Theoretical spin relaxation by diffusion on curved surfaces

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A comprehensive theoretical analysis is presented which accounts for nuclear spin relaxation due to molecular surface diffusion on spheroidal aggregates undergoing restricted rotational diffusion in a uniaxial potential of mean torque. The model is formulated primarily with surfactant systems in mind, and should provide a realistic description of spin relaxation in nematic and smectic liquid crystals as well as in isotropic micellar solutions. Two efficient numerical schemes are developed to compute the joint time correlation functions and spectral density functions. In addition, a variety of useful analytical results are derived for special cases. Numerical calculations suggest that nuclear spin relaxation may be a unique method for monitoring small deviations from spherical aggregate shape.

I. INTRODUCTION

The technique of nuclear spin relaxation is finding increasing use in the study of molecular organization and dynamics in complex fluids. In particular, it is now firmly established as one of the principal experimental tools for investigating surfactant systems, be it isotropic micellar solutions, microemulsions, or liquid-crystalline mesophases of the smectic, nematic, or cubic types.

Experimental sophistication has now reached a stage where accurate measurements of individual spectral densities and extensive frequency dispersions are routinely feasible. In contrast, the theoretical modeling of time correlation functions and spectral density functions is often comparatively crude and not always based on sufficiently realistic structural-dynamic models. The present work attempts to remedy this situation for systems where molecular diffusion on curved surfaces is an important cause of spin relaxation. This widely occurring mechanism for modulating the anisotropic spin-lattice coupling is sometimes referred to as translationally induced rotation.\(^{1,2}\)

In surfactant systems, curved oil-water interfaces are ubiquitous and frequently define the boundary of closed nonspherical aggregates. We model such aggregates as prolate or oblate spheroids (ellipsoids of revolution). Encompassing a wide range of shapes—from spherical to long needle-like or extended disk-like aggregates—the spheroid model captures the essential structural features of many surfactant systems.

While the emphasis in this work is on surface diffusion, our treatment also incorporates the orientational degrees of freedom of the spheroidal aggregates. We thus consider a system where the aggregates exhibit long-range orientational order and undergo restricted reorientational motion subject to a uniaxial potential of mean torque. The isotropic solution of freely rotating aggregates emerges as a special case: the limit of vanishing mean torque. Our treatment thus has considerable generality and should be applicable to most types of surfactant systems where the aggregates can be modeled as spheroids. Within the theoretical framework developed here, spin-relaxation data can, in principle, be used to determine aggregate size, shape, and orientational order, as well as the surface diffusion coefficient of the spin-bearing species and the rotational diffusion coefficients of the aggregate.

In general, the spin-lattice coupling is also modulated by local (internal) motions. Since these are usually much faster than the motions treated explicitly here, they act merely to establish a residual spin-lattice coupling to be modulated by the slower motions and to give an independent additive contribution to the spin-relaxation rates. In view of the complexity of the local dynamics,\(^{3,4}\) this contribution usually cannot be realistically described by simple diffusional models and will not be considered here.

The assumption that the observed nucleus is confined to a surface of simple geometry is always an approximation. For nuclei residing in or near the headgroup of typical surfactant molecules, this should be an excellent approximation. (Headgroup diffusion normal to the surface is expected to be either fast and of small amplitude, in which case it merely contributes to the local motions referred to above, or of larger amplitude but too infrequent to contribute significantly to spin relaxation.) For small mobile species, such as counterions, it is not so obvious that the surface-diffusion approximation can be justified. In fact, one would then expect contributions from "radial" motion (normal to the surface) as well as from lateral motion. Moreover, these contributions are not independent, as the diffusion equation separates into independent radial and lateral parts only in the trivial case of planar geometry. However, unless the system is dilute and the aggregates are very extended (as in semidilute polyelectrolyte solutions\(^{5,6}\)), radial diffusion does not give a significant direct contribution to the spin-relaxation rates, but acts mainly to renormalize the spin-lattice coupling (already reduced by local motions).

The outline of this paper is as follows. In Sec. II we establish our notation and obtain some basic (essentially model-independent) results for the joint time correlation functions, making extensive use of symmetry. Known results for the reorientational correlation functions are given in compact form in Sec. III. The mathematical analysis of the surface-diffusion problem, contained in Secs. IV and V,
forms the central part of this work. Two different numerical schemes—the eigenfunction method and the direct method—are developed and compared. In addition, we obtain analytical results in a number of special cases. In Sec. VI we discuss the convergence properties of our numerical methods and investigate certain single-exponential approximations to the correlation functions. Finally, in Sec. VII, we illustrate the application of the theory by two specific examples relating to lyotropic nematics and to isotropic micellar solutions.

II. THEORETICAL FOUNDATIONS

When analyzing spin-relaxation problems, it is often helpful to proceed in two stages. In the first stage (Sec. II), the theoretical analysis is taken as far as possible without invoking detailed models, i.e., without specifying the form of the time-dependent distribution functions for the relevant molecular degrees of freedom. By exploiting the known or assumed general properties of the system, such as time-scale separation or statistical independence of different degrees of freedom and various symmetry properties, the problem can often be greatly simplified. A complete model for the relevant molecular degrees of freedom is then specified in the second stage of the analysis (Sec. III–V), thus permitting explicit calculation of static ensemble averages (mean-square fluctuations and order parameters) and of reduced time correlation functions (or correlation times).

A. Statement of the problem

We consider a system of nuclear spins whose interaction with the molecular environment is described by a second-rank irreducible tensor \( V \), e.g., an electric-quadrupole-field-gradient coupling or an intramolecular magnetic-dipole–dipole coupling. In the motional-narrowing regime, where the spin system evolves according to Redfield's equation of motion, the response of the spin system to external magnetic perturbations (as in a spin-relaxation experiment) is governed by the three lab-frame spectral density functions \( J_k(\omega), k = 0, 1, 2 \), which constitute the real part of the frame, of the spin-lattice coupling tensor \( V \): of the \( k \)th spherical component \( V^k \), in a laboratory-fixed frame, of the correlation functions, \( \gamma_k(t) \), of the fluctuating part, \( \gamma^k(t) \), governed by the three lab-frame spectral density functions \( J_k(\omega), k = 0, 1, 2 \), which constitute the real part of the Fourier–Laplace transform of the corresponding time auto-correlation functions, \( g^k(t) \), of the fluctuating part, \( \gamma(t) \), of the \( k \)th spherical component \( V^k \), in a laboratory-fixed frame. of the spin-lattice coupling tensor \( V \):

\[
j_k(\omega) = \text{Re} \int_0^\infty dt \exp(i\omega t) g^k(t),
\]

\[
g^k(t) = \langle \gamma^k(t) \rangle = \langle \gamma(t) \rangle - \langle \gamma^0(t) \rangle,
\]

\[
\langle \gamma^k(t) \rangle = \langle \gamma(t) \rangle - \langle \gamma^0(t) \rangle.
\]

The imaginary counterpart of (2.1) determines the second-order dynamic shift, \( \gamma_k(\omega) \), which, although of potential value, is rarely measured.

In the organized fluid systems that we have in mind, a variety of molecular motions may cause the spin-lattice coupling to fluctuate in time. Typically, there are fast fluctuations of relatively small spatial amplitude, due to highly localized motions, superimposed on slower fluctuations of larger amplitude, due to modulation of the magnitude and orientation of the locally averaged coupling tensor. If these two classes of motion occur on different time scales, the correlation functions can be decomposed into two independent parts associated with fast and slow motions. (The time-scale separation ensures that the cross-correlation functions vanish.) In this work we focus on the part of the correlation functions that is due to slow motions. Accordingly, all coupling tensor components should be interpreted as locally averaged quantities.

We consider a fluid system (isotropic solution or liquid crystal) containing "aggregates" (this term will be used throughout as a generic label for surfactant micelles, micromulsion droplets, macromolecules, etc.), which, for simplicity, are assumed to be monodisperse in size and shape. The aggregate shape is taken to be uniaxial; more specifically, prolate or oblate spheroidal. The slow fluctuation of the locally averaged spin-lattice coupling is considered to be the result of (i) translatonal motion of the spin-bearing species laterally along the spheroidal aggregate surface, and (ii) reorientation of the entire aggregate with respect to the lab frame. These two processes may occur on the same time scale. However, if the aggregate is much larger than the spin-bearing molecule, the two processes will be essentially statistically independent. We assume that this is the case.

Our analysis refers to a system where the aggregates exhibit long-range orientational order and, hence, undergo restricted reorientational motion. The spheroidal aggregates are taken to be nonpolar, hence the phase must also be uniaxial and nonpolar; slightly less restrictively, we require that the potential of mean torque experienced by an aggregate possess at least \( D_{4h} \) symmetry. The isotropic solution of freely reorienting aggregates emerges as a special case: the limit of vanishing mean torque. Finally, the locally averaged spin-lattice coupling tensor is assumed (i) to possess at least threefold rotational symmetry \( C_3 \) with its symmetry axis everywhere perpendicular to the aggregate surface, and (ii) to be spatially uniform over the spheroidal surface, i.e., only its orientation is modulated by molecular surface diffusion.

B. Decomposition of correlation functions

In order to identify contributions from different motional degrees of freedom, we introduce four coordinate systems denoted \( L, D, A, \) and \( M \), defined in Table I and illustrated in Fig. 1. The lab-frame components \( \gamma^k(t) \) of the coupling tensor are then transformed to the molecular frame, via the director and aggregate frames,

\[
\gamma^k(t) = \langle \gamma(t) \rangle - \langle \gamma^0(t) \rangle = \sum_{n} \sum_{m} D_{nm}^2 \{ \Omega_{LM}(t) \} D_{nm}^2 \{ \Omega_{DA}(t) \}.
\]

where \( D_{ab}^2 \{ \Omega_{LM}(t) \} = \delta_{ab} \delta_{mn} S \).

In (2.4) and elsewhere the range of the summation indices is from \( -2 \) to \( +2 \), unless otherwise specified. Since the major molecular-frame residual coupling tensor component \( V^2 \) in (2.4) merely acts as a scale factor, we shall set it equal to unity. The properly scaled correlation functions and
spectral density functions are then obtained simply by multiplying our results by \((V_0^M)^2\). The quantity \(S\) in (2.4) is a second-rank orientational order parameter which, on account of the assumed symmetry (see above), can be factorized as

\[ S = S_{DA} S_{AM}. \]  

(2.5)

\(S_{DA}\) describes the orientational order of the aggregates with respect to the director, while \(S_{AM}\) is a measure of the orientational averaging brought about by molecular diffusion over the spheroidal surface.

When (2.4) is inserted into (2.2), we obtain a four-dimensional sum involving correlation functions of the type

\[ \langle D_{nm}^{2*} (\Omega_{DA}) D_{nm'}^{2*} (\Omega_{DA}) D_{nm}^{2*} (\Omega_{AM}) D_{nm'}^{2*} (\Omega_{AM}) \rangle, \]  

(2.6)

where the zero superscript signifies initial time. This can be simplified in two respects. First, the statistical independence of aggregate reorientation and molecular surface diffusion allows us to factorize (2.6). Secondly, the fivefold rotational symmetry around the director and aggregate axes imply, according to a powerful (but apparently not widely known) symmetry theorem,\(^9\) that the individual correlation functions vanish unless \(n = n'\) and \(m = m'\). Hence, (2.6) may be replaced by

\[ \delta_{nm} \delta_{nm'} \langle D_{nm}^{2*} (\Omega_{DA}) D_{nm}^{2*} (\Omega_{DA}) \rangle \times \langle D_{nm'}^{2*} (\Omega_{AM}) D_{nm'}^{2*} (\Omega_{AM}) \rangle. \]  

(2.7)

The lab-frame correlation functions in (2.2) can now be expressed as

\[ g_n^{LM} (\theta_{LD}) = \sum_n \left[ (d^2 - \delta_n \theta_{LD}) \right] \gamma_n^{LM} (t), \]  

(2.8)

explicitly displaying the dependence on the angle \(\theta_{LD}\) between the magnetic field and the director. The director-frame correlation functions, with \(n = 0, \pm 1, \pm 2\), are given by

\[ g_n^{LM} (t) = \sum_n \left\{ \langle D_{nm}^{2*} (\Omega_{DA}) D_{nm}^{2*} (\Omega_{DA}) \rangle \langle D_{nm'}^{2*} (\Omega_{AM}) D_{nm'}^{2*} (\Omega_{AM}) \rangle \right\}, \]  

(2.9)

and it follows that (2.8) may be expressed as

\[ g_n^{LM} (t) = g_n^{LM} (-t) = g_n^{LM} (t), \]  

(2.10)

Using a contraction formula for products of Wigner functions\(^1\) and expressing the resulting Clebsch–Gordan coefficients in algebraic form, we find that the orientational functions in (2.11) may be expressed as

\[ F_{kn} (\theta_{LD}) = \frac{1}{2} + \alpha_k \alpha_n P_2 (\cos \theta_{LD}) + \beta_k \beta_n P_4 (\cos \theta_{LD}), \]  

(2.12)

in terms of the coefficients

\[ \alpha_k = \frac{1}{\sqrt{14}} (k^2 - 2), \]  

(2.13a)

\[ \beta_k = \frac{1}{12 \sqrt{70}} (35k^4 - 155k^2 + 72), \]  

(2.13b)
and the Legendre polynomials
\[ P_2(\cos \theta_{LD}) = \frac{1}{2}(3 \cos^2 \theta_{LD} - 1), \]  
\[ P_4(\cos \theta_{LD}) = \frac{1}{8}(35 \cos^4 \theta_{LD} - 30 \cos^2 \theta_{LD} + 3). \]  
(2.14a, 2.14b)

It is evident from (2.12) that \( F_{kn}(\theta_{LD}) = F_{nk}(\theta_{LD}) \), so there are only six distinct angular functions.

