small probe could well be located in a clathrate-type cavity such that it samples the relaxation of a "single" local structure.

VI. MAGNETIC RESONANCE RELAXATION

A. NMR

The spectral density of Eq. (3.2) may now be combined with the usual treatment of NMR relaxation[28] to yield for the contribution from relaxation by intramolecular dipole–dipole interaction of like nuclei of spin I by rotational reorientation:

$$(1/T_1)_{\rm rot} = (2\gamma^4\hbar^2/b^6)I(I+1)\sum_{K=-2}^{2}|f^{(K)}|^2 \times[J_{K1}(\omega_0)+4J_{K2}(\omega_0)]\ , \qquad (6.1)$$

$$(1/T_2)_{\rm rot} = (\gamma^4\hbar^2/b^6)I(I+1)\sum_{K=-2}^{2}|f^{(K)}|^2 \times[3J_{K0}(0)+5J_{K1}(\omega_0)+2J_{K2}(2\omega_0)]\ , \qquad (6.2)$$

where

$$|f^{(0)}|^2 = [\tfrac{1}{2}(1-3\cos^2\beta')]^2\ ,$$

$$|f^{(\pm1)}|^2 = \tfrac{3}{2}\sin^2\beta'\cos^2\beta'\ ,$$

$$|f^{(\pm2)}|^2 = \tfrac{3}{8}\sin^4\beta'\ ,$$

where β' is the polar angle between the molecular axis which is aligned relative to the director and the vector between the two dipoles. Also b is the internuclear separation and γ is the nuclear gyromagnetic ratio. Similar expressions may be written for unlike nuclei (cf. Ref. 28). The spectral densities in Eqs. (6.1) and (6.2) are given, for example, by Eqs. (3.28), (4.12b), or (5.5).[28] In general, it will be necessary to add to Eqs. (6.1) and (6.2) the contributions due to intermolecular dipole–dipole interactions.[29]

For quadrupolar relaxation we consider the simple special case of $I=1$, and an axially symmetric electric-field gradient. Then we get

$$1/T_1)_{\rm quadr} = \tfrac{3}{8}(e^2qQ/\hbar)^2\sum_{K=-2}^{2}|f^{(K)}|^2[J_{K1}(\omega_0)+4J_{K2}(2\omega_0]\ , \qquad (6.3)$$

$$(1/T_2)_{\rm quadr} = \tfrac{1}{16}(e^2qQ/\hbar)^2\sum_{K=-2}^{2}|f^{(K)}|^2 \times[9J_{K0}(0)+15J_{K1}(\omega_0)+6J_{K2}(2\omega_0)]\ . \qquad (6.4)$$

The $|f^{(K)}|^2$ are defined as before, but with β' the polar angle between the molecular axis which aligns along the director and the symmetry axis of the electric-field gradient tensor. [Because of the general frequency dependence of Eq. (3.28), it is not useful to solve for the other special case[28] of $J_{KM}(\omega)=J_{KM}(0)$].

Note that in the above equations it is only the $J_{0\pm1}(\omega_0)$ terms that are affected by the director fluctuations (cf. Sec. III), while all the $J_{0M}(\omega)$ terms are affected by order parameter fluctuations (cf. Sec. IV).

B. ESR

We consider the motional-narrowing linewidth for an unpaired electron interacting with a single nucleus of spin I. We include axially symmetric dipolar and g-tensor contributions with the same principle axes. One obtains as a function of nuclear-spin quantum number $m_{\rm I}$:

$$1/T_2 = A + Bm_{\rm I} + Cm_{\rm I}^2\ , \qquad (6.5)$$

where

$$(A-A') = \tfrac{1}{3}I(I+1)\gamma_e^2|D_0|^2\sum_{K=-2}^{2}|f^{(K)}|^2[J_{K,0}(\omega_e)+3J_{K,1}(\omega_a) + 6J_{K,2}(\omega_e)] + \frac{\hbar^2\gamma_e^2}{16\beta_e^2}\sum_{K=-2}^{2}|f^{(K)}|^2 \times[4J_{K,0}(0)+3J_{K,1}(\omega_e)]\ , \qquad (6.6)$$

$$B = \frac{\hbar\gamma_e^2}{\sqrt{6}\beta_e}D_0F_0\sum_{K=-2}^{2}|f^{(K)}|^2[4J_{K,0}(0)+3J_{K,1}(\omega_e)]\ , \qquad (6.7)$$

$$C = \tfrac{1}{3}\gamma_e^2(D_0)^2\sum_{K=-2}^{2}|f^{(K)}|^2[8J_{K,0}(0)-3J_{K,1}(\omega_a)-J_{K,0}(\omega_e) + 6J_{K,1}(\omega_e)-6J_{K,2}(\omega_e)]\ , \qquad (6.8)$$

with A' containing the remaining nuclear-spin independent linewidth contributions. Here $D_0=(6)^{-1/2}(a_\perp - a_\parallel)$, and $F_0=\tfrac{2}{3}\beta_e B_0[g_\parallel - g_\perp]$, with $a_\parallel$ and $a_\perp$ the parallel and perpendicular components respectively of the hyperfine tensor, $g_\parallel$ and $g_\perp$ the equivalent components of the g tensor, B_0 the magnetic field strength, β_e the Bohr magneton, γ_e the electron–spin gyromagnetic factor, ω_e the electron spin Larmor frequency, and $\omega_a=\tfrac{1}{2}a|\gamma_e| \pm \omega_n$ the nuclear-spin flip frequencies. Note that the $|f^{(K)}|^2$ have the same meaning as before with β' the polar angle between the principal symmetry axis of the axially symmetric magnetic tensors and the molecular axis which is aligned relative to the director. More general line width expressions (e.g., for nonaxially symmetric magnetic tensors) may be written in an analogous manner with the aid of results given by PF and in Ref. 17. (Also, we have neglected the high-field corrections needed for vanadyl[30] but unnecessary for nitroxides).

