Theory of intramolecular spin relaxation by translational diffusion in locally ordered fluids

I. Continuum diffusion versus discrete-state exchange in systems with planar interfaces

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In locally ordered fluids, such as macromolecular solutions, clays and lyotropic liquid crystals, nuclear spin relaxation can be induced by modulation, through translational diffusion of the fluid molecules, of the magnitude and orientation of the residual intramolecular spin-lattice coupling tensor, which is only partially averaged by local molecular motions near an interface. A theory of spin relaxation in locally ordered fluids bounded by planar interfaces is developed, with special emphasis on effects of translational diffusion. The theory is based on a continuous diffusion model (CDM) which, in contrast to the commonly adopted discrete exchange model (DEM), treats equilibrium and time-dependent distribution functions in a self-consistent way. A striking feature of translational diffusion in heterogeneous systems is the abundance of reencounters with previously visited interracial regions. It is demonstrated that these diffusional reencounters, which are inherent in the CDM theory, may lead to a relaxation behaviour which is qualitatively different from that predicted by the DEM theory. Furthermore, it is seen that the widespread concept of intrinsic relaxation rate (associated with a spatial region) and the fast/slow exchange classification are not generally valid. The formal framework of the CDM theory allows molecular interactions of any complexity to be introduced. In this paper a mean-field model based on the nonlinear Poisson–Boltzmann equation is used to obtain analytic expressions for the spectral density functions that determine the relaxation behaviour in the presence and in the absence of spectral line splittings.

1. INTRODUCTION

During the past 15 years nuclear spin relaxation has emerged as a powerful technique for unravelling the structure and dynamics of complex molecular systems. Solutions of macromolecules or amphiphilic aggregates, clays, lyotropic liquid crystals, protein crystals, oriented polymers and intact biological tissue have all been subjected to extensive spin relaxation studies. A common feature of these diverse systems is that the molecules in the fluid regions experience a locally ordered environment created by the anisotropic interactions in the vicinity

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The theory of nuclear spin relaxation may be divided into three stages as shown in figure 1. Starting with a model for the relevant intermolecular forces and structural features of the system, the methods of statistical mechanics are used to construct certain equilibrium and time-dependent distribution functions. In the next stage the fluctuating spin-lattice coupling is averaged over these distribution functions. This results in a time autocorrelation function and, by way of a Fourier transform, a spectral density function. In the third stage the macroscopic response of the spin system to various kinds of externally applied perturbations is related to the structure and dynamics of the molecular system. A general solution to this problem is available only in the so-called perturbation regime (also referred to as the motional narrowing regime), where time-dependent second-order perturbation theory can be used to express the various experimentally accessible relaxation rates in terms of the spectral density function. The perturbation regime is defined by the condition that all molecular fluctuations are fast compared to the spin relaxation which they induce [1, 2].

In N.M.R. studies of locally ordered fluids one encounters two qualitatively different cases within the perturbation regime. We shall refer to these cases as systems with long-range order and systems with medium-range order [3]. Strictly speaking this is an operational classification; it refers to the N.M.R. properties of certain nuclear spins in the system. Not only the spatial extension of
ordered structures, but also the molecular dynamics, the magnitude of the spin–lattice coupling, etc. determine whether a system is classified as having long-range or medium-range order in this sense.

In systems with long-range order the degenerate N.M.R. spectrum is split into two or more lines, the spacing of which is proportional to the residual, locally averaged, static spin–lattice coupling and which contains information about the extent of preferential orientation with respect to the interface. In systems with medium-range order this static coupling is eliminated by molecular motions which completely randomize the orientation of the residual coupling tensor with respect to a laboratory-fixed frame. While these motions must be fast compared to the frequency of the residual coupling which they modulate, they are nevertheless much slower than the typical local motions in the interfacial region. As a consequence, the orientational correlation function exhibits a slowly decaying tail, which may or may not be exponential and which often dominates the spin relaxation behaviour. The crucial importance of local order (and the consequent anisotropy) in determining the N.M.R. properties of complex systems was emphasized by Berendsen and Edzes [3] in connection with $^{23}$Na N.M.R. studies on biological material. A general theoretical foundation for nuclear spin relaxation in locally ordered systems was laid down ten years ago by Wennerström et al. [4] and later elaborated with special reference to water nuclei [5]. Theoretical work in this area has been reported also by Packer et al. [6, 7], Woessner [8] and Burnell et al. [9].

The long-time tail of the orientational correlation function in systems with medium-range order is typically associated with aggregate reorientation and/or translational diffusion of the spin–bearing species among differently oriented interfacial regions (on the same or on different aggregates). The effect of translational diffusion on spin relaxation is most naturally introduced at stage I (cf. figure 1) via a continuous diffusion equation. This is the standard approach in the theory of spin relaxation through modulation of the intermolecular magnetic dipole–dipole coupling in simple fluids [1]. However, in the case of spin relaxation through modulation of the intramolecular residual coupling (magnetic dipole–dipole or electric quadrupole) in locally ordered fluids, this approach has not been pursued. Instead one has taken over and extended the longstanding terminology and concepts developed in connection with N.M.R. studies of chemical exchange processes.

The study of the kinetics of chemical exchange processes, such as proton transfer, ligand exchange and conformational equilibria, is one of the earliest and most fruitful chemical applications of the N.M.R. technique. Theories that link the N.M.R. spectral lineshape to the rate parameters have been developed on the basis of the Bloch equations [10–12] and, for the case of negligible chemical shift differences, from the general theory of stochastic processes [13]. With locally ordered systems in mind, the chemical exchange theory has been generalized to multexponentially relaxing nuclei with spin quantum number $I \geq 3/2$ [14, 15] including also dynamic shift effects [15].

The chemical exchange theories mentioned so far are all based on the assumption that the exchange is slow compared to the local molecular motions which are responsible for the intrinsic spin relaxation rate in each site. The chemical exchange effects can then be incorporated at stage III of figure 1. When the mean residence time of a nucleus in a particular site is not long compared to the
correlation times characterizing the local motions in that site, then it is no longer possible, in general, to define an intrinsic relaxation rate and the chemical exchange must be introduced already at stage I. This has been done in several ways \[16-19\], but only under rather restrictive assumptions.

The transplantation of the chemical exchange theory, as outlined above, from its native domain of elementary processes in simple fluids to the considerably more complex situation of translational diffusion in locally ordered fluids is, as might be expected, not without its problems. In this approach, which we shall label the discrete exchange model (DEM), the translational diffusion process is modelled as a markovian (uncorrelated) random walk among discrete states (or sites). In the simplest version, only two discrete states are distinguished: an unperturbed bulk region, with the properties of a simple fluid, and a perturbed interfacial region, in which the rate of local motions as well as the magnitude of the locally averaged residual spin–lattice coupling may differ from the bulk region. These two states are often loosely referred to as ‘free’ and ‘bound’.

According to the two-state DEM theory, the spin relaxation rate in a system with medium-range order may be written, in the typical fast-exchange regime, as a population-weighted average,

$$R = P_F R_F + P_B R_B,$$

where $P_B (=1-P_F)$ is the probability of finding a given nuclear spin in the perturbed (or ‘bound’) state and where $R_F$ and $R_B$ are the intrinsic relaxation rates in the two states. In the DEM a spin which resides just outside the perturbed region is dynamically equivalent to one that is far removed from any interface and the translational diffusion process is fully characterized by the mean residence time, $\tau_B$, in the perturbed state. Furthermore, in the case of systems with medium-range order, it is invariably assumed that the orientational correlation induced by the surface is irretrievably lost at the moment the spin leaves the perturbed region. Were it not for this assumption, it would not be possible to express the relaxation rate in terms of intrinsic rates as in (1.1). The long-time tail of the orientational correlation function for the perturbed state now decays exponentially with an effective correlation time, $\tau^*_B$, given by \[18, 19\]

$$\frac{1}{\tau^*_B} = \frac{1}{\tau_B} + \frac{1}{\tau_r},$$

where $\tau_r$ is the correlation time for aggregate reorientation (here taken to be isotropic).

There are two prominent differences between the simple fluids for which the chemical exchange theories were originally developed and the more complex locally ordered fluids of interest here. The first difference pertains to the nature of the sites or states. The early N.M.R. studies of chemical exchange processes were usually concerned with stoichiometrically well-defined sites created by strong specific forces of short range, often of a covalent nature. In locally ordered fluids, on the other hand, one is usually dealing with exchange between much less well-defined regions of space. However, if the surface-induced orientational perturbation is short-ranged (a few solvent diameters), it is reasonable to approximate its continuous decay by a step function defining two discrete states.

The second major difference between simple and locally ordered fluids has more far-reaching consequences for the spin relaxation behaviour. In the DEM,
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Figure 2. Sample trajectory of an unbiased random walk on a one-dimensional lattice with a reflecting barrier. Each of the six consecutive strips records the position (40 lattice sites shown) during 400 steps.

with its postulate of complete randomization of the residual spin–lattice coupling upon exchange, one does not take into account that a spin which has left the perturbed state always has a finite probability of returning, thus delaying the loss of orientational correlation with the interface. The effect of site reencounters is not important in simple fluids, in which reorientation is sufficiently fast to randomize the orientation before any reencounters have occurred. However, if the fluid contains relatively immobile macromolecules or large molecular aggregates there is ample time for reencounter events to affect the slowly decaying correlation function. Furthermore, the large aggregate size and, in the case of counterions, the Coulomb interaction, vastly enhance the reencounter probability. As a simple illustration of the effect of aggregate size, we show in figure 2 a segment of an unbiased random walk starting at a planar reflecting interface. Note that during the time it takes the diffusing particle to explore the available space, and thus become spatially randomized, a large number of surface reencounters take place. The reencounter problem for counterion diffusion in a mean electrostatic potential given by the Poisson–Boltzmann (PB) equation has recently been studied for several surface geometries [20].

As the spin–bearing species diffuses back and forth between the perturbed and unperturbed states, the locally averaged residual spin–lattice coupling fluctuates in time. Translational diffusion thus becomes a relaxation mechanism in locally ordered fluids. For systems with long-range order this contribution to the spin relaxation has been treated within the DEM by assuming that the orientational correlation with the interface is retained on exchange [4–6, 9]. However, because of the assumption that all spins in a given state are dynamically equivalent, the DEM results are not generally valid.

In the case of systems with medium-range order, the effects of translational diffusion on the spin relaxation have been treated in an even cruder way in the DEM, namely by stipulating that the orientational correlation with the interface is completely lost on exchange. The dynamical description is thus truncated after
the first exchange event and all subsequent reencounters are neglected. In this approximation, the only effect of the diffusional modulation of the residual spin–lattice coupling is a shortening of the effective correlation time in equation (1.2). However, because of the reencounters the time required for randomization of the residual spin–lattice coupling by translational diffusion may be orders of magnitude longer than the mean residence time, \( \tau_B \), in the perturbed state. Consequently, the DEM result (1.2) may be grossly inaccurate. We are thus in a curious situation in which reencounter effects have been treated crudely for systems with long-range order, where, as we shall see, they usually are of minor importance, while they have been completely neglected for systems with medium-range order, where they may dominate the relaxation behaviour.

The purpose of the present work is to replace the DEM by a more realistic continuous diffusion model (CDM), in which the translational diffusion of the spin–bearing species is governed by the Smoluchowski diffusion equation \([20, 21]\). A peculiar, and potentially confusing, feature of the DEM is that effects of translational diffusion are incorporated into the relaxation theory at stage III as well as at stage I (cf. figure 1), corresponding to the state averaging in (1.1) and the effective correlation time in (1.2), respectively. In contrast, by introducing translational diffusion explicitly at the correlation function level, the CDM theory treats all effects of translational diffusion self-consistently. Since the reencounter events are fully included in the CDM, the correlation function becomes non-local in space. As a consequence, it is not possible to define intrinsic relaxation rates for each state as in (1.1).