By measuring a set of quadrupolar spin-relaxation rates at a given magnetic field, corresponding to a Larmor frequency \( \omega_0 \), one can separately determine the three lab-frame frequencies \( \omega, \omega_a, \) and \( 2\omega_0 \) by measuring a set of quadrupolar spin-relaxation rates at a given magnetic field, corresponding to a Larmor frequency \( \omega_0 \), one can separately determine the three lab-frame frequencies \( \omega, \omega_a, \) and \( 2\omega_0 \) if the alignment angle \( \theta_{LD} \) can be varied, then (2.10)–(2.14) enable one to extract the values of each of the three director-frame spectral density functions \( j_k^2(\omega) \) at the three frequencies 0, \( \omega_0 \), and \( 2\omega_0 \).

In the limit where the mean torque goes to zero, the system becomes isotropic (with respect to aggregate orientation) and the director frame is then superfluous. We may thus set \( \theta_{LD} = 0 \) and, since \( (2 - \delta_{mk})F_{kn}(0) = \delta_{kn} \), (2.10) reduces to the trivial result \( g_k^2(t) = g_k^2(t) \). Further, according to Hubbard's symmetry theorem for time correlation functions of irreducible tensor components [which, incidentally, is a special case of the general group-theoretical theorem used to obtain (2.7)], the correlation functions in a rotationally invariant frame are the same for all tensor components, i.e., they are independent of the projection index. Hence, in the isotropic limit,

\[ g_k^2(t) = g_k^2(t), \]

(2.15)

where we have suppressed the redundant projection index. [The independence of the director-frame projection index is explicitly borne out by (3.4) for the particular case of rotational diffusion of a symmetric top.]

Returning now to the director-frame correlation functions \( g_k^m(t) \), we express (2.9) more compactly as

\[ g_k^m(t) = S_{AM}^2 \delta_{AM}^2 g_{00}^m(t) + \delta_{m0}^2 S_{DA0}^2 g_{00}^m(t) + \sum_m g_{0m}^m(t) g_m^AM(t), \]

(2.16)
in terms of the correlation functions \( g_{0m}^m(t) \) for aggregate reorientation and \( g_m^AM(t) \) for surface diffusion:

\[ g_{0m}^m(t) = \langle D_{nm}^2 (\Omega_{DA}^2) - \delta_{m0}^2 S_{DA0}^2 \rangle, \]

(2.17)

\[ g_m^AM(t) = \langle D_{nm}^2 (\Omega_{DA}^2) - \delta_{m0}^2 S_{DA0}^2 \rangle. \]

(2.18)

These correlation functions are defined so as to vanish in the limit \( t \to \infty \).

The number of distinct terms in the sum in (2.16) can be reduced by making use of symmetry. By the same arguments that were used in going from (2.8) to (2.10), it follows that \( g_m^AM(t) = g_{-m}^AM(t) \). Further, the assumed symmetry of the potential of mean torque (see above) implies that \( g_{-m}^m(t) = g_{m0}^m(t) \). Hence, there are (at most) nine independent reorientational correlation functions \( g_{nm}^m(t) \) and three independent surface diffusion correlation functions \( g_{0m}^m(t) \), and the summation index in (2.16) may be restricted to non-negative values:

\[ g_k^m(t) = S_{AM}^2 g_{00}^m(t) + \delta_{m0}^2 S_{DA0}^2 g_{00}^m(t) + \sum_{m=0}^{\infty} (2 \delta_{m0}) g_{0m}^m(t) g_m^AM(t). \]

(2.19)

III. CORRELATION FUNCTIONS FOR AGGREGATE REORIENTATION

Before addressing the central problem in this work, viz., the calculation of the correlation functions \( g_m^AM(t) \) for molecular surface diffusion, we shall briefly discuss the reduced reorientational correlation functions \( g_{nm}^m(t) \) and \( g_{-m}^m(t) \). The former are considered in Sec. III, while the latter are calculated in Secs. IV and V.

The correlation functions \( g_{nm}^m(t) \) and \( g_{-m}^m(t) \) in (2.19) may be formally factorized as

\[ g(t) = g(0)g(t). \]

(2.20)

The mean-square fluctuation \( g(0) \) is fully determined by the equilibrium orientational distribution, while the reduced correlation function \( g(t) \) depends on the details of the underlying dynamic process. Proceeding as in the derivation of (2.12) and appealing to the even parity of the potential of mean torque (which causes all odd-rank order parameters to vanish), we find that the initial values of (2.17) and (2.18) take the form

\[ g_{nm}^m(0) = \frac{1}{2} + \alpha_n \alpha_m S_{DA} + \beta_n \beta_m Q_{DA} - \delta_{n0} \delta_{m0} S_{DA}^2, \]

(2.21)

\[ g_{m0}^m(0) = \frac{1}{2} + \alpha_n \alpha_m S_{AM} + \beta_n \beta_m Q_{AM} - \delta_{m0}^2 S_{AM}^2. \]

(2.22)

where the coefficients are defined in (2.13), while \( S \) and \( Q \) are the second-rank and fourth-rank order parameters

\[ S = \langle P_2(\cos \theta) \rangle, \]

(2.23a)

\[ Q = \langle P_4(\cos \theta) \rangle. \]

(2.23b)

The explicit forms obtained by combining (2.13) and (2.21) agree with previous results, e.g., in Ref. 15.

This is as far as we can go without invoking dynamic models that specify the statistical properties of the five Euler angles (cf. Table II) whose fluctuations govern the decay of the reduced correlation functions \( g_{nm}^m(t) \) and \( g_{-m}^m(t) \). The former are considered in Sec. III, while the latter are calculated in Secs. IV and V.
where the effective reorientational correlation time $\tau_{nm}$ is obtained as the inverse of the corresponding diagonal element of the matrix representation of the symmetrized rotational diffusion operator for a symmetric top in a modified Wigner basis. Explicitly, one finds for an even potential of mean torque

$$\frac{1}{\tau_{nm}} = c_{nm} D_1 + m^2 (D_\parallel - D_1), \quad (3.2a)$$

$$c_{nm} = c_{mn} = (\frac{3}{2} + 3 \alpha_n \alpha_m S_{DA} - 4 \beta_n \beta_m Q_{DA}) / g_{nm}^2(0). \quad (3.2b)$$

The quantities required to calculate $c_{nm}$ from (3.2b) are defined in (2.13), (2.21), and (2.23). The approximation defined by (3.1) and (3.2) is exact in the limits of vanishing order (isotropic system) and perfect order ($S_{DA} = 1$), and is reasonably accurate throughout the high-order regime, say $S_{DA} > 0.6$. For many applications to surfactant systems, there is thus no need to go beyond the single-exponential approximation.

Under the aforementioned conditions, the approximation (3.2) yields accurate correlation times $\tau_{nm}$ for all cases except $n = m = 1$, where the rotational diffusion operator couples Wigner functions of different parity. For this case, one should therefore use the following second-order approximation:

$$\tau_{11} = \frac{\delta \tau_{11}^0}{\delta - \epsilon D_\parallel^2 \tau_{11}^0}, \quad (3.3a)$$

where $\tau_{11}^0$ is obtained from (3.2), and

$$\delta = 2(1 - S_{nA}) D_1 + (2 + S_{nA}) D_\parallel, \quad (3.3b)$$

$$\epsilon = \frac{10 S_{DA}^2}{14 + 5 S_{DA} + 16 Q_{DA}}. \quad (3.3c)$$

It should be noted that, within the approximation scheme described above, the potential of mean torque, $w(\theta_{DA})$, does not appear explicitly, but is reflected in the values of the two order parameters $S_{DA}$ and $Q_{DA}$. Now if $w(\theta_{DA})$ involves a single coupling parameter, e.g., $w(\theta_{DA}) = - \lambda \cos^2(\theta_{DA})$, then it defines a one-to-one correspondence between $S_{DA}$ and $Q_{DA}$. Since the resulting functional relationship $Q_{DA} - f(S_{DA})$ is rather insensitive to the detailed shape of the (even) potential of mean torque, the fourth-rank order parameter $Q_{DA}$ is almost universally determined by the second-rank order parameter $S_{DA}$ for this class of potentials of mean torque.

Next we consider some special cases. In the isotropic limit ($S_{DA} = 0$), (3.1) and (3.2) reduce to the exact result

$$g_{DA}^0(t) = \exp\left(-t/\tau_0\right), \quad (3.4)$$

$$\frac{1}{\tau_0} = 6 D_1 + 2 D_\parallel^2 \tau_0. \quad (3.5)$$

As expected on symmetry grounds, this result is independent of the director projection index $n$. With $g_{DA}^0(0) = 1/3$ from (2.21), we thus obtain from (2.15) and (2.19) the isotropic correlation function

$$g^L(t) = \left[ S_{DA}^2 \exp\left(-t/\tau_0\right) + \sum_{m=0}^{\infty} \left(2 - \delta_{m0}\right) \right] \exp\left(-t/\tau_m\right) g_{m0}^m(t). \quad (3.6)$$

In the limit of perfect order ($S_{DA} = 1$), the spheroid can only undergo spinning motion and the above results yield

$$g_{DA}^0(t) = \delta_{m0} \left(1 - \delta_{m0}\right)^\frac{1}{3} \exp\left(-m^2 D_\parallel t\right), \quad (3.7)$$

whence (2.19) reduces to

$$g_{DA}^0(t) = \exp\left(-m^2 D_\parallel t\right) g_{m0}^m(t). \quad (3.8)$$

Another limiting case, which may be appropriate for nuclei residing in small mobile molecules or ions, is that of fast surface diffusion and perfect order, (3.8) and (3.9) both reduce to the expected result

$$g_{DA}^0(t) = g_{m0}^m(0). \quad (3.9)$$

In the special case of fast surface diffusion and perfect order, (3.8) and (3.9) may be an accurate approximation to (2.19) even though time-scale separation does not obtain for all $n$ and $m$. Thus if the order parameter $S_{DA}$ is sufficiently large, the two spinning modes ($n = m = 1$) may be slow compared to the surface diffusion modes, whereas the remaining tumbling modes are faster than, or on the same time scale, as the surface diffusion modes, but have so small amplitudes $d_{DA}^0(0)$ that they make a negligible contribution to the sum in (2.19).