C. Tilt of director axis

When the director axis is not parallel to the applied magnetic field, the spectral densities of Eq. (3.28) or

(4.13) depend upon the angle θ' between the director and the field.[31–33] We give the expressions for $J_{KM}(\omega, \theta')$ in terms of the $J_{KM}(\omega, 0) \equiv J_{KM}(\omega)$ given in Secs. III–V, which were developed for director axis parallel to the applied magnetic field (we suppress ω):

$$J_{K0}(\theta') = \tfrac{1}{5}(J_{K0} + 2J_{K1} + 2J_{K2}) + \tfrac{2}{7}P_2(\theta')(J_{K0} + J_{K1} - 2J_{K2}) + \tfrac{6}{35}P_4(\theta')(3J_{K0} - 4J_{K1} + J_{K2}) , \quad (6.9)$$

$$J_{K1}(\theta') = \tfrac{1}{5}(J_{K0} + 2J_{K1} + 2J_{K2}) + \tfrac{1}{7}P_2(\theta')(J_{K0} + J_{K1} - 2J_{K2}) - \tfrac{4}{35}P_4(\theta')(3J_{K0} - 4J_{K1} + J_{K2}) , \quad (6.10)$$

$$J_{K2}(\theta') = \tfrac{1}{5}(J_{K0} + 2J_{K1} + 2J_{K2}) - \tfrac{2}{7}P_2(\theta')(J_{K0} + J_{K1} - 2J_{K2}) + \tfrac{1}{35}P_4(\theta')(3J_{K0} - 4J_{K1} + J_{K2}) , \quad (6.11)$$

where

$$P_2(\theta') = \mathfrak{D}^2_{00}(0, \theta', 0) = \tfrac{1}{2}(3x^2 - 1)$$

and

$$P_4(\theta') = \mathfrak{D}^4_{00}(0, \theta', 0) = \tfrac{1}{8}(35x^4 - 30x^2 + 3)$$

with $x \equiv \cos\theta'$. One uses these $J_{KM}(\omega, \theta')$ in Eqs. (6.1)–(6.8).

VII. SUMMARY AND CONCLUSIONS

The main objective of this work was to remove the assumption of statistical independence between the overall molecular reorientational motion and the order (and local structure) fluctuations in the theory of spin relaxation in nematics. This has been accomplished by treating both types of dynamics as a composite Markov process and solving for the physically meaningful limit wherein τ_R is significantly shorter than the τ_q (or τ_x) characterizing the order (or local structure) fluctuations. Simple analytic results are achieved in the limit of very small fluctuations such that only lowest order terms need be retained, but our methods could be extended to effects of larger fluctuations.

It is possible to separate the motional correlation functions into several terms: the first one corresponds to rotational relaxation under a static restoring potential (which, however, contains corrections for the equilibrium distribution of potentials). Another term is characteristic of the correlation function for director (order parameter, or local structure) fluctuations, and a third (and negative) term represents a cross-correlation between the statistically dependent processes. In lowest order in director (etc.) fluctuations, the second term is identical to the results previously obtained,[5,6] but with the aid of a formalism developed in Appendix A and discussed further in Appendix B, one could develop the higher order corrections from our expressions. The negative cross-correlation term has been shown to have a very simple relationship to the second term by evaluating it using the simple strong-collision model of rotational reorientation. It is not expected that its primary features would be altered by the use of more realistic models of reorientation, although the mathematical analysis becomes more complex. It is found in the lowest order analysis that this cross-term, which is of some theoretical interest, is in general rather small.

The results we have obtained are also characterized by the feature that as the order parameter $S \to 0$, one achieves the correct physical limit, such that the overall correlation functions become independent of any director (etc.) fluctuations. This confirms the point made by PF on the need to neglect physically unsound terms in the earlier analyses, which have, however, been retained by Doane *et al.*[5] in their recent analysis. Furthermore our results given here for the correlation functions for molecular reorientation are based on the most complete solutions of the correct reorientational diffusion equations[6,13,14] and should therefore be considerably more accurate than the highly approximate treatment used by Doane *et al.*[5,47]

We discuss in Appendix B the question of the applicability of motional-narrowing theory in these situations where director fluctuations have very slowly relaxing components. It appears that for typical spin-relaxation situations, motional-narrowing theory should be applicable in terms of a description based on complete independence of the normal modes and the neglect of any higher-order cross-terms involving different modes. Such an analysis has the unpleasant feature of depending on sample volume (but it does have the satisfactory feature that any such higher-order terms approach zero as $V \to \infty$). It is pointed out that proper higher-order corrections, which are V independent, and nonzero in general, may be obtained from cross-terms involving the statistically independent modes provided one is dealing with the nonsecular perturbation terms in the spin Hamiltonian which will lead to *nonzero* spectral densities. A procedure for carrying out such an analysis has been briefly outlined. However, it may also be necessary to consider mode–mode coupling effects to carry out meaningful calculations in higher order.

In the local structure model, however, as τ_x becomes long enough, it would be necessary to use a slow tumbling theory. This may be carried out by combining the methods in this paper with the stochastic–Liouville equation approach to this problem as outlined by PF.

APPENDIX A: THE PROBABILITY FUNCTION FOR DIRECTOR FLUCTUATIONS

We now consider how one may obtain explicit forms for $\mathbf{P}(\Psi(\mathbf{r}), t)$. That is, the value of $\Psi(\mathbf{r})$ at $\mathbf{r}$ is a stochastic variable determined by the projection of the normal modes $\Psi(\mathbf{q})$ at local site $\mathbf{r}$. But the correlation between $\Psi(\mathbf{r}_i)$ and $\Psi(\mathbf{r}_j)$ at different points $\mathbf{r}_i$ and $\mathbf{r}_j$, due to the cooperative nature of the motion, must be included in a complete specification of $\mathbf{P}(\Psi(\mathbf{r}), t)$, which then becomes a multidimensional Markov process (in the Hilbert space of $\mathbf{r}$). It is, of course, much simpler to consider the normal modes $\Psi(\mathbf{q})$ and first develop the expression for $\mathbf{P}(\Psi(\mathbf{q}), t)$. In the approximation of independent modes in q space, we can write a separate Markovian distribution $P_i(\Psi(\mathbf{q}), t)$ corresponding to the ith q value. We are then guided by (1) the known mean-square fluctuations for each mode predicted by equipartition and (2) the known dissipative character for each mode. We then may write (by use of results in Appendix B of PF) the Markovian equation