The mean residence time, \( \tau_B \), of the DEM is replaced in the CDM by the parameters that enter into the diffusion equation and its associated boundary conditions, namely the self-diffusion coefficient of the spin–bearing species, the effective potential experienced by the diffusing species and the geometry of the diffusion space. In the CDM the geometry of the fluid region and the potential of mean force acting on the spin–bearing species determine the equilibrium distribution of spins (characterized by \( P_n \) in a two-state model) as well as their translational dynamics. This internal consistency is lacking in the DEM.

In this paper we develop the CDM theory of nuclear spin relaxation in locally ordered fluids with planar interfaces. The theory is restricted to the case of intramolecular spin–lattice coupling, which includes the electric quadrupole coupling as well as the intramolecular part of the magnetic dipole–dipole coupling. Examples of systems with long-range order and planar interfaces include clays and lamellar lyotropic mesophases, both of which have been thoroughly investigated by N.M.R. techniques. Systems with medium-range order and planar interfaces are less common in practice. However, our main motivation for treating this case in detail is pedagogical. Being free from the complications associated with the additional diffusional degrees of freedom in cylindrical and spherical geometry, the treatment of the planar case clearly brings out the essential difference between the DEM and the CDM. Furthermore, for planar geometry the diffusion equation can be solved analytically in terms of elementary functions. This is true not only for free diffusion (zero mean field) but also in the case of counterions subject to the mean electrostatic potential derived from the nonlinear PB equation \([20]\).

We begin by deriving formal expressions for the appropriate time correlation functions in terms of the equilibrium distribution function, \( f(x) \), and the trans-
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lational diffusion propagator, \( f(x, t | x_0) \). This is stage II of figure 1. Systems with long-range and medium-range order are treated in §§2 and 3, respectively. The results obtained are quite general in that they are valid for any model of the intermolecular forces in the system. Stage I is addressed in §4, where we present the equilibrium distributions and diffusion propagators for the appropriate boundary conditions and for two extreme interaction models: the field-free case (relevant to water nuclei, for example) and the no-salt PB mean field case (relevant to counterion nuclei). In the next two sections we substitute the analytic results for \( f(x) \) and \( f(x, t | x_0) \) into the formal expressions for the correlation functions thus obtaining explicit results for the two interaction models. This enables us to make a detailed comparison of the spectral density functions predicted by the DEM and CDM theories. Next comes a discussion of the approximations inherent in the CDM theory, followed by a summary of the main conclusions of the present work.

2. FORMAL RESULTS FOR SYSTEMS WITH LONG-RANGE ORDER

In this section we derive formal expressions for the time auto-correlation functions

\[
G_k(t) \equiv \langle \hat{V}_L^*(0) \hat{V}_L^L(t) \rangle, \quad k = 0, 1, 2, \tag{2.1}
\]

which govern the spin relaxation behaviour in the presence of a static coupling. \( \hat{V}_L(t) \) is the \( k \)th spherical component, expressed in a lab-fixed frame (L), of the second-rank irreducible coupling tensor \( \mathbf{V} \). The quantity appearing in (2.1) is that part of \( \hat{V}_L(t) \) which fluctuates at a rate which is higher than the static coupling frequency, i.e.

\[
\hat{V}_L(t) \equiv V_L(t) - \langle V_L \rangle. \tag{2.2}
\]

The coupling tensor \( \mathbf{V} \) is usually specified in its principal frame (P), where it is diagonal. We therefore transform the components \( V_L(t) \) to this frame by means of the second-rank Wigner rotation matrix \( \mathbf{D}^2(\Omega) \). In order to separate contributions to \( G_k(t) \) from various molecular degrees of freedom, it is convenient to carry out this transformation via the director frame (D), the z-axis of which is perpendicular to the planar interface (see figure 3). For the successive transformations \( L \rightarrow D \rightarrow P \), we have [22]

\[
V_L(t) = \sum_m \sum_n D_{km}^2(\Omega_{LD}) D_{nm}^2(\Omega_{DP}) \langle V^P_m \rangle \Gamma(t) \tag{2.3}
\]

where the sums run from \(-2\) to \(+2\). By means of these transformations, we have factorized the time dependence in \( V_L(t) \) into two sets of stochastic variables: the three Euler angles \( \Omega_{DP}(t) \), specifying the instantaneous orientation of the P frame with respect to the interface, and the state variable \( \Gamma(t) \). For simplicity, we consider only two discrete states: a perturbed state, which extends a distance \( \delta \) out from either interface, and an unperturbed state, which encompasses the rest of the system (see figure 3). Mainly for historic reasons, we denote the states by \( B \) and \( F \), respectively. The random variable \( \Gamma \) has the effect of ‘switching on’ different distribution functions (see below) depending on the instantaneous x-coordinate of the spin: inside \((2b - \delta < x < \delta)\) or outside \((\delta < x < 2b - \delta)\) the perturbed B state. The \( \Gamma \)-dependence in (2.3) also accounts for any differences between the two states in the magnitude of the instantaneous spin–lattice coup-
Figure 3. The fluid region between two parallel planar surfaces is divided into two identical cells by the symmetry plane at $x = b$. Each cell is subdivided into a $B$ state, extending a distance $\delta$ from the surface, and an $F$ state.

We assume that the Euler angles $\Omega_{L0}$ are time-independent, as indicated in (2.3).

The correlation function $G_k(t)$ involves averages over the joint equilibrium probability density and over the joint transition probability density for the stochastic variables $\Omega_{DP}$ and $\Gamma$. The equilibrium probability density may be written

$$f(\Omega_{DP}, \Gamma) = f(\Omega_{DP}|\Gamma)P(\Gamma),$$

indicating that the orientational distribution function for the $P$ frame with respect to the interface depends on $\Gamma$. $P(\Gamma)$ is the probability of finding a given spin in state $\Gamma$. The quantities appearing in (2.4) are normalized according to

$$\int d\Omega_{DP} f(\Omega_{DP}|\Gamma) = 1,$$

$$\sum_{\Gamma} P(\Gamma) = P_F + P_B = 1.$$  

We assume that the fluctuations in $\Omega_{DP}(t)$ occur on a much shorter timescale than those in $\Gamma(t)$. As a consequence of this timescale separation, the joint transition probability density factorizes as

$$f(\Omega_{DP}, \Gamma; t|\Omega_{DP0}, \Gamma^0) = f(\Omega_{DP}; t|\Omega_{DP0}; \Gamma^0)P(\Gamma; t|\Gamma^0),$$

where a superscript zero denotes the initial value of the respective variable. As indicated in (2.7), the rate of reorientation of the $P$ frame is state-dependent. It may be noted that (2.7) reduces to (2.4) in the limit $t \to \infty$.

Because of the timescale separation, it is convenient to divide $\bar{V}_k^L(t)$ into two parts as

$$\bar{V}_k^L(t) = V_{kF}^L(t) + V_{ks}^L(t),$$

with

$$V_{kF}^L(t) \equiv \bar{V}_k^L(t) - V_{ks}^L(t),$$

$$V_{ks}^L(t) = \int d\Omega_{DP} f(\Omega_{DP}|\Gamma)\bar{V}_k^L(t).$$
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The averaging in (2.10) over the rapidly fluctuating variable $\Omega_{DP}$ ensures that $V_{ks}(t)$ contains only the slow time dependence associated with $\Gamma$. The static coupling appearing in (2.2) is obtained by averaging over $\Omega_{DP}$ as well as over $\Gamma$

$$\langle V_k \rangle \equiv \sum P(\Gamma) \int d\Omega_{DP} f(\Omega_{DP} | \Gamma) V_k^L(t).$$

(2.11)

With the reasonable assumption that $f(\Omega_{DP} | \Gamma)$ possesses at least threefold rotation symmetry with respect to the director (the $z_0$-axis), equations (2.2), (2.3) and (2.9)–(2.11) yield

$$\langle V_k \rangle = D_{\Omega_{LD}}^2(\Omega_{LD}) P_B \tilde{V}_B,$$

(2.12)

$$V_{kj}(t) = \sum_m D_{\Omega_{LD}}^2(\Omega_{LD}) \left\{ \sum_m D_{\Omega_{DP}}^2(\Omega_{DP}) [\Gamma(t)] - \delta_{m0} \tilde{V}[\Gamma(t)] \right\},$$

(2.13)

$$V_{ks}(t) = D_{\Omega_{LD}}^2(\Omega_{LD}) [\tilde{V}[\Gamma(t)] - P_B \tilde{V}_B],$$

(2.14)

where we have introduced the locally averaged residual coupling in state $\Gamma$

$$\tilde{V}(\Gamma) \equiv \sum_m \langle D_{\Omega_{DP}}^2(\Omega_{DP}) \rangle_\Gamma \tilde{V}_m^L(\Gamma).$$

(2.15)

In the unperturbed state, $f(\Omega_{DP} | F) = 1/(8\pi^2)$ by definition so that $\tilde{V}_F = 0$, which was used in obtaining (2.12). We note that, even if the principal components $V_{m}^L$ are independent of $\Gamma$, the residual coupling $\tilde{V}(\Gamma)$ will still depend on $\Gamma$ via the orientational distribution function $f(\Omega_{DP} | \Gamma)$.

The correlation function $G_k(t)$ may be expressed as

$$G_k(t) = \int d\Omega_{DP} f(\Omega_{DP}, \Gamma) V_{ks}(\Omega_{LD}, \Omega_{DP}, \Gamma)$$

(2.16)

$$\sum_{\Gamma} \int d\Omega_{DP} f(\Omega_{DP}, \Gamma; t | \Omega_{DP}, \Gamma) V_{ks}^L(\Omega_{LD}, \Omega_{DP}, \Gamma).$$

Because of the statistical independence of the fluctuations in $\Omega_{DP}(t)$ and $\Gamma(t)$, as expressed by (2.7), the cross-correlations between $V_{kj}(t)$ and $V_{ks}^L(t)$ vanish and $G_k(t)$ may be written as a sum of two independent parts [23]

$$G_k(t) = G^0_k(t) + G^0_{k}(t),$$

(2.17)

where

$$G^0_k(t) \equiv \langle V_{kj}^{A}(0) V_{kj}^L(t) \rangle$$

$$= \sum_{\Gamma} P(\Gamma) \int d\Omega_{DP} f(\Omega_{DP}, \Gamma) V_{kj}^{A}(\Omega_{LD}, \Omega_{DP}, \Gamma)$$

(2.18)

$$\times \int d\Omega_{DP} f(\Omega_{DP}, t | \Omega_{DP}, \Gamma) V_{kj}^{L}(\Omega_{LD}, \Omega_{DP}, \Gamma),$$

and

$$G^0_k(t) \equiv \langle V_{ks}^{A}(0) V_{ks}^L(t) \rangle$$

$$= \sum_{\Gamma} P(\Gamma) V_{ks}^{L}(\Omega_{LD}, \Gamma) \sum_{\Gamma} P(\Gamma; t | \Gamma) V_{ks}^{L}(\Omega_{LD}, \Gamma).$$

(2.19)
In deriving (2.17)–(2.19), we made use of equations (2.1), (2.4) and (2.7)–(2.10). The ‘fast’ correlation function, \( G_f(t) \), describes the partial randomization of the orientation, \( \Omega_{DP} \), of the principal coupling frame with respect to the interface by local motions such as molecular reorientation. The ‘slow’ correlation function, \( G_s(t) \), describes the randomization of the state variable, \( \Gamma \), brought about by translational diffusion of the spin-bearing species through the system.

Because of the orientational constraint imposed by the interface, the fast correlation function, \( G_f(t) \), will have a complicated (non-exponential) behaviour. However, it is usually neither possible nor desirable to extract a more detailed picture of the local motions than that provided by an effective (state-dependent) correlation time. Accordingly, we assume that the effect on \( G_f(t) \) of the interface is contained in the effective correlation time for the perturbed state and that this correlation time is independent of the orientation of the interface with respect to the external magnetic field. Using this approximation, we show in the Appendix that (2.13) and (2.18) yield (independent of \( k \))

\[
G_f(t) = \frac{1}{2} \left[ P_F V_F^2 \tilde{G}_f(t) + P_B V_B^2 \tilde{G}_B(t) \right],
\]

where we have introduced

\[
V(\Gamma) \equiv \left[ \sum_m | V_m^2(\Gamma) |^2 \right]^{1/2}.
\]

\( V(\Gamma) \) is often written as \( V_0^2(1 + \eta^2/3)^{1/2} \), where \( \eta \) is the asymmetry parameter of the coupling tensor. The effective correlation functions \( \tilde{G}(t | \Gamma) \), which are formally defined in the Appendix, have the properties \( \tilde{G}(0 | \Gamma) = 1 \) and \( \tilde{G}(\infty | \Gamma) = 0 \) and the respective effective correlation times are obtained by integrating over time.