**IV. CORRELATION FUNCTIONS FOR SURFACE DIFFUSION: GENERAL RESULTS**

The surface-diffusion correlation functions $g_{m0}^m(t)$, defined in (2.18), may be expressed as

$$g_{m0}^m(t) = \int d\Omega_{AM} f(\Omega_{AM}) \tilde{D}_{m0}^2(\Omega_{AM}) \times \int d\Omega_{AM} f(\Omega_{AM}) g_{m0}^m(\Omega_{AM}), \quad (4.1)$$

where

$$\tilde{D}_{m0}^2(\Omega_{AM}) = D_{m0}^2(\Omega_{AM}) - \delta_{m0} S_{AM}. \quad (4.2)$$

Here $f(\Omega_{AM})$ is the equilibrium distribution function for the Euler angles $\Omega_{AM}$ and $f(\Omega_{AM}, t | \Omega_{AM}^0)$ is the surface-diffusion propagator which, when multiplied by $d\Omega_{AM}$, yields the conditional probability of having Euler angles in the range $d\Omega_{AM}$ around $\Omega_{AM}$ at time $t$, given the initial Euler angles $\Omega_{AM}^0$. Since one index is zero on the Wigner functions (on account of the $C_2$ symmetry of the locally averaged coupling tensor), we need only consider two Euler angles: the angle $\theta_{AM}$ between the symmetry axes of the spheroidal aggregate and the coupling tensor, and the azimuthal angle $\phi_{AM}$ with...
where we have introduced the reduced propagator
\[ F_m(\eta, t | \eta_0) = \int_0^{2\pi} d\phi \cos(m\phi) f(\eta, \phi, t | \eta_0). \] (4.11)

### B. The surface-diffusion equation

Since the equilibrium surface distribution is uniform, the diffusing molecule experiences no mean force, i.e., the propagator \( f(\eta, \phi, t | \eta_0) \) describes free diffusion on a spheroidal surface. For the case of an "isotropic" (same in all directions on the surface) and uniform (independent of \( \eta \) and \( \phi \)) surface-diffusion coefficient \( D_s \), the propagator then satisfies the surface-diffusion equation
\[ \frac{\partial}{\partial t} f(\eta, \phi, t | \eta_0) = D_s \nabla^2 f(\eta, \phi, t | \eta_0), \] (4.12)
and the initial condition
\[ f(\eta, \phi, 0 | \eta_0) = \frac{\delta(\eta - \eta_0)\delta(\phi)}{h(\eta_0)}. \] (4.13)

By considering the net flow out of an area element \( h_\eta h_\phi \eta d\eta d\phi \) on the spheroidal surface, one can show that the surface Laplacian \( \nabla^2 \) takes the form
\[ \nabla^2 = \frac{1}{h_\eta h_\phi} \left[ \frac{\partial}{\partial \eta} \left( \frac{h_\phi}{h_\eta} \frac{\partial}{\partial \eta} \right) + \frac{\partial}{\partial \phi} \left( \frac{h_\eta}{h_\phi} \frac{\partial}{\partial \phi} \right) \right], \] (4.14)
where the surface metric coefficients \( h_\phi \) and \( h_\eta \) are functions of \( \eta \) (see below). It should be stressed that (4.14) is not obtained by taking the limit \( \xi \to \text{const} \) of the three-dimensional Laplacian (whose angular part contains \( \xi \) only in a factor multiplying the angular derivatives), as one does in the case of spherical polar coordinates. Rather, one should set the radial metric coefficient \( h_\eta(\xi, \eta) \) equal to unity in the three-dimensional Laplacian in order to obtain (4.14). Unfortunately, I did not realize this in a previous study of surface diffusion on spheroids. Physically, this problem is illustrated by the fact that the shell between two confocal spheroids is of nonuniform thickness, so a uniform space distribution cannot be reduced to uniform surface distribution by letting the shell thickness go to zero.

The metric factor \( h(\eta) \) defined by (4.6) is related to the conventional metric coefficients in (4.14) through
\[ h(\eta) = \frac{1}{a^r} h_\eta(\xi, \eta) h_\phi(\xi, \eta) = \frac{1}{a^r} h_\eta(\xi, \eta) h_\phi(\xi, \eta), \] (4.15)
where \( h_\eta(\xi, \eta) \) and \( h_\phi(\xi, \eta) \) are the usual three-dimensional metric coefficients and the fixed radial coordinate \( \xi \) is \( r^{-1}(1 - r^2)^{-1/2} \).

Combination of (4.12), (4.14), and (4.15) yields the surface-diffusion equation
\[ \frac{\partial}{\partial t} f(\eta, \phi, t | \eta_0) = \frac{D_s}{a^r} \left( \frac{1}{h(\eta)} \frac{\partial}{\partial \eta} \left[ \frac{1 - \eta^2}{h(\eta)} \frac{\partial}{\partial \eta} f(\eta, \phi, t | \eta_0) \right] \right) \]
\[ + \frac{r^{-2s}}{1 - \eta^2} \frac{\partial^2}{\partial \phi^2} f(\eta, \phi, t | \eta_0). \] (4.16)
We now multiply (4.16) by \( \cos(m\phi) \) and integrate over \( \phi \), using (4.11). The azimuthal term is integrated by parts twice, using the periodic boundary conditions in \( \phi \). We thus obtain
\[
\frac{\partial}{\partial \tau} f_m(\eta, \tau | \eta_0) = \frac{1}{h(\eta)} \frac{d}{d\eta} \left[ \frac{(1 - \eta^2)}{h(\eta)} \frac{d}{d\eta} f_m(\eta, \tau | \eta_0) \right] - \frac{(m^2)}{r^2} \frac{1}{1 - \eta^2} f_m(\eta, \tau | \eta_0),
\]
where we have introduced the reduced time variable
\[
\tau = D_s \frac{t}{a^2}.
\]
In connection with the surface-diffusion spectral density functions, we will use the corresponding reduced angular frequency
\[
\bar{\omega} = \omega a^2 / D_s.
\]
It follows from the foregoing that the correlation functions \(g_m^M(t)\) depend on the absolute dimensions of the spheroid solely through the scaling \((4.18)\) of the time. To calculate these correlation functions, we must now solve the partial differential equation \((4.17)\) subject to the initial condition
\[
f_m(\eta, 0 | \eta_0) = \delta(\eta - \eta_0) / h(\eta_0),
\]
and the boundary conditions
\[
f_m(\eta, \tau | \eta_0) \text{ bounded at } \eta = \pm 1.
\]

### C. Eigenfunction method: Formal theory

In more compact notation \((4.17)\) reads as
\[
\frac{\partial}{\partial \tau} f_m(\eta, \tau | \eta_0) = - \frac{1}{h(\eta)} \mathcal{L}_m f_m(\eta, \tau | \eta_0),
\]
where the differential operators \(\mathcal{L}_m\) are defined as
\[
\mathcal{L}_m = - \frac{1}{h(\eta)} \frac{d}{d\eta} p(\eta) \frac{d}{d\eta} + \left( \frac{m^2}{r^2} \right) \frac{1}{h(\eta)},
\]
where \(p(\eta) = (1 - \eta^2) / h(\eta)\).

The method of separation of variables provides a general solution to \((4.22)\) of the form
\[
f_m(\eta, \tau | \eta_0) = \sum_{k} c_k^m \psi_k^m(\eta) \exp\left(-\lambda_k^m \tau\right),
\]
where \(\psi_k^m(\eta)\) is a generalized eigenfunction of the operator \(\mathcal{L}_m\), i.e.,
\[
\mathcal{L}_m \psi_k^m(\eta) = \lambda_k^m h(\eta) \psi_k^m(\eta),
\]
\(\lambda_k^m\) being the corresponding eigenvalue. The ordinary differential equation \((4.26)\) has singularities at \(\eta = \pm 1\) and, to obtain the physically relevant, regular solutions, it should be solved subject to the boundary conditions
\[
\psi_k^m(\eta) \text{ bounded at } \eta = \pm 1,
\]
\[
\frac{d\psi_k^m(\eta)}{d\eta} \text{ bounded at } \eta = \pm 1.
\]

Equations \((4.26)\) and \((4.27)\) constitute a Sturm–Liouville problem and, proceeding in the usual manner, one can readily establish the following properties.

(i) The differential operator \(\mathcal{L}_m\) is self-adjoint.

(ii) \(\mathcal{L}_m\) has a discrete spectrum of real, non-negative, nondegenerate eigenvalues \(\lambda_k^m\), which we take to be arranged in ascending order (with \(\lambda_k^m \to \infty\) as \(k \to \infty\)). For \(m \neq 0\), all eigenvalues are positive, whereas, for \(m = 0\), the smallest eigenvalue is \(\lambda_0^0 = 0\).

(iii) The real-valued eigenfunctions \(\psi_k^m(\eta)\) form a complete set, orthogonal on the interval \(-1 < \eta < 1\) with respect to the weight function \(h(\eta)\). Since \((4.26)\) is a homogeneous differential equation, the eigenfunctions can be normalized, which we take to be the case. Hence,
\[
\int_{-1}^{1} d\eta h(\eta) \psi_k^m(\eta) \psi_n^m(\eta) = \delta_{kk}.
\]

It follows from \((4.8)\) and \((4.26)-(4.28)\) that the normalized eigenfunction corresponding to the zero eigenvalue is
\[
\psi_0^0(\eta) = \frac{1}{\sqrt{\sigma}}.
\]
(iv) Since the operator \(\mathcal{L}_m\) is invariant with respect to reflection through the equator plane \(\eta = 0\), its eigenfunctions are of definite parity. If the eigenvalues \(\lambda_k^m\) are arranged in ascending order and labeled with \(k = m, m + 1, \ldots\), then the eigenfunction \(\psi_k^m(\eta)\) has precisely \(k - m\) nodes in the interval \(-1 < \eta < 1\). Consequently, we have the symmetry relation
\[
\psi_k^m(-\eta) = (-1)^{k-m} \psi_k^m(\eta).
\]

C. Eigenfunction method: Formal theory

The coefficients \(c_k^m\) in the eigenfunction expansion \((4.25)\) must now be chosen so that the initial condition \((4.20)\) is satisfied. Setting \(\tau = 0\) in \((4.25)\), substituting \(c_k^m h(\eta) \psi_k^m(\eta)\) and integrating over \(\eta\), we find that
\[
f_m(\eta, \tau | \eta_0) = \sum_{k} c_k^m(\eta_0) \psi_k^m(\eta) \exp(-\lambda_k^m \tau).
\]

It follows from property (ii) that \(f_m(\eta, \tau | \eta_0)\), as given by \((4.30)\), reduces correctly to the equilibrium distribution \(f(\eta) = 1 / \sigma \) as \(r \to \omega_\circ\).

Combination of \((4.10)\), \((4.18)\), and \((4.30)\) now yields for the surface-diffusion correlation functions
\[
g_m^M(t) = \sum_{k} c_k^m(\eta_0) \psi_k^m(\eta) \exp(-t / \tau_k^m),
\]
where we have defined the amplitude factors
\[
c_k^m = \frac{1}{\sqrt{\tau_k^m}} \int_0^1 d\eta h(\eta) \psi_k^m(\eta) \delta_{m0}(\xi),
\]
and the correlation times
\[
\tau_k^m = a^2 / (D_s \lambda_k^m).
\]

According to \((4.4)\) and \((4.5)\), we have the symmetry relation
\[
\tilde{a}_{k0}(\xi - \eta) = (-1)^{k-m} \tilde{a}_{k0}(\xi),
\]
which, together with \((4.6)\) and \((4.29)\), implies that the parity of the integrand in \((4.32)\) is \((-1)^k\). Hence,
\[
a_k^0 = 0 \text{ for odd } k.
\]

Further, it follows from \((2.23a)\), \((4.4)\), \((4.8)\), and \((4.32)\) that
\[
f_0^0 = \langle \tilde{a}_{k0}(\xi) \rangle = 0.
\]

On account of \((4.55)\), we may express \((4.31)\) as
\[
g_m^M(t) = \sum_{k=1}^{\infty} (a_k^m)^2 \exp(-t / \tau_k^m).
\]

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D. Eigenfunction method: Matrix solution

A finite number \( N \) of approximate eigenvalues and eigenvectors can be obtained numerically by discretizing the \( \eta \) space. For simplicity, we consider a uniformly spaced grid of \( N \) grid points:

\[
\eta_\alpha = -1 + (\alpha - \frac{1}{2}) \Delta, \quad \alpha = 1, 2, \ldots, N, \tag{4.37}
\]

separated by the grid spacing \( \Delta = 2/N \).