$$\partial P_i(\Psi(\mathbf{q}),t)/\partial t = -\Gamma_{i\Psi(\mathbf{q})} P_i(\Psi(\mathbf{q},t)) \ , \tag{A1}$$

where

$$\Gamma_{i\Psi(\mathbf{q})} = -D_\Psi \nabla^2_\Psi + 2D_\Psi \alpha_q[\cos\theta_\mathbf{q} \sin\theta_\mathbf{q}\, \partial/\partial\theta_\mathbf{q} + (3\cos^2\theta_\mathbf{q} - 1)] \ , \tag{A2}$$

with

$$D_\Psi = kT/\eta V \tag{A3a}$$

and

$$\alpha_q = \tfrac{1}{2} KVq^2/kT \ . \tag{A3b}$$

This is the equation for a simple "hindered rotational diffusion," as discussed in Appendix B of PBF. The specific values for D_Ψ and α_q are the ones required to agree with above-noted requirements (1) and (2) as will be shown below, and as PF have previously pointed out.[34]

Now, except for the smallest values of q (i.e., $q \lesssim (2kT/KV)^{1/2}$ which is negligible—cf. Appendix B), the effective potential α_q will guarantee that the fluctuations are small, so we take the limit for $\alpha_q \gg 1$ and $\theta_\mathbf{q}$ very small. We then symmetrize the resulting $\Gamma_{i,\Psi(q)}$ to yield[6]

$$\tilde{\Gamma}_{i,\Psi(\mathbf{q})} = D_\Psi[(\partial^2/\partial\theta^2_\mathbf{q}) + \theta^{-1}_\mathbf{q}(\partial/\partial\theta_\mathbf{q}) - \theta^{-2}_\mathbf{q}(\partial^2/\partial\phi^2_\mathbf{q}) - \alpha^2_q\theta^2_\mathbf{q} + 2\alpha_q] \tag{A4}$$

The solution to this type of diffusion operator has been discussed elsewhere.[13] One finds eigenfunctions

$$Y^M_N(\Psi(\mathbf{q})) = y^M_N(\theta_\mathbf{q})\, e^{iM\phi}(2\pi)^{-1/2} \ , \tag{A5}$$

where

$$y^M_N(\theta_\mathbf{q}) = [2\alpha_q N!/(N+|M|)!]^{1/2} e^{-\alpha_q\theta^2_\mathbf{q}/2} (\alpha_q^{1/2}\theta_\mathbf{q})^{|M|} \times L^{|M|}_N(\alpha_q\theta^2_\mathbf{q}) \tag{A5$'$}$$

and the $L^M_N(z)$ are the generalized Laguerre polynomials. The $Y^M_N(\Psi(q))$ are normalized when integrated over $\int_0^\infty \theta d\theta \int_0^{2\pi} d\phi$ as is appropriate for small fluctuations such that $\sin\theta \sim \theta$. The eigenvalues of $\tilde{\Gamma}_{q,\Psi}$ are

$$W^M_{q,N} \equiv (\tau^{-1}_q)^M_N = 2\alpha_q D_\Psi(2N + |M|) \ . \tag{A6}$$

Also we have

$$\Gamma_{i\Psi}(\mathbf{q}) = y^0_0(\theta_\mathbf{q})\tilde{\Gamma}_{i\Psi(\mathbf{q})}[y^0_{q,0}(\theta_\mathbf{q})]^{-1} \tag{A7}$$

and

$$P_{\text{eq}}(\Psi(\mathbf{q})) = y^0_0(\theta_\mathbf{q})\, Y^0_0(\Psi(\mathbf{q}))/\sqrt{2\pi} = 2(\alpha_q/2\pi) e^{-\alpha_q\theta^2_\mathbf{q}} , \tag{A8}$$

which is a "one-sided Gaussian" in $\theta_\mathbf{q}$ with mean square fluctuation $\langle\theta_\mathbf{q}\rangle^2 = \alpha^{-1}_q$ that is consistent with the hydrodynamic model. When we employ bra–ket notation for the complete orthonormal set $Y^M_N(\Psi(\mathbf{q}))$, we may write for the conditional probability of the qth mode[6]

$$P_i(\Psi_0(\mathbf{q})|\Psi(\mathbf{q}),t) = \sum_{N,M} |\tilde{Y}^M_N(\Psi(\mathbf{q}))\rangle\, e^{-W^M_{qN}t} \langle\tilde{Y}^M_N(\Psi_0(\mathbf{q}))| \ , \tag{A9}$$

where

$$|\tilde{Y}^M_N(\Psi(\mathbf{q}))\rangle \equiv y^0_0(\theta_\mathbf{q})\,|Y^M_N(\Psi(\mathbf{q}))\rangle \ . \tag{A9$'$}$$

Now the complete $\mathbf{P}(\Psi(\mathbf{q}),t)$ is given as

$$\mathbf{P}(\Psi(\mathbf{q}),t) = \prod_i P_i(\Psi(\mathbf{q}),t) \ . \tag{A10}$$

It is, of course, possible to construct a formal Markovian expression for $\mathbf{P}(\Psi(\mathbf{r}),t)$, based upon the fact that we are able to treat the $\Psi(\mathbf{q})$ as independent Markovian variables and the $\Psi(\mathbf{r})$ are obtained as linear combinations of them by Fourier inversion. One may accomplish this most straightforwardly by writing

$$\partial\mathbf{P}(\Psi(\mathbf{q}),t)/\partial t = -\sum_i \Gamma_{i\Psi(\mathbf{q})}\mathbf{P}(\Psi(\mathbf{q}),t)$$

and then perform the linear transformations of $\sum_i \Gamma_{i\Psi(\mathbf{q})}$ to obtain $\Gamma_{\Psi(\mathbf{r})}$. Such procedures are described by Lax[35] and by Wang and Uhlenbeck[15] for multidimensional Fokker–Planck equations in nonperiodic variables. It is only necessary to apply such procedures to the angular variables $\Psi(\mathbf{r})$ and $\Psi(\mathbf{q})$. When this is done one may then write

$$\partial\mathbf{P}(\Psi(\mathbf{r}),t)/\partial t = -\Gamma_{\Psi(\mathbf{r})}\mathbf{P}(\Psi(\mathbf{r}),t) \ .$$