The slow correlation function, \( G_s(t) \), is obtained by inserting (2.14) into (2.19), noting that by definition \( V_f = 0 \) and using the normalization requirements (2.6) as well as

\[
\sum_{\Gamma} P(\Gamma; t | \Gamma^0) = 1,
\]

and

\[
\sum_{\Gamma^0} P(\Gamma^0)P(\Gamma; t | \Gamma^0) = P(\Gamma).
\]

The result is

\[
G_s(t) = \left[ d_{k_0}^2(\theta_{LD} + \pi) \right] P_B [P(B; t | B) - P_B].
\]

Note that \( G_s(t) \) depends on the orientation of the interface.

The discrete-state propagator \( P(B; t | B) \) in (2.24) is a measure of the probability of finding the spin in state \( B \) at time \( t \), given that it was in that state initially. This quantity must now be related to the continuous diffusion propagator \( f(x, t | x_0) \). Since \( d_{k_0}^2(\theta_{LD} + \pi) = d_{k_0}^2(\theta_{LD}) \), the two opposite interfaces are indistinguishable and the diffusion equation needs to be solved only in half the interlamellar space, i.e. in one ‘cell’ (e.g. \( 0 < x < b \) in figure 3). We thus impose perfectly reflecting boundaries at \( x = 0 \) and at \( x = b \) and denote the resulting propagator by \( f_{RR}(x, t | x_0) \). The equilibrium distribution of spins within the system is given by

\[
f(x) = \exp \left( -\tau(x) \right) \left[ \int_0^b dx \exp \left( -\tau(x) \right) \right]^{-1},
\]

(2.25)
where \( v(x) \) is the potential of mean force (in units of \( k_B T \)) experienced by a spin-bearing species at \( x \). Note that \( f(x) \) is normalized on half the interlamellar interval (one cell). From figure 3, it follows that

\[
P_B = \int_0^\delta dx f(x),
\]

(2.26)

and

\[
P(B; t | B) = \int_0^\delta dx_0 f(x_0) \int_0^\delta dx f_{RR}(x, t | x_0) \left[ \int_0^\delta dx f(x) \right]^{-1}.
\]

(2.27)

Finally, (2.26) and (2.27) are substituted into equation (2.24), which becomes

\[
G^2(t) = \left[ d_{\Omega(0 \Omega)} V^2_B \right]^2 \int_0^\delta dx_0 f(x_0) \int_0^\delta dx \left[ f_{RR}(x, t | x_0) - f(x) \right].
\]

(2.28)

### 3. Formal results for systems with medium-range order

In the previous section, we assumed that the Euler angles \( \Omega_{LD} \), describing the orientation of the interface in the cell where the spin resides, are time-independent. However, this is not always the case. If the planar interface belongs to a dispersed aggregate, this may reorient as a whole and thus modulate \( \Omega_{LD} \). Alternatively, if the system contains cells with different orientations between which the spin-bearing species can diffuse, then \( \Omega_{LD} \) can vary in time even though the interfaces remain fixed. As noted in the Introduction, such modulation of the residual coupling adds to the correlation function a slowly decaying tail, which can be decisive for the relaxation behaviour. In this section we derive a formal expression for the correlation function which governs the relaxation in the case that the residual static coupling has been completely eliminated by the slow motion.

For the residual coupling to be completely eliminated, two conditions must be fulfilled: (1) the motion which modulates \( \Omega_{LD} \) must be fast compared to the (state-averaged) residual coupling frequency, and (2) all director orientations must be equally probable, i.e.

\[
f(\Omega_{LD}) = \frac{1}{8\pi^2}.
\]

(3.1)

(The magnetic dipole–dipole coupling between two protons in the same molecule can be eliminated by intermolecular proton exchange even though (3.1) does not hold. This situation, which involves a true discrete-site chemical exchange, has been discussed in the literature [6, 9].) According to Hubbard’s theorem [24], relaxation in systems with medium-range order is governed by the \( k = 0 \) correlation function

\[
G(t) = \langle V^2_{\Omega(0 \Omega)} \rangle,
\]

(3.2)

where \( V^2_{\Omega(t)} \) is given by (2.3) with \( k = 0 \) and a time-dependent \( \Omega_{LD}(t) \).

The joint equilibrium probability density for the three sets of stochastic variables may be written

\[
f(\Omega_{LD}, \Omega_{DP}, \Gamma) = f(\Omega_{LD}) f(\Omega_{DP} | \Gamma) P(\Gamma).
\]

(3.3)
The $\Omega_{LD}$-factorization follows because all interactions within a cell are independent of its orientation. (Although large aggregates with anisotropic magnetic susceptibility may be oriented by a strong magnetic field, the small spin-bearing species in the fluid region do not interact significantly with external magnetic or gravitational fields.) As in §2, we assume that the fluctuations in $\Omega_{DP}(t)$ occur on a much shorter timescale than those in $\Gamma(t)$ and $\Omega_{LD}(t)$. However, we do not assume timescale separation between $\Gamma(t)$ and $\Omega_{LD}(t)$. The joint transition probability density now factorizes as

$$f(\Omega_{LD}, \Omega_{DP}, \Gamma; t | \Omega_{LD}^0, \Omega_{DP}^0, \Gamma^0) = f(\Omega_{LD}, \Gamma; t | \Omega_{LD}^0, \Gamma^0) f(\Omega_{DP}; t | \Omega_{DP}^0, \Gamma^0).$$

As in (2.8)–(2.10), we divide $V_{0L}(t)$ into two parts, assuming that $f(\Omega_{DP} | \Gamma)$ has at least threefold rotation symmetry with respect to the director,

$$V_{0L}(t) = \sum_m D_{0m}^2[\Omega_{LD}(t)] \left\{ \sum_m D_{mm}^2[\Omega_{DP}(t)] V_{m}^m[\Gamma(t)] - \delta_{m0} \bar{V}[\Gamma(t)] \right\},$$

$$V_{0s}(t) = D_{00}^2[\Omega_{LD}(t)] \bar{V}[\Gamma(t)],$$

where (2.15) has been used. Because of the factorization in (3.4), the correlation function may be written as a sum of a rapidly and a slowly decaying part, as in (2.17), with

$$G(t) \equiv \langle V_{0L}^*(0) V_{0L}(t) \rangle$$

$$= \int d\Omega_{LD} f(\Omega_{LD}) \sum_{\Gamma} \Gamma P(\Gamma) \int d\Omega_{DP} f(\Omega_{DP} | \Gamma) V_{0L}^*(\Omega_{LD}, \Omega_{DP}^0, \Gamma^0) \times \int d\Omega_{DP} f(\Omega_{DP}; t | \Omega_{DP}^0, \Gamma^0) V_{0L}(\Omega_{LD}, \Omega_{DP}, \Gamma^0),$$

and

$$G^\gamma(t) \equiv \langle V_{0s}^*(0) V_{0s}(t) \rangle$$

$$= \int \int d\Omega_{LD} f(\Omega_{LD}) \sum_{\Gamma} \Gamma P(\Gamma) V_{0s}^*(\Omega_{LD}, \Gamma^0) \times \int \int d\Omega_{LD} f(\Omega_{LD}; t | \Omega_{LD}^0, \Gamma) V_{0s}(\Omega_{LD}, \Gamma).$$

In the Appendix we show that equations (3.1), (3.5) and (3.7), without further approximations, lead to

$$G(t) = \frac{1}{2}[P_{F} V_{B}^2 \tilde{G}(t) + P_{B}(V_{B}^2 - \bar{V}_{F}^2) \tilde{G}(t)],$$

where, as in §2, the quantities $\tilde{V}(\Gamma)$, $V(\Gamma)$ and $\tilde{G}(t | \Gamma)$ are defined by (2.15), (2.21) and (A3), respectively. We note that if $\bar{V}_{B} \ll V_{B}$, as often is the case, then (3.9) is identical to (2.20).

We now turn our attention to the slow correlation function, $G^\gamma(t)$. As noted in the Introduction, our main concern in this section is the effect on $G^\gamma(t)$ of diffusional surface reencounters in a dispersion of large aggregates, without the complications of interfacial curvature. Accordingly, we shall develop the CDM theory for a particularly simple model system. While this model system is artificial in some respects, its great virtue is that it explicitly reveals the essential difference...
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between the DEM and CDM theories. Moreover, it allows us (in §6) to express all results in terms of elementary functions. Results of quantitative validity for actual systems can be obtained within the same general theoretical framework, albeit usually at the cost of numerical computation. The important cases of cylindrical and spherical aggregates will be treated in subsequent papers.

We assume that $\Omega_{LD}$ can be modulated by two processes only: (1) reorientation of the planar aggregate surface, and/or (2) translational diffusion of the spin to another, differently oriented, aggregate surface. In any real system virtually all reencounters with the initial interface occur before the spin has diffused very far away from this interface. It should therefore suffice to solve the diffusion equation within a relatively small subsystem and to postulate that the remaining correlation is completely lost as the spin diffuses out of the subsystem. In the DEM the subsystem is simply identified with the perturbed $B$-state. In this zeroth-order ansatz, surface reencounters are thus completely neglected. A more realistic ansatz would be to take the cell $0 < x < b$ (see figure 3) as the subsystem.

According to this dynamic cell approximation (DCA), which we shall adopt here, $\Omega_{LD}$ is completely randomized as the spin reaches the cell boundary, $x = b$, for the first time.

The assumptions of the previous paragraph allow us to decompose the joint transition probability density in (3.8), with $\Gamma = \Gamma^{0} = B$, as follows

$$f(\Omega_{LD}, B; t | \Omega_{LD}^{0}, B) = f_{r}(\Omega_{LD}; t | \Omega_{LD}^{0})P_{cell}(B; t | B) + f(\Omega_{LD})[P(B; t | B) - P_{cell}(B; t | B)].$$

(3.10)

Here, $f_{r}(\Omega_{LD}; t | \Omega_{LD}^{0})$ is the propagator for aggregate reorientation and $P_{cell}(B; t | B)$ is the probability of finding a spin in state $B$ at time $t$, given that it was initially in state $B$ and that it has not left the cell in the meantime. The limiting properties of (3.10) are

$$f(\Omega_{LD}, B; 0 | \Omega_{LD}^{0}, B) = \delta(\Omega_{LD} - \Omega_{LD}^{0}),$$

(3.11)

$$f(\Omega_{LD}, B; \infty | \Omega_{LD}^{0}, B) = P_{B} f(\Omega_{LD}).$$

(3.12)

The $t \to \infty$ limit agrees with (3.3), as required.

Combining equations (3.6), (3.8) and (3.10), noting that $V_{F} = 0$ and using (3.1) and the orthogonality relation for the $D$-elements, we obtain

$$G^{\ast}(t) = \frac{1}{2} V_{B}^{2} P_{B} P_{cell}(B; t | B) G_{\ast}(t).$$

(3.13)

The reduced orientational correlation function is defined by

$$G_{\ast}(t) = \frac{5}{8\pi^{2}} \int d\Omega_{LD}^{0} \int d\Omega_{LD} f_{r}(\Omega_{LD}; t | \Omega_{LD}^{0})D_{00}(\Omega_{LD}^{0})D_{00}(\Omega_{LD})$$

$$= \frac{5}{8} \int_{-1}^{1} d\cos \theta_{LD} f_{r}(\theta_{LD}; t | 0) P_{2}(\cos \theta_{LD}),$$

(3.14)

where $P_{2}$ is the second-rank Legendre polynomial. The limits of (3.14) are $G_{\ast}(0) = 1$ and $G_{\ast}(\infty) = 0$.