The Sturm–Liouville equation (4.26) is approximated by the generalized matrix eigenvalue problem

\[
L^m \psi_k^\alpha = \lambda_k^m \psi_k^\alpha, \tag{4.38}
\]

where the column eigenvector \( \psi_k^\alpha \) has elements \( \psi_k^\alpha (\eta_\alpha) \), \( L^m \) is the \( N \times N \) matrix representation of the differential operator \( \mathcal{L}^m \) (see below), and \( H \) is a diagonal matrix with elements \( h(\eta_\alpha) \). Similarly, the orthonormality relation (4.28) is expressed in matrix notation as

\[
\tilde{\psi}_k^\alpha H \psi_n^\alpha = \delta_{kn}, \tag{4.39}
\]

where the tilde denotes transposition.

For computational convenience, we define the modified eigenvectors

\[
\phi_k^\alpha = \Delta^{1/2} H^{1/2} \psi_k^\alpha, \tag{4.40}
\]

where the diagonal matrix \( H^{1/2} \) has elements \( \sqrt{h(\eta_\alpha)} \). The orthonormality relation (4.39) then becomes simply

\[
\tilde{\phi}_k^\alpha \phi_n^\alpha = \delta_{kn}, \tag{4.41}
\]

without explicit reference to the weight function or to the number of grid points. In terms of the modified eigenvectors, (4.38) reduces to the standard matrix eigenvalue problem

\[
M^m \phi_k^\alpha = \lambda_k^m \phi_k^\alpha, \tag{4.42}
\]

with

\[
M^m = H^{-1/2} L^m H^{-1/2}. \tag{4.43}
\]

Since the operator \( \mathcal{L}^m \) is self-adjoint, its matrix representation \( L^m \) must be symmetric. Further, since \( H^{-1/2} \) is symmetric (in fact, diagonal), it follows that also \( M^m \) is a symmetric matrix.

The amplitudes \( a_k^\alpha \), required to calculate the correlation functions \( g_m^{\alpha \nu}(t) \) via (4.36), are defined by (4.32), which may be expressed in matrix notation as

\[
d_k^\alpha = \tilde{d}_k^\alpha \phi_k^\alpha, \tag{4.44}
\]

where \( d^\alpha \) is a column vector with elements

\[
d_k^\alpha = \left[ \frac{\Delta}{\sigma} h(\eta_\alpha) \right]^{1/2} \tilde{d}_m \zeta(\eta_\alpha). \tag{4.45}
\]

We must now construct the matrix \( M^m \) on the basis of (4.23) and (4.43). Adopting the symmetric finite-difference approximation

\[
\frac{d}{d \eta} \left[ p(\eta) \frac{d u}{d \eta} \right] \eta_\alpha = \frac{1}{\Delta} \left[ p(\eta_\alpha + 1/2) - p(\eta_\alpha - 1/2) \right] \left[ u(\eta_\alpha + 1/2) - u(\eta_\alpha - 1/2) \right], \tag{4.46}
\]

we obtain a symmetric tridiagonal matrix with nonzero elements given by

\[
M_{\alpha \alpha + 1}^m = M_{\alpha + 1 \alpha}^m = \frac{p(\eta_\alpha + 1/2) - p(\eta_\alpha - 1/2)}{\Delta^2 \left[ h(\eta_\alpha) h(\eta_{\alpha + 1}) \right]^{1/2}}. \tag{4.47a}
\]

Two comments are in order concerning this result. First, it is seen that \( p(\eta) \) should be evaluated at points halfway between the grid points \( \eta_\alpha \) defined by (4.37). Secondly, Eqs. (4.47) are valid at all grid points, including the “boundary” points \( \alpha = 1 \) and \( \alpha = N \). By constructing the grid as in (4.37), we avoid the singularities of \( 1/p(\eta) \) in (4.47a).

The symmetric matrix eigenvalue problem (4.42) may be solved with any standard numerical routine. (In the interest of computing efficiency, the sparsity of the tridiagonal matrix \( M^m \) should be exploited.) This results in a set of \( N \) approximate eigenvalues \( \lambda_k^m \), eigenvectors \( \phi_k^\alpha \), and, via (4.44), amplitudes \( a_k^\alpha \). These are then inserted into (4.36) to give an approximation (corresponding to truncation of the infinite sum after \( \text{Int} \{ (N + 1)/2 \} \) terms) to the correlation function \( g_m^{\alpha \nu}(t) \). The desired accuracy is achieved by increasing the number \( N \) of grid points, which enables more terms to be included in the expansion (4.36) and, at the same time, increases the accuracy of any given term.

E. Direct method: Formal theory

The eigenfunction expansion approach described above is conceptually transparent and readily transcribed into a general numerical algorithm. For many purposes, however, an alternative approach is preferable. In this approach, which we refer to as the direct method, one focuses, not on the eigenfunctions \( \psi_k^\alpha \), but on an integral quantity defined as

\[
e_{\eta_0 \tau} = \int_{\eta_0}^{\eta_\tau} d \eta h(\eta) f_m(\eta, \tau) d_\eta^2 (\xi). \tag{4.48}
\]

The connection to the eigenfunction method is established by substituting into (4.48) the eigenfunction expansion (4.30) and then using (4.32) and (4.35). This yields

\[
e_{\eta_0 \tau} = \sqrt{\sigma} \sum_{k=1}^{\infty} a_k^m \phi_k^\alpha(\eta_0) \exp(-\lambda_k^m \tau). \tag{4.49}
\]

Now consider the differential operator \( \mathcal{L}^m \), defined by (4.23) except that, as indicated by the zero superscript, it acts on the initial coordinate \( \eta_\alpha \) rather than on \( \eta \). By operating with \( \mathcal{L}^m \) on (4.49) and using the eigenvalue equation (4.26), it is seen that \( e_{\eta_0}^{\alpha \nu}(\eta, \tau) \) satisfies the adjoint (or backward) surface-diffusion equation.22,24
\[
\frac{\partial}{\partial \tau} q_m(\eta_0 \tau) = - \frac{1}{h(\eta_0)} \varphi^0_m q_m(\eta_0 \tau). 
\]

From (4.20) and (4.48), we obtain the initial condition
\[
q_m(\eta_0 0) = \hat{2}^m_{m0} (\xi_0). 
\]
Further, since all eigenvalues appearing in (4.49) are positive, we have
\[
q_m(\eta_0 \tau \to \infty) = 0. 
\]

From (4.29) and (4.49), we also obtain the symmetry relation
\[
q_m(- \eta_0 \tau) = (-1)^m q_m(\eta_0 \tau). 
\]

The relation of the quantity \( q_m(\eta_0 \tau) \) to the correlation function \( g_{mM}^M(\tau) \) follows from (4.10) and (4.48):
\[
g_{mM}^M(\tau) = \begin{array}{c} \frac{2}{\sigma} \int_0^\infty d\eta_0 h(\eta_0) \hat{2}_{m0}^2 (\xi_0) q_m(\eta_0 \tau), \end{array} 
\]
where we have also used the symmetries (4.34) and (4.53). The corresponding spectral density function is, according to (2.1):
\[
J_m^{M}(\tilde{\omega}) = \frac{\alpha^2}{D}\Re \int_0^\infty d\tau \exp(i \tilde{\omega} \tau) g_{mM}^M(\tau) 
\]
where \( \tilde{\omega} \) is the reduced frequency defined in (4.19) and \( Q_m(\eta_0 \tilde{\omega}) \) is the Fourier–Laplace transform of \( q_m(\eta_0 \tau) \), i.e.,
\[
Q_m(\eta_0 \tilde{\omega}) = \int_0^\infty d\tau \exp(i \tilde{\omega} \tau) q_m(\eta_0 \tau). 
\]

Fourier–Laplace transforming (4.50), using (4.51) and (4.52), we find that \( Q_m(\eta_0 \tilde{\omega}) \) satisfies the inhomogeneous ordinary differential equation
\[
\left[ 1 - \frac{\varphi^0_m}{h(\eta_0) \tilde{\omega}} \right] Q_m(\eta_0 \tilde{\omega}) = \hat{2}^2_{m0} (\xi_0). \tag{4.57} 
\]

As will be seen in Sec. V, the direct method is often better suited than the eigenfunction method for deriving exact results in special cases. Thus the calculation of the zero-frequency limit of the spectral density functions can sometimes be reduced to quadratic (or even to closed analytical form) by directly integrating (4.57) with \( \tilde{\omega} = 0 \). This is illustrated in Sec. V A for the case \( m = 0 \). Further, in Secs. V C and V D, we employ the direct method to derive closeform asymptotic results for highly eccentric spheroids (\( \tau \to 0 \)). Another important advantage of the direct method is that its numerical implementation is usually much more computationally efficient than the eigenvector approach.

**F. Direct method: Matrix solution**

The eigenvector method described in Sec. IV D has the virtue of providing the entire correlation function \( g_{mM}^M(t) \) or, equivalently, the entire spectral density function \( J_m^{M}(\omega) \). However, since a nuclear spin-relaxation experiment at a given external magnetic field strength probes the spectral density function at only a few discrete frequencies (usually multiples of the Larmor frequency), it may be extremely wasteful to compute the full frequency dependence. In such situations, the direct method provides a more economical approach.

By discretizing the \( \eta \) space as in (4.37), we may express (4.57) in matrix notation as
\[
(M^m - \tilde{\omega} U) R^m = d^m, \tag{4.58} 
\]
where \( U \) is the \( N \times N \) unit matrix, and
\[
R^m = H^{1/2} Q^m, \tag{4.59} 
\]
where \( Q^m \) is a column vector with elements \( Q_m(\eta_o \tilde{\omega}) \), and the matrices \( M^m, H, \) and \( d^m \) have been defined in Sec. IV D. According to (4.55), the spectral density can be obtained as
\[
J_m^{M}(\tilde{\omega}) = \frac{\alpha^2}{D} d^m \Re R^m. \tag{4.60} 
\]

Now if we want to solve (4.58) simultaneously for all frequencies, then we must find the orthogonal matrix \( X^m \) which diagonalizes \( M^m \) through the similarity transformation
\[
\bar{X}^m M^m X^m = \Lambda^m. \tag{4.61} 
\]

It is readily shown that the diagonal elements of \( \Lambda^m \) are the eigenvalues \( \lambda^m_k \), and that the columns of \( X^m \) are the eigenvectors \( \phi^m_k \) and, hence, that the description (4.58)–(4.61) is computationally equivalent to the eigenvector method in Sec. IV D. The above formalism has been used extensively, e.g., by Freed and co-workers for solving relaxation problems involving the relative diffusion of two species in a three-dimensional space and, more recently, by the present author for calculating spectral densities for a spin-lattice coupling tensor whose magnitude and orientation is modulated by diffusion in a spatially restricted and locally anisotropic system.

If we need to know the value of the spectral density function at a few frequencies, then it is computationally much simpler to solve the matrix equation (4.58) directly for each frequency. This is readily accomplished using any standard complex matrix equation solving routine (preferably one that capitalizes on the tridiagonality of the matrix \( M^m \)). It is straightforward to transform (4.58) into a matrix equation for the real part of \( R^m \), which, however, is more time consuming to solve [mainly due to the extra matrix multiplication required to form the pentadiagonal matrix \( (M^m)^2 \)]. It should be noted that to solve (4.58) we do not have to find the inverse of the matrix \( (M^m - \tilde{\omega} U) \), which is more demanding computationally. In fact, for \( m = 0 \) and \( \tilde{\omega} = 0 \), the inverse does not even exist, since the matrix \( M^0 \) is singular of rank \( N - 1 \). The singularity of this matrix is just a reflection of the probability conservation law or normalization of the propagator \( f_{00}(\eta_0 | \eta_0) \), which introduces a degeneracy in the set of simultaneous linear equations (4.58). The consequent nonuniqueness of the solution vector \( \mathbf{R}^0 \) does not pose any problem for the same reason that the zero eigenvalue \( \lambda_0 \) does not appear in the expansion (4.36).

