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Director fluctuations and nuclear-spin relaxation in lyotropic nematic liquid crystals

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Lyotropic nematic liquid crystals, like their thermotropic counterparts, exhibit collective reorientation modes known as director fluctuations. In this work we consider the effect of director fluctuations on the transverse spin relaxation of quadrupolar nuclei in uniaxial lyotropic nematic liquid crystals, reporting ^{2}H (labeled surfactant) and ^{23}Na (counterion) relaxation data from the calamitic (N_C^+) and discotic (N_D^-) phases of the system sodium dodecyl sulphate-decanol-water. The transverse relaxation is found to be dominated by a large contribution to the secular zero-frequency spectral density from diffusion-modulated (counterion) or viscoelastic (surfactant) director fluctuations. The existing theory of nuclear-spin relaxation by director fluctuations is extended to include the effect of translational diffusion on the fourth-order director-fluctuation time correlation functions. In contrast to thermotropic nematics, the second-order director-fluctuation contribution to the nonsecular high-frequency spectral densities is negligible in lyotropic nematic liquid crystals at conventional magnetic fields. This is a consequence of the much longer short-wavelength cutoff in lyotropic liquid crystals. The large zero-frequency spectral density, however, allows us to deduce the viscoelastic properties of the nematic phases, obtaining effective elastic constants of 0.3–1.0 pN in the investigated temperature range. The nematic order parameter is found to be significantly influenced by collective modes as well as by local micelle reorientation. For the oblate micelles in the N_D^- phase, the local modes are most important, whereas the reverse is true for the prolate micelles in the N_C^+ phase. In the surfactant case, the longest-wavelength-director-fluctuation modes are too slow to motionally average the nuclear-quadrupole coupling, resulting in a static broadening of the ^{2}H satellites.

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I. INTRODUCTION

Nematic liquid crystals differ from isotropic fluids in that the constituent molecules or molecular aggregates are orientationally correlated over macroscopic distances. Phenomenologically, this long-range orientational order is described by a second-rank ordering tensor [1], which, in the case of uniaxial nematic mesophases, is characterized by three independent quantities: the order parameter S and the two Euler angles that specify the orientation of the principal frame in which the ordering tensor is diagonal. More commonly, however, the set of three independent quantities is chosen as S and the two transverse components, n_x and n_y, of a unit vector referred to as the nematic director [1].

Because of thermal motion in the nematic fluid, the director orientation fluctuates in time. (Fluctuations in the order parameter S, which may be important near the nematic-isotropic phase transition [2–4] are not considered here.) Such director fluctuations may be regarded as collective reorientation modes for the nematic molecules or molecular aggregates emerging as a direct consequence of the long range of the orientational correlations. The principal cause of the characteristic light scattering from nematic mesophases, director fluctuations are also manifested in the spin-relaxation rates of nuclei residing in the nematic molecules or aggregates [1,4–6]. As the collective reorientation modes are expected to be slow, they should be reflected most strongly in the low-frequency-spin-relaxation behavior.

Nuclear-spin-relaxation studies of director fluctuations have been largely confined to thermotropic nematics, where the characteristic angular dependence and $\omega^{-1/2}$ dispersion of the longitudinal relaxation rate [4–6] have been experimentally verified for several systems [7]. In this work, however, we are concerned with *lyotropic* (surfactant-based) nematic liquid crystals. Whereas the light scattering from lyotropic nematic liquid crystals is much less intense than from thermotropic nematics [2,3] (due to the much smaller dielectric anisotropy), there is no reason for expecting director fluctuations to be a less efficient spin-relaxation mechanism for lyotropic than for thermotropic nematic liquid crystals. To our knowledge, this has not yet been experimentally demonstrated. In the case of lyotropic *smectic* mesophases (most notably phospholipid bilayers), on the other hand the importance of director fluctuations has been established for the longitudinal relaxation at low frequencies [7–9] and for the transverse relaxation [10].

The aim of the present work is to quantitatively assess the importance of director fluctuations for the spin-relaxation behavior from lyotropic nematic liquid crystals. To this end we have measured the transverse relaxation rates of ^{2}H in the specifically deuterated sodium dodecyl sulphate (SDS) surfactant and of ^{23}Na in the counterion from the calamitic (N_C^+) and discotic (N_D^-) uniaxial nematic mesophases of the system sodium dodecyl sulphate-decanol-water [11]. These phases are composed of prolate and oblate spheroidal micelles, respectively, with an essentially temperature-independent axial ratio in the range 3–4 [12].