It remains to relate the discrete-state propagator $P_{cell}(B; t | B)$ in (3.13) to the continuous diffusion propagator $f(x, t | x_{0})$. The difference between $P(B; t | B)$ and $P_{cell}(B; t | B)$ is that the latter includes only diffusional paths that are fully contained within the cell, $0 < x < b$. An expedient way of excluding those diffu-
sional paths that cross the cell boundary is to impose an absorbing boundary at
\(x = b\) (the interface at \(x = 0\) still being reflecting). The resulting propagator is
denoted \(f_{RA}(x, t | x_0)\) and
\[
P_{\text{cell}}(B; t | B) = \int_0^b dx_0 \ f(x_0) \int_0^b dx \ f_{RA}(x, t | x_0) \left[ \int_0^b dx \ f(x) \right]^{-1}. \quad (3.15)
\]
On combining equations (2.26), (3.13) and (3.15), we arrive at the final result of
this section
\[
G^s(t) = \frac{1}{2} \bar{V}_B^2 \bar{G}_s(t) \int_0^b dx_0 \ f(x_0) \int_0^b dx \ f_{RA}(x, t | x_0). \quad (3.16)
\]
The close formal resemblance between the results (2.28) and (3.16) for systems
with long-range and medium-range order, respectively, reflects the unified treat-
ment of these two cases in the CDM theory.

4. DIFFUSION PROPAGATORS

The formal expressions (2.28) and (3.16) for the slow correlation functions are
valid for any model of the molecular interactions in the system. Given a potential
of mean force, \(u(x)\), the equilibrium distribution, \(f(x)\), and the dynamics of the
spin–bearing species may be calculated from (2.25) and the Smoluchowski diffu-
sion equation \[20, 21\]
\[
\frac{\partial}{\partial t} f(x, t | x_0) = \frac{\partial}{\partial x} \left\{ D(x) f(x) \frac{\partial}{\partial x} \left[ f(x, t | x_0)/f(x) \right] \right\}, \quad (4.1)
\]
where \(D(x)\) is the (possibly spatially varying) self-diffusion coefficient of the
spin–bearing species. Equation (4.1) is to be solved subject to the initial condition
\[
f(x, 0 | x_0) = \delta(x - x_0), \quad (4.2)
\]
and the boundary conditions
\[
\frac{\partial}{\partial x} \left[ f(x, t | x_0)/f(x) \right] \bigg|_{x=0} = 0, \quad (4.3)
\]
and either
\[
\frac{\partial}{\partial x} \left[ f_{RA}(x, t | x_0)/f(x) \right] \bigg|_{x=b} = 0, \quad (4.4)
\]
or
\[
f_{RA}(b, t | x_0) = 0. \quad (4.5)
\]
In the present work we shall neglect any short-ranged features of the potential
of mean force that may exist in the perturbed interfacial region. The adopted
interaction model, which we shall call the PB model, identifies \(u(x)\) with the
mean electrostatic potential obtained by solving the nonlinear Poisson–Boltzmann
equation for counterions in a region bounded by two parallel charged interfaces.
This choice of interaction model is motivated partly by anticipated applications of
the theory to counterion spin relaxation. Furthermore, the PB model leads to
analytical results for planar geometry and the coupling to the interface can be
continuously varied through a single parameter, from the free-diffusion limit
(zero mean field) and upwards. We shall also assume that the bulk self-diffusion
coefficient, \(D_0\), applies throughout the system.
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When the spin-bearing species is electrically neutral, we set

$$w(x) = 0,$$  \hspace{1cm} (4.6)

whereby equations (2.25) and (2.26) yield

$$f(x) = \frac{1}{b},$$  \hspace{1cm} (4.7)

$$P_B = \frac{\delta}{b}.$$  \hspace{1cm} (4.8)

The one-dimensional free-diffusion propagators with boundary conditions given by (4.3)–(4.5) are [25]

$$f_{RR}(x, t | x_0) - f(x) = \frac{2}{b} \sum_{n=1}^{\infty} \cos \left( \frac{n\pi x_0}{b} \right) \cos \left( \frac{n\pi x}{b} \right) \exp \left[ - \left( \frac{n\pi}{b} \right)^2 D_0 t \right],$$  \hspace{1cm} (4.9)

$$f_{RA}(x, t | x_0) = \frac{2}{b} \sum_{n=0}^{\infty} \cos \left[ \frac{(2n + 1)\pi x_0}{2b} \right] \cos \left[ \frac{(2n + 1)\pi x}{2b} \right] \times \exp \left\{ - \left[ \frac{(2n + 1)\pi}{2b} \right]^2 D_0 t \right\}. \hspace{1cm} (4.10)

When the spin-bearing species is ionic, $w(x)$ is obtained by solving the nonlinear PB equation in the lamellar region of figure 3. We consider here the case with only one type of counterions and no additional electrolyte. The ions are modelled as point charges, $z\varepsilon$, immersed in a dielectric continuum of relative permittivity $\varepsilon_r$ and the balancing interfacial charge is represented by a uniform surface charge density, $\sigma$. The solution to the Poisson–Boltzmann equation for this case is [26]

$$w(x) = w(b) + 2 \ln \cos \left[ \kappa(b - x) \right].$$  \hspace{1cm} (4.11)

The Debye parameter, $\kappa$, which lies in the range $0 - \pi/(2b)$, is obtained from

$$\kappa b \tan (\kappa b) = - \frac{z\sigma b}{2\varepsilon_0 \varepsilon_r k_B T} \equiv \frac{b}{\lambda_C},$$  \hspace{1cm} (4.12)

which defines the coupling parameter, $\lambda_C$ (with the dimension of length). Substitution of (4.11) into equations (2.25) and (2.26) leads to

$$f(x) = \kappa \cot (\kappa b) \sec^2 \left[ \kappa(b - x) \right],$$  \hspace{1cm} (4.13)

$$P_B = 1 - \cot (\kappa b) \tan \left[ \kappa(b - \delta) \right].$$  \hspace{1cm} (4.14)

When $f(x)$ from (4.13) is inserted into (4.1) one obtains the planar Smoluchowski–Poisson–Boltzmann equation, which has recently been solved analytically [20]. With the present boundary conditions, we have

$$f_{RR}(x, t | x_0) - f(x) = \frac{2}{b} \cos \left[ \kappa(b - x_0) \right] \cos \left[ \kappa(b - x) \right] \times \sum_{n=1}^{\infty} \left( \frac{n\pi}{b} \right)^2 \phi_n(x_0) \phi_n(x) \exp \left\{ - \left[ \left( \frac{n\pi}{b} \right)^2 - \kappa^2 \right] D_0 t \right\},$$  \hspace{1cm} (4.15)
\[ f_{RA}(x, t | x_0) = \frac{2 \cos \left[ \kappa(b - x_0)b \right]}{b \cos \left[ \kappa(b - x) \right]} \sum_{n=0}^{\infty} \frac{\psi_n(x_0)\psi_n(x)}{(2n + 1)\pi^2} \frac{1}{2b} \]
\[ \times \exp \left\{ - \left[ \left( \frac{(2n + 1)\pi}{2b} \right)^2 - \kappa^2 \right] D_0 t \right\}, \quad (4.16) \]

where we have defined
\[ \phi_n(x) \equiv \kappa \tan \left[ \kappa(b - x) \right] \sin \left( \frac{n\pi x}{b} \right) - \frac{n\pi}{b} \cos \left( \frac{n\pi x}{b} \right), \quad (4.17) \]
\[ \psi_n(x) \equiv \kappa \tan \left[ \kappa(b - x) \right] \sin \left[ \left( \frac{(2n + 1)\pi x}{2b} \right) - \frac{(2n + 1)\pi}{2b} \right] \cos \left[ \left( \frac{(2n + 1)\pi x}{2b} \right) \right]. \quad (4.18) \]

We note that the zero field results (4.6)-(4.10) emerge from equations (4.11)-(4.18) in the limit \( \lambda_c \to \infty \) (or \( \kappa b = 0 \)).

We end this section by presenting some additional results which will be used later. Consider the self-diffusion of a particle in the cell, \( 0 < x < b \), with \( x = 0 \) reflecting and \( x = b \) absorbing. The probability, \( Q_{cell}(t) \), that the particle remains in the cell at time \( t \), i.e. that it has not yet been absorbed at \( x = b \), is
\[ Q_{cell}(t) = \int_0^b dx_0 \int_0^b dx f_{RA}(x, t | x_0). \quad (4.19) \]

Now \( -(d/dt)Q_{cell}(t) dt \) is clearly the probability that the particle is absorbed between \( t \) and \( t + dt \). The mean time, \( \tau_{cell} \), that the particle resides in the cell is therefore
\[ \tau_{cell} = - \int_0^\infty dt \int_0^\infty t \frac{dQ_{cell}(t)}{dt} = \int_0^\infty dt Q_{cell}(t). \quad (4.20) \]

As was first shown by Pontrjagin, Andronoff and Witt [27], \( \tau_{cell} \) can be obtained without solving the Smoluchowski equation (4.1). Their result, which has recently been rederived [28] by direct integration of (4.1), is
\[ \tau_{cell} = \frac{1}{D_0} \int_0^b dx \int_0^x dy f(x) f(y) \left[ \int_0^y d\alpha f(\alpha) \right]^2. \quad (4.21) \]

With (4.7) and (4.13), one obtains, in the field-free case
\[ \tau_{cell} = \frac{b^2}{3D_0}, \quad (4.22) \]
and in the PB case
\[ \tau_{cell} = \frac{b^2}{2D_0} \frac{1}{\kappa b} \left[ \tan (\kappa b) + \cot (\kappa b) - \frac{1}{\kappa b} \right], \quad (4.23) \]
with \( \kappa b \) given by (4.12). These expressions can, of course, also be derived by the more laborious method of integrating the appropriate propagator over \( x, x_0 \) and \( t \), according to (4.19) and (4.20).
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In the strong coupling regime \( \lambda_c \ll b, \kappa b \approx \pi/2 \), the decay of \( Q_{\text{cell}}(t) \) is very nearly exponential [20]

\[
Q_{\text{cell}}(t) = \exp \left( -t/\tau_{\text{cell}} \right).
\] (4.24)

The physical interpretation of (4.24) is that the position of the diffusing particle has become essentially equilibrated before it has reached the absorbing boundary. The fast initial equilibration phase is followed by a quasi-stationary situation characterized by first-order kinetics according to (4.24). In this strong coupling regime, (4.23) becomes

\[
\tau_{\text{cell}} = \frac{b^2}{D_0} \left[ \frac{\pi}{2} - (\kappa b)^2 \right]^{-1} = \frac{2b^3}{\pi^2 D_0 \lambda_c}.
\] (4.25)

When both boundaries are reflecting, \( Q_{\text{cell}} = 1 \) at all times so that \( \tau_{\text{cell}} \) diverges. It is possible to define another characteristic time for the self-diffusion process whereby an initial delta-function distribution relaxes towards the equilibrium distribution, \( f(x) \). However, this characteristic time is essentially independent of the coupling parameter, \( \lambda_c \), so that the slow correlation function never becomes dominated by a single exponential (see below). Consequently, it is not useful to introduce a characteristic time in this case.

5. EXPLICIT RESULTS FOR SYSTEMS WITH LONG-RANGE ORDER

In this section we combine the formal expression (2.28) for the slow correlation function in the presence of a static coupling with the mean-field distribution functions of §4. We also present explicit formulas for the corresponding spectral density

\[
J_k(\omega) \equiv \int_0^\infty dt \cos(\omega t)G_k(t), \quad k = 0, 1, 2,
\] (5.1)

The values of the spectral density at \( \omega = k\omega_0 \), where \( \omega_0 \) is the resonance frequency, enter into the relaxation matrix elements, which determine the various experimentally accessible relaxation rates [1].