The direct solution of the complex matrix equation (4.58) is typically between one and two orders of magnitude faster than the eigenvector method.
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(4.42). So if one needs to know the value of the spectral density function at much less than 10–100 frequencies, the direct method is to be preferred. On the other hand, if we are concerned, not with the surface-diffusion spectral densities $j_m^A(\omega)$, but with the joint spectral densities $j_m^A(\omega)$, defined by (2.1) and (2.19), then the direct method may not be applicable since it does not, like the eigenfunction method, yield the correlation functions $g_m^A(t)$ in (2.19). In many cases, however, the reorientational correlation functions $g_m^A(t)$ in (2.19) are single exponential as in (3.1). Then the direct method can still be used to calculate the joint spectral density. It is readily shown that to obtain the contributions from the cross terms in (2.19), one simply replaces $\tilde{\omega}$ by $\tilde{\omega} + \omega^2/(D_\tau m)$ in (4.58) and multiplies the resulting spectral density term by $g_m^A(0)$. The same procedure can, of course, be used also if $g_m^A(t)$ is represented as a linear combination of exponentials. In conclusion, the eigenfunction method should be used (i) if the spectral density function needs to be accurately evaluated at a large number of frequencies, (ii) if the reorientational correlation functions cannot be expressed as linear combinations of a small number of exponentials, or (iii) if one wants to investigate the breakdown of the motional-narrowing approximation (cf. Sec. V D). For most other purposes, however, the direct method is to be preferred.

V. CORRELATION FUNCTIONS FOR SURFACE DIFFUSION: SPECIAL CASES

Although the treatment in Sec. IV provides general methods for numerically calculating the correlation functions $g_m^A(t)$ and the spectral density functions $j_m^A(\omega)$, we shall now show that further analytical progress is possible in the zero-frequency limit as well as in the geometrical limits (sphere, needle, disk) of the spheroid. The results thus obtained are useful in several respects. The zero-frequency spectral density provides a convenient reference point against which the rate of convergence of the general numerical algorithms can be assessed. The results for the limiting geometries are important for establishing the range of behavior encompassed by the model. Closed-form analytical results are particularly valuable here, as the rate of convergence of the eigenfunction method deteriorates for extremely eccentric spheroids (cf. Sec. VI A). Although the strict needle and disk limits ($r$→0) are of little practical interest, the understanding of the asymptotic behavior afforded by analytical results is valuable since these results remain accurate even for moderately eccentric spheroids.

A. The zero-frequency limit

We now demonstrate, using the direct approach of Sec. IV E, how the calculation of the $m = 0$ spectral density at zero frequency, $j_0^A(0)$, can be reduced to simple quadrature. The starting point is (4.57), which for $m = 0$ and $\tilde{\omega} = 0$ reads as

$$\frac{d}{d\eta_0} \left[ \frac{p(\eta_0)}{d\eta_0} Q_0(\eta_0,0) \right] = - h(\eta_0) \hat{a}_0^2(\xi_0),$$

(5.1)

with $p(\eta_0)$ given by (4.24). The special form of this second-order differential equation enables us to transform it into an iterated integral. Integrating (5.1) from 0 to $\eta$, we obtain

$$\frac{d}{d\eta_1} Q_0(\eta_1,0) = - \frac{1}{p(\eta_1)} \int_0^{\eta_1} d\eta_2 h(\eta_2) \hat{a}_0^2(\xi_2),$$

(5.2)

where we have used the symmetry property

$$\frac{d}{d\eta} Q_0(\eta,0) \mid_{\eta = 0} = 0$$

(5.3)

which follows from (4.53). A second integration from 0 to $\eta_0$ yields

$$Q_0(\eta_0,0) = Q_0(0,0) - \int_0^{\eta_0} \frac{d\eta_1}{p(\eta_1)} \int_0^{\eta_1} d\eta_2 h(\eta_2) \hat{a}_0^2(\xi_2).$$

(5.4)

The zero-frequency spectral density is given by (4.55) as

$$j_0^A(0) = \frac{2a^2}{\sigma D_s} \int_0^1 d\eta_0 h(\eta_0) \hat{a}_0^2(\xi_0) Q_0(\eta_0,0).$$

(5.5)

From the definition (4.4), it follows that the constant term in (5.4) does not contribute to the integral in (5.5). Hence, $j_0^A(0)$ becomes

$$j_0^A(0) = \frac{2a^2}{\sigma D_s} \int_0^1 d\eta_0 h(\eta_0) \hat{a}_0^2(\xi_0) \times \int_0^{\eta_0} \frac{d\eta_1}{p(\eta_1)} \int_0^{\eta_1} d\eta_2 h(\eta_2) \hat{a}_0^2(\xi_2).$$

(5.6)

By interchanging the order of integration and relabeling dummy variables, this threefold iterated integral can be reduced to the form

$$j_0^A(0) = \frac{2a^2}{\sigma D_s} \int_0^1 d\eta h(\eta) \frac{1}{1 - \eta'^2} I(\eta),$$

(5.7)

where (4.24) has been used, and

$$I(\eta) = \int_0^\eta d\eta' h(\eta') \hat{a}_0^2(\xi').$$

(5.8)

Expressing the integrand explicitly with the aid of (4.4)–(4.6) and evaluating the resulting standard integrals, we obtain

$$j_0^A(0) = \frac{2a^2 b^2}{2(1 - \rho^2)^3 \sigma D_s} \int_0^1 d\eta h(\eta) \frac{1}{1 - \eta'^2} [J(\eta)],$$

(5.9)

with

$$J_{pr}(\eta) = r \arcsin[(1 - \rho^2)^{1/2} \eta]$$

$$- \eta h_{pr}(\eta) \arccos(r),$$

(5.10a)

$$J_{ob}(\eta) = r \arcsin[(1 - \rho^2)^{1/2} \eta/r]$$

$$- \eta h_{ob}(\eta) \arccosh(1/r),$$

(5.10b)

where we have also used (4.9) and (A5). Inserting $J(\eta)$ from (5.10) into (5.9), we find that $j_0^A(0)$ may be expressed as a linear combination of three integrals—all of which are divergent! However, it can be shown that $J(\eta)$ goes as 1 − η when η → 1, so the integral in (5.9) is convergent and is readily performed numerically.
B. The sphere limit

As an instructive example of the use of the eigenfunction expansion formalism, we consider now the sphere limit. As the axial ratio $r \to 1$, (4.5), (4.6), and (4.9) yield $h = 1$, $\sigma = 2$, and $\eta = \xi$. The Sturm–Liouville problem (4.26) thus reduces to

$$\frac{d}{d\xi} \left[ (1 - \xi^2) \frac{d}{d\xi} \psi_k^m(\xi) \right] + \left( \lambda^2 - \frac{m^2}{1 - \xi^2} \right) \psi_k^m(\xi) = 0.$$  

(5.11)

This is nothing but the associated Legendre equation, which is satisfied by the reduced Wigner functions $d_k^m(\xi)$. The orthonormal eigenfunctions and corresponding eigenvalues are then

$$\psi_k^m(\xi) = (k + \frac{1}{2})^{1/2} d_k^m(\xi),$$  

(5.12)

$$\lambda^2 = k(k + 1), \quad k = m, m + 1, \ldots$$  

(5.13)

Using (4.32) and (4.33), we thus obtain $d_k^m = \delta_{k2}/\sqrt{5}$ and $1/r_2 = k(k + 1)D_2/a^2$. Substitution into (4.36) yields finally (for all $m$ values)

$$g_m^A(t) = \frac{1}{4} \exp(-6D_2t/a^2),$$  

(5.14)

which is the well-known result for surface diffusion on a sphere of radius $a$. (This problem is isomorphic to that of rotational diffusion of a spherical top with rotational diffusion coefficient $D_2/a^2$.)

C. The needle limit

The prolate spheroid has two distinct $r \to 0$ limits, which we refer to as the needle and the line. The needle is obtained by fixing the minor semiaxis $b$ and letting the major semiaxis $a \to \omega$. As suggested by its name, the needle differs from a rod by having a nonuniform curvature. If, on the other hand, $a$ is held fixed while $b \to 0$, the prolate spheroid degenerates into a line of length $2a$ (the generator of the prolate spheroid coordinate system). As might be expected, and as explicitly borne out by (5.23) and (5.24), all surface-diffusion correlation functions and spectral density functions vanish identically in the line limit.

Before examining the needle limit, we consider the related case of a straight circular cylinder of radius $b$ and of infinite length. In this geometry the surface normal is everywhere orthogonal to the symmetry axis, i.e., $f(\xi) = \delta(\xi)$ and, hence,

$$S_{cyl} = - \frac{1}{2},$$  

(5.15)

$$\tilde{d}_{2/m}^m(\xi) = \delta_{m2}(\frac{\xi}{2}).$$  

(5.16)

Further, the surface-diffusion propagator factorizes into an (irrelevant) axial part and an azimuthal part of the form

$$f(\phi,t) = \frac{1}{2\pi} \left[ 1 + 2 \sum_{n=1}^{\infty} \cos(n\phi) \exp(-n^2D_2t/b^2) \right].$$  

(5.17)

Substitution of these results into (4.3) leads to the exponential correlation function

$$g_m^A(t) = \delta_{m2} \frac{1}{4} \exp(-4D_2t/b^2).$$  

(5.18)

We now consider the needle limit. Letting $r \to 0$ in (A5) (A8), we obtain

$$S_{cyl} = - \frac{1}{2},$$  

$$g_m^A(0) = \delta_{m2} \frac{1}{4},$$  

in accord with the cylinder results (5.15) and (5.18). While the order parameter $S_{cyl}$ and the mean-square fluctuation $g_m^A(0)$ happen to be the same for the needle and the cylinder, the nonuniform curvature of the needle is manifested in the time dependence of the correlation function, which we now derive using the direct method of Sec. IV E. With the aid of (4.6a), (4.18), (4.23), (4.24), and (5.16), we obtain for the $r \to 0$ limit of (4.50) and (4.51)

$$\frac{\partial}{\partial t} q_m(\eta,t) = - \frac{D_2}{b^2} \frac{m^2}{1 - \eta^2} q_m(\eta,t),$$  

(5.21a)

$$q_m(\eta,0) = \delta_{m2} \frac{1}{2} \eta^{1/2}.$$  

(5.21b)

The solution to (5.21) is

$$q_m(\eta,t) = \delta_{m2} \frac{1}{2} \eta^{1/2} \exp \left[ - \frac{4D_2t}{b^2(1 - \eta^2)} \right].$$  

(5.22)

Substituting (5.16) and (5.22), along with $\sigma = \pi/2$ and $h(\eta) = (1 - \eta^2)^{1/2}$ into (4.54), we obtain for the correlation functions in the needle limit

$$g_m^A(t) = \delta_{m2} \frac{3}{2\pi} \int_0^1 d\eta (1 - \eta^2)^{1/2} \exp \left[ - \frac{4D_2t}{b^2(1 - \eta^2)} \right]$$  

$$= \delta_{m2} \left[ (1 - 2\tau) \text{erfc}\left( \frac{\tau}{\sqrt{\tau}} \right) + \frac{2}{\sqrt{\pi}} \tau \exp(-\tau) \right]$$  

(5.23)

where now $\tau = t/\tau_{cyl}$ and $\tau_{cyl} = b^2/(4D_2)$. The $m = 2$ spectral density function thus becomes

$$f_2^A(\omega) = \frac{3}{4} \tau_{cyl} \frac{1}{2\pi} \text{Re} \left[ 1 - (1 - i\tau)^{-1/2} \right]$$  

$$= \frac{3}{4} \tau_{cyl} \frac{1}{2\pi} \left( 1 - \frac{z^2}{2(1 + z^2)} \left( \frac{1 + z^2}{(1 + z^2)^{1/2} - 1} \right) \right)^{1/2}$$  

(5.24)

where $z = \omega \tau_{cyl}$. In the zero-frequency limit, this reduces to

$$f_2^A(0) = \frac{9b^2}{128D_2} = \frac{3}{4} \frac{b^2}{2\pi}$$  

(5.25)

where the last result follows from (5.18). It can be shown that $g_2^A(t)$ in (5.23) has a uniformly faster decay than the cylinder correlation function in (5.18). This is to be expected, as the local radius of the needle equals $b$ only at the equator ($\eta = 0$) and is smaller everywhere else. Consequently, the zero-frequency spectral density, $f_2^A(0)$, is smaller for the needle than for the cylinder.