In Sec. II we recapitulate relevant aspects of the theory of spin relaxation by nematic director fluctuations and extend the theory in certain respects. The emphasis is on transverse relaxation, which is dominated by *fourth-order* director-fluctuation contributions to the zero-frequency spectral density. As compared to previous treatments of higher-order director-fluctuation contributions [13,14] our development differs in that we consider in more detail the secular (zero-frequency) contribution and the effect of translational diffusion.

In contrast to typical thermotropic nematics, the *second-order* director-fluctuation contribution to the nonsecular high-frequency spectral densities $J_1^L(\omega_0)$ and $J_2^L(2\omega_0)$ is negligible for the investigated N_C^+ and N_D^- phases. This is mainly due to the much larger short-wavelength cutoff λ_c in the lyotropic mesophases, which makes the cutoff frequency ω_c much smaller than the Larmor frequency at conventional magnetic fields. The zero-frequency spectral density $J_0^L(0)$, however, is very large and dominated by diffusion-modulated (counterions) or viscoelastic (surfactants) director fluctuations, allowing us to estimate the viscoelastic constants of the mesophases. In the case of the surfactant, the longest-wavelength-director-fluctuation modes are too slow to motionally average the nuclear-quadrupole coupling, resulting in a static broadening of the ^{2}H satellites. Invoking also the results of our previous study of the longitudinal relaxation behavior [12], we decompose the nematic order parameter into contributions from local micelle reorientation and collective director fluctuations. The relative importance of the two contributions is found to be qualitatively different in the two nematic mesophases.

II. THEORY

A. Quadrupole relaxation in uniaxial nematics

The frequency spectrum and the spin-relaxation behavior of the ^{2}H and ^{23}Na nuclei used in this work are governed by the interaction of the nuclear electric-quadrupole moment with the electric-field gradient generated by the surrounding charge distribution [15]. The quadrupole coupling is manifested to first order in the quadrupole splitting ν_Q and to second order in the various spin-relaxation rates, which are linear combinations of the motional spectral densities $J_0^L(0)$, $J_1^L(\omega_0)$, and $J_2^L(2\omega_0)$ [16]. The high-frequency spectral densities $J_1^L(\omega_0)$ and $J_2^L(2\omega_0)$ are usually not significantly affected by motions that are slow compared to the Larmor frequency ω_0. The zero-frequency spectral density, on the other hand, may be influenced by much slower motions and is therefore an appropriate experimental quantity for investigating director fluctuations. In the following we focus on $J_0^L(0)$.

Nematic mesophases are readily aligned by the magnetic torque exerted by the static magnetic field used to polarize the nuclear-spin system. For uniaxial nematic phases the angle θ_{LD} between the magnetic field and the macroscopic (mean) phase director is determined by the sign of the diamagnetic susceptibility anisotropy in the director frame $\Delta\chi_D=\chi_\parallel^D-\chi_\perp^D$; $\theta_{LD}=0$ for $\Delta\chi_D>0$ and $\theta_{LD}=\pi/2$ for $\Delta\chi_D<0$ [1]. In this work we study a calamitic nematic phase with $\Delta\chi_D>0$ (denoted N_C^+) and a discotic nematic phase with $\Delta\chi_D<0$ (denoted N_D^-).

In order to exploit the uniaxial symmetry of the nematic phases, the lab-frame spectral density $J_0^L(0)$ is transformed to the director frame [4,17]. For the N_C^+ phase ($\theta_{LD}=0$) we have (trivially)

$$J_0^L(0)=J_0^D(0)\ , \tag{2.1a}$$

and for the N_D^- phase ($\theta_{LD}=\pi/2$)