In the field-free case, we substitute (4.7)–(4.9) into (2.28) and carry out the integration, to obtain

\[
G_k(t) = 2[d_{k\theta}(\theta_{LD})V_B]\sum_{n=1}^\infty \sin^2 \left( \frac{n\pi b}{D_0} \right) \exp \left( -\frac{n\pi^2 D_0 t}{b^3} \right),
\] (5.2)

and, with (5.1),

\[
J_k(\omega) = [d_{k\theta}(\theta_{LD})V_B]^2 \frac{2b^2}{D_0} \sum_{n=1}^\infty \frac{\sin^2 \left( \frac{n\pi b}{D_0} \right)}{(n\pi)^4 + (b^2\omega/D_0)^2}.
\] (5.3)

The infinite series in (5.3) can be summed exactly with the result

\[
J_k(\omega) = [d_{k\theta}(\theta_{LD})V_B]^2 \frac{b^2}{D_0} \left[ \sin x \cos x + \sinh x \cosh x \right]
\]
\[
- \sin [(1 - 2P_B)x] \sinh [(1 - 2P_B)x] \left[ \sin x \cosh x - \cos x \sinh x \right]
\]
\[
- \cos [(1 - 2P_B)x] \cosh [(1 - 2P_B)x] \left[ \sin x \cosh x + \cos x \sinh x \right]
\]
\[
\times \{(2x)^3[\sin^2 x + \sinh^2 x]\}^{-1},
\] (5.4)
where we have defined
\[ x \equiv \left( \frac{\omega b^2}{2D_0} \right)^{1/2}. \] (5.5)

In the zero-frequency limit, (5.4) reduces to
\[ J^i_k(0) = \left[ d^2_{\theta LD}(\theta LD) \right]^2 (1 - \rho B)^2 \frac{\delta^2}{3D_0}. \] (5.6)

In the PB case, we substitute (4.13) and (4.15) into (2.28) and carry out the integration, to obtain
\[ G_\omega(t) = \left[ d^2_{\theta LD}(\theta LD) \rho B \right]^2 2D_0 \cot (\kappa b) \sec^2 [\kappa(b - \delta)] \]
\[ \times \sum_{n=1}^{\infty} \frac{\sin^2 (n\pi \delta/b)}{(n\pi)^2 - (\kappa b)^2} \exp \left\{ -\left[ (n\pi)^2 - (\kappa b)^2 \right] \frac{D_0 t}{b^2} \right\}, \] (5.7)

and, with (5.1),
\[ J^i_k(\omega) = \left[ d^2_{\theta LD}(\theta LD) \rho B \right]^2 \frac{2b^2}{D_0} \kappa b \cot (\kappa b) \sec^2 [\kappa(b - \delta)] \]
\[ \times \sum_{n=1}^{\infty} \frac{\sin^2 (n\pi \delta/b)}{(n\pi)^2 - (\kappa b)^2} + (\omega b^2/D_0)^2. \] (5.8)

In the zero-frequency limit, the infinite series in (5.8) can be summed exactly with the result
\[ J^i_k(0) = \left[ d^2_{\theta LD}(\theta LD) \rho B \right]^2 \frac{b^2}{4D_0} \cos (\kappa b) \left( \cos (\kappa b) - \cos [\kappa(b - 2\delta)] \right) \]
\[ + \kappa b \csc (\kappa b) [1 - \cos (2\kappa \delta)] + 2\kappa \delta \sin [\kappa(b - 2\delta)] \]
\[ \times \{ \kappa b \sin (\kappa b) \cos [\kappa(b - \delta)] \}^{-2}. \] (5.9)

In the limit of vanishing Coulomb coupling ($\lambda_{C} \rightarrow \infty$, $\kappa b = 0$), equations (5.7)–(5.9) reduce to the preceding zero-field results.

In the dilute regime ($\delta \ll b$) (5.9) becomes
\[ J^i_k(0) = \left[ d^2_{\theta LD}(\theta LD) \rho B \right]^2 \frac{\delta^2}{2D_0} \sec^2 [\kappa(b - \delta)](\kappa b)(\kappa \lambda) \left( 1 + (\kappa \lambda)^2 - \frac{\lambda \epsilon}{b} \right), \] (5.10)

where (4.12) was also used. In the weak coupling regime ($\kappa b \ll 1$), (5.10) reduces to (5.6) (with $P_B = 0$), while in the strong coupling regime ($\lambda_{C} \ll b$, $\kappa b \approx \pi/2$) it yields
\[ J^i_k(0) = \left[ d^2_{\theta LD}(\theta LD) \rho B \right]^2 \frac{\delta^2}{2D_0} \left( \frac{\lambda \epsilon}{b} \right)^2, \] (5.11)

demonstrating that, as $\lambda_{C}$ is varied, $J^i_k(0)$ goes through a maximum (at $\lambda_{C} = \delta$).

It is of interest to compare the preceding results of the CDM theory with the predictions of the DEM theory, in which the continuous translational diffusion process is replaced by an uncorrelated random walk among the discrete states. In the two-state DEM, one departs from equation (2.24), which contains the discrete-state propagator $P(B; t | B)$. It is easy to show that the DEM propagator is [13]
\[ P(B; t | B) = P_B + (1 - P_B) \exp (-t/\tau_{\epsilon}), \] (5.12)
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where

\[ \frac{1}{\tau_{ex}} \equiv \frac{1}{\tau_F} + \frac{1}{\tau_B} = \frac{1}{(1 - P_B)\tau_B}, \] (5.13)

with \( \tau_F \) and \( \tau_B \) being the mean residence times in the respective states. Using equations (2.24), (5.1) and (5.12), we get

\[ J_0^F(\omega) = \left[ d^2_0(\theta_{LD})\bar{V}_B^2 \right]^2 P_B(1 - P_B) \frac{\tau_{ex}}{1 + (\omega\tau_{ex})^2}, \] (5.14)

in agreement with previous work [4-6, 9]. In the zero-frequency limit (5.13) and (5.14) yield

\[ J_0^F(0) = \left[ d^2_0(\theta_{LD})\bar{V}_B^2 \right]^2 P_B(1 - P_B)^2 \tau_B. \] (5.15)

The comparison of the DEM and CDM results will be made for the same model of the molecular interactions in the system. Any differences are then due entirely to the more realistic dynamical description in the CDM. The quantities \( P_B \) and \( \tau_B \) in (5.15) are evaluated in the PB model described in §4, with \( \tau_B \) being identified as the mean time taken to reach \( x = \delta \), with the initial position Boltzmann-averaged over the B state, \( 0 < x < \delta \). In analogy with (4.21),

\[ \tau_B = \frac{1}{D_0 P_B} \int_0^\delta \frac{dx}{f(x)} \left[ \int_0^x dy f(y) \right]^2. \] (5.16)

In the field-free case, (5.16) yields \( \tau_B = \delta^2/(3D_0) \). On comparing (5.6) and (5.15), we thus see that the DEM underestimates \( J_0^F(0) \) by a factor of \( P_B^{-1} = b/\delta \). As a consequence, the two models predict qualitatively different behaviour of \( J_0^F(0) \) as the lamellar spacing \( (2b) \) is varied. This is illustrated in figure 4. The

Figure 4. Variation of the reduced zero-frequency spectral density, \( \mathcal{J}_0^F(0) \equiv J_0^F(0) \left[ d^2_0(\theta_{LD})\bar{V}_B^2 \delta^2/(3D_0) \right]^{-1} \), with surface-to-surface separation, \( 2b \), in units of \( \delta \), in the field-free case.
comparison of the two models in the presence of a PB mean field is shown in figure 5 for $\lambda_c = \delta/3$ (typical of counterions in lamellar liquid crystalline phases of ionic amphiphiles). Whereas, in the DEM, $J_\lambda(0)$ levels off with increasing lamellar spacing, the CDM predicts that translational diffusion becomes an increasingly efficient relaxation mechanism as $b$ increases. In fact, over most of the $b$-range of figure 5, $J_\lambda(0)$ is nearly proportional to $b$, as predicted by (5.11).

The large discrepancy between the DEM and CDM predictions of the zero-frequency spectral density, as seen in figures 4 and 5, reflects the fact that $P(B; t | B)$ has a slower decay in the CDM than in the DEM. As a consequence, $J_\lambda(0)$ decays at lower frequencies in the CDM than in the DEM. This is illustrated in figure 6, which reveals a frequency shift of about two orders of magnitude for $\delta/b = 0.05$. Depending on the value of $b^2/D_0$, the dispersion of $J_\lambda(0)$ may thus occur in the neighbourhood of the resonance frequency, thereby rendering the relaxation rates frequency dependent. (Note that the only effect of $b^2/D_0$ in figure 6 is to scale the frequency axis; an increase in $b^2/D_0$ shifts the curves to lower frequency by the same factor.) Furthermore, it is seen that the dispersion is non-Lorentzian, with a much slower decay on the high-frequency side.

In order to estimate the relative contributions to the observable spin relaxation rates from translational diffusion and from local motions, it is useful to compare $J_\lambda(0)$ with the spectral density, $J_{\text{bulk}}(0)$, in the absence of interfaces. The latter is expected to be of the same order of magnitude as $J(0)$, given by the time integral of (2.20).

As an example of the field-free case, we take water $^2$H relaxation in an aqueous region bounded by two planar interfaces. At ambient temperatures

$$R_{\text{bulk}} = \frac{5}{4} \left( \frac{eQ}{\hbar} \right)^2 J_{\text{bulk}}(0) \approx 2 \text{ s}^{-1}. \quad (5.17)$$

![Figure 5](image-url)  
As in figure 4, but in the presence of a PB mean field with coupling strength $\lambda_c = \delta/3$. 

The large discrepancy between the DEM and CDM predictions of the zero-frequency spectral density, as seen in figures 4 and 5, reflects the fact that $P(B; t | B)$ has a slower decay in the CDM than in the DEM. As a consequence, $J_\lambda(0)$ decays at lower frequencies in the CDM than in the DEM. This is illustrated in figure 6, which reveals a frequency shift of about two orders of magnitude for $\delta/b = 0.05$. Depending on the value of $b^2/D_0$, the dispersion of $J_\lambda(0)$ may thus occur in the neighbourhood of the resonance frequency, thereby rendering the relaxation rates frequency dependent. (Note that the only effect of $b^2/D_0$ in figure 6 is to scale the frequency axis; an increase in $b^2/D_0$ shifts the curves to lower frequency by the same factor.) Furthermore, it is seen that the dispersion is non-Lorentzian, with a much slower decay on the high-frequency side.

In order to estimate the relative contributions to the observable spin relaxation rates from translational diffusion and from local motions, it is useful to compare $J_\lambda(0)$ with the spectral density, $J_{\text{bulk}}(0)$, in the absence of interfaces. The latter is expected to be of the same order of magnitude as $J(0)$, given by the time integral of (2.20).

As an example of the field-free case, we take water $^2$H relaxation in an aqueous region bounded by two planar interfaces. At ambient temperatures
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Figure 6. Dispersion of the spectral density, $\mathcal{J}(\omega)$, in the field-free case (dashed curves) and in the presence of a PB mean field with $\lambda_c = \delta/3$ (solid curves). All curves correspond to $\delta/b = 0.05$ and $b^2/D_0 = 1 \times 10^{-8}$ s.

With $P_B \ll 1$ and $d_{k_0}^2(\theta_{LD}) = 1$, (5.6) yields an upper bound of

$$
\mathcal{J}_k(0) \leq \frac{P_B^2}{3D_0} \delta^2. \tag{5.18}
$$

With the plausible [5, 29] values $\delta = 0.5$ nm, $D_0 = 2 \times 10^{-9}$ m$^2$ s$^{-1}$ and $eQV_B/h = 1 \times 10^4$ s$^{-1}$, we find

$$
\mathcal{J}_b(0) \ll 0.1. \tag{5.19}
$$

It thus appears that, in this case, translational diffusion does not contribute significantly to the relaxation rates. It should be noted, however, that it may not be appropriate to neglect the effect of short-range forces on the water diffusion near the interface. This point will be examined in detail in a subsequent paper.