A useful insight can be gained by rewriting the integral in (5.23) as

$$g_2^A(t) = \frac{3}{8} \exp \left[ - \frac{4D_2t}{b^2(1 - \eta^2)} \right].$$  

(5.26)

where the angular brackets denote a surface average. Noting that the local radius $R$ of a prolate spheroid with minor semiaxis $b$ is

$$R = b(1 - \eta^2)^{1/2},$$  

(5.27)

we see that (5.26) may be interpreted as a surface average of the local cylinder correlation function, i.e.,
\[ g_2^{br}(t) = \langle g_2^{br}(t;R) \rangle, \]  
where \( g_2^{br}(t;R) \) is given by (5.18) with \( b \) replaced by the local radius \( R \). This result shows that, in the needle limit, the decay of the correlation function is entirely due to azimuthal surface diffusion (modulation of the angle \( \phi \)), whereas \( \eta \) appears only in the static averaging in (5.28).

In the needle limit (where \( a \to \infty \)), any finite change of the angular coordinate \( \eta \) by surface diffusion requires an infinite time. Consequently, we have what might be termed a slow-exchange situation and the averaging in (5.28) is, in fact, never realized in practice. Rather, the observed spin-relaxation behavior in the needle limit would be a superposition of that for nuclei with different \( \eta \) coordinates, each described by a correlation function \( g_2^{br}[t;R(\eta)] \). This complication is not of much practical interest, however, as the spheroid model hardly provides an accurate description of highly eccentric aggregates. The value of the foregoing analysis derives instead from the fact that the analytical results (5.23)–(5.25) can serve as useful approximations for finite axial ratios \( \rho \) (where a fast-exchange situation obtains). In fact, as may be inferred from Fig. 5, (5.25) is accurate to better than 5% already at \( \rho = 5 \) (cf. Sec. VI C). The limiting frequency dependence in (5.24) is accurate over an even wider range of axial ratios. For example, Fig. 2(a) reveals an excellent agreement between (5.24) and the exact (numerically obtained) dispersion even for \( \rho = 3 \). The deviation of the exact dispersion from Lorentzian shape is quite small for all axial ratios. This is illustrated in Fig. 2(b), where the exact dispersion is compared with the reduced Lorentzian \( 1/(1 + 2\sigma^2/3) \).

D. The disk limit

As in the prolate case, there are two distinct \( r \to 0 \) limits for the oblate spheroid. The nontrivial limit, which we refer to as the disk, is obtained by letting \( a \to \infty \) while keeping \( b \) fixed. In the trivial limit, obtaining by letting \( b \to 0 \) at fixed \( a \), the oblate spheroid degenerates into a flat disk of radius \( a \) (the generator of the oblate spheroidal coordinate system). As shown by (5.33), all surface-diffusion spectral density functions vanish identically in this limit.

Before examining the disk limit, we consider the related case of a lamella of thickness \( 2b \) and of infinite lateral extent. In this geometry the surface normal everywhere coincides with the symmetry axis, hence the trivial results

\[ S_{\text{lam}} = 1, \]  
\[ g_m^{\text{lam}}(t) = 0. \]  

Letting \( r \to 0 \) in (4.9b) and (A5)–(A8), we obtain in the disk limit

\[ S_{AM} = 1, \]  
\[ g_m^{AM}(0) = 0, \]  
in accord with the lamella results (5.29) and (5.30). However, the lamella and disk do not give the same results for \( g_m^{AM}(t) \) and \( j_m^{AM}(\omega) \), as we now demonstrate.

According to (4.23), (4.24), (4.55), and (4.57), the spectral density functions for an oblate spheroid of arbitrary axial ratio may be formally expressed as

\[ j_m^{AM}(\omega) = \begin{align*} &- \frac{2a^2}{\sigma D_\lambda} \int_0^1 d\eta \, h(\eta) \hat{d}_{m0}^2(\xi) \\ &\times \text{Re} \left[ \frac{1}{h(\eta)} \frac{d}{d\eta} \left[ \frac{(1 - \eta^2)}{h(\eta)} \frac{d}{d\eta} \right] - \frac{m^2}{1 - \eta^2} + i \frac{\omega a^2}{D_\lambda} \right]^{-1} \hat{d}_{m0}^2(\xi). \end{align*} \]  

(5.33)

Now, in the disk limit, (4.5) and (4.6) imply that \( h(\eta) = |\eta| \) and that \( \hat{d}_{10}^2(\xi) \) vanishes as \( r \), while \( \hat{d}_{20}^2(\xi) \) and \( \hat{d}_{30}^2(\xi) \) vanish as \( r^2 \). It then follows from (5.33) that, in the disk limit, \( j_0^{AM}(\omega) \) and \( j_2^{AM}(\omega) \) are identically zero, while \( j_1^{AM}(\omega) \) becomes

\[ j_1^{AM}(\omega) = \begin{align*} &- \frac{2b^2}{D_\lambda} \int_0^1 d\eta \, \eta D(\eta) \\ &\times \text{Re} \left[ \frac{1}{\eta} \frac{d}{d\eta} \left[ \frac{(1 - \eta^2)}{\eta} \frac{d}{d\eta} \right] - \frac{1}{1 - \eta^2} + i \frac{\omega a^2}{D_\lambda} \right] D(\eta). \end{align*} \]  

(5.34)

where \( D(\eta) = \hat{d}_{10}^2(\xi)/r \). As seen from (5.34), \( j_1^{AM}(\omega) \) may be nonzero if \( \omega a^2 \) is bounded. In the following, we therefore restrict our attention to the zero-frequency spectral density \( j_1^{AM}(0) \). Considering the vanishing mean-square fluctuation, as expressed by (5.32), a nonzero \( j_1^{AM}(0) \) can result only if the decay of \( g_1^{AM}(t) \) is infinitely slow. Using the eigenfunction formalism of Sec. IV C, one can indeed show that all the
correlation times $\tau_{2k}$ diverge as $r^{-2}$ and that this is precisely offset by the vanishing of the amplitudes $a_{2k}$ as $r$.

According to (4.4)–(4.6),

$$\hat{a}^{2}_{10}(\xi) = -\frac{\sqrt{6}}{2} r \eta (\frac{1-\eta^2}{\eta})^{1/2}$$

(5.35)

which is inserted into (5.55) and (5.57) to give

$$j^{1M}(0) = -\frac{3b^2}{\sigma D_s} \int_{0}^{1} d\eta \eta (1-\eta^2)^{1/2} S(\eta),$$

(5.36)

where we have defined the quantity

$$S(\eta) = 2Q_s(\eta,0)/\sqrt{6}\eta(\eta),$$

(5.37)

which is obtained by solving the differential equation

$$\eta \frac{d}{d\eta} \left[ (1-\eta^2) \frac{d}{d\eta} \left[ h(\eta) S(\eta) \right] \right] - \left[ h(\eta) \right]^3 S(\eta) = \eta (1-\eta^2)^{1/2},$$

(5.38)

subject to the boundary conditions, established by (4.27a), (4.29), (4.49), and (4.56),

$$S(0) = 0,$$

(5.39a)

$$S(\eta) \text{ bounded at } \eta = \pm 1.$$  

(5.39b)

Taking the $r \to 0$ limit in (5.38), we obtain

$$\eta^2 (1-\eta^2)^2 S''(\eta) + \eta (1-\eta^2) (1-3\eta^2) S'(\eta) - S(\eta) = \eta^2 (1-\eta^2)^{1/2},$$

(5.40)

where the prime denotes differentiation with respect to $\eta$. The general solution to (5.40) may be expressed as

$$S(\eta) = c_1 S_1(\eta) + c_2 S_2(\eta) + S_3(\eta).$$

(5.41)

As can readily be verified by substitution into (5.40), the two independent solutions of the homogeneous equation are

$$S_1(\eta) = 1/\left[ \eta (1-\eta^2)^{1/2} \right],$$

(5.42a)

$$S_2(\eta) = \eta/(1-\eta^2)^{1/2},$$

(5.42b)

while the particular solution of the inhomogeneous equation is

$$S_3(\eta) = \text{sgn}(\eta) \eta^2/[3(1-\eta^2)^{1/2}],$$

(5.42c)

The boundary condition (5.39a) clearly requires that $c_1 = 0$. This leaves us with $S(\eta) = \eta(|\eta| + 3c_2)/(1-\eta^2)^{1/2}$, which is bounded at $\eta = \pm 1$, as required by (5.39b), only if $c_2 = -1/3$. The desired solution to (5.40) is therefore

$$S(\eta) = \eta(|\eta| - 1)/[3(1-\eta^2)^{1/2}].$$

(5.43)

Finally, we insert (5.43) into (5.36), set $\sigma = 1$ [the $r \to 0$ limit of (4.9b)], and integrate, thus obtaining the remarkably simple result

$$j^{1M}(0) = b^2/(12D_s).$$

(5.44)

As discussed above, this result derives from a sum of terms, each of which is a product of a vanishing amplitude and a diverging correlation time. It is clear, therefore, that the motional-narrowing approximation, which assumes that the molecular motions described by the correlation function are fast on the time scale of nuclear-spin relaxation, cannot be valid in the disk limit. In fact, $j^{1M}(\omega)$ must be identically zero in this limit, just as for the lamella [cf. (5.30)]. Nevertheless, (5.44) may still be a useful approximation for oblate spheroids that are relatively large, but not so large as to violate the motional-narrowing condition.

A rigorous treatment of spin dynamics in the transition region between the static limit and the motional-narrowing limit requires a theory wherein spin dynamics and molecular diffusion appear at the same level of description, as in the stochastic Liouville equation.\(^{31,32}\) For our purposes, however, a cruder approach will do. According to (4.36), the secular contribution to a transverse nuclear-spin relaxation rate from the $k$ th eigenmode of the $m = 1$ surface-diffusion operator, may be expressed as (we omit the $m = 1$ superscript here)

$$R_k = \alpha Q_s(a_{2k})^2 \tau_{2k},$$

(5.45)

where $\alpha Q_s$ is the root-mean-square spin-lattice coupling frequency (incorporating any numerical factors as well as the angular factor discussed in Sec. II B). The effect of the breakdown of motional-narrowing theory may be approximately described by introducing a cutoff time $\tau_{2k}$ for each mode, such that

$$R_k \tau_{2k} = 1 \text{ when } \tau_{2k} = \tau_{2k}^R,$$

(5.46)

and then expressing the motionally narrowed zero-frequency spectral density as [cf. (4.36)]

$$j^{1M}(0) = \sum_{k=1}^{\infty} (a_{2k})^2 \left( \frac{1}{\tau_{2k}} + \frac{1}{\tau_{2k}^R} \right)^{-1},$$

(5.47)

where the last result follows from (5.45) and (5.46).

Computing the amplitudes $a_{2k}$ and the correlation times $\tau_{2k}$ as described in Sec. IV D and setting $\alpha Q_s = 10^4, 10^5,$ or $10^6$ rad s$^{-1}$, we obtain from (5.47) the solid curves in Fig. 3. This should be compared with the dashed curve, which was computed on the assumption that motional-narrowing theory remains valid for all axial ratios $[\alpha Q_s = 0$ in (5.47)] and

![FIG. 3. Shape dependence of the normalized $m = 1$ spectral density at zero frequency for surface diffusion on oblate spheroids, showing the effect of incomplete motional narrowing for the indicated values of the residual coupling frequency $\alpha Q_s$. The dashed curve is the result for complete motional narrowing.](image-url)
which has essentially reached the disk limit (5.44) at $\rho \approx 100$. For a typical value of $\omega_0 = 10^3 \text{ rad s}^{-1}$, it is seen that a significant departure from motional-narrowing theory occurs only at axial ratios that are so large as to be without practical interest. Further, it can be inferred that the simple limiting result (5.44) is accurate to better than 7% for axial ratios $\rho > 2.5$ (cf. Sec. VI C).

VI. NUMERICAL RESULTS FOR SURFACE-DIFFUSION CORRELATION FUNCTIONS AND SPECTRAL DENSITIES

A. Numerical convergence

Before presenting numerical results, we briefly consider the convergence properties of the numerical methods, described in Sec. IV, for computing the surface-diffusion spectral density functions $f^\text{AM}_m(\omega)$. There are two basic criteria for judging the performance of a numerical algorithm: speed and accuracy. As discussed in Sec. IV F, the direct method is usually superior to the eigenfunction method in terms of computing time. But we also desire a high rate of convergence, i.e., as the number $N$ of grid points (and the size of the matrix $M$) is increased, the numerical approximation should rapidly approach the exact result. Since the reduced Wigner functions $d^{\omega,0}_\mathbf{m} \{ \xi(\eta) \}$ vary strongly with $\eta$ near the poles ($\eta = \pm 1$) of the prolate spheroid, it might be expected that a very fine grid (large $N$) would be required to obtain accurate results. One way to improve accuracy for a given $N$ (at the expense of reducing the sparsity of the matrix $M$) is to replace (4.46) by a higher-order finite-difference approximation. A more effective strategy, however, is to replace (4.37) by a nonuniform grid with smaller grid spacings in regions where the Wigner functions vary rapidly.