$$J_0^L(0)=\tfrac{1}{4}J_0^D(0)+\tfrac{3}{4}J_2^D(0)\ . \tag{2.1b}$$

The director-frame spectral densities $J_m^D(0)$ reflect dynamic processes on several time scales. Among these processes we consider explicitly only director fluctuations, i.e., the process(es) whereby the orientation of the local director experienced by a given spin fluctuates in time (cf. Sec. IV D). All other processes are referred to as local. As discussed in detail elsewhere [12,18], the local motions include noncollective micelle reorientation, molecular diffusion over the curved micelle surface, and various "internal" motions. We assume that the local motions are uncorrelated with, and much faster than, the director fluctuations. The director-frame spectral densities can then be decomposed as

$$J_m^D(0)=J_{m,\mathrm{loc}}^D(0)+J_{m,\mathrm{dir}}^D(0)\ . \tag{2.2}$$

As shown in Sec. II C, the director-fluctuation (denoted by the subscript "dir") contributions to these spectral densities are related by

$$J_{0,\mathrm{dir}}^D(0)=3J_{2,\mathrm{dir}}^D(0)\ . \tag{2.3}$$

We need, therefore, consider only $J_{0,\mathrm{dir}}^D(0)$, which can be expressed as

$$J_{0,\mathrm{dir}}^D(0)=c_R(\pi\chi_{\mathrm{loc}})^2 j_{\mathrm{dir}}(0)\ , \tag{2.4}$$

where c_R is a spin-dependent numerical factor: $c_R=\frac{3}{2}$ for $I=1$ (^{2}H) and $c_R=1$ for $I=\frac{3}{2}$ (^{23}Na). χ_{loc} is the quadrupole coupling constant averaged over all local motions [18]. The reduced spectral density $j_{\mathrm{dir}}(0)$ can be formally factorized into a fluctuation amplitude $g_{\mathrm{dir}}(0)$ and an effective correlation time τ_{dir} as

$$j_{\mathrm{dir}}(0)=g_{\mathrm{dir}}(0)\tau_{\mathrm{dir}}\ , \tag{2.5}$$

with

$$\tau_{\mathrm{dir}}=\int_0^\infty dt\, g_{\mathrm{dir}}(t)/g_{\mathrm{dir}}(0)\ , \tag{2.6}$$

$$g_{\mathrm{dir}}(t)=\langle P_2(\cos\theta_{Dd}^0)P_2(\cos\theta_{Dd})\rangle-S_{\mathrm{dir}}^2\ , \tag{2.7}$$

where $\theta_{Dd}=\theta_{Dd}(t)$ is the angle between the macroscopic (mean) director and the local director (the uniaxial symmetry of the phase is assumed to persist down to the local level), and S_{dir} is the associated order parameter

$$S_{\mathrm{dir}}=\langle P_2(\cos\theta_{Dd})\rangle\ . \tag{2.8}$$

The locally averaged quadrupole coupling constant χ_{loc} depends on the size and shape of the micelle as well as on the details of the interfacial region [12]. In our analysis of director fluctuations, however, we can eliminate χ_{loc} by invoking the quadrupole splitting ν_Q, given by

$$\nu_Q = c_Q P_2(\cos\theta_{LD}) S_{\mathrm{dir}} \chi_{\mathrm{loc}} , \tag{2.9}$$

where c_Q is a spin-dependent numerical factor: $c_Q = \frac{3}{2}$ for $I=1$ and $c_Q = \frac{1}{2}$ for $I = \frac{3}{2}$.

B. Continuum description of the local director field

To relate the order parameter S_{dir}, the fluctuation amplitude $g_{\mathrm{dir}}(0)$, and the effective correlation time τ_{dir} to the macroscopic properties of the nematic phase, we adopt the usual continuum description, where the deformational fluctuations of the (locally uniaxial) nematic fluid are described entirely in terms of a unit vector field $\mathbf{n}(\mathbf{r})$ referred to as the local director [1]. The macroscopic phase director $\mathbf{n}_0$ is simply the average $\langle \mathbf{n}(\mathbf{r}) \rangle$. We define two Cartesian coordinate systems D and d, such that the z_D axis is along $\mathbf{n}_0$ and the z_d axis along $\mathbf{n}(\mathbf{r})$. Because of the local uniaxial symmetry, the local director components $n_x(\mathbf{r})$ and $n_y(\mathbf{r})$ in the D frame are statistically equivalent.