This transformation into the Hilbert space of $\mathbf{r}$ will, however, lead to more complicated forms because of the cross correlations[35] between the values of $\Psi(\mathbf{r}_1)$ and $\Psi(\mathbf{r}_2)$ at points $\mathbf{r}_1$ and $\mathbf{r}_2$. The main point is that $\mathbf{P}(\Psi(\mathbf{r}),t)$ and $\mathbf{P}(\Psi(\mathbf{q}),t)$ contain equivalent information about the Markovian process, so one is free to choose the simpler of the two.

Now one actually needs the more complete distribution function

$$\mathbf{P}(\Psi(\mathbf{q}),\mathbf{r}_B,t) = \mathbf{P}(\Psi(\mathbf{q}),t)P(\mathbf{r}_B,t) \ , \tag{A11}$$

where $\mathbf{r}_B$ is the location of the molecule at time t, and the equality is based on the assumption that the translational diffusion of the molecule is uncorrelated with the director fluctuations.

We assume that $P(\mathbf{r}_B,t)$ obeys a normal translational diffusion equation, so that[28]

$$\begin{aligned} P(\mathbf{r}_{B,0}|\mathbf{r}_B,t) &= \sum_\mathbf{q} e^{i\mathbf{q}\cdot(\mathbf{r}_B-\mathbf{r}_{B,0})}\, e^{-Dq^2t} \\ &= \sum_\mathbf{q} |\mathbf{r}_{B,0,\mathbf{q}}\rangle\, e^{-Dq^2t} \langle\mathbf{r}_{B,\mathbf{q}}| \end{aligned} \tag{A12}$$

with D the translational diffusion coefficient of the molecule, assumed isotropic for simplicity. The sum over $\mathbf{q}$ may also be replaced by an integration involving the volume V.

We now seek the correlation function

$$\begin{aligned} C(\Psi(\mathbf{r}_B,t)) &\equiv \langle\Psi^*(\mathbf{r}_{B,0},t=0)\Psi(\mathbf{r}_B,t)\rangle = \sum_{\substack{i,k,l\\N,M}} \langle P_{\text{eq}}(\Psi,\mathbf{r}_B)|\, e^{-i\mathbf{q}_i\cdot\mathbf{r}_B}\Psi(\mathbf{q}_i)\,|\mathbf{r}_{B,\mathbf{q}_k}\rangle\, e^{-Dq^2t} \prod_{q_j} [\,|Y^M_{q_j,N}(\Psi)\rangle\, e^{-W^M_{q_j,N}t} \langle Y^M_{q_j,N}(\Psi_0)|\,] \\ &\times \langle\mathbf{r}_{B,0,\mathbf{q}_k}|\, e^{+i\mathbf{q}_l\cdot\mathbf{r}_{B,0}}\Psi^*(\mathbf{q}_l)\,|\mathbf{P}_0(\Psi,\mathbf{r}_B)\rangle = \sum_{k,N,M} |\langle P_{\text{eq}}(\Psi(\mathbf{q}_k))|\,\Psi(\mathbf{q}_k)\,|Y^M_{q_k,N}(\Psi)\rangle|^2 \exp[-(W^M_{q_k,N} + Dq^2_k)t] \end{aligned} \tag{A13}$$

using the orthonormality of the $|\mathbf{r}_B, \mathbf{q}_k\rangle$, [i.e., one has $\int \exp[-i(\mathbf{q}_i - \mathbf{q}_j)\mathbf{r}_B]d^3r_B = \delta(\mathbf{q}_i - \mathbf{q}_j)$]. The matrix elements of $\Psi(\mathbf{q}_k)$ needed for Eq. (A13) are given by Eq. (B15) of Ref. 13 (but with λ_2^{-1} replaced by $\lambda_2^{-1/2}$) or equivalently by Eq. (A23) of PF. One may then obtain Eq. (3.20) as the final result. Note that only the $W^1_{q,0} = 2\alpha_q D_\Psi = Kq^2/\eta \equiv \tau_q^{-1}$ enter into the final result in agreement with the hydrodynamic model. Actually the effect of the translational diffusion term requires that $1/K^{3/2}$ in Eq. (3.19) be replaced by $1/[K(K+D)]^{1/2}$. This correction for finite D was first introduced by Pincus in an *ad hoc* fashion.[36] Our treatment here is a more formal demonstration of its validity.

APPENDIX B: LOW FREQUENCY SPECTRAL DENSITIES AND VALIDITY OF MOTIONAL NARROWING APPROACH

There are two general questions which exist with regard to a spin–relaxation theory involving director fluctuations. The first is exemplified by the divergence in the second term of the spectral density in Eq. (3.28) as $\omega \to 0$. It was suggested by PF that this divergence should be removed by a proper consideration of the coupling between Ψ and Ω. This has not been borne out by the present analysis. Also, it has been suggested that the τ_q's associated with director fluctuations are too long to permit the latter to "motionally average" the large spin Hamiltonian terms in ESR, although they should be adequate for NMR.[30] Thus, the second question pertains to the validity of the motional narrowing approach. We consider these two questions.

