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Spin relaxation in cubic liquid crystals

The role of symmetry

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Cubic liquid-crystalline phases are usually regarded as isotropic systems. This view is justified for physical properties that transform as second rank tensors. However, the time correlation functions describing spin relaxation in cubic phases include components that transform as fourth rank tensors, which distinguish between cubic and spherical symmetry. In this work we explore the consequences of this fact for spin relaxation behaviour in cubic phases using group theoretical methods. We identify the two irreducible crystal frame time correlation functions of a cubic phase, derive the orientation dependence of the laboratory frame time correlation functions for single crystal samples, and discuss the relation of the cubic (fourth rank) order parameter to the microstructure of the phase. Finally, as an illustration of the general results, we derive the time correlation functions for a specific model of a micellar cubic phase.

1. Introduction

Liquid-crystalline phases of cubic symmetry have been identified in a variety of surfactant–water systems, ranging from simple detergents to complex mixtures of membrane lipids [1–3], but are not as well understood as the classical lamellar and hexagonal phases. Most recent work on cubic phases has focused on their microstructure, i.e. the symmetry, topology, and local geometry of the dividing interface that separates the polar and apolar regions. While small-angle X-ray (and neutron) scattering can provide information about crystal symmetry (space group) and translational order (lattice parameter), spin relaxation can yield more detailed information about the interface geometry. Several nuclear spin relaxation studies of bicontinuous [4–9] and micellar [7, 9–13] cubic phases have been reported.

The unit cell of a cubic liquid crystal exhibits a high degree of rotational symmetry. Any physical quantity that transforms under rotation as a second rank tensor vanishes when averaged over the unit cell. For this reason cubic phases are non-birefringent (optically isotropic) and usually yield high resolution NMR spectra characteristic of isotropic fluids [14, 15]. These properties led early workers in the field to use the term viscous isotropic phase. However, cubic phases are not isotropic; the unit cell exhibits the symmetry of the octahedral point group rather than that of the full three dimensional rotation group [16]. The purpose of the present work is to explore the consequences of this fact for the spin relaxation behaviour.

Since NMR spectra from cubic liquid crystals do not usually exhibit frequency shifts associated with a static spin–lattice coupling, it has generally been assumed that the spin relaxation behaviour is also analogous to that of isotropic liquids [4–13]. This is not the case. Since the second rank spin–lattice coupling tensor (for example an

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electric field gradient tensor, an intramolecular magnetic dipole–dipole interaction tensor, or an anisotropic chemical shift tensor) vanishes when averaged over the cubic unit cell, the Zeeman transitions remain degenerate and the equation of motion for the spin density operator takes the same form as for isotropic fluids. As a result, the spectral lineshape is qualitatively the same for cubic phases and isotropic fluids. However, the relaxation superoperator, being of second order in the spin–lattice coupling, has components transforming as fourth rank tensors, which behave differently in cubic and spherically symmetric systems. As regards the spin relaxation behaviour, it is important, therefore, to recognize that cubic liquid crystals are in fact anisotropic fluids.

The most obvious NMR consequence of the anisotropy of cubic phases is the dependence of the spin relaxation rates on the orientation of the crystal with respect to the static magnetic field. These rates are linear combinations of three distinct laboratory frame spectral density functions, which are the cosine transforms of the corresponding laboratory frame time correlation functions. Each of these three functions is a different function of the crystal orientation. Although single crystal samples of cubic phases can be prepared [17], all spin relaxation studies so far reported have been performed on powder samples with an isotropic distribution of cubic unit cell orientations. If the inter-domain diffusion is fast compared to the orientational variation of the spin relaxation rates, the three isotropically averaged laboratory frame spectral density functions become identical, just as for an isotropic fluid.

Even in a powder sample, however, the cubic symmetry plays an important role for the spin relaxation. In liquid crystals, molecular motions are naturally referred to a crystal frame chosen according to the symmetry of the unit cell. For a cubic phase of octahedral symmetry, the axes of the crystal frame would thus be identified with the orthogonal four-fold axes in the unit cell. The single isotropically averaged laboratory frame time correlation function can then be expressed as a linear combination of crystal frame time correlation functions. The question then arises: how many distinct crystal frame time correlation functions are there for a cubic liquid crystal, and what is their form? This question can be answered by invoking a group theoretical selection rule [18, 19]. We thus find that there are two distinct crystal frame time correlation functions for a cubic phase and we refer to these as the irreducible time correlation functions, since they are associated with irreducible representations of the symmetry group of the liquid crystal. This result may be contrasted with the well-known cases of isotropic fluids [20], with only one irreducible time correlation function, and uniaxial or hexagonal liquid-crystalline phases [21–23], with three irreducible time correlation functions. Group theoretical analyses of orientational time correlation functions have previously been presented in connection with the theory of quasi-elastic neutron scattering and Raman spectroscopy in molecular crystals [24, 25]. General discussions of the symmetry imposed constraints on orientational time correlation functions in isotropic fluids have also appeared [26, 27]. Although the present case of an axially symmetric interaction tensor in a cubic liquid crystal is formally analogous to the case of an octahedral molecule in an isotropic fluid, explicit results for the orientation dependence of the laboratory frame time correlation functions and the relation of the crystal frame irreducible time correlation functions to the cubic order parameter have not, to our knowledge, been presented previously.

In complex fluids, spin relaxation is generally induced by a variety of motions of different symmetries and on different time scales. Although the faster local motions may be quite complex, the slowest motion reflects the full symmetry of the system. It is this motion that is described by the crystal frame irreducible time correlation functions. Thus, in isotropic fluids the single irreducible time correlation function describes the isotropic motion, whereas, in cubic liquid crystals, the two crystal frame irreducible time correlation functions describe the cubic motion.