The director components $n_\alpha(\mathbf{r})$ ($\alpha = x$ or y) can be Fourier expanded as

$$n_\alpha(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{q}} \hat{n}_\alpha(\mathbf{q}) \exp(-i\mathbf{q}\cdot\mathbf{r}) , \tag{2.10a}$$

where V is the averaging volume used to define the mean director $\mathbf{n}_0$. (For a uniformly aligned sample, free from orientational defects [1], V is simply the sample volume.) The complex-valued mode amplitudes $\hat{n}_\alpha(\mathbf{q})$ are related to the $n_\alpha(\mathbf{r})$ by the inverse transform

$$\hat{n}_\alpha(\mathbf{q}) = \int_V d\mathbf{r}\, n_\alpha(\mathbf{r}) \exp(i\mathbf{q}\cdot\mathbf{r}) . \tag{2.10b}$$

The deformational free energy of the nematic fluid, associated with its curvature elasticity and its interaction with the external magnetic field B_0, may be expressed, to second order in the mode amplitudes $\hat{n}_\alpha(\mathbf{q})$ as [1]

$$A = \frac{\kappa}{2V} \sum_{\mathbf{q}} (q^2 + \xi_m^{-2}) [|\hat{n}_x(\mathbf{q})|^2 + |\hat{n}_y(\mathbf{q})|^2] , \tag{2.11}$$

where κ is an effective elastic constant (neglecting the anisotropy in the elasticity tensor) and ξ_m is the magnetic coherence length. For the latter, we obtain

$$\xi_m = \left[\frac{\mu_0 \kappa S_{\mathrm{dir}}}{\Delta\chi_D P_2(\cos\theta_{LD})} \right]^{1/2} \frac{1}{B_0} , \tag{2.12}$$

where μ_0 is the vacuum permeability. This expression differs in two respects from that usually encountered in the literature. First, the factor $P_2(\cos\theta_{LD})$ reflects the dependence of the magnetic free energy of deformation on the orientation θ_{LD} of the *mean* director. Second, this energy involves the diamagnetic susceptibility anisotropy in the *local* director frame $\Delta\chi_d$, which has been expressed in terms of the experimentally accessible susceptibility anisotropy in the *mean* director frame $\Delta\chi_D = S_{\mathrm{dir}} \Delta\chi_d$.

Like the director components $n_\alpha(\mathbf{r})$, the mode amplitudes $\hat{n}_\alpha(\mathbf{q})$ are regarded as stochastic variables. From the quadratic form of the free-energy expression (2.11) it follows that the equilibrium distribution for $\hat{n}_\alpha(\mathbf{q})$ is Gaussian with the variance [1]

$$\langle |\hat{n}_\alpha(\mathbf{q})|^2 \rangle = \frac{k_B T V}{\kappa(q^2 + \xi_m^{-2})} . \tag{2.13}$$

Furthermore, director-fluctuation modes of different wave vectors are uncorrelated (strictly true only in the limit $V \to \infty$), i.e.,

$$\langle \hat{n}_\alpha(\mathbf{q}) \hat{n}_\alpha^*(\mathbf{q}') \rangle = \delta_{\mathbf{q}\mathbf{q}'} \langle |\hat{n}_\alpha(\mathbf{q})|^2 \rangle . \tag{2.14}$$

The order parameter S_{dir} defined by (2.8) can be expressed (exactly) as

$$S_{\mathrm{dir}} = 1 - 3\langle [n_x(\mathbf{r})]^2 \rangle . \tag{2.15}$$

Inserting the Fourier expansion (2.10a) and using (2.13) and (2.14), one obtains

$$S_{\mathrm{dir}} = 1 - \frac{3k_B T}{\kappa V} \sum_{\mathbf{q}} (q^2 + \xi_m^{-2})^{-1} . \tag{2.16}$$

At this point we encounter the fundamental limitation of continuum theory; it is valid only over length scales that are large compared to typical intermicellar separations. If we use the macroscopic ($q=0$ limit) elastic constant κ in (2.16), we should, therefore, truncate the sum over $\mathbf{q}$ modes beyond a certain wave number q_c, corresponding to a lower continuum cutoff wavelength $\lambda_c = 2\pi/q_c$. (The problem of choosing an appropriate λ_c value is discussed in Sec. IV B.)