One way to remove the divergence as $\omega \to 0$ is to recognize that the correct value of τ_q^{-1} (in the single force-constant approximation) is $(K/\eta)[q^2 + \xi_H^{-2}]$, where $\xi_H^2 = K/\chi H^2$, with ξ_H the coherence length due to the presence of the magnetic field H, and χ is the anisotropic part of the molecular diamagnetic susceptibility. Also, the mean square values of Eq. (3.17) become $kT/K[q^2 + \xi_H^{-2}]V$. When these changes are substituted into the calculation of $C^{(2)}_{0,\pm1}(t)$ or $J^{(2)}_{KM}(\omega)$, one obtains (for $\omega_c \to \infty$)

$$C^{(2)}_{0,\pm1}(t) = 3S^2 \frac{1}{4\pi^{3/2}} \frac{k_B T\eta}{K^{3/2}} e^{-a^2 t}[t^{-1/2} - \sqrt{\pi} a e^{a^2 t} \operatorname{erfc}(at^{1/2})] \tag{B1}$$

with $a^2 = K/\eta\xi_H^2$, and

$$J^{(2)}_{0,\pm1}(\omega) = 3S^2 \frac{1}{4\sqrt{2}\pi} \frac{k_B T\eta\xi_H}{K^2} \left(\frac{1}{1+\sqrt{1+(\omega/a^2)^2}}\right)^{1/2}, \tag{B2}$$

where we have neglected the translational diffusion term. When that term is included, in the manner discussed in Appendix A, one gets

$$C^{(2)}_{0,\pm1}(t) = 3S^2 \frac{1}{4\pi^{3/2}} \frac{kT}{K} \times \left[\sqrt{\frac{\eta}{tK'}} e^{-a^2 t} - \frac{\sqrt{\pi}}{\xi_H} e^{+D/\xi_H^2} \operatorname{erfc}(a' t^{1/2})\right] \tag{B3}$$

and

$$J^{(2)}_{0,\pm1}(\omega) = 3S^2 \frac{1}{4\pi} \frac{kT\xi_H}{K'} \left[\frac{D[1-\sqrt{x^2+(\omega/a'^2)^2}] + (\omega\xi_H^2/\sqrt{2})\sqrt{\sqrt{x^2+(\omega/a'^2)^2} - x}}{\omega^2\xi_H^4 + D^2}\right], \tag{B4}$$

with $a'^2 = K'/\eta\xi_H^2$, $K' = K + \eta D$, $x = K/K'$. Thus, for example, Eq. (B2), in the limit $\omega/a^2 \to 0$, is given by

$$J^{(2)}_{0,\pm1}(\omega) = \frac{1}{4\sqrt{2}\pi} 3S^2 \frac{k_B T\eta\xi_H}{K^2}[1 - \tfrac{1}{8}(\omega/a^2)^2] \tag{B5}$$

and it shows no divergence for finite ξ_H. The important frequency here is $\omega_{\xi_H} \equiv a^2 \sim 20\ \mathrm{sec}^{-1}$ corresponding to $\xi_H \sim 2\times10^{-4}$ cm (where we have taken $K \sim 4\times10^{-7}$ dyn, $\eta \sim 0.5$ P (e.g., MBBA), $\chi \sim 10^{-7}$ cgs units, $H \sim 10^4$ G). This frequency is quite small, so even though there is no divergence at $\omega = 0$, it follows that for $\omega > \omega_{\xi_H}$ the high frequency limiting form, such as the second term in Eq. (3.28), applies. We should now ask whether motional narrowing theory applies for such small relaxation frequencies as $\tau_q^{-1} \sim \omega_{\xi_H}$. We thus turn our attention to the question of the validity of the motional-narrowing approach in these problems.

The simplest statement of a sufficiency condition for motional narrowing that is applicable to the present problem is one given by Redfield.[37] He defines a characteristic frequency ω^* of the bath (which in our problem is some measure of the range and weighting of the τ_q^{-1}) by the requirement that the associated spectral densities obey

$$J^{(2)}_{KM}(\omega) \cong J^{(2)}_{KM}(\omega') \text{ if } |\omega - \omega'| < \omega^* . \tag{B6}$$

Then motional narrowing theory is valid if

$$\mathrm{Re}(R), \mathrm{Im}(R) \ll \omega^* < kT/\hbar \tag{B7}$$

where the R are the relaxation matrix elements; typically Re(R) are the T_1^{-1} and T_2^{-1} terms associated in the present case with $J^{(2)}_{KM}(\omega)$. [The Im(R) give the dynamic frequency shifts[38] and they are also important in determining the validity of motional narrowing, as discussed below.[39]] In order that the definition of ω^* given by Eq. (B6) apply to expressions like Eq. (B2) we have $\omega^* \sim \omega_{\xi_H} \sim 20\ \mathrm{sec}^{-1}$. Typically the T_1^{-1} and T_2^{-1} terms from director fluctuations are much greater than ω_{ξ_H}, especially for ESR, so this sufficiency condition is *not* satisfied.

Actually, we can attempt to be more detailed in developing the conditions for motional narrowing theory for the present case of independent q modes. The nature of our development in this paper and Appendix A suggests that we apply conditions like Eqs. (B6) and (B7) to the contributions from each q mode. If we let $T_{1,q}^{-1} \sim T_{2,q}^{-1} \sim |\mathcal{H}^2_{1,q}|\tau_q$, where $\mathcal{H}_{1,q}$ is the component of $\mathcal{H}_1(\Psi)$ which is modulated by the qth mode of director fluctuations, then we would require $|\mathcal{H}^2_{1,q}|\tau_q^2 \ll 1$ in order that the qth mode satisfy a motional narrowing criterion.[39] In particular, we have from Eq. (3.28)

$$|\mathcal{H}^2_{1,q}| \sim 3S^2(kT/Kq^2V)\omega_s^2 , \tag{B8}$$

where ω_s is the magnitude of a typical term in the spin Hamiltonian, $\tau_q = \eta/Kq^2$, and we are neglecting ξ_H for the moment. Thus we have that as $q \to 0$, $|\mathcal{H}_{1,q}^2| \tau_q^2 \to \infty$ for finite V. Clearly, the low q modes are ineffective in causing relaxation (for finite V). Let us define the reference frequency $\tau_{\bar{q}}^{-1}$ such that $|\mathcal{H}_{1,q}^2| \tau_{\bar{q}}^2 = 1$. This yields from Eq. (B8)

$$\tau_{\bar{q}}^{-3} \equiv (Kq^2/\eta)^3 = (3S^2kT/V\eta)\omega_s^2 \sim 8 \times 10^{-14}\, \omega_s^2$$