On the basis of the topology of the dividing interface, lyotropic cubic phases are classified as either bicontinuous cubic phases, where both the polar and apolar regions are connected over macroscopic distances in three dimensions, or micellar cubic phases, containing closed surfactant aggregates. In bicontinuous cubic phases the dividing interface directly reflects the cubic symmetry. The cubic motion is then the diffusion of interfacial species (for example nuclei belonging to the surfactant molecule or its counterion, which are effectively confined to the interface) over the dividing interface. Using concepts from the differential geometry of minimal surfaces, we have recently [28] considered in detail the cubic irreducible time correlation functions. describing surface diffusion in bicontinuous cubic phases whose microstructure can be modelled in terms of triply periodic minimal surfaces. In micellar cubic phases it is the spatial arrangement of the micelles that reflects the cubic symmetry and the cubic motion is the process that allows the spin-bearing species to sample all of the inequivalent micelles of the cubic unit cell. Molecular diffusion over the surface of the individual micelles also contributes to the spin relaxation in micellar cubic phases, but this contribution is not described by cubic irreducible time correlation functions. If the micelles are uniaxial, surface diffusion is instead described by the three uniaxial irreducible time correlation functions, which, in the case of spheroidal micelles, have been considered in detail elsewhere [29].

The outline of this paper is as follows. In § 2 we define the laboratory frame and crystal frame time correlation functions, and in § 3 we make use of group theory to identify the two cubic irreducible time correlation functions. These results are then used in § 4 to derive the orientation dependence of the observed laboratory frame time correlation functions for single crystal cubic phases and the observed linear combination of irreducible time correlation functions for powder samples. In § 5 we express the initial time correlation functions in terms of the cubic order parameter, which is the average of the fourth rank Legendre polynomial over the cubic orientational distribution function. The cubic order parameter contains information about the geometry of the interface in bicontinuous phases and about the spatial arrangement of the aggregates in micellar phases. Results for specific microstructural and dynamic models are then presented for bicontinuous and micellar phases in §§ 6 and 7, with the emphasis on micellar cubic phases.

2. Laboratory frame and crystal frame time correlation functions

We consider a system of nuclear spins whose interaction with the molecular environment is described by a second rank irreducible tensor **V**, for example an electric quadrupole–field gradient coupling, an intra-molecular magnetic dipole–dipole coupling, or an anisotropic chemical shift coupling [30]. In the motional narrowing regime, where the spin system evolves according to the Bloch–Wangsness–Redfield equation of motion [30], the relaxation behaviour of the spin system is governed by the three laboratory frame time correlation functions $G_k^L(\tau)$, with $k = 0, 1, 2$, of the kth spherical component V_k^L, in a laboratory fixed frame, of the spin–lattice coupling tensor **V**,

$$G_k^L(\tau) = \langle V_k^{L*}(0) V_k^L(\tau) \rangle. \tag{2.1}$$

In a liquid crystal of cubic symmetry, if the diffusion of the spin-bearing molecule across the unit cell is fast compared to the spin–lattice coupling frequency, the diffusionally averaged coupling tensor vanishes,

$$\langle V^L_k \rangle = 0. \tag{2.2}$$

(The minimum symmetry requirement is two orthogonal three-fold axes [31].) In a cubic liquid crystal, the static (diffusionally averaged) spin-lattice coupling (and the associated frequency shift) thus vanishes, and the time correlation functions $G^L_k(\tau)$ in equation (2.1) decay to zero as $\tau \to \infty$; just as in an isotropic (spherically symmetric) liquid.

In order to identify contributions from different motional degrees of freedom, we introduce three coordinate systems denoted by L, C, and D. The z_L, z_C, and z_D axes are defined, respectively, by the static magnetic field, a four-fold axis in the (octahedral) cubic unit cell, and the local director. In bicontinuous cubic phases the local director is the normal to the dividing interface at the current position of the spin-bearing molecule, whereas in micellar cubic phases it defines the preferred orientation of a particular micellar aggregate in the unit cell. For simplicity, we assume that the local director is (at least) a three-fold axis. This should be a good approximation in most cases (cf. §§ 6 and 7). In this section we focus on the fluctuations in $V^L_k(\tau)$ associated with the cubic motion, i.e. the stochastic time dependence of the orientation $\Omega_{CD}(\tau)$ of the local director in the crystal frame. We assume that the motions modulating the director frame components $V^D_p(\tau)$ are much faster than those modulating $\Omega_{CD}(\tau)$. After averaging over the former motions, the transformation of the laboratory frame components $V^L_k(\tau)$ to the local director frame takes the form

$$V^L_k(\tau) = (-1)^k \sum_n D^2_{-kn}(\Omega_{LC}) D^2_{n0}[\Omega_{CD}(\tau)] \langle V^D_0 \rangle, \tag{2.3}$$

where $D^2_{\alpha\beta}(\Omega_{XY})$ are the elements of the second rank Wigner rotation matrix and Ω_{XY} denotes the set of Euler angles specifying the relative orientation of the X and Y frames [32]. In equation (2.3) and elsewhere the range of the summation indices is from -2 to $+2$, unless otherwise specified. The orientation, Ω_{LC}, of the cubic unit cell with respect to the static magnetic field is taken to be time independent. It should be noted that, unless the cubic phase is uniformly aligned, spatial diffusion through the sample causes Ω_{LC} to fluctuate in time. Typically, such fluctuations are fast compared to the spread of Ω_{LC} dependent spin relaxation rates. The contribution to the relaxation rates from Ω_{CD} fluctuations is then obtained simply by averaging the orientation dependent rates (and time correlation functions) over the Ω_{LC} distribution. In the following we make the assumption that the residual coupling $\langle V^D_0 \rangle$ in equation (2.3) is not modulated by the motions that induce Ω_{CD} fluctuations. For notational convenience, we set it equal to unity.