We choose a grid spacing that decreases geometrically in going from the equator towards either pole, i.e., we replace (4.37) by

$$
\eta_\alpha = -1 + \frac{\alpha - 1}{N/2}, \quad \alpha = 1, 2, \ldots, N/2 
$$

$$
\Delta_\alpha = \left\{ \begin{array}{ll}
\frac{\epsilon^\gamma}{\epsilon^{N/2}} & \alpha = 1, 2, \ldots, N/2 \\
\frac{1}{\epsilon^{N/2}} & \alpha = N/2 + 1, N/2 + 2, \ldots, N
\end{array} \right. 
$$

where it is understood that $\epsilon < 1$ and that $N$ is an even integer. The parameters $\epsilon$ and $\Delta$ are not independent; in fact $\Delta = (1 - \epsilon)/(1 - \epsilon^N)$. If the ratio $\gamma$ of the smallest to the largest grid spacing is held constant as $N$ is increased, then $\epsilon$ approaches unity with increasing $N$ as $\gamma^{1/(N - 1)}$. Finally, we make the straightforward generalization of (4.46) to a non-uniform grid.6,13 (The matrix $M$ remains symmetric and tridiagonal.)

Table III gives some examples of the rate of convergence achieved with the nonuniform grid (6.1) in the calculation of the surface-diffusion spectral densities $f^\text{AM}_m(0)$. (The $\gamma$ value was roughly optimized in the range 0.01–1 depending on the projection index $m$, the axial ratio, and on whether the spheroid is prolate or oblate.) In all cases shown in Table III, the exact result is known analytically or can be obtained by simple quadrature (cf. Sec. V). In general, four-digit precision requires $N = 50–100$. Using the direct method, this entails a computing time on the order of 1 s on a Macintosh IIcx. (The eigenfunction method is slower by a factor 10–20 for single-frequency calculations with this precision.) The advantage of using a nonuniform grid is clearly shown for the prolate case with $\rho = 10$ and $m = 0$; the relative error at $N = 60$ is reduced by a factor 400.

B. Single-exponential approximations

The surface-diffusion correlation functions $g^\text{AM}_m(t)$ may be expressed as superpositions of decaying exponentials as in (4.36). Since $g^\text{AM}_m(t)$ is strictly exponential in the sphere limit (cf. Sec. V B), it may be thought that the sum in (4.36) could be truncated after the first term to give a useful single-exponential approximation to $g^\text{AM}_m(t)$. Such an approximation is, however, of little value since (i) the correlation times $\tau_m^\omega$ in (4.36) cannot be obtained without considerable computational effort, and (ii) the combined relative weight of the discarded terms amounts to 0.25 (somewhat less for $m = 2$) already at an axial ratio $\rho = 2$.

In general, the most useful single-exponential approximation is obtained, not by truncating the infinite series, but by expressing the correlation function as

$$
S^\text{AM}_m(t) = \frac{d^\omega,0}_m \{ \xi(\eta) \} \exp \left[ -\frac{d^\omega,0}_m(0) t / f^\text{AM}_m(0) \right].
$$

This form has the correct limiting values at $t = 0$ and $t \to \infty$.

### Table III. Rate of convergence in computation of $f^\text{AM}_m(\omega = 0)$ using a nonuniform grid.

<table>
<thead>
<tr>
<th>$m$</th>
<th>Prolate</th>
<th>Oblate</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N$</td>
<td>$\rho$</td>
<td>$\gamma$</td>
</tr>
<tr>
<td>10</td>
<td>1.0447</td>
<td>1.0050 (0.9334)</td>
</tr>
<tr>
<td>20</td>
<td>1.0104</td>
<td>1.0067 (0.7399)</td>
</tr>
<tr>
<td>40</td>
<td>1.0223</td>
<td>1.0007 (0.8667)</td>
</tr>
<tr>
<td>60</td>
<td>1.0010</td>
<td>1.0002 (0.9161)</td>
</tr>
<tr>
<td>100</td>
<td>1.0003</td>
<td>1.0000 (0.9571)</td>
</tr>
<tr>
<td>200</td>
<td>1.0001</td>
<td>1.0000 (0.9852)</td>
</tr>
</tbody>
</table>

*The entries in the table give $f^\text{AM}_m(\omega = 0; N)$ divided by the exact value. The numerical calculations were performed with the nonuniform grid (6.1) with optimized $\gamma$ values, except for the values within parentheses, which were obtained using the uniform grid (4.37).
and, moreover, yields the exact zeroth-order moment (i.e., time integral). It may thus be regarded as a time-dependent Padé approximant. Whereas the initial-time correlation functions \( g_0^{M}(0) \) can be expressed in closed form (cf. the Appendix), the zero-frequency spectral densities \( j_0^{M}(0) \) cannot. However, \( j_0^{M}(0) \) can be obtained by simple quadrature as shown in Sec. V A. Here we shall use (6.2) mainly as a reference for examining the deviations of the exact correlation functions from single-exponential behavior.

Figure 4(a) shows the reduced correlation function \( \tilde{g}_0^{M}(t) = g_0^{M}(t)/g_0^{M}(0) \) for prolate axial ratios. The single-exponential approximation (6.2) is seen to be reasonably accurate for \( p = 2 \), but fails badly for \( p = 5 \). Very similar results are obtained in the prolate case for \( m = 1 \) and in the oblate case for all \( m \). However, \( g_2^{M}(t) \) for prolates turns out to be very nearly exponential over the entire range of axial ratios. This is illustrated in Fig. 4(b) for \( p = 5 \). In fact, the reduced correlation function \( \tilde{g}_2^{M}(t) \) is virtually independent of axial ratio for \( p > 3 \) and is then virtually equal to the bracketed expression in (5.23). This point was also made in Sec. V C. Fig. 2 demonstrates the nonobvious fact that (5.24) describes a virtually Lorentzian dispersion and that the reduced spectral density function \( j_2^{M}(\omega)/j_2^{M}(0) \) has practically reached its \( \rho \to \infty \) limit already at \( p = 3 \).

The single-exponential approximation, discussed in Sec. III, for the reorientational correlation functions was derived by Moro and Nordio using a perturbation approach. Interestingly, identical results have been obtained by Szabo using a short-time expansion. While these two approaches are equivalent to first order, the perturbation approach readily yields second-order approximations as needed for the \( n = m = 1 \) spinning mode (cf. (3.3)). Nevertheless, it might be of interest to consider the analogous short-time approximation for the surface-diffusion correlation functions. In place of (6.2), we thus write

\[
\tilde{g}_2^{M}(t) = \tilde{g}_2^{M}(0) \exp \left[ \frac{d}{dt} \ln \tilde{g}_2^{M}(t) \right]_{t = 0},
\]

which is seen to be exact to linear order in time (and, trivially, at \( t \to \infty \)). Differentiating (4.10) with respect to time, substituting (4.17), integrating by parts, and using the initial condition (4.20), we find

\[
\frac{d}{dt} \tilde{g}_2^{M}(t) \mid_{t = 0} = - \frac{D_2}{\sigma^2} \int_0^1 d\eta \left[ \frac{1 - \eta}{\eta} \right] \frac{d}{d\eta} \left[ \frac{d}{d\eta} \tilde{g}_2^{M}(\eta) \right]^2 + \left( \frac{m^2}{\rho^2} \right) \frac{b^2}{1 - \eta^2} \left[ \frac{d}{d\eta} \tilde{g}_2^{M}(\eta) \right]^2.
\]

Using (4.5) and (4.6), the integral in (6.4) can be performed analytically in all cases. For example, in the prolate case, we obtain from (6.1) and (A6a) for the effective correlation time in (6.3)

\[
\tau_0 = \frac{\frac{d}{dt} \ln \tilde{g}_2^{M}(t) \mid_{t = 0}}{105 \rho^2 (\sigma - 2r - r^2) b^2} = \frac{105 \rho^2 (\sigma - 2r - r^2) b^2}{8(3 + 4r^2)(1 - r^2)^3 \sigma D_i}.
\]

Under conditions where the true correlation function is single exponential, (6.3) is obviously exact. The usefulness of the corresponding approximation in the reorientational problem derives from the fact that these correlation functions are single exponential in the limit of vanishing orientational order and in the limit of complete order. In contrast, the surface-diffusion correlation functions are single exponential only in the sphere limit and, consequently, the approximation defined by (6.3) and (6.4), which may be regarded as a first-order shape perturbation on the sphere limit, is of marginal interest. While it has the advantage of analytical simplicity, it yields respectable accuracy only very close to the sphere limit. [In particular, it is much less accurate than the integral approximation (6.2).] As an example, for a prolate spheroid of axial ratio \( \rho = 1.1 \), the exact \( g_2^{M}(t) \) has a relative weight of 0.994 for the first exponential in (4.36) with correlation time \( \tau_2 = 1.110 \) [in units of \( b^2 / (6D_i) \)]. The integral approximation (6.2) yields \( \tau_0 = j_0^{M}(0)/j_2^{M}(0) = 1.014 \), while the perturbation approximation (6.5) yields \( \tau_0 = 1.094 \).

C. Shape dependence of the zero-frequency spectral densities

Figure 5 summarizes the shape dependence of the six different zero-frequency spectral densities \( j_0^{M}(0) \) in the
range of axial ratios where the spheroidal-aggregate model is thought to be physically relevant. Two different cases are considered: (i) increasing $\rho$ while keeping the minor semiaxis $b$ fixed (as in the growth of an originally spherical surfactant micelle$^{27}$), and (ii) increasing $\rho$ while keeping the aggregate volume fixed (as in the deformation of an originally spherical microemulsion droplet$^{28}$). It is helpful to regard $j^M_m(0)$ as the product of the mean-square fluctuation $g^M_m(0)$ and an effective correlation time (the time integral of the reduced correlation function). The former is independent of the absolute dimensions of the spheroid and, hence, the same in cases (i) and (ii).

In the limit $\rho \to \infty$, all the $g^M_m(0)$ vanish, except $g^M_2(0)$ for prolates which tends to $3/8$ (cf. Sec. V and the Appendix). As for the six zero-frequency spectral densities $j^M_m(0)$, all but two vanish in the limit $\rho \to \infty$. As we approach the needle limit of the prolate spheroid (Sec. V C), the effective correlation time in $j^M_2(0)$, which essentially describes "azimuthal" surface diffusion, tends to a constant value and $j^M_2(0)$ approaches a value which is a factor $135/64 \approx 2.11$ larger than for the sphere. This limiting result is accurate to better than 5% for $\rho > 5$. The other nontrivial limit is the disk limit of the oblate spheroid (Sec. V D), where the effective correlation time diverges in such a way as to give a finite $j^M_1(0)$; a factor $5/2$ larger than for the sphere. It is seen that this limiting value is approached from above, after going through a maximum at $\rho \approx 6$, and that the limiting result is accurate to better than 7% for $\rho > 2.5$.

The $m = 0$ spectral densities are only affected by "polar" surface diffusion (modulation of $\theta_M$). The pronounced maximum in $j^M_0(0)$ for oblates growing at fixed $b$, due to a sharp increase in the effective correlation time, may be exploited as a convenient signature of that geometry. The qualitatively different behavior of $j^M_m(0)$ for prolates and oblates in case (i) is, of course, mainly due to the fact that the oblate grows in two dimensions while the prolate is extended in only one dimension. The differences in $j^M_m(0)$ between prolates and oblates are generally smaller in case (ii), but the nonzero needle limit of $g^M_2(0)$ is still reflected in $j^M_2(0)$ for prolates.

VII. SELECTED APPLICATIONS

The present theoretical description of the effect on nuclear spin relaxation of aggregate reorientation and molecular surface diffusion encompasses a rich diversity of behavior, ranging from isotropic solutions to perfectly ordered liquid crystals, from a static surface distribution to rapid translational averaging, and from spherical to extended disk-like or needle-like aggregates. Here we cannot explore the full range of this behavior, but shall merely present two specific examples, both taken from the field of surfactant physical chemistry, of situations where the present theory can be used to extract valuable molecular-level information from nuclear spin-relaxation data.