(using $V \sim 1$ cm^3, $\frac{3}{2}S^2 \sim \frac{1}{2}$, $T \sim 300$ °K, $\eta \sim 0.5$ P). In ESR, $\omega_s \sim 10^8$–10^9 sec^{-1}, so $\tau_{\bar{q}}^{-1} \sim 10$–$44$ sec^{-1}, and for NMR $\omega_s \lesssim 10^5$ sec^{-1} corresponding to $\tau_{\bar{q}}^{-1} < 0.1$ sec^{-1}. When the effects of ξ_H from the finite magnetic field are introduced, this causes the effective lower limit of $\tau_{\bar{q}}^{-1}$ (as $q \to 0$) to be ω_{ξ_H}, since $\tau_q^{-1} = (K/\eta)(q^2 + \xi_H^{-2})$ and q^2 in Eq. (B7) is replaced by $q^2 + \xi_H^{-2}$. Thus, for NMR, motional narrowing theory is applicable, based on this type of an argument. For ESR, $\tau_{\bar{q}}^{-1}$ is at least of the same order of magnitude as ω_{ξ_H} (for the finite volumes used). [The inclusion of a finite diffusion coefficient D improves matters by decreasing the value of $\bar{q}$, although $\tau_{\bar{q}}^{-1}$ is increased somewhat.[40]] However, for nonsecular (and pseudosecular) perturbations, i.e., $\omega \neq 0$, one has contributions to $T_{1,q}^{-1} \sim T_{2,q}^{-1} \sim |\mathcal{H}_{1,q}|^2 \tau_q/(1 + \tau_q^2\omega^2)$, and we require this quantity to be much smaller than τ_q^{-1} for motional narrowing theory to apply. In ESR $\omega_{\text{psec}} \sim 10^8$–$10^9$ sec^{-1} or much greater than τ_q^{-1} as $\tau_q \to \infty$ [Note from Eqs. (3.28) and (6.5)–(6.8) that it is the pseudosecular terms which are the important ESR ones that result from director fluctuations]. For these slow q modes, we can let $\tau_q/(1 + \tau_q^2\omega_{\text{psec}}^2) \to 1/\tau_q\omega_{\text{psec}}^2$. However, in this limit, the stricter criterion for motional narrowing is determined by the dynamic frequency shift terms [i.e., the ImR terms in Eq. (B7)].[37,38] Then we require

$$|\mathcal{H}_{1,q}|^2 [\omega\tau_q^2/(1 + \omega^2\tau_q^2)]\, \tau_q \approx |\mathcal{H}_{1,q}|^2\, \tau_q/\omega \ll 1. \qquad \text{(B9)}$$

If we again define a $\tau_{\bar{q}}$ such that this inequality becomes an equality, then we get (for the same values as above) $\tau_{\bar{q}}^{-2} = 8 \times 10^{-4}\, \omega_s^2/\omega_{\text{psec}}$. Then since $\omega_{\text{psec}} \sim \omega_s \sim 10^8$–$10^9$ sec^{-1}, one obtains $\tau_{\bar{q}} \sim 310$–80 sec, so that motional-narrowing theory should apply for all τ_q^{-1} down to ω_{ξ_H} for the pseudosecular terms in ESR.

In the case of quasicritical fluctuations near the nematic–isotropic phase transition, one may use the above arguments, but with $\omega_\xi \sim 2 \times 10^6$ sec^{-1} (cf. Sec. IV) replacing ω_{ξ_H}, to show that motional-narrowing theory is applicable for the independent q modes.

The treatment we have just given is a reasonable one in terms of the complete statistical independence of the q modes. It does, however, lead to criteria which do depend on sample volume, although such terms are commonly neglected in discussing properties in the bulk. A more rigorous analysis of this problem is to utilize a more complete slow-motional theory to correct for any breakdown in the application of motional-narrowing theory. This task can be accomplished in any of several ways,[9,10,38,41–43] but for present purposes the most useful would be the partial time ordered cumulant (PTOC) method employed by Freed[38,41,42] based on Kubo's[44] generalized cumulant expansion theorems. One can systematically introduce higher-order terms in the calculation of the T_1^{-1}, T_2^{-1}, and more generally the line-shape and relaxation contributions which arise from the slowly fluctuating components. The formalism developed in Appendix A becomes essential in order to generate the higher-order correlations. Such an analysis is, however, beyond the scope of the present work, so we content ourselves with some general observations.

The leading term, which is second order in $\mathcal{H}_{1q}$ is just the motional-narrowing result. The nature of the matrix elements of the $\Psi(\mathbf{q}_k)$ that appear in Eq. (A16) (cf. Ref. 13) lead to a vanishing of terms third order in $\mathcal{H}_{1q}$. The fourth order terms are of the order of $|\mathcal{H}_{1,q}^2|^2(\tau_q^{-1} - i\omega)^{-3}$ (where ω in each term in the product may, in general, be different), which will be small when the narrowing condition Eq. (B9) or (B8′) is fulfilled.[45] When integrated over the q modes, this contribution will have a V^{-1} dependence as is consistent with the motional narrowing-conditions obtained above. However, a new feature arises in fourth order. It is, in principle, possible to have cross-terms involving the qth mode and the q'th mode each taken to second order. There are here some formal analogies to the classic problem of spin relaxation by the two-phonon Raman process in solids.[46] An important difference is the pure dissipative character of the fluctuating director modes. When, as in the Raman process, one performs a double integral over $\mathbf{q}$ and $\mathbf{q}'$ to get such cross terms, then the final result is indeed independent of V. Thus the question arises as to the importance of such Raman-like processes in spin relaxation by the (dissipative) cooperative modes of director fluctuations. When we use the Markovian theory of Appendix A along with the PTOC method, one immediately finds that such cross-terms make zero contribution to the zero frequency spectral densities arising from secular perturbations, because then one is dealing with the simple cumulants of the stochastic process, and these cumulants vanish when they contain any cross-terms involving uncorrelated variables. For perturbations which do not commute with $\mathcal{H}_0$, this is no longer necessarily true, and detailed calculations appear to be required. (One might also find at this level, that it is important to include effects of a breakdown of the simplifying assumption of the statistical independence of the different q modes).