Substitution of equation (2.3) into equation (2.1) yields

$$G^L_k(\tau; \Omega_{LC}) = \sum_n \sum_{n'} D^{2*}_{-kn}(\Omega_{LC}) D^2_{-kn'}(\Omega_{LC}) G^C_{nn'}(\tau), \tag{2.4}$$

where we have introduced the crystal frame time correlation functions

$$G^C_{nn'}(\tau) = \langle D^{2*}_{n0}(\Omega^0_{CD}) D^2_{n'0}(\Omega_{CD}) \rangle, \tag{2.5}$$

with the zero superscript denoting the initial time. Since n and n' range from -2 to $+2$, there are 25 (complex-valued) crystal frame time correlation functions to consider. Fortunately, this number can be reduced by exploiting the symmetries of the dynamic process and of the liquid-crystalline phase. If the stochastic process $\Omega_{CD}(\tau)$ obeys detailed balance, as is the case for all diffusion and exchange processes of interest in lyotropic liquid crystals, then the time correlation functions are invariant under time reversal [33], i.e.

$$G^C_{nn'}(-\tau)=G^C_{nn'}(\tau), \tag{2.6}$$

implying that the time correlation function matrix is hermitian,

$$G^{C*}_{nn'}(\tau)=G^C_{n'n}(\tau). \tag{2.7}$$

This symmetry relation reduces the number of crystal frame time correlation functions from 25 to 15. On account of the conjugation symmetry of the Wigner functions [32], we have the additional symmetry relation

$$G^{C*}_{nn'}(\tau)=(-1)^{n+n'}G^C_{-n-n'}(\tau), \tag{2.8}$$

which further reduces the number of time correlation functions from 15 to 9. Of these, 6 are off-diagonal (cross) time correlation functions and, hence, complex-valued. Consequently, there are actually 15 distinct real-valued quantities.

3. Irreducible time correlation functions

As a consequence of the cubic symmetry of the unit cell, there are only two distinct (real-valued) crystal frame time correlation functions. To demonstrate this, we make use of a group-theoretical selection rule for time correlation functions [19, 24–27]:

> If the functions A^k_q and $B^{k'}_{q'}$ transform as the components q and q' of the irreducible representations k and k' of the symmetry group of the system, then their time correlation function is non-zero only if $q=q'$ and $k=k'$, and is then independent of q, i.e.
>
> $$\langle A^{k*}_q(0)B^{k'}_{q'}(\tau)\rangle=\delta_{qq'}\delta_{kk'}\langle A^{k*}(0)B^k(\tau)\rangle. \tag{3.1}$$

The derivation of this selection rule is straightforward; it is entirely analogous to the well-known selection rule for matrix elements of the hamiltonian (or any other scalar operator) [34]. Alternatively, it may be regarded as a special case (scalar operator) of the generalized Wigner–Eckart theorem (for arbitrary groups) [18, 35]. The time correlation function on the right hand side of equation (3.1), which is independent of the component index, will be referred to as an irreducible time correlation function. It is analogous to the reduced matrix element in the Wigner–Eckart theorem. If $A=B$, as in our case, and if the stochastic process obeys detailed balance, it follows from equations (2.7) and (3.1) that all irreducible time correlation functions are real-valued.

We consider a cubic unit cell with the symmetry of the octahedral point group O (or 432 in the short Hermann–Mauguin notation). (The results are the same for the full octahedral group O_h (or m$\bar{3}$m), which also contains the inversion element.) While the Wigner functions (or spherical harmonics) $D^2_{n0}(\Omega)$ with $n=0, \pm 1, \pm 2$ form a basis for representing the group O, this representation is not irreducible (as it is for the full three dimensional rotation group K). In order to apply the symmetry theorem from equation (3.1) we therefore construct linear combinations of Wigner functions that transform as components of the irreducible representations of the group O. The required symmetry adapted functions, first employed to solve the one electron Schrödinger equation with an octahedral lattice potential [36, 37], are referred to as cubic harmonics. We define them as

$$K^E_0(\Omega)=D^2_{00}(\Omega), \tag{3.2 a}$$

$$K_2^E(\Omega)=\frac{1}{\sqrt{2}}[D_{20}^2(\Omega)+D_{-20}^2(\Omega)], \tag{3.2 b}$$

$$K_1^T(\Omega)=D_{10}^2(\Omega), \tag{3.2 c}$$

$$K_{-1}^T(\Omega)=D_{-10}^2(\Omega), \tag{3.2 d}$$

$$K_2^T(\Omega)=\frac{1}{\sqrt{2}}[D_{20}^2(\Omega)-D_{-20}^2(\Omega)]. \tag{3.2 e}$$

As indicated by the superscripts, the cubic harmonics of rank 2 belong either to the two dimensional irreducible representation E or to the three dimensional irreducible representation T_2 of the group O (we use Mulliken's notation for the irreducible representations). Furthermore, they obey the orthogonality relation

$$\int d\Omega[K_n^{(j)}(\Omega)]^*K_{n'}^{(j')}(\Omega)=\delta_{jj'}\delta_{nn'}\frac{4\pi}{5}, \tag{3.3}$$

where the integration is over the two Euler angles $\Omega=(\phi_C, \theta_{CD}, -)$ and $d\Omega=d\phi_C d\theta_{CD} \sin\theta_{CD}$.

With the aid of equation (3.2) we can now express the crystal frame time correlation functions in equation (2.5) in terms of cubic harmonics, and then apply the symmetry theorem in equation (3.1). We thus find that the three laboratory frame time correlation functions in equation (2.4) take the form

$$G_k^L(\tau;\theta_{LC},\phi_C)=F_k^E(\theta_{LC},\phi_C)G_E^C(\tau)+F_k^T(\theta_{LC},\phi_C)G_T^C(\tau), \tag{3.4}$$

where we have introduced the two cubic irreducible time correlation functions

$$\begin{aligned}G_E^C(\tau)&=\langle K^{E*}(\Omega_{CD}^0)K^E(\Omega_{CD})\rangle\\&=G_{00}^C(\tau)=G_{22}^C(\tau)+\operatorname{Re}[G_{2-2}^C(\tau)],\end{aligned} \tag{3.5 a}$$

$$\begin{aligned}G_T^C(\tau)&=\langle K^{T*}(\Omega_{CD}^0)K^T(\Omega_{CD})\rangle\\&=G_{11}^C(\tau)=G_{22}^C(\tau)-\operatorname{Re}[G_{2-2}^C(\tau)].\end{aligned} \tag{3.5 b}$$

Note that, in contrast to isotropic fluids and uniaxial phases, the cross correlation function $G_{2-2}^C(\tau)$ does not vanish in a cubic phase.