For a sufficiently large volume V (strictly, in the limit $V \to \infty$), we can replace the discrete-director-fluctuation-mode spectrum by a continuous one. The sum in (2.16) is then converted to an integral using the correspondence rule

$$\sum_{\mathbf{q}} \to (2\pi)^{-3} V \int d\mathbf{q} . \tag{2.17}$$

After performing the integration in (2.16) one obtains the well-known result [1]

$$S_{\mathrm{dir}} = 1 - \frac{3k_B T}{\pi \kappa \lambda_c} [1 - \epsilon \arctan(1/\epsilon)] , \tag{2.18}$$

where

$$\epsilon = (q_c \xi_m)^{-1} . \tag{2.19}$$

As typically $\epsilon \ll 1$ (cf. Sec. IV D), we can safely replace the expression within square brackets in (2.18) by unity.

According to (2.7) and (2.8), the initial-time correlation function $g_{\mathrm{dir}}(0)$ can be expressed (exactly) as

$$g_{\mathrm{dir}}(0) = \frac{9}{4} [\langle |n_+(\mathbf{r})|^4 \rangle - \langle |n_+(\mathbf{r})|^2 \rangle^2] , \tag{2.20}$$

where $n_+ = n_x + i n_y$. Using the Fourier expansion (2.10a), the statistical independence (2.14) of the $\mathbf{q}$ modes and the Gaussian property of $\hat{n}_\alpha(\mathbf{q})$, one finds [13]

$$\langle |n_+(\mathbf{r})|^4 \rangle = 8 \langle [n_x(\mathbf{r})]^2 \rangle^2 . \tag{2.21}$$

Combination of (2.15), (2.20), and (2.21) then yields

$$g_{\mathrm{dir}}(0)=(1-S_{\mathrm{dir}})^2 \ . \tag{2.22}$$

This simple result can also be obtained by noting that, for small θ_{Dd}, $g_{\mathrm{dir}}(0)=\frac{9}{4}[\langle\theta_{Dd}^4\rangle-\langle\theta_{Dd}^2\rangle^2]$ and $S_{\mathrm{dir}}=1-\frac{3}{2}\langle\theta_{Dd}^2\rangle$, and that, for a Gaussian distribution $f(\theta_{Dd})\sim\exp(-\theta_{Dd}^2/\langle\theta_{Dd}^2\rangle)$, one has $\langle\theta_{Dd}^4\rangle=2\langle\theta_{Dd}^2\rangle^2$. The exact result is [4,17]

$$g_{\mathrm{dir}}(0)=\tfrac{1}{5}+\tfrac{2}{7}S_{\mathrm{dir}}+\tfrac{18}{35}Q_{\mathrm{dir}}-S_{\mathrm{dir}}^2 \ , \tag{2.23}$$

where $Q_{\mathrm{dir}}=\langle P_4(\cos\theta_{Dd})\rangle$. The approximation (2.22) thus implies a relation between the second-rank and fourth-rank order parameters S_{dir} and Q_{dir}.

C. Effective correlation times

As shown in Sec. II A, the zero-frequency spectral density $J_0^L(0)$ for a uniaxial nematic phase involves the time correlation functions $g_0^{\mathrm{dir}}(t)$ and $g_2^{\mathrm{dir}}(t)$. The former, simply denoted $g_{\mathrm{dir}}(t)$ in Sec. II A, is given by (2.7) while the latter is

$$g_2^{\mathrm{dir}}(t)=\langle D_{20}^{2*}[\Omega_{Dd}(0)]D_{20}^2[\Omega_{Dd}(t)]\rangle \ . \tag{2.24}$$

The Euler angles $\Omega_{Dd}(t)=[\theta_{Dd}(t),\phi_D(t)]$ specify the orientation of the local director, at the current location of the spin, with respect to the D frame. These angles fluctuate in time as a result of two dynamic processes: (i) translational diffusion of the spin-bearing molecule through the inhomogeneous director field $\mathbf{n}(\mathbf{r})$, and (ii) viscoelastic director fluctuations that render time-dependent the orientation of the local director $\mathbf{n}(\mathbf{r},t)$ at a given "point" $\mathbf{r}$. In general both processes occur; in the following, however, we consider only the two limiting cases of (i) translational diffusion in a static director field (corresponding to a diffusion coefficient $D\gg\kappa/\eta$), and (ii) an immobile spin subject to viscoelastic director fluctuations ($D\ll\kappa/\eta$). Since the two processes can be considered statistically independent, the extension to the general case is straightforward (cf. Sec. IV D).