The PB mean field case will be exemplified by $^{23}$Na relaxation of sodium counterions in an aqueous region bounded by two charged planar interfaces. At ambient temperatures

$$
R_{\text{bulk}} = \frac{1}{3} \left( \frac{eQ}{\hbar} \right)^2 J_{\text{bulk}}(0) \approx 20 \text{ s}^{-1}. \tag{5.20}
$$

With $\lambda_c = \delta$ and $d_{k_0}^2(\theta_{LD}) = 1$, (5.11) yields an upper bound of

$$
\mathcal{J}_k(0) \leq \frac{P_B^2 \delta b}{8D_0}. \tag{5.21}
$$

With the plausible [23] values of $\delta = 0.5$ nm, $D_0 = 1 \times 10^{-9}$ m$^2$ s$^{-1}$ and $eQV_B/h = 1 \times 10^5$ s$^{-1}$, we find

$$
\frac{\mathcal{J}_b(0)}{J_{\text{bulk}}(0)} \ll 0.4 \text{ b(nm)}, \tag{5.22}
$$

$\text{nm}$.
which shows that, even in the absence of short-range forces, translational diffusion may be of importance for counterion spin relaxation in lamellar systems with fluid regions of sufficient thickness. Since \( \mathcal{J}^s_\phi(\omega) \) starts to fall at \( \omega \sim D_0/b^2 \) (see figure 4) and since \( \omega_0(\text{Na}) \) typically lies in the range \( 10^8-10^9 \text{ rad s}^{-1} \), it may be possible to observe a relaxation dispersion.

6. Explicit results for systems with medium-range order

When (4.7) and (4.10) are substituted into (3.16) and the integration performed, we obtain for the field-free case

\[
G^s(t) = \frac{1}{2} \vec{V}_B^2 \vec{G}_t(t) \sum_{n=0}^{\infty} \frac{\sin^2 \left[ (2n+1)(\pi/2)P_B \right]}{[(2n+1)(\pi/2)]^2} \exp \left\{ -\left[ (2n+1)\frac{\pi}{2} \right]^2 \frac{D_0 t}{b^2} \right\}. \tag{6.1}
\]

For simplicity, we assume henceforth that the reduced orientational correlation function, defined by (3.14), is exponential, i.e.

\[
\vec{G}_t(t) = \exp \left( -\frac{t}{\tau_t} \right). \tag{6.2}
\]

Combination of equations (5.1), (6.1) and (6.2) leads to the spectral density

\[
\mathcal{J}^s(\omega) = \frac{1}{2} \vec{V}_B^2 \frac{2b^2}{D_0} \sum_{n=0}^{\infty} \frac{[\{(2n+1)(\pi/2)\}^2 + (b^2/D_0 \tau_t)] \sin^2 \left[ (2n+1)(\pi/2)P_B \right]}{[(2n+1)(\pi/2)]^2 \left\{ [(2n+1)(\pi/2)]^2 + (b^2/D_0 \tau_t) \right\}^2 + [b^2\omega/D_0]^2}. \tag{6.3}
\]

In the zero-frequency limit, the infinite series in (6.3) can be summed exactly with the result

\[
\mathcal{J}^s(0) = \frac{1}{2} \vec{V}_B^2 P_B \tau_t \left\{ 1 - \frac{\sinh (P_B \beta)}{P_B \beta} [\cosh (P_B \beta) - \tanh \beta \sinh (P_B \beta)] \right\}, \tag{6.4}
\]

where we have defined

\[
\beta \equiv \left( \frac{b^2}{D_0 \tau_t} \right)^{1/2}. \tag{6.5}
\]

In the case where the overall rotation is so slow that \( \beta \ll 1 \), (6.3) can be summed for arbitrary frequency with the result

\[
\mathcal{J}^s(\omega) = \frac{1}{2} \vec{V}_B^2 \frac{b^2}{D_0} \left\{ [\sinh \alpha \cosh \alpha - \sin \alpha \cos \alpha] - \sin \left[ (1 - 2P_B) \alpha \right] \cosh \left[ (1 - 2P_B) \alpha \right][\sin \alpha \sin \alpha - \cos \alpha \cos \alpha] - \cos \left[ (1 - 2P_B) \alpha \right] \sin \left[ (1 - 2P_B) \alpha \right][\sin \alpha \sin \alpha + \cos \alpha \cos \alpha] \right\} \times \left\{ (2\alpha)^2 [\cos^2 \alpha + \sin^2 \alpha] \right\}^{-1}, \tag{6.6}
\]

with \( \alpha \) given by (5.5). In the \( \omega = 0 \) limit, (6.6) reduces to

\[
\mathcal{J}^s(0) = \frac{1}{2} \vec{V}_B^2 (1 - \frac{2}{3}P_B) \frac{b^2}{D_0}. \tag{6.7}
\]

This result also follows from (6.4) in the limit \( \beta \ll 1 \). With the help of (4.8) and (4.22), equation (6.7) can be expressed in terms of the cell residence time, \( \tau_{cell} \), as

\[
\mathcal{J}^s(0) = \frac{1}{3} (3 - 2P_B)P_B \vec{V}_B^2 \tau_{cell}. \tag{6.8}
\]
In the PB case, we substitute (4.13) and (4.16) into (3.16) and carry out the integration, to obtain

\[ G_S(t) = V_B^2 \sum_{n=0}^{\infty} \sin^2 \left\{ \left[ (2n + 1)(\pi/2) / (\delta/b) \right]^2 - (\kappa b)^2 \right\} \exp \left\{ - \left[ \left( (2n + 1) \pi / 2 \right)^2 - (\kappa b)^2 \right] D_0 t / b^2 \right\}. \]  

(6.9)

In the strong coupling regime ($\lambda_c \ll b$), where according to (4.12) $\kappa b \approx \pi/2$, the first term in (6.9) will clearly have a much larger amplitude and a much slower decay than the following terms. For this reason, it is convenient to split the correlation function into two parts

\[ G_S(t) = G_0^s(t) + G_\infty(t), \]  

(6.10)

where $G_0^s(t)$ is the $n = 0$ term in (6.9) and $G_\infty(t)$ is the remainder.

Assuming that $G_S(t)$ is given by (6.2) and taking the Fourier cosine transform of $G^s(t)$ according to (5.1), we get

\[ J_S(\omega) = \frac{2b^2}{D_0} \frac{\kappa b \cot(\kappa b) \sec^2(\kappa(b - \delta))}{\left[ ((2n + 1)(\pi/2))^2 - (\kappa b)^2 \right]} \sin \left\{ \left[ (\pi/2) / (\delta/b) \right] \right\} \frac{1}{1 + (\omega \tau^*_s)^2}, \]  

(6.11)

with $\beta$ defined by (6.5), and

\[ J_S(\omega) = \frac{2b^2}{D_0} \frac{\kappa b \cot(\kappa b)}{\left[ ((\pi/2))^2 - (\kappa b)^2 \right]} \frac{\sin \left[ (\pi/2) / (\delta/b) \right]}{\cos \left[ \kappa(b - \delta) \right]} \frac{1}{1 + (\omega \tau^*_s)^2}, \]  

(6.12)

where we have introduced an effective correlation time, $\tau^*_s$, given by

\[ \frac{1}{\tau^*_s} = \frac{1}{\tau_{cell}} + \frac{1}{\tau_s}, \]  

(6.13)

with

\[ \tau_{cell} = \frac{b^2}{D_0} \left[ ((\pi/2))^2 - (\kappa b)^2 \right]. \]  

(6.14)

Note that it is only in the strong coupling regime that $\tau_{cell}$ can be identified as the cell residence time (see §4). The infinite series in (6.11) may be summed when $\beta \ll 1$ and $\omega = 0$, to give for the total spectral density

\[ J_S(\omega) = \frac{2b^2}{D_0} \left( \frac{1}{\kappa b} csc(\kappa b) \right) \sec^2(\kappa(b - \delta)) \sin \left[ \kappa(b - 2\delta) \right] \]  

\[ - \sin(\kappa b) + \kappa b \sec(\kappa b)[1 - \cos(2\kappa b)] + 2\kappa b \cos(\kappa(b - 2\delta)), \]  

(6.15)

which reduces to (6.7) in the limit of vanishing coupling ($\lambda_c \to \infty$, $\kappa b = 0$).

In the dilute ($\delta \ll b$), strong coupling ($\lambda_c \ll b$) regime (4.14) yields $P_B = (1 + \lambda_c / (\delta b))^{-1}$, so that (6.12) becomes

\[ J_S(\omega) = \frac{1}{2} \left( P_B V_B^2 \right) \frac{\tau^*_s}{1 + (\omega \tau^*_s)^2}, \]  

(6.16)
and, if also $\beta \ll 1$,

$$J_1(0) = \frac{1}{2} (P_B \bar{V}_B)^2 \tau_{\text{cell}} = \frac{1}{2} \bar{V}_B^2 \frac{2b^3}{\pi^2 D_0 \lambda_C (1 + \lambda_C/\delta)^2}.$$  

(6.17)

Equation (6.17) shows that $J_1(0)$ increases strongly upon dilution, $b$ being the concentration variable, and that it increases without bound as the Coulomb coupling becomes stronger ($\lambda_C \rightarrow 0$). In the same regime (dilute, strong coupling, $\beta \ll 1$), we subtract (6.12) from (6.15) to obtain

$$\bar{V}_B \delta^2 \frac{\lambda_C b}{\pi k b D_0 (\lambda_C + \delta)^2},$$

which shows that $J_2(0)$ varies linearly with $b$ and passes through a maximum (at $\lambda_C = \delta$) as the coupling strength is varied. Equation (6.18) agrees to within a factor of order unity with the isotropic average of (5.11). In the dilute, strong coupling regime, we can thus associate $J_1(0)$ with the randomization of the locally averaged coupling, $P_B \bar{V}_B$, within the cell and $J_2(0)$ with the much slower randomization of the cell-averaged coupling, $P_B \bar{V}_B$, as the spin–bearing species diffuses from one cell to another. A comparison of (6.17) and (6.18) shows that $J_1(0) / J_2(0) \approx \lambda_C / b \ll 1$. In the dilute, strong coupling regime, $J_1(0)$ may thus be neglected relative to $J_2(0)$. This neglect of $J_1(0)$ may be called a steady-state approximation (SSA) since it is related to the quasi-stationary behaviour discussed in connection with (4.24). Alternatively, the SSA may be introduced into the theory from the beginning by assuming timescale separation between $\Omega_{LD}(t)$ and $\Gamma(t)$ and including only the $\Omega_{LD}$-fluctuations in the slow correlation function. Such an approach was adopted in a recent study of counterion relaxation in polyelectrolyte solutions [23].

We now compare the results derived in this section with the predictions of the DEM theory. In the two-state DEM for systems with medium-range order, such as solutions of macromolecules or large molecular aggregates, one usually assumes that the orientational correlation induced by the surface is completely lost once the spin has left the perturbed region (state $B$). The discrete-state propagator then takes the simple form

$$P(B; t | B) = \exp (-t/\tau_B).$$

(6.19)

In this approximation, surface reencounters are thus not included in the dynamical description. On combining equations (3.13), (5.1), (6.2) and (6.19), we obtain the DEM result

$$J^*(\omega) = \frac{1}{2} \bar{V}_B^2 P_B \frac{\tau_B^*}{1 + (\omega \tau_B^*)^2},$$

(6.20)

with the effective correlation time, $\tau_B^*$, defined by (1.2). As before, the comparison of the DEM and CDM results is made for the same interaction model, with $P_B$ and $\tau_B$ given by (2.26) and (5.16), respectively, and with $f(x)$ from the PB model of §4.