4. Orientation dependence

The angular functions in equation (3.4), which determine the dependence of the spin relaxation rates on the orientation (θ_{LC}, ϕ_C) of the crystal frame with respect to the static magnetic field, can be expressed as

$$F_0^E=1-F_0^T=1-3\sin^2\theta_{LC}+\tfrac{3}{2}H, \tag{4.1 a}$$

$$F_1^E=1-F_1^T=2\sin^2\theta_{LC}-H, \tag{4.1 b}$$

$$F_2^E=1-F_2^T=\tfrac{1}{2}\cos^2\theta_{LC}+\tfrac{1}{4}H, \tag{4.1 c}$$

$$H=\tfrac{1}{4}\sin^4\theta_{LC}[7+\cos(4\phi_C)]. \tag{4.1 d}$$

The dependence on the azimuthal angle ϕ_C is a characteristic feature of symmetries where z_C is an n-fold axis with $n<5$. As seen from equation (2.4) the ϕ_C dependence in cubic phases is directly related to the non-zero cross correlation function $G_{2-2}^C(\tau)$. Since the octahedral unit cell contains three orthogonal four-fold axes, the angular functions in equations (4.1) must be invariant under a 90° rotation about any of these axes. This property is readily verified from equations (4.1). For example, for any of the orientations $(\theta_{LC}, \phi_C) = (0°, 0°)$, $(0°, 90°)$, $(90°, 0°)$, and $(90°, 90°)$ we obtain from equations (3.4) and (4.1)

$$G_0^L(\tau) = G_E^C(\tau), \tag{4.2 a}$$

$$G_1^L(\tau) = G_T^C(\tau), \tag{4.2 b}$$

$$G_2^L(\tau) = \tfrac{1}{2}[G_E^C(\tau) + G_T^C(\tau)]. \tag{4.2 c}$$

The angular functions in equations (4.1) are shown in the figure for $\phi_C = 0°$ and 45°. The dependence on ϕ_C, i.e. the angle of rotation about the four-fold axis, is seen to be weak for $\theta_{LC} < 30°$.

The full information content of the quadrupolar (or homonuclear dipolar) spin relaxation behaviour (at a given Larmor frequency ω_0) of a cubic single crystal consists of the six irreducible spectral densities $J_E^C(k\omega_0)$ and $J_T^C(k\omega_0)$ with $k = 0, 1, 2$, where, for example

$$J_E^C(\omega) = \int_0^\infty d\tau \cos(\omega\tau) G_E^C(\tau). \tag{4.3}$$

To extract these six quantities it is necessary to determine three linearly independent spin relaxation rates at two different crystal orientations. For example, by choosing the orientations (θ_{LC}, ϕ_C) as $(0°, 0°) = A$ and $(90°, 45°) = B$, we obtain

$$J_E^C(0) = J_0^L(0, A), \tag{4.4 a}$$

$$J_E^C(\omega_0) = 2J_1^L(\omega_0, B) - J_1^L(\omega_0, A), \tag{4.4 b}$$

$$J_E^C(2\omega_0) = 5J_2^L(2\omega_0, A) - 4J_2^L(2\omega_0, B), \tag{4.4 c}$$

$$J_T^C(0) = \tfrac{1}{3}[4J_0^L(0, B) - J_0^L(0, A)], \tag{4.4 d}$$

$$J_T^C(\omega_0) = J_1^L(\omega_0, A), \tag{4.4 e}$$

$$J_T^C(2\omega_0) = 4J_2^L(2\omega_0, B) - 3J_2^L(2\omega_0, A). \tag{4.4 f}$$

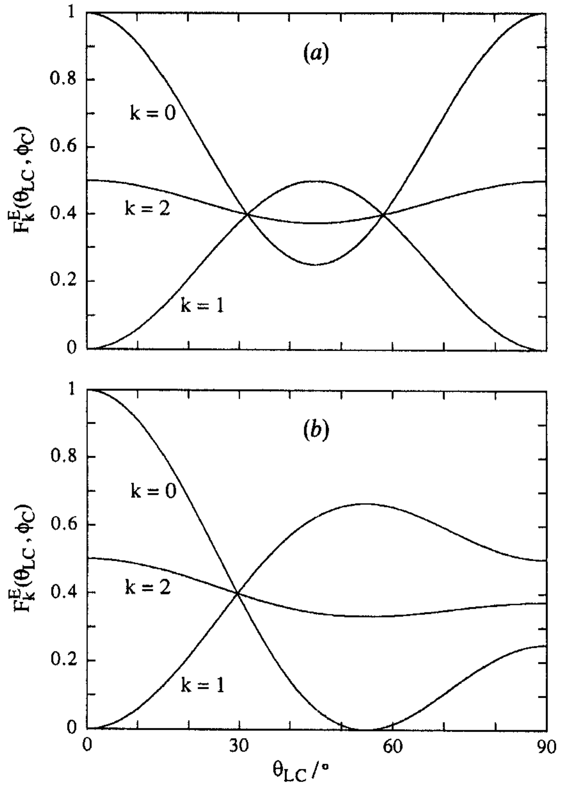
For a powder sample, with a random distribution of unit cell orientations, the information content of the spin relaxation rates is reduced. If diffusion among spatial regions with different unit cell orientations is fast compared to the corresponding difference in relaxation rates, the laboratory frame time correlation function that is probed is simply the isotropic average of equation (3.4), i.e.

$$\begin{aligned} G_{\text{iso}}^L(\tau) &= \frac{1}{4\pi} \int_0^{2\pi} d\phi_C \int_0^\pi d\theta_{LC} \sin\theta_{LC} G_k^L(\tau; \theta_{LC}, \phi_C), \\ &= \tfrac{2}{5} G_E^C(\tau) + \tfrac{3}{5} G_T^C(\tau). \end{aligned} \tag{4.5}$$

As seen from the figure, a single crystal can yield the same relaxation behaviour as a powder sample for particular crystal orientations, for example $(\theta_{LC}, \phi_C) = (31{\cdot}72°, 0°)$, $(58{\cdot}28°, 0°)$, or $(29{\cdot}67°, 45°)$.