APPENDIX C: FREE ENERGY FLUCTUATIONS AT THE NEMATIC-ISOTROPIC PHASE TRANSITION

The basis of our analysis of the correlation function is the expression Eq. (14) of Stinson *et al.*[19] for the orientational free energy, which is

$$\begin{aligned}\overline{\Delta F} = \frac{V}{2} A \sum_{\mathbf{q}} \Big| &|Q^{(0)}(\mathbf{q})|^2 (1 + \xi_1^2 q^2 + \tfrac{2}{3}\xi_2^2 q^2) \\ &+ (|Q^{(1)}(\mathbf{q})|^2 + |Q^{(-1)}(\mathbf{q})|^2)(1 + \xi_1^2 q^2 + \tfrac{1}{2}\xi_2^2 q^2) \\ &+ (|Q^{(2)}(\mathbf{q})|^2 + |Q^{(-2)}(\mathbf{q})|^2)(1 + \xi_1^2 q^2)\Big| \qquad \text{(C1)}\end{aligned}$$

where

$$Q^{(0)} = \sqrt{3/2}\, Q_{zz}\,,$$

$$Q^{(\pm 1)} = \mp Q_{zx} - iQ_{zy}\,,$$

$$Q^{(\pm 2)} = \tfrac{1}{2}(Q_{xx} - Q_{yy} \pm 2iQ_{xy})\,.$$

If, for simplicity, we ignore ξ_2 and let $\xi_1 = \xi$ then we get the simple equipartition values:

$$\langle |Q^{(M)}(\mathbf{q})|\rangle^2 = \tfrac{3}{2}\langle |Q(\mathbf{q})|\rangle^2 = AV/kT(1+\xi^2 q^2) . \qquad \text{(C2)}$$

One can, of course, use the more accurate expressions but this does not seem warranted to the extent that we follow the usual approach of employing a single

$$\tau_q^{-1} = L(\xi^{-2} + q^2)/\nu .$$

(This includes neglect of coupling to shear flow).[2] That is we have

$$\dot{Q}^{(i)}(\mathbf{q}) = -\tau_q^{-1} Q^{(i)}(\mathbf{q}) . \qquad \text{(C3)}$$

We further have from Eqs. (C1) and (C2) that

$$\langle (Q^{(M')*}(\mathbf{q}))_0 (Q^{(M)}(\mathbf{q}))_t \rangle = \langle |Q^{(M)}(\mathbf{q})|\rangle^2 e^{-t/\tau_q} \delta_{M,M'} , \qquad \text{(C4)}$$

i.e., the fluctuations of the different tensor components of the ordering are uncorrelated. It is also in the spirit of neglecting the term in L_2, that we can use the form

$$\overline{\Delta F} = \tfrac{1}{2} V\tilde{A} \sum_{\mathbf{q}} Q(\mathbf{q})^2 (1+\xi^2 q^2) \text{ with } \tilde{A} = \tfrac{3}{2} A .$$

Following Landau[20] one has $\tilde{A} = a(T - T^*)$, and also

$$\xi^2 \equiv L/\tilde{A} = L/a(T - T^*) ,$$

where ξ is the coherence length of the order fluctuations. Below the phase transition we again let[19,21]

$$\Delta F = \tfrac{1}{2} AQ_{\alpha\beta}Q_{\alpha\beta} - \tfrac{1}{3} BQ_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha} + \tfrac{1}{4} CQ_{\alpha\beta}Q_{\alpha\beta}Q_{\gamma\delta}Q_{\gamma\delta} - \tfrac{1}{2}\chi_\alpha H_\alpha Q_{\alpha\beta} H_\beta \qquad \text{(C5)}$$

where ΔF is the difference in free-energy density between nematic and isotropic states, and the summation convention is implied. Then we substitute in Eq. (4.6a) to obtain

$$\Delta F = \tfrac{1}{2}\tilde{A}Q^2 - \tfrac{1}{3}\tilde{B}Q^3 + \tfrac{1}{4}\tilde{C}Q^4$$
$$(\tilde{A} = \tfrac{3}{2}A, \quad \tilde{B} = \tfrac{3}{4}B, \quad \tilde{C} = \tfrac{9}{4}C) \qquad \text{(C6)}$$

(neglecting the magnetic field term). When ΔF is minimized with respect to Q (i.e., $\tilde{A}Q - \tilde{B}Q^2 + \tilde{C}Q^3 = 0$) one obtains the nematic value of

$$Q_N = \tilde{B}/2\tilde{C}\,[1 + (1 - 4\tilde{A}\tilde{C}/\tilde{B}^2)^{1/2}] . \qquad \text{(C7)}$$

The phase transition occurs at T_c where $\Delta F = 0$ corresponding to $\tilde{A} = 2\tilde{B}^2/9\tilde{C}$, and thus $Q_N = 2\tilde{B}/3\tilde{C}$ at the transition. Thus in the nematic phase we replace Q by $Q_N + \Delta Q$ and keep only lowest order terms in ΔQ.[23] This gives

$$\Delta F_N \approx \tfrac{1}{2}\bar{A}\Delta Q^2 \qquad \text{(C8)}$$

where ΔF_N is the free energy density deviation from the equilibrium value for the nematic phase and $\bar{A} \equiv \tilde{A} - 2\tilde{B}Q_N + 3\tilde{C}Q_N^2$. We now add the lowest order terms for the inhomogeneous part of the free energy density[19,21]:

$$\tfrac{1}{2}L_1[\nabla_\alpha(\Delta Q)_{\beta\gamma}][\nabla_\alpha(\Delta Q_{\beta\gamma})] + \tfrac{1}{2}L_2[\nabla_\alpha(\Delta Q_{\alpha\gamma})][\nabla_\beta(\Delta Q_{\beta\gamma})] . \qquad \text{(C9)}$$