1. Static director field

The time correlation functions $g_m^{\mathrm{dir}}(t)$ involve the Euler angles Ω_{Dd}, which are related to the local director components $\mathbf{n}_\alpha$ through

$$n_+\equiv n_x+in_y=\sin\theta_{Dd}\exp(i\phi_D) \ . \tag{2.25}$$

Substitution into (2.7) and (2.24) yields the exact results

$$g_0^{\mathrm{dir}}(t)=\tfrac{9}{4}[\langle\langle|n_+(\mathbf{r}_0)|^2|n_+(\mathbf{r})|^2\rangle\rangle_{\mathrm{dif}}-\langle|n_+(\mathbf{r})|^2\rangle^2] \ , \tag{2.26a}$$

$$g_2^{\mathrm{dir}}(t)=\tfrac{3}{8}\langle\langle[n_+(\mathbf{r}_0)]^2[n_+^*(\mathbf{r})]^2\rangle\rangle_{\mathrm{dif}} \ , \tag{2.26b}$$

where the time dependence enters implicitly via the fluctuating position of the spin $\mathbf{r}=\mathbf{r}(t)$ and $\mathbf{r}_0=\mathbf{r}(0)$.

The orientational variable n_+ is stochastic at two levels: (i) the local director orientation and hence $n_+(\mathbf{r})$ varies stochastically *in space,* and (ii) the position $\mathbf{r}(t)$ of the diffusing spin varies stochastically *in time.* Accordingly, the time correlation functions involve a double ensemble average; $\langle\ \rangle$ refers to an average over the joint director-orientation distribution at positions $\mathbf{r}_0$ and $\mathbf{r}$, and $\langle\ \rangle_{\mathrm{dif}}$ refers to an average over all positions $\mathbf{r}_0$ and $\mathbf{r}$ connected by a diffusional trajectory in time t. [It may be noted that the stochastic process $\Omega_{Dd}(t)$ is non-Markovian in the presence of translational diffusion.]

The latter diffusional average may be formulated explicitly as

$$\langle\langle\ \rangle\rangle_{\mathrm{dif}}=\frac{1}{V}\int d\mathbf{r}_0\int d\mathbf{r}\,f(\mathbf{r},t|\mathbf{r}_0)\langle\ \rangle \ , \tag{2.27}$$

where $f(\mathbf{r},t|\mathbf{r}_0)$ is the translational diffusion propagator

$$f(\mathbf{r},t|\mathbf{r}_0)=(4\pi Dt)^{-3/2}\exp\left[\frac{|\mathbf{r}-\mathbf{r}_0|^2}{4Dt}\right] , \tag{2.28}$$

with an effective self-diffusion coefficient D for the spin-bearing molecule in the nematic fluid. (In keeping with the neglect of anisotropy in the elasticity tensor, we neglect the anisotropy in the diffusivity tensor $\mathbf{D}$ and take $D=\mathrm{Tr}\mathbf{D}/3$. Unless the micelles are very large, this is a reasonable approximation.) Because of the translational invariance we can set $\mathbf{r}_0=0$. [The propagator (2.28) is strictly valid only for an unbounded system ($V\to\infty$).] After Fourier expanding the diffusion propagator, we obtain

$$\langle\langle\ \rangle\rangle_{\mathrm{dif}}=\frac{1}{V}\sum_{\mathbf{q}}\exp(-q^2Dt)\int d\mathbf{r}\langle\ \rangle\exp(-i\mathbf{q}\cdot\mathbf{r}) \ . \tag{2.29}$$

Using (2.10a), (2.14), and the Gaussian property of the $\hat{n}_\alpha(\mathbf{q})$, as in the derivation of (2.21), we find

$$\begin{aligned}\langle|n_+(0)|^2|n_+(\mathbf{r})|^2\rangle-\langle|n_+(\mathbf{r})|^2\rangle^2 &= \left[\frac{2}{V^2}\sum_{\mathbf{q}}\langle|\hat{n}_x(\mathbf{q})|^2\rangle\exp(i\mathbf{q}\cdot\mathbf{r})\right]^2\\ &=\tfrac{1}{2}\langle[n_+(0)]^2[n_+^*(\mathbf{r})]^2\rangle \ . \end{aligned}\tag{2.30}$$