5. The cubic order parameter

The initial values of the crystal frame time correlation functions in equation (2.5) can all be expressed entirely in terms of the fourth rank orientational order parameter



Angular functions $F_k^E(\theta_{LC}, \phi_C) = 1 - F_k^T(\theta_{LC}, \phi_C)$ with $k = 0, 1, 2$, for $\phi_C = 0°$ (*a*) and $\phi_C = 45°$ (*b*).

Q, defined as the average over the cubic unit cell of the fourth rank Legendre polynomial

$$Q = \langle P_4(\cos \theta_{CD}) \rangle. \tag{5.1}$$

We refer to this as the cubic order parameter. Expanding the product of Wigner functions in equation (2.5) in a Clebsch–Gordan series [32], we obtain

$$G^C_{nn'}(0) = \delta_{nn'} \frac{1}{5} + (-1)^n \frac{9\sqrt{2}}{\sqrt{35}} \begin{pmatrix} 2 & 2 & 4 \\ n & -n' & n'-n \end{pmatrix} \langle D^4_{n-n',0}(\Omega_{CD}) \rangle. \tag{5.2}$$

Although there is only one unique order parameter of rank $1 \leqslant k \leqslant 4$ for an axially symmetric interaction tensor in a cubic crystal [38, 39], there are actually two non-zero order parameters of rank $1 \leqslant k \leqslant 4$, namely

$$\langle D^4_{00}(\Omega_{CD}) \rangle = Q, \tag{5.3}$$

$$\langle D^4_{\pm 40}(\Omega_{CD}) \rangle = \frac{\sqrt{5}}{\sqrt{14}} Q. \tag{5.4}$$

Combination of equations (5.2)–(5.4) yields the following non-zero initial time correlation functions

$$G^C_{00}(0) = \tfrac{1}{5} + \tfrac{18}{35} Q, \tag{5.5 a}$$

$$G^C_{11}(0) = G^C_{-1-1}(0) = \tfrac{1}{5} - \tfrac{12}{35} Q, \tag{5.5 b}$$

$$G^C_{22}(0) = G^C_{-2-2}(0) = \tfrac{1}{5} + \tfrac{3}{35}Q, \tag{5.5 c}$$

$$G^C_{2-2}(0) = G^C_{-22}(0) = \tfrac{3}{7}Q. \tag{5.5 d}$$

For the irreducible time correlation functions in equation (3.5) we thus have

$$G^C_E(0) = \tfrac{1}{5} + \tfrac{18}{35}Q, \tag{5.6 a}$$

$$G^C_T(0) = \tfrac{1}{5} - \tfrac{12}{35}Q. \tag{5.6 b}$$

Substitution into equation (4.5) yields $G^L_{\text{iso}}(0) = \frac{1}{5}$, as expected for a motionally averaged powder sample.

Although we have assumed that the cubic unit cell possesses octahedral symmetry (O or O_h), all of our results are in fact valid also for the tetrahedral point groups T_h and T_d [16]. In the case of tetrahedral symmetry the z_C axis should be taken as one of the three orthogonal two-fold axes. (There is no four-fold axis in these groups.)

From its definition equation (5.1), it follows that the fourth rank order parameter is confined to the range

$$-\tfrac{3}{7} \leqslant Q \leqslant 1, \tag{5.7}$$

which is simply the range of $P_4(\cos\theta)$ for $0 \leqslant \theta \leqslant \pi$. The cubic symmetry further restricts Q to the range

$$-\tfrac{7}{18} \leqslant Q \leqslant \tfrac{7}{12}. \tag{5.8}$$

These limits follow directly from equation (5.5) by noting that any auto correlation function must have a non-negative initial value. The cubic point groups are unique in that the symmetry not only selects the non-zero order parameters, but also imposes restrictions on the value of the fourth rank order parameter.

The cubic order parameter is determined by the distribution function $f(\theta_{CD})$ for the angle θ_{CD} between the local director and the crystal fixed z_C axis. This distribution function must be invariant under all symmetry operations of the cubic point group. The upper limit, $Q = \frac{7}{12}$, corresponds to a distribution with the local director pointing with equal probability in any of the six orthogonal directions along the four-fold axes. The lower limit, $Q = -\frac{7}{18}$, corresponds to a distribution with the local director pointing with equal probability toward any of the eight corners of the cubic unit cell.

6. Biconlinuous cubic phases

In the case of bicontinuous cubic phases the local director is identified with the normal to the dividing interface at the current position of the spin-bearing molecule or ion. The stochastic time dependence of the Euler angles $\Omega_{CD}(\tau)$ then reflects the diffusion of the spin-bearing species over the dividing interface. In recent years bicontinuous cubic phases have been successfully modelled in terms of triply periodic minimal surfaces [40–45], in particular Schwarz's diamond (D) and primitive (P) surfaces and Schoen's gyroid (G) surface, which are the three cubic triply periodic minimal surfaces of simplest topology [46–49]. A theoretical description of spin relaxation induced by surface diffusion on these cubic triply periodic minimal surfaces as well as on their parallel surfaces has been presented elsewhere [28].

For the D, P, and G triply periodic minimal surfaces and their parallel surfaces, the cubic order parameter, which determines the initial irreducible time correlation functions through equation (5.6), is confined to the range [28]

$$-0{\cdot}24584 \leqslant Q \leqslant -0{\cdot}10423, \tag{6.1}$$

the upper limit pertaining to the minimal surface and the lower limit to the maximally displaced parallel surface. The cubic order parameter is negative because the normal vector distribution for these surfaces is peaked at the eight flat points (with vanishing gaussian curvature) of the surface, where the normal vector points towards a corner of the cubic unit cell (cf. § 5).