To the same level of accuracy as our simple approach to the isotropic phase (i.e., neglect of L_2), one obtains for the Fourier transform $\Delta Q_{\mathbf{q}}$ of ΔQ the free energy expression[23]:

$$\overline{\Delta F_N} = \tfrac{1}{2} V \sum_q (\bar{A} + L_N q^2)\,|\Delta Q(\mathbf{q})|^2 \qquad \text{(C10)}$$

Then

$$\tfrac{3}{2}\langle |\Delta Q^{(M)}(\mathbf{q})|^2\rangle = \langle |\Delta Q(\mathbf{q})|^2\rangle = \bar{A}V/kT(1+\xi^2 q^2) . \qquad \text{(C11)}$$

Then, by analogy to the arguments for τ_q in the isotropic phase, we would obtain here

$$\tau_q^{-1} = L_N(\bar{\xi}^{-2} + q^2)/\nu_N \qquad \text{(C12)}$$

with $\bar{\xi}^2 \equiv L_N/\bar{A}$. We have allowed for the first-order transition by introducing an L_N and ν_N which need not be equal to L or ν at T_c. Also, our use of Eqs. (C5), (C6), and (C9) for the nematic is probably not quantitatively sound: Q_N is typically large, ≈ 0.4, so that higher order terms in Q are probably needed for a quantitative agreement.[24] In the limit of small A (i.e., near T^*), one may expand the expression for Q_N to lowest order in A to obtain $\bar{A} \approx 3a(T^+ - T)$, where $T^+ = T_c + \tfrac{1}{2}(T_c - T^*)$, so that $\xi_N \propto (T^+ - T)^{-1/2}$. Actually it is possible to show that even over a reasonable temperature range one still has $\xi_N \propto (T^+ - T)^{-1/2}$. In particular, for the range $-4\,^\circ\mathrm{K} \le (T - T^*) \le 0.7\,^\circ\mathrm{K}$, it was found that $\bar{A}$ is well represented by $\bar{A} = 2.7a(T^+ - T)$ with $T^+ = T_c + 0.6(T_c - T^*)$ when $T_c - T^* \sim 1°$.[23]

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[24] One may adopt a mean field point of view here such that $y(\Omega) \propto S$. This, then, would lend itself to an analysis like that of Maier–Saupe to obtain an expression for the instantaneous value of the free-energy. One could then use this form (plus inhomogeneous terms) to study fluctuations instead of incorporating the Landau–de Gennes results as we have done here.

[25] The effect of the cutoff is important only for ω such that $\omega/\omega_c \gtrsim 1$ (cf. Sec. III). However we have $\omega/\omega_c \ll 1$ (see below). Thus when cutoff effects are important we can let $(\omega_\xi^{1/2}\{1 + [1 + (\omega/\omega_\xi)^2]^{1/2}\}^{1/2})^{-1} \rightarrow \omega^{-1/2}$ in Eq. (4.12b). This form is now equivalent to the frequency dependence in Eq. (3.28) and it would be appropriate to let $\omega^{-1/2}$ become $u(\omega/\omega_c)\omega^{-1/2}$ in Eq. (4.12b) in this limit. In the example given below $u(\omega/\omega_c) \sim 0.77$.

[26] Actually the results of PF show a correction term linear in S, but it is small compared to the higher power terms. It undoubtedly arises from the linear combinations of numerical least squares fits to a cubic in S that were used, and they cannot be expected to be exact.

[27] Cf. Eqs. (A14)–(A28) of PF. In Eq. (A23) of PF the factor 3/2 should be $\sqrt{3/2}$. The same correction is required in Eq. (A24); the factors 9/4 in Eq. (A25) and (A27) become 3/2; and 9/8 in Eq. (A28) becomes 3/4.

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[34] Cf. Footnote 61 of Ref. 6. The numerical error referred to in Footnote 27 of this work is one source of the small difference between Eqs. (A3) and the expressions given by that footnote. The other source of the difference is that Eq. (A9) of Ref. 6 does not have the factor of 2, which correctly appears in Eq. (3.17) of this work.

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[39] It is important to note that we are applying this Redfield condition as though the fluctuating director contribution to spin relaxation were additive to the contribution from the overall reorientational model (i.e., statistical independence of these motions) even though such an assumption was not invoked in the main body of this paper. Actually, this is reasonable from a result like Eq. (3.26). Furthermore, it appears from more complete analyses referred to below (in particular the stochastic Liouville approach) that this should be legitimate when a motional narrowing condition applies to the overall reorientation, and the slow director fluctuations yield a small perturbation in the sense of Eqs. (2.10).

[40] Another point one may make regards the validity of using a strongly damped model like Eq. (A4) for the director fluctuations. It requires $\frac{1}{2}q^2 < kT/KV \sim 10^{-7}$ cm^{-2} $<<< \xi_H^{-2} \sim 1/4 \times 10^8$ cm^{-2}. Thus, once α_q is redefined as $KV(q^2 + \xi_H^{-2})/2kT$ throughout Appendix A, there is no problem with this model in finite magnetic fields.

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[45] These fourth order terms are then of order $|(kT/q^2KV)\omega_s^2|^2 \times (\tau_q^{-1} - i\omega)^{-3}$. There are other terms which appear as fourth order in director fluctuations but second order in ω_s. They arise from second-order corrections involving θ^2 in the matrix elements of $\Psi(q)$ needed in Eq. (A13) and given by PF. They are of order $(kT/q^2KV)^2\omega_s^2(\tau_q^{-1} - i\omega)^{-1}$.

[46] Reference 28, Chap. IX.

[47] Added in proof: Our theory has now been applied to an analysis of NMR experiments by C. G. Wade, Ann. Rev. Phys. Chem. (in press). We thank Professor Wade for his helpful communication.