In the field-free case, with $\tau_B = \delta^2/(3D_0)$, (6.7) and (6.20) show that, in the absence of overall rotation ($\tau_r \rightarrow \infty$), the DEM underestimates $J^*(0)$ by a factor of $(3 - 2P_B)/P_B$. As a consequence, the concentration (measured by $1/b$) dependence of $J^*(0)$ is qualitatively different in the two models. Figure 7 shows that, in the DEM, $J^*(0)$ decreases on dilution, whereas the reverse is true in the CDM.
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Figure 7. Variation of the reduced zero-frequency spectral density, \( P(0) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \delta^2 (3D_0) \), with 'concentration', \( \delta/b \), in the field-free case. The constant value of \( P \beta = \frac{3Z}{(D_0^2 \tau_c^2)} \) is given by each curve (solid: CDM, dashed: DEM).

Equation (1.2) implies that when \( \tau_c \lesssim \tau_B \), then the overall rotation causes a reduction of \( \tau_B^* \) and, according to the DEM, also of \( P(0) \). In the CDM, however, it is only necessary that \( \tau_c \lesssim b^2/D_0 \) for the overall rotation to affect \( P(0) \) (cf. equation (6.5)). This is illustrated in figure 7. It is the surface reencounters in the CDM which, by slowing down the decay of \( G(t) \), makes it sensitive to slow isotropic motions. The reencounters also displace the dispersion of \( P(\omega) \) to lower frequencies, as seen by comparing the CDM and DEM curves in figure 8. In the

Figure 8. Dispersion of the spectral density, \( P(\omega) \), in the field-free case with \( \delta/b = 0.01 \) and \( b^2/D_0 = 1 \times 10^{-6} \) s. The correlation time, \( \tau_c \), for aggregate reorientation is given (in seconds) by each curve (solid: CDM, dashed: DEM).
CDM, there is a pronounced deviation from Lorentzian shape. In the absence of overall rotation, $\mathcal{P}(\omega)$ starts to fall at $\omega \sim D_0/b^2$ but then decays quite slowly over several decades in frequency. If the overall rotation is so fast that $\tau_r \lesssim b^2/D_0$, then the 'late' reencounters have no effect on the correlation function and $\mathcal{P}(\omega)$ is essentially Lorentzian (provided that equation 6.2 is valid).

Consider now the case of a PB mean field with $\lambda_c = \delta$. For $\delta \ll b$ we are then in the strong coupling regime ($\lambda_c \ll b$), where $\mathcal{P}(\omega)$ is associated with the positional randomization within the cell while $\mathcal{P}'(\omega)$ reflects the escape from the cell. Figure 9 shows how $\mathcal{P}(\omega)$ varies with concentration ($1/b$) in the two models. As predicted by (6.18), $\mathcal{P}(\omega)$ increases in proportion to $b$ in the dilute regime. Overall rotation with $\tau_r \lesssim b^2/D_0$ causes the $\mathcal{P}(\omega)$ curve to level out. As in the field-free case, the dispersion of $\mathcal{P}(\omega)$ is spread over a wide range of frequencies and extends to much lower frequencies in the CDM than in the DEM (see figure 10). The effect of overall rotation is the same as in figure 8.

The dominant contribution to $\mathcal{P}(0)$ comes from the randomization of the surface orientation, $\Omega_{LD}$, as the spin escapes from the cell. Figure 11 shows that this contribution, $\mathcal{P}'(0)$, increases strongly upon dilution: for $\delta \ll b$, $\mathcal{P}(0) \propto b^3$ as predicted by (6.17). Because of the vastly enhanced reencounter probability in the electrostatic field, $G_s(t)$ decays very slowly and translational diffusion becomes an extremely efficient relaxation mechanism, especially in dilute systems where the cell residence time, $\tau_{cell}$, is long. As can be inferred from (6.13), overall rotation imposes an upper limit for $\mathcal{P}(0)$ so that the curves in figure 11 begin to level out when $\tau_r \lesssim \tau_{cell}$. As evident from (6.12) and (6.13), the dispersion of $\mathcal{P}'(\omega)$ occurs around $\omega \sim 1/\tau_{cell} + 1/\tau_i$ and is purely Lorentzian (see figure 12). In the absence of overall rotation, the dispersion occurs at lower frequency than in the zero-field case (figure 8), since in the strong coupling regime $\tau_{cell} \gg b^2/D_0$ (cf. equation...
Figure 10. Dispersion of the spectral density, $J_\omega(\omega)$, in the presence of a PB mean field with $\lambda_c = \delta$. All curves correspond to $\delta/b = 0.01$ and $b^2/D_0 = 1 \times 10^{-6}$ s. The correlation time, $\tau_r$, for aggregate reorientation is given (in seconds) by each curve (solid: CDM, dashed: DEM). The DEM curve represents the total $J(\omega)$.

4.25. A comparison of figures 10 and 12 shows that the dispersion of $J_\omega(\omega)$ occurs at much lower frequency than that of $J_\omega(\omega)$. Whereas one always has $J_\omega(\omega) \gg J_\omega(\omega)$ for $\omega \lesssim 1/\tau_{cell} + 1/\tau$, the reverse may therefore be true at higher frequencies.

As in §5, we estimate the relative contributions to the spin relaxation rates from translational diffusion and from local motions by comparison with the spectral density, $J_{bulk}(0)$, in the absence of interfaces. Again, we take the relaxation of water $^2$H and counterion $^{23}$Na as examples. In the case of water (zero mean
field), (6.7) yields an upper bound for \( J(0) \) which is 60 per cent of that given by (5.18). The conclusion of §5 (with the proviso regarding the effect of short-range forces) thus applies also to systems with medium-range order, i.e. translational diffusion does not contribute significantly to the relaxation in the zero mean field case.

In the case of \(^{23}\text{Na} \) counterion relaxation, (6.18) with \( \lambda_c = \delta \) and the parameter values of §5 yields

\[
\frac{J_{\|}(0)}{J_{\text{bulk}}(0)} \lesssim 0.03 \, \text{b (nm)},
\]

which shows that \( J_{\|}(0) \) may contribute substantially to the total spectral density at high dilution. In the same way, we get from (6.17)

\[
\frac{J_{\perp}(0)}{J_{\text{bulk}}(0)} \lesssim 0.1 \, [\text{b (nm)}]^3.
\]

In reasonably dilute systems, say \( b \gtrsim 3 \) nm, \( J_{\perp}(0) \) may thus dominate the transverse relaxation rate and the much smaller contributions from positional randomization within the cell \( (J_{\|}(0)) \) and from local motions \( (J_{\perp}(0)) \) may be neglected. For the longitudinal relaxation, however, the reverse may be true: with the parameter values of figures 10 and 12, \( J_{\|}(w_0) \gg J_{\perp}(w_0) \) for \( w_0 \gtrsim 10^7 \) rad s\(^{-1} \) (in the absence of overall rotation).

7. Discussion

7.1. The local motions

The formal expressions (2.20) and (3.9) for the fast correlation function, \( G^f(t) \), were derived without specifying a detailed model for the local motions that
modulate the spin–lattice coupling on the fast timescale. On the other hand, it
was assumed that the spin–lattice coupling is of purely intramolecular origin so
that its magnitude $V(\Gamma)$, defined by (2.21), is independent of time. In practice
this is rarely so. In the case of water nuclei, for example, the $^2H$ and $^{17}O$ electric
field gradients depend to some extent on hydrogen bond interactions [29], while
the $^1H$ dipole–dipole interaction also couples protons in different molecules. In
the case of simple ions, the electric field gradient is due mainly to instantaneous
asymmetries in the primary solvation shell [30]. It is clear, therefore, that a more
sophisticated treatment of $G'(t)$ is required if one wants to extract detailed infor-
modation about the local motions.

The emphasis of the present work is on relaxation induced by modulation of
the locally averaged residual coupling, $\bar{V}_B$, as defined by (2.15). In this pursuit
we have made only one assumption about the local motions, namely that they are
fast compared to the motions that modulate the residual coupling. This timescale
separation enabled us to factorize the joint propagators in (2.7) and (3.4) and, as a
consequence, split the total correlation function into a fast and a slow part as in
(2.17). The timescale separation also guarantees that $G'(t)$ can be written as a
simple average over states as in (2.20) and (3.9). In other words, equation (1.1) is
valid for the fast local motions.

In the case of water and simple ions, the local motions, including molecular
rotation and translation, librations and hydrogen bond rearrangements, have cor-
relation times in the range $10^{-13}$–$10^{-11}$ s at ambient temperatures. The modu-
lation of the state parameter, $\Gamma(t)$, takes place on a broad timescale, typically
ranging from $10^{-11}$ s and upwards. The assumption of timescale separation thus
appears justified. The possibility (for water more than for counterions) of a slight
overlap of timescales around $10^{-11}$ s is of little consequence since it only affects
the extreme end of the high-frequency tail of the spectral density (cf. figures 6, 8
and 10).

7.2. The two-state approximation

On a molecular scale any interface is heterogeneous. The molecules of the
fluid thus sample a variety of environments in the interfacial region. However,
because of the fast motions at the interface it is usually not possible to distinguish
among these local environments in an N.M.R. experiment. Only the average
properties in the perturbed region can be deduced. In keeping with this lateral
course-graining, one usually distinguishes between only two fluid regions outside
the interface, namely the $B$ and $F$ states. If the residual spin–lattice coupling
decayed to zero only slowly with the distance from the interface, it would be
pertinent to introduce a continuous function $\bar{V}(x)$. There is strong evidence [31],
however, that the residual coupling vanishes a few solvent diameters away from
the interface. A two-state treatment thus appears reasonable except for highly
heterogeneous aggregate interfaces, such as globular proteins, where additional
(specific) discrete states may be required.

In the formal theory of §§2 and 3, we assumed that the orientational distribu-
tion function in the perturbed state, $f(\Omega_{Dp}|B)$, has at least threefold rotation
symmetry with respect to the director (surface normal). In view of the lateral
averaging and the essentially free rotation of the molecular residues at most
interfaces of interest, this seems a reasonable assumption.
7.3. The dynamic cell approximation

The effect of translational diffusion in systems with long-range order is to average the residual coupling from its local value \( D_0^2(\Omega_{LD})V_B \) in the perturbed region to its static cell average \( D_0^2(\Omega_{LD})P_B \bar{V}_B \). In systems with medium-range order, on the other hand, the local residual coupling \( D_0^2(\Omega_{LD})V_B \) is averaged to zero. This cannot be accomplished solely by translational diffusion within the cell; in addition the orientation, \( \Omega_{LD} \), of the interface must become randomized. In the absence of aggregate reorientation, this requires translational diffusion among cells with different orientations. If the cell orientations are uncorrelated (see below), then the slow correlation function is given by

\[
G^*(t) = \frac{1}{2} \bar{V}_B^2 P_B P^*(B; \ t | B),
\]

(7.1)

where \( P^*(B; \ t | B) \) is the probability of finding the spin in state \( B \) at time \( t \), given that it was initially in state \( B \) in the same cell. Strictly speaking the propagator \( P^*(B; \ t | B) \) can decay to zero only in an infinite three-dimensional system with aggregates of finite extent. This behaviour is a consequence of the continuum version of Pólya's theorem [32], which states that any finite region of space will be visited with unit probability by a particle diffusing in an infinite space of less than three dimensions. This is true not only for free diffusion but also in the presence of a periodic and bounded potential of mean force. In practice, however, the ultimate decay of \( G^*(t) \) is ensured through the intervention of other motions such as aggregate reorientation (cf. equation (3.13)).

In the dynamic cell approximation (DCA) introduced in §3, \( P^*(B; \ t | B) \) in (7.1) is replaced by the propagator \( P_{cell}(B; \ t | B) \), which is prematurely forced to zero by imposing an absorbing cell boundary. This guarantees that \( G^*(t) \) will have an asymptotically exponential tail and, accordingly, that the spectral density will approach Lorentzian shape at the low-frequency end of the dispersion region (cf. figures 8 and 10). The neglect in the DCA of those reencounters that occur after extracellular excursions is reasonable only under special circumstances, e.g. when the aggregate rotational correlation time, \( \tau_r \), is of the same order of magnitude as the cell residence time, \( \tau_{cell} \). In general, however, the DCA is a rather crude approximation. Our excuse for using it here is that it greatly simplifies the task of displaying the essential features of the relaxation behaviour in a system with medium-range order and planar interfaces. Since this model system is somewhat artificial in itself, it does not seem worthwhile to proceed beyond the DCA. We shall return to this problem in subsequent papers, where we discuss systems with cylindrical and spherical interfaces.