While the two irreducible time correlation functions $G_E^C(\tau)$ and $G_T^C(\tau)$ have different initial values, they have the same initial slope [28]

$$\left.\frac{d}{d\tau}G_E^C(\tau)\right|_{\tau=0}=\left.\frac{d}{d\tau}G_T^C(\tau)\right|_{\tau=0}=\tfrac{6}{5}D_S\langle K\rangle, \tag{6.2}$$

where D_S is the surface diffusion coefficient of the spin-bearing species, and $\langle K\rangle$ is the average over the cubic unit cell of the (negative) gaussian curvature of the minimal surface. This exact result can be used to construct single exponential approximations to the two cubic irreducible time correlation functions [28].

The only microstructural model used previously to interpret spin relaxation data from bicontinuous cubic phases is the inscribed sphere model [7–9], where the actual bicontinuous dividing interface is replaced by a sphere of diameter equal to the cubic lattice parameter. The spin relaxation is then ascribed to force-free diffusion on the surface of this immobile (non-rotating) sphere. If used to determine the lattice parameter, this model may lead to an underestimate by as much as a factor of two [28]. Furthermore, since the inscribed sphere model does not possess the required cubic symmetry (of the unit cell), it fails to predict orientation-dependent spin relaxation rates from single crystal samples.

7. Micellar cubic phases

The case of micellar cubic phases, where the unit cell contains several micelles that may differ in shape and orientational constraints, is more complicated than the case of bicontinuous phases. In addition to molecular diffusion over the closed micellar surfaces, we must also consider the restricted reorientation of the micelles, and the cubic motion whereby the spin-bearing species is allowed to sample the full cubic symmetry of the unit cell (cf. § 1). The cubic process may be molecular interchange among the micelles, interchange of entire micelles, or something intermediate such as a fusion–fission process.

The simplest case is a cubic spatial arrangement of identical spherical micelles. The results of sections 3–5 are then applicable for the combined molecular surface diffusion and micelle rotation in the cubic potential set up by the surrounding micelles. In practice, however, the effect of inter-micellar (mainly electrostatic) interactions on the diffusion of a spin-bearing ionic species over the spherical interface may be sufficiently small that the spin relaxation behaviour can be treated as in an isotropic fluid of spherical micelles.

The currently favoured structural models of micellar cubic phases involve non-spherical micelles [50, 51]. We consider, therefore, a cubic unit cell composed of N non-spherical micelles of identical size and shape. For simplicity, we assume that the micelle shape is uniaxial and that the potential of mean torque experienced by each micelle is also uniaxial. We let these symmetry axes define the z axes of the aggregate (A) frame and the local director (D) frame, respectively. Further, the z_M axis of the M frame is identified with the normal to the micellar surface at the current position of the spin-bearing species. As before, we assume that the local surface normal is (at least) a threefold axis. In place of equation (2.3) we then have

$$V_k^L(\tau) = (-1)^k \sum_n \sum_p \sum_q D^2_{-kn}(\Omega_{LC}) D^2_{np}[\Omega_{CD}(\tau)] D^2_{pq}[\Omega_{DA}(\tau)] D^2_{q0}[\Omega_{AM}(\tau)]. \tag{7.1}$$

The three sets of Euler angles Ω_{CD}, Ω_{DA}, and Ω_{AM} are modulated by cubic motions, restricted micelle reorientation, and molecular diffusion over the micelle surface, respectively. For convenience the residual coupling $\langle V_0^M \rangle$, which is assumed to be uniform over the micelle surface, has been set equal to unity. The further treatment of this model depends on the relative rates of the three classes of motion. If the cubic motions are much slower than the other motions, the laboratory frame time correlation functions can be decomposed into a sum of two independent parts as [19]

$$G_k^L(\tau) = G_{k,CD}^L(\tau) + G_{k,DM}^L(\tau). \tag{7.2}$$

We consider first the contribution from cubic motions, i.e. the first term in equation (7.2). This is the time correlation function of the partially averaged quantity

$$\begin{aligned} V_{k,CD}^L(\tau) &= \langle V_k^L(\tau) \rangle_{DM} \\ &= S_{DA} S_{AM} (-1)^k \sum_n D^2_{-kn}(\Omega_{LC}) D^2_{n0}[\Omega_{CD}(\tau)], \end{aligned} \tag{7.3}$$

where we have exploited the uniaxial symmetries (and the assumed statistical independence of Ω_{DA} and Ω_{AM}), and defined the second rank order parameters

$$S_{DA} = \langle P_2(\cos\theta_{DA}) \rangle$$

and

$$S_{AM} = \langle P_2(\cos\theta_{AM}) \rangle.$$

These order parameters are determined by the shape of the potential of mean torque and by the shape of the micelle, respectively. Since the micelles are of identical shape, S_{AM} is the same for all N micelles. The orientational distribution $f(\Omega_{DA})$ and hence S_{DA}, however, may differ among the N micelles. The cubic processes then modulate not only the Euler angles Ω_{CD} but also the order parameter S_{DA}. If, on the other hand, S_{DA} is the same for all N micelles, then equation (7.3) differs from equation (2.3) merely by a constant scaling factor and all the results of sections 3–5 apply. In particular,

$$G_{k,CD}^L(\tau; \theta_{LC}, \phi_C) = (S_{DA} S_{AM})^2 [F_k^E(\theta_{LC}, \phi_C) G_E^C(\tau) + F_k^T(\theta_{LC}, \phi_C) G_T^C(\tau)], \tag{7.4}$$

with the cubic irreducible time correlation functions given by equation (3.5).