It follows from (2.26), (2.29), and (2.30) that

$$g_0^{\mathrm{dir}}(t)=3g_2^{\mathrm{dir}}(t) \ , \tag{2.31}$$

which proves (2.3) for the special case of translational diffusion in a static director field. It suffices, therefore, to consider the correlation function $g_0^{\mathrm{dir}}(t)\equiv g_{\mathrm{dir}}(t)$, which becomes

$$\begin{aligned}g_{\mathrm{dir}}(t)=\frac{9}{(2\pi)^6V^2}&\int d\mathbf{q}\int d\mathbf{q}'\langle|\hat{n}_x(\mathbf{q})|^2\rangle\langle|\hat{n}_x(\mathbf{q}')|^2\rangle\\ &\times\exp(-|\mathbf{q}+\mathbf{q}'|^2Dt) \ , \end{aligned}\tag{2.32}$$

where we have also made the transition to a continuous-mode spectrum according to (2.17).

Because of the exponential cross term $\exp(-2\mathbf{q}\cdot\mathbf{q}'Dt)$, the two-dimensional integral in (2.32) cannot be reduced to the square of a one-dimensional integral as in the limit of an immobile spin (cf. below). For this reason, translational diffusion cannot in general be incorporated into the director-fluctuation theory simply through the replacement $\kappa/\eta \rightarrow D+\kappa/\eta$ in the expression for the mode relaxation time [1]. Such a procedure is correct for the *second-order* (in n_α or θ_{Dd}) contribution to $g_1^{\rm dir}(t)$ [4,6], but not for the *fourth-order* time correlation functions $g_0^{\rm dir}(t)$ and $g_2^{\rm dir}(t)$ considered here.

Inserting the mean-square mode amplitude (2.13) into (2.32), introducing spherical polar coordinates, and carrying out the angular integrations, we find

$$\frac{g_{\rm dir}(t)}{g_{\rm dir}(0)}=\frac{1}{2q_c^2Dt}\int_0^{q_c}dq\int_0^{q_c}dq'\,\frac{qq'\sinh(2qq'Dt)\exp[-(q^2+q'^2)Dt]}{(q^2+\xi_m^{-2})(q'^2+\xi_m^{-2})}\,, \tag{2.33}$$

where we have also used (2.18) and (2.22) for $g_{\rm dir}(0)$. The effective correlation time $\tau_{\rm dir}$, defined by (2.6), is now obtained by integrating (2.33) over time,

$$\tau_{\rm dir}=\frac{1}{q_c^2D}\int_0^1 dx\int_0^x dy\frac{xy}{(x^2+\epsilon^2)(y^2+\epsilon^2)}\ln\left[\frac{x+y}{x-y}\right]\,, \tag{2.34}$$

with ϵ defined by (2.19). The double integral in (2.34) cannot be expressed in closed form; however, since typically $\epsilon \ll 1$ we can expand the nondivergent part in powers of ϵ to obtain

$$\tau_{\rm dir}=\frac{\lambda_c^2}{16D}[\ln(1/\epsilon)-1.12+O(\epsilon)]\,. \tag{2.35}$$

To obtain a convergent zero-frequency spectral density $j_{\rm dir}(0)$ it is thus essential to introduce a finite short-wavelength cutoff λ_c as well as a finite magnetic coherence length ξ_m (or long-wavelength cutoff). However, the dependence of $j_{\rm dir}(0)$ on λ_c and ξ_m is weak; the λ_c^2 factor in $\tau_{\rm dir}$ is cancelled by a λ_c^{-2} factor in $g_{\rm dir}(0)$ [cf. (2.18) and (2.22)] leaving only the logarithmic dependence on the ratio ξ_m/λ_c. This fortunate circumstance allows us, in the limit of a static director field, to determine the elastic constant κ from $j_{\rm dir}(0)$ without the need for accurate estimates of ξ_m and λ_c. It should be emphasized that to obtain the results (2.22) and (2.35) for $j_{\rm dir}(0)$, we have introduced only one approximation above those inherent in the standard continuum theory of elastic fluctuations [1], viz., the (reasonable) neglect of anisotropy in the translational diffusion tensor.