A. Nematic lyotropic liquid crystals

A variety of surfactant systems exhibit nematic liquid-crystalline phases, which are macroscopically aligned by the magnetic torque exerted by the polarizing $B_0$ field used in NMR experiments. The two most widely occurring uniaxial nematic phases (usually denoted $N_c^+$ and $N_c^-$) are believed to be composed of either prolate spheroidal aggregates aligned with the field or oblate micelles with their symmetry axis orthogonal to the field. The present theory is well suited to describe the spin relaxation of surfactant-bound or counterion nuclei in such nematic phases. In fact, our current spin-relaxation studies of lyotropic nematics$^{39}$ provided the impetus for this work.
FIG. 6. Shape dependence of the lab-frame spectral densities for surface diffusion on spheroidal aggregates in idealized nematic phases. The axial ratio is varied at fixed minor semiaxis. The diffusional time scale is fixed at $\frac{6}{D}$, $\tau_0 = 10$ ns and the angular Larmor frequency is $\omega = 0.1665$ rad ns$^{-1}$. (These values are appropriate for Na$^+$ counterions in a $B_0$ field of 2.3 T.)

Since the effects of molecular surface diffusion are likely to dominate over the effects of restricted reorientation of the highly ordered micelles, we idealize this illustrative example by neglecting the latter effects. We thus consider a nematic phase composed of uniformly oriented, immobile spheroids. We assume that the three distinct lab-frame spectral densities $j_k^M(k\omega_0)$ have been determined by an appropriate combination of spin-relaxation experiments. According to (2.10)–(2.14), we then have for micelles oriented parallel to the $B_0$ field

$$j_k^M(k\omega_0) = j_k^M(k\omega_0),$$

and for micelles oriented perpendicular to the field

$$j_0^M(0) = \frac{1}{2} [j_{4/2}^{AM}(0) + 2j_2^{AM}(0)],$$

$$j_1^M(\omega_0) = \frac{1}{4} [j_{1/2}^{AM}(\omega_0) + j_{1/2}^{AM}(\omega_0) + j_{1/2}^{AM}(\omega_0)] + j_{2/2}^{AM}(\omega_0),$$

$$j_2^M(2\omega_0) = \frac{1}{2} [j_{2/2}^{AM}(2\omega_0) + j_{2/2}^{AM}(2\omega_0) + j_{2/2}^{AM}(2\omega_0)].$$

The shape (or size) dependence of the lab-frame spectral densities predicted for the idealized nematic phases are shown in Fig. 6. It is seen that this dependence is rather strong in the most interesting range $\rho < 5$, suggesting that the micelle size may be determined rather accurately from spin-relaxation data. Two qualitative features are noteworthy: (i) the inequality $j_2^M(2\omega_0) > j_0^M(\omega_0)$ for prolate spheroids (except very close to the sphere limit), and (ii) the pronounced maximum in $j_0^M(0)$ for oblate spheroids. The former constitutes a useful signature of the $\mathcal{N}$ phase, while the latter may be used as a simple indicator of micelle size ($\rho < 2$ or $\rho > 3$) by measuring the temperature dependence of $j_0^M(0)$. A complete analysis, incorporating also the partial orientational disorder and the restricted rotational diffusion of the micelles, is somewhat more involved, but can be carried out entirely within this theoretical framework presented here. In addition to providing the micelle size, such an analysis could yield valuable dynamic information, e.g., the lateral diffusion coefficient of the spin-bearing molecule or ion.

### B. Isotropic micellar solutions

In isotropic systems, where the tensorial spin-lattice coupling is isotropically averaged by sufficiently fast motions, there is only one lab-frame spectral density function. According to (3.6)

$$j_k^M(\omega) = \frac{1}{2} S_{AM}^2 \frac{\tau_0}{1 + (\omega \tau_0)^2} + \frac{1}{2} \sum_{m=0}^{2} (2 - \delta_m)$$

$$\times \int_0^{\infty} dt \cos(\omega t) \exp(-t/\tau_m) g_m^{AM}(t).$$

where the symmetric top correlation times $\tau_m$ are related to the rotational diffusion coefficients $D_\parallel$ and $D_\perp$ through (3.5).

In the sphere limit, (3.5) and (5.14) show that (7.3) reduces to the Lorentzian

$$j_k^M(\omega) = \frac{1}{2} \frac{\tau_0}{1 + (\omega \tau_0)^2},$$

with the joint correlation time $\tau_\alpha$ being related to the rotational-diffusion correlation time $\tau_\alpha$ and the surface-diffusion correlation time $\tau_s$ by

$$\frac{1}{\tau_\alpha} = \frac{1}{\tau_\alpha} + \frac{1}{\tau_s},$$

$$\frac{\tau_\alpha}{1} = \frac{4\pi n b^3}{3k_B T},$$

As compared to nematic liquid crystals, isotropic systems pose a more difficult interpretational problem since the three surface-diffusion correlation functions $g_m^{AM}(t)$ are inextricably mixed in (7.3). A unique molecular-level interpretation, therefore, usually requires spin-relaxation studies over an extended frequency range. Typically, one measures the dispersion of the longitudinal relaxation rate $R_1(\omega_0)$, which, in the case of exponential quadrupolar relaxation, may be decomposed as

$$R_1(\omega_0) = R_{int} + C [j_0^M(\omega_0) + j_1^M(2\omega_0)],$$

where $R_{int}$ is the contribution from "internal" motions which are assumed to be much faster than the motions described by (7.3) and also much faster than the Larmor frequency $\omega_0$ of interest. The constant $C$, which is proportion


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al to the square of the residual quadrupole coupling constant, will not concern us here.

Surfactant aggregates in micellar solutions are believed to adopt more or less spheroidal shapes under certain conditions. It is therefore of interest to examine how relatively small deviations from spherical shape are reflected in the shape of the frequency dispersion (7.8). We have thus computed, for a few typical cases, the joint spectral density function (7.3), with the rotational diffusion coefficients for the spheroid given by the Perrin equations, and then plotted the resulting frequency dispersion of \( R_1(\omega_0) - R_{\text{int}} \) as given by (7.8).

The results are shown in Fig. 7, where we have taken \( \tau_{sd} = 20 \) ns (which corresponds to a spherical micelle of radius \( \approx 2.5 \) nm) and \( \tau_{rd} = 1 \) or 100 ns (corresponding to surface diffusion coefficients, \( D_s \approx 10^{-9} \) or \( 10^{-11} \) m\(^2\) s\(^{-1}\), typical of counterners and surfactants, respectively). The dashed curves refer to a spherical micelle, while the solid curves refer to a prolate spheroidal micelle of axial ratio \( \rho = 1.3 \). The corresponding dispersion curves for oblate spheroids have closely similar shape, but are slightly displaced towards lower frequencies.

The shape of the dispersion curve is completely determined by the axial ratio and the ratio \( \tau_{sd}/\tau_{rd} \) (the change in the dispersion shape is thus the same for deformation at constant volume as for growth of the major semiaxis), while the magnitude of either correlation time determines the location of the dispersion curve on an absolute frequency scale. Now if \( \tau_{sd} \approx \tau_{rd} \), as for surfactant-bound nuclei, then micelle rotation is more important than surface diffusion. The shape of the \( R_1 \) dispersion is then rather insensitive to the axial ratio. This is particularly true for oblate spheroids, where \( \mathcal{U}_b \) and \( D_s \) differ by less than 25% for all axial ratios. However, for relatively eccentric prolaters (say \( \rho > 3 \)), \( D_s \) is considerably smaller than \( \mathcal{U}_b \) and the dispersion curve develops a high-frequency tail. If, on the other hand, \( \tau_{sd} < \tau_{rd} \), as for countermion nuclei, then surface diffusion and micelle rotation give rise to distinct dispersion steps. [While conventional NMR spectrometers only provide access to the frequency range 1–100 MHz for typical quadrupolar nuclei, the magnitude of the low-frequency step can be inferred from measurements of the transverse relaxation rate \( R_2 \), which involves the zero-frequency spectral density \( f' \).] Figure 7 shows that the departure from a Lorentzian dispersion can be substantial already at \( \rho = 1.3 \). For a prolate micelle, this corresponds to an increase in the aggregation number by 30%. While changes in aggregation number of this order of magnitude can probably be determined by other techniques, such as fluorescence quenching and neutron scattering, nuclear spin relaxation appears to be a unique method for revealing small deviations from spherical shape.

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APPENDIX: ORDER PARAMETERS AND MEAN-SQUARE FLUCTUATIONS FOR SURFACE DIFFUSION ON A SPHEROID

For reference purposes, we collect here some analytical results for static properties that are used in the main text. The second- and fourth-rank order parameters for surface diffusion are

\[
S_{AM} = \langle P_2(\cos \theta_{AM}) \rangle = \frac{1}{2} (\xi^2 - 1),
\]

\[
Q_{AM} = \langle P_4(\cos \theta_{AM}) \rangle = 3 \xi (\xi^4 - 10 \xi^2 + 3),
\]

where \( \xi = \cos \theta_{AM} \). From (4.5) and (4.8),

\[
(\xi^k)_{pr} = \frac{\mathcal{R}(\sigma - 2r)}{(1 - r^2)\sigma},
\]

\[
(\xi^2)_{ob} = \frac{2 - \sigma}{(1 - r^2)\sigma},
\]

\[
(\xi^4)_{pr} = \frac{r^2(2 + 4\sigma^2 - 3r^2)}{(1 - r^2)^2\sigma},
\]

\[
(\xi^4)_{ob} = \frac{4 + 2r^2 - 3\sigma}{(1 - r^2)^2\sigma},
\]

Combination of (A1a) and (A3) yields for the second-rank order parameter

\[
S_{AM}^{pr} = \frac{4r^2 - 6\sigma^2 - 2\sigma}{(1 - r^2)^2\sigma},
\]

\[
S_{AM}^{ob} = \frac{6 - 4\sigma + \rho^2 \sigma}{(1 - r^2)^2\sigma},
\]

in agreement with previous work. The initial-time correlation functions are obtained by inserting \( \alpha_m \) and \( \beta_m \) from (2.13), \( S_{AM} \) from (A5), and \( Q_{AM} \) as given by (A1b), (A3), and (A4), into (2.22). The results are

\[
[\xi^m(0)]_{pr} = \frac{9r^2(\sigma - 2r - r^2)}{2(1 - r^2)^2\sigma^2 - 7},
\]

FIG. 7. Normalized frequency dispersion of isotropic longitudinal relaxation rate due to surface diffusion on freely rotating spheres (dashed curves) and prolate spheroids of axial ratio \( \rho = 1.3 \) (solid curves). The rotational correlation time is \( \tau_{rd} = 20 \) ns.
\[ [g_1^{Ab}(0)]_c = \frac{9[r^2\sigma - 2(\sigma - 1)^2]}{2(1 - r^2)^2\sigma}, \quad (A6b) \]

\[ [g_1^{Ab}(0)]_r = \frac{3r^2[1 + 2\sigma(1 + 2r^2)]}{2(1 - r^2)^2\sigma}, \quad (A7a) \]

\[ [g_2^{Ab}(0)]_c = \frac{3(2 + r^2)\sigma - 2(1 + 2\sigma)}{2(1 - r^2)^2\sigma}, \quad (A7b) \]

\[ [g_2^{Ab}(0)]_pr = \frac{3[6r^3 - (4r^3 - 1)\sigma]}{8(1 - r^2)^2\sigma}, \quad (A8a) \]

\[ [g_2^{Ab}(0)]_c = \frac{3r^2[6 - (4 - r^2)\sigma]}{8(1 - r^2)^2\sigma}. \quad (A8b) \]

20. B. Halle, Mol. Phys. 61, 963 (1987). In this work the metric coefficients are not correctly placed in the surface-diffusion equation. The consequent errors in the spectral density functions are relatively small, except for the case \( m = 0 \). Thus, in Fig. 6, the \( m = 1 \) dispersion should not cross the \( m = 0 \) dispersion, but should always be below (prolate) or above (oblate) the latter. However, all results for static averages and for the limits of fast and slow surface diffusion are unaffected by the error in the diffusion equation.
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