The second term in equation (7.2), i.e. the contribution from restricted micelle reorientation and molecular surface diffusion, is the time correlation function of the quantity

$$\begin{aligned} V_{k,DM}^L(\tau) &= V_k^L(\tau) - \langle V_k^L(\tau) \rangle_{DM} \\ &= (-1)^k \sum_p D^2_{-kp}(\Omega_{LD}) \tilde{D}^2_{p0}[\Omega_{DM}(\tau)], \end{aligned} \tag{7.5}$$

where we have temporarily contracted the C and A frames by summing over n and q in equations (7.1) and (7.3), and defined

$$\tilde{D}^2_{p0}(\Omega_{DM}) = D^2_{p0}(\Omega_{DM}) - \delta_{p0} S_{DM}. \tag{7.6}$$

We thus obtain for a particular micelle in the cubic unit cell

$$G^L_{k,DM}(\tau;\Omega_{LD}) = \sum_p \sum_{p'} D^{2*}_{-kp}(\Omega_{LD}) D^2_{-kp'}(\Omega_{LD}) \langle \tilde{D}^{2*}_{p0}(\Omega^0_{DM}) \tilde{D}^2_{p'0}(\Omega_{DM}) \rangle. \tag{7.7}$$

As the Wigner functions $D^2_{p0}(\Omega_{DM})$ transform as components of the irreducible representations $A_{1g}\,(p=0)$, $E_{1g}\,(p=\pm1)$, and $E_{2g}\,(p=\pm2)$ of the symmetry group $D_{\infty \mathrm{h}}$ of the potential of mean torque, the selection rule in equation (3.1) tells us that the time correlation functions on the right hand side of equation (7.7) vanish if $p \neq p'$ and are distinct irreducible time correlation functions if $p = p'$. Consequently [21–23, 29]

$$G^L_{k,DM}(\tau;\theta_{LD}) = \sum_{p=0}^{2} F^p_k(\theta_{LD}) G^D_{pp}(\tau), \tag{7.8}$$

with the angular functions

$$F^p_k(\theta_{LD}) = (1 - \delta_{p0}/2)\{[d^2_{kp}(\theta_{LD})]^2 + [d^2_{k-p}(\theta_{LD})]^2\}. \tag{7.9}$$

The irreducible time correlation functions in equation (7.8) may be expressed as [29]

$$G^D_{pp}(\tau) = S^2_{AM} G^{DA}_{p0}(\tau) + \delta_{p0} S^2_{DA} G^{AM}_{00}(\tau) + \sum_{q=0}^{2} (2 - \delta_{q0}) G^{DA}_{pq}(\tau) G^{AM}_{q0}(\tau), \tag{7.10}$$

where the time correlation functions

$$G^{DA}_{pq}(\tau) = \langle D^{2*}_{pq}(\Omega^0_{DA}) D^2_{pq}(\Omega_{DA}) \rangle - \delta_{p0}\delta_{q0} S^2_{DA} \tag{7.11}$$

describe restricted micelle reorientation, while the time correlation functions

$$G^{AM}_{q0}(\tau) = \langle D^{2*}_{q0}(\Omega^0_{AM}) D^2_{q0}(\Omega_{AM}) \rangle - \delta_{q0} S^2_{AM} \tag{7.12}$$

describe molecular diffusion over the micellar surface. The explicit calculation of these time correlation functions has been described elsewhere for prolate or oblate spheroidal micelles [29].

It should be noted that the result in equation (7.8) makes no reference to the cubic symmetry of the liquid crystal. However, this result holds only for a particular micelle, subject to a potential of mean torque whose symmetry axis makes an angle θ_{LD} with the static magnetic field. To obtain the desired time correlation functions, we must, therefore, average equation (7.8) over the cubic distribution function $f(\Omega_{CD})$. If the irreducible time correlation functions $G^D_{pp}(\tau)$ are the same for all N micelles, we need only average the angular functions $F^p_k(\theta_{LD})$. Performing the $L \to D$ transformation in two steps as $L \to C \to D$, averaging over $f(\Omega_{CD})$, and making use of equations (5.3) and (5.4), we obtain

$$\begin{aligned} G^L_{k,DM}(\tau;\theta_{LC},\phi_C) = \langle G^L_{k,DM}(\tau;\theta_{LD}) \rangle_{CD} &= G^L_{\mathrm{iso},DM}(\tau) \\ &+ \tfrac{2}{7} Q[F^E_k(\theta_{LC},\phi_C) - \tfrac{2}{5}][3G^G_{00}(\tau) - 4G^D_{11}(\tau) + G^D_{22}(\tau)], \end{aligned} \tag{7.13}$$

where the angular functions $F^E_k(\theta_{LC},\phi_C)$ are given by equations (4.1), and

$$G^L_{\mathrm{iso},DM}(\tau) = \tfrac{1}{5}[G^D_{00}(\tau) + 2G^D_{11}(\tau) + 2G^D_{22}(\tau)] \tag{7.14}$$

is the isotropically averaged time correlation function. For a powder sample, with a random distribution of crystal orientations, the second term in equation (7.13) vanishes since $\langle F^E_k(\theta_{LC},\phi_C) \rangle_{\mathrm{iso}} = \frac{2}{5}$, and we are left with equation (7.14) as expected. (This result can also be derived directly from equation (7.8) by noting that $\langle F^p_k(\theta_{LD}) \rangle_{\mathrm{iso}} = (2 - \delta_{p0})/5$.) For the special case where the micelles are oriented along the four-fold axes of the cubic unit cell ($Q=\frac{7}{12}$) and one of these axes is aligned with the magnetic field ($\theta_{LC}=0$), equation (7.13) yields

$$G_{0,DM}^{L}(\tau)=\tfrac{1}{2}[G_{00}^{D}(\tau)+G_{22}^{D}(\tau)], \tag{7.15 a}$$

$$G_{1,DM}^{L}(\tau)=\tfrac{1}{3}[2G_{11}^{D}(\tau)+G_{22}^{D}(\tau)], \tag{7.15 b}$$

$$G_{2,DM}^{L}(\tau)=\tfrac{1}{12}[3G_{00}^{D}(\tau)+4G_{11}^{D}(\tau)+5G_{22}^{D}(\tau)]. \tag{7.15 c}$$