In a system with medium-range order, all director orientations with respect to a lab-fixed frame are, by definition, equally probable (cf. equation (3.1)). This requirement, however, does not exclude the possibility that the relative orientation of nearby cells is nonrandom. For example, there may exist a preference for parallel arrangements of neighbouring interfaces. Such orientational correlations between different cells have no effect within the DCA, which postulates that the \( \Omega_{LD} \)-correlation is completely lost at the cell boundary. In a more general version of the theory, however, these correlations will tend to slow down the randomization of the residual coupling \( D_0^2(\Omega_{LD})\bar{V}_B \). It can be shown [23], under certain conditions, that this effect can be incorporated into the theory simply by replacing \( \tau_{cell} \) by \( \tau_{cell}/(1 - S_2) \), where the second-rank order parameter \( S_2 \) is obtained by averaging the second-degree Legendre polynomial over the orientational pair correlation function.
7.4. The interaction model

The molecular interactions enter into the CDM theory via the equilibrium distribution, as reflected in $P_B$, and via the discrete-state diffusion propagator, $P(B; t | B)$. (The implicit dependence of the residual spin–lattice coupling, $\tilde{V}_B$, on the molecular interactions will not concern us here.) In this work we have adopted an electrostatic mean-field model, the PB model described in §4, based on a continuum description of the fluid and of the interface. However, within a few solvent diameters of an interface any continuum theory must fail. It is of interest, therefore, to extend the theory to more realistic interaction models which include short-range forces in the interfacial region. One way to incorporate effects of short-range forces on the propagator, $P(B; t | B)$, is via the potential of mean force, $\psi(x) \propto -\ln f(x)$, in the Smoluchowski diffusion equation (4.1). Alternatively, one can solve the diffusion equation for the $B$ and $F$ regions separately and match the propagators with a partially absorbing boundary condition at $x = \delta$.

It is important to recognize that short-range forces are manifest in qualitatively different ways for solvent (e.g. water) and solute (e.g. counterions) species. In a dilute solution the displacement of a solvent molecule is strongly correlated with displacements of other solvent molecules. The transfer of a solvent molecule from state $B$ to state $F$ will thus, on the average, be coupled to a reverse transfer of another solvent molecule. As a consequence, the potential of mean force is the same in the two states and $P_B$ is unaffected. The short-range forces do, however, affect the dynamics and hence $P(B; t | B)$. This dynamic effect may be modelled by a barrier in the potential of mean force which the solvent molecule has to surmount in order to pass from the $B$ state to the $F$ state or vice versa. In general, the barrier will have a mechanical (direct interactions) as well as an entropic contribution. The latter is present even in a hard sphere fluid at a hard wall [33]. Dilute solute molecules, on the other hand, are not as strongly correlated in the above sense and short-range forces will be manifest in $P_B$ as well as in $P(B; t | B)$.

The PB model not only ignores short-range forces by treating the solvent as a structureless continuum; it also neglects long-range electrostatic correlations among ionic solute species. The accuracy of this electrostatic mean-field approximation has recently been examined by computer simulation of the counterion distribution [34, 35] and of the diffusion propagator [36] in the lamellar geometry of figure 3. For the continuum model (excluding short-range forces and image effects) excellent agreement with the PB model was found for monovalent counterions (in water), whereas substantial deviations occurred for divalent counterions. For divalent ions, however, the neglect of electrostatic correlations may be less serious than the neglect of short-range forces.

8. Conclusions

In this paper we have presented a theory of intramolecular spin relaxation by translational diffusion in locally ordered fluids with planar interfaces. In contrast to previous treatments of this problem, the present CDM theory is based on a self-consistent description of the equilibrium distribution and the continuous translational diffusion of the spin–bearing species. An important feature of this description is that it accounts for diffusional reencounters with the interfacial region. We have demonstrated that such reencounters may produce a spin relaxation behaviour which is qualitatively different from that predicted by the commonly employed DEM theory.
Explicit formulas for the spectral density function have been derived for systems with long-range order (which exhibit line splittings) as well as for systems with medium-range order. In the former case our results should be directly applicable to real systems such as clays and lyotropic liquid crystals, while in the latter case the results are indicative of the qualitative relaxation behaviour to be expected. Corresponding results for systems with cylindrical or spherical interfaces will be reported in subsequent papers. While the formal framework of the CDM theory allows molecular interactions of any complexity to be introduced, we have here focused on the so-called PB model, based on the mean electrostatic potential obtained from the non-linear Poisson–Boltzmann equation.

When the residual spin–lattice coupling is modulated by translational diffusion, it is not possible, in general, to define intrinsic spin relaxation rates for each state or site. As a consequence, the concept of fast and slow exchange, as used in connection with the DEM theory, is not valid. When translational diffusion is the relaxation mechanism, the secular (zero-frequency) contribution to the relaxation rate increases monotonically with decreasing temperature until the diffusion becomes so slow that one leaves the perturbation regime. However, before this breakdown of the theory occurs other motions, such as aggregate reorientation, may take over the modulation of the residual spin–lattice coupling.

The CDM theory has been developed with two important applications in mind, namely relaxation of counterion nuclei and water nuclei in locally ordered fluids. We are not aware of any detailed study of counterion relaxation in systems with long-range order. However, in conjunction with the CDM theory such studies may provide valuable information about counterion diffusion near interfaces. As regards systems with medium-range order, a large amount of counterion relaxation data has been reported. When these data are analysed in terms of the CDM theory, previous interpretations may, in some cases, have to be revised. The CDM theory (in the SSA limit and adapted to cylindrical geometry) was recently tested [23] against an extensive set of data on $^{23}$Na counterion (secular) relaxation in polyelectrolyte solutions [37]. Quantitative agreement was obtained.

In the case of water nuclei, there have been reports [6, 9] of relaxation by translational diffusion in systems with long-range order. In our opinion, these findings are not entirely conclusive; further studies on well-defined model systems would be of value. Recent water $^{17}$O relaxation studies [38, 39] on locally ordered aqueous solutions demonstrate that translational diffusion can be a relaxation mechanism in systems with medium-range order. However, it appears that the results can be explained only if short-range forces are invoked.

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**APPENDIX**

*The fast correlation function*

In this Appendix we derive equations (2.20) and (3.9) for the fast correlation function. In the case of systems with long-range order, we insert (2.13) into (2.18) and use (2.15), to obtain
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\[ G_k(t) = \sum_m \sum_q D_{km}^2(\Omega_{LD})D_{kq}^2(\Omega_{LD}) \sum_{\Gamma^0} P(\Gamma^0) \times \left\{ \sum_m \sum_q \frac{V_m(\Gamma^0) V_q(\Gamma^0)}{2 \sigma_0^m(\Gamma^0) \sigma_0^q(\Gamma^0)} \int d\Omega_{DP} f(\Omega_{DP}^0 | \Gamma^0) \int d\Omega_{DP} f(\Omega_{DP}; t | \Omega_{DP}^0; \Gamma^0) \times D_{mm}^2(\Omega_{DP})D_{qq}^2(\Omega_{DP}) - \delta_{m0} \delta_{q0} [V(\Gamma^0)]^2 \right\}. \]  

(A 1)

Assuming that \( f(\Omega_{DP} | \Gamma) \) has at least fivefold rotation symmetry with respect to the director and using a symmetry theorem due to Wennerström [5], we find

\[ G_k(t) = \sum_m \left[ d_{km}^2(\theta_{LD}) \right]^2 g_m(t), \]  

(A 2)

with

\[ g_m(t) = \sum_{\Gamma^0} P(\Gamma^0) \times \left\{ \sum_m \sum_q \frac{V_m(\Gamma^0) V_q(\Gamma^0)}{2 \sigma_0^m(\Gamma^0) \sigma_0^q(\Gamma^0)} \int d\Omega_{DP} f(\Omega_{DP}^0 | \Gamma^0) \times \int d\Omega_{DP} f(\Omega_{DP}; t | \Omega_{DP}^0; \Gamma^0) D_{mm}^2(\Omega_{DP})D_{mq}^2(\Omega_{DP}) - \delta_{m0} [V(\Gamma^0)]^2 \right\} \]

\[ = \sum_{\Gamma^0} P(\Gamma^0) \times \left\{ \sum_m \sum_q \frac{V_m(\Gamma^0) V_q(\Gamma^0)}{2 \sigma_0^m(\Gamma^0) \sigma_0^q(\Gamma^0)} \int d\Omega_{DP} f(\Omega_{DP}^0 | \Gamma^0) \times D_{mm}^2(\Omega_{DP})D_{mq}^2(\Omega_{DP}) - \delta_{m0} [V(\Gamma^0)]^2 \right\} \]

\[ G_k(t), \]  

(A 3)

where the last step defines the effective reduced correlation function \( \bar{G}_k(t | \Gamma^0) \) associated with the reorientation of the principal coupling frame in state \( \Gamma^0 \).

From the product formula for the \( D \)-elements and the orthogonality of the \( 3-j \) symbols [22], it follows that

\[ \sum_m \left[ d_{km}^2(\theta_{LD}) \right]^2 D_{mm}^2(\Omega_{DP})D_{mq}^2(\Omega_{DP}) \]

\[ = (-1)^{\lambda + q} \sum_{j=0}^4 (2j + 1) \binom{2}{k} \binom{2}{m'} \binom{2}{q'} \binom{2}{j} \begin{pmatrix} 2 & 2 & j \\ -k & k & 0 \end{pmatrix} \begin{pmatrix} 2 & 2 & j \\ -m' & q' & m' - q' \end{pmatrix} d_{00}^j(\theta_{LD})D_{0, m' - q}^j(\Omega_{DP}). \]  

(A 4)

We assume that the surface-induced orientational bias is small so that we may write

\[ \int d\Omega_{DP} f(\Omega_{DP}^0 | \Gamma^0)D_{0, m' - q}^j(\Omega_{DP}) = \delta_{j0} \delta_{m' q'}. \]  

(A 5)

From (2.15) and (A 5), it follows that \( \bar{V}(\Gamma^0) = 0 \). On combining equations (A 2)–(A 5), we then arrive at the desired result

\[ G_k(t) = \frac{1}{5} \sum_{\Gamma^0} P(\Gamma^0)[V(\Gamma^0)]^2 \bar{G}_k(t | \Gamma^0), \]  

(A 6)

with \( V(\Gamma) \) defined by (2.21). For a two-state system, (A 6) reduces to (2.20).

In the case of systems with medium-range order, we insert (3.5) into (3.7) and use (2.15). The result is given by (A 1) with the replacement

\[ D_{km}^2(\Omega_{LD})D_{kq}^2(\Omega_{LD}) \rightarrow \int d\Omega_{LD} f(\Omega_{LD})D_{km}^2(\Omega_{LD})D_{kq}^2(\Omega_{LD}) = \delta_{mq \frac{1}{2}}. \]  

(A 7)
The equality in (A7) is a consequence of (3.1) and the orthogonality of the D-elements. This leads to

$$G(t) = \frac{1}{5} \sum_m g_m(t), \quad (A8)$$

with $g_m(t)$ given by (A3), which in the present case may be simplified by noting that

$$\sum_m D_{mm'}(\Omega_{dp}) D_{mq'}(\Omega_{dp}) = \delta_{m,q'}, \quad (A9)$$

by virtue of the unitarity of the Wigner matrices. Collecting results and using (2.21), we arrive at

$$G(t) = \frac{1}{5} \sum \{ P(\Gamma^0) [V(\Gamma^0)]^2 - \{ \tilde{V}(\Gamma^0) \}^2 \} G(t|\Gamma^0), \quad (A10)$$

which is equation (3.9) for our two-state system. If the residual coupling, $\tilde{V}(\Gamma^0)$, is small, (A10) reduces to (A6), as expected.

REFERENCES

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[31] For example, [5, 23] and work cited therein.