As an illustration of the previous rather general results, we now consider in more detail the structural model for micellar cubic phases of space group Pm$\bar{3}$n (point group O_h) proposed by Fontell *et al.* [50]. This model is based on the structure deduced from single crystal X-ray diffraction studies of certain solid phases of a few homonuclear diatomic molecules (N_2, γ-O_2, β-F_2) [52]. The eight micelles per unit cell are of the same size and shape, but are orientationally disordered in different ways: two micelles are spherically disordered, while of the remaining six micelles two are randomly oriented in each of the three orthogonal mirror planes. The cubic order parameter Q for this model is $\frac{7}{16}$. The laboratory frame time correlation function for the cubic motion is given by equation (7.4) with $S_{DA}=-\frac{1}{2}$. Since $D_{10}^{2}(\Omega_{CD})=0$ for all eight micelles also $G_{T}^{C}(\tau)=0$, so that only the irreducible time correlation function $G_{E}^{C}(\tau)$ of E symmetry needs to be considered. If the cubic motion is intermicellar exchange of the spin-bearing species it can be modelled as a discrete stationary Markov process. If exchange takes place with equal probability from a given micelle to either of $N-1$ surrounding micelles (N is not necessarily equal to 8), the irreducible time correlation function decays exponentially as

$$G_{E}^{C}(\tau)=G_{E}^{C}(0)\exp(-\lambda_{N}\tau). \tag{7.16}$$

The rate constant λ_N is related to the mean residence time τ_M of the spin-bearing species in a micelle through

$$\lambda_{N}=\frac{N}{(N-1)\tau_{M}}. \tag{7.17}$$

The initial time correlation function in equation (7.16) is obtained from equation (5.6 *a*) as

$$G_{E}^{C}(0)=\tfrac{1}{5}+\tfrac{18}{35}Q=\tfrac{17}{40}. \tag{7.18}$$

For a powder sample we thus obtain (cf. equation (4.5))

$$G_{\mathrm{iso},CD}^{L}(\tau)=\tfrac{17}{400}S_{AM}^{2}\exp(-\lambda_{N}\tau). \tag{7.19}$$

The contribution from (restricted) micelle reorientation and surface diffusion to the laboratory frame time correlation function for a powder sample is obtained from equation (7.14) as

$$G_{\mathrm{iso},DM}^{L}(\tau)=\tfrac{2}{8}G_{00}^{L,I}(\tau)+\tfrac{6}{8}[\tfrac{1}{5}G_{00}^{D}(\tau)+\tfrac{2}{5}G_{11}^{D}(\tau)+\tfrac{2}{5}G_{22}^{D}(\tau)], \tag{7.20}$$

where the first term is associated with the two isotropically tumbling micelles and the second term with the six micelles that tumble freely in a plane. Using equation (7.10) and the explicit expressions for the reorientational time correlation functions $G_{pq}^{DA}(\tau)$ [29], and assuming that micelle tumbling (rotation about the short axes of the micelle, with diffusion coefficient $D_\perp$) is much slower than surface diffusion, we find

$$G_{00}^{L,I}(\tau)=\tfrac{1}{5}S_{AM}^{2}\exp(-6D_{\perp}\tau)+\tfrac{1}{5}\sum_{q=0}^{2}(2-\delta_{q0})G_{q}(\tau), \tag{7.21}$$

$$G_{00}^{D}(\tau)=\tfrac{1}{4}G_{0}(\tau)+\tfrac{3}{4}G_{2}(\tau), \tag{7.22 a}$$

$$G^D_{11}(\tau)=\tfrac{1}{2}G_1(\tau)+\tfrac{1}{2}G_2(\tau), \qquad (7.22\,b)$$

$$G^D_{22}(\tau)=\tfrac{3}{8}S^2_{AM}\exp(-4D_\perp\tau)+\tfrac{3}{8}G_0(\tau)+\tfrac{1}{2}G_1(\tau)+\tfrac{1}{8}G_2(\tau). \qquad (7.22\,c)$$

Here we have introduced the time correlation functions

$$G_q(\tau)=\exp(-q^2D_\parallel\tau)G^{AM}_{q0}(\tau) \qquad (7.23)$$

for surface diffusion on the uniaxial micelle and rotation of the micelle about its symmetry axis (with diffusion coefficient $D_\parallel$).

Combination of equations (7.2) and (7.19)–(7.23) yields for the laboratory frame time correlation function in a powder sample

$$G^L_{\text{iso}}(\tau)=\tfrac{1}{20}S^2_{AM}[\tfrac{17}{20}\exp(-\lambda_N\tau)+\exp(-6D_\perp\tau)+\tfrac{9}{4}\exp(-4D_\perp\tau)]$$
$$+\tfrac{1}{5}[G^{AM}_{00}(\tau)+2\exp(-D_\parallel\tau)G^{AM}_{10}(\tau)+2\exp(-4D_\parallel\tau)G^{AM}_{20}(\tau)]. \qquad (7.24)$$

The three exponentials in the first term refer to intermicellar exchange, isotropic micelle tumbling, and in-plane micelle tumbling, respectively. The second term represents surface diffusion on all eight micelles in the unit cell as well as micelle rotation about the symmetry axis. The order parameter S_{AM} is determined by the shape (relative dimensions) of the micelles, while the surface diffusion time correlation functions $G^{AM}_{q0}(\tau)$ also depend on the surface diffusion coefficient D_S of the spin-bearing species. The calculation of S_{AM} and $G^{AM}_{q0}(\tau)$ for spheroidal micelles has been described in detail elsewhere [29].

In recent studies [9, 13] of spin relaxation in micellar cubic phases, a simpler form of the laboratory frame time correlation function was used. In the second part of equation (7.24) only the third term was retained; this was taken to be of the form

$$G^{AM}_{20}(\tau)=\exp(-4D_S\tau/b^2),$$

as for surface diffusion on an infinitely long cylinder of radius b. In the first part of equation (7.24), the expression within square brackets was represented by a single exponential. By using the more accurate form of equation (7.24) the inconsistencies encountered with the semi-empirical time correlation function [9, 13] could probably be removed, leading to a more reliable picture of the microstructure of these cubic phases.

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