2. *Immobile spin*

In this limiting case, previously treated by Vold, Vold, and Warner [13] and by van der Zwan and Plomp [14], one considers the temporal fluctuations of the local director orientation at a fixed point in space. The time correlation functions $g_m^{\rm dir}(t)$ are now spatially local (and translationally invariant in the limit $V\rightarrow\infty$), and $n_+(\mathbf{r},t)$ varies only as a result of viscoelastic fluctuations;

$$g_0^{\rm dir}(t)=\tfrac{9}{4}[\langle|n_+(\mathbf{r},0)|^2|n_+(\mathbf{r},t)|^2\rangle-\langle|n_+(\mathbf{r})|^2\rangle^2]\,, \tag{2.36a}$$

$$g_2^{\rm dir}(t)=\tfrac{3}{8}\langle[n_+(\mathbf{r},0)]^2[n_+^*(\mathbf{r},t)]^2\rangle\,. \tag{2.36b}$$

In this case it is necessary to make the *additional* assumption [13,14] that the different wave-vector components of the local director field behave as independent Gaussian Markov processes. Whereas in the limit of a static director field we only needed the Gaussian form of the *equilibrium* distribution $f[\hat{n}_\alpha(\mathbf{q})]$, in the present case we must make the stronger assertion that the stochastic *process* $\hat{n}_\alpha(\mathbf{q},t)$ is Gaussian, i.e., that the director-fluctuation propagator $f[\hat{n}_\alpha(\mathbf{q},t),t|\hat{n}_\alpha(\mathbf{q},0)]$ is of the Ornstein-Uhlenbeck form [14,19]. (The latter property clearly implies the former.) It then follows that the mode autocorrelation functions decay exponentially as [1,19]

$$\langle\hat{n}_\alpha(\mathbf{q},0)\hat{n}_\alpha^*(\mathbf{q}',t)\rangle=\delta_{\mathbf{qq}'}\langle|\hat{n}_\alpha(\mathbf{q})|^2\rangle\exp[-t/\tau_v(q)]\,, \tag{2.37}$$

with the viscoelastic mode relaxation time $\tau_v(q)$ given by [20]

$$\frac{1}{\tau_v(q)}=\frac{\kappa}{\eta}(q^2+\xi_m^{-2})\,, \tag{2.38}$$

where η is an effective nematic viscosity (any q dependence in η is neglected).

Proceeding as in the case of a static director field, one finds that the relation (2.31), and hence also (2.3), remains valid, and that

$$g_{\rm dir}(t)=\left[\frac{3}{(2\pi)^3V}\int d\mathbf{q}\langle\hat{n}_x(\mathbf{q},0)\hat{n}_x^*(\mathbf{q},t)\rangle\right]^2\,. \tag{2.39}$$

Combination of (2.13), (2.18), (2.22), and (2.37)–(2.39) then yields the reduced time correlation function

$$\frac{g_{\rm dir}(t)}{g_{\rm dir}(0)}=\left[\frac{1}{q_c}\int_0^{q_c}dq\frac{q^2}{(q^2+\xi_m^{-2})}\times\exp\left[-(q^2+\xi_m^{-2})\frac{\kappa}{\eta}t\right]\right]^2\,. \tag{2.40}$$

The effective correlation time becomes

$$\begin{aligned}\tau_{\rm dir}&=\frac{\eta}{q_c^2\kappa}\int_0^1dx\int_0^1dy\frac{x^2y^2}{(x^2+\epsilon^2)(y^2+\epsilon^2)(x^2+y^2+2\epsilon^2)}\\&=\frac{\lambda_c^2\eta}{8\pi\kappa}[\ln(1/\epsilon)-1.52+O(\epsilon)]\,.\end{aligned} \tag{2.41}$$

To leading order in ϵ, i.e., keeping only the logarithmic term in (2.41), our result for τ_{dir} is a factor 2 larger than that obtained by Vold, Vold, and Warner [13]. This difference is due to the further approximations invoked by these authors to evaluate the q integrals. It may also be noted that, to leading order in ϵ, the substitution $\kappa/\eta \rightarrow D$ in (2.41) yields an effective correlation time that differs by $2/\pi$ from the correct result (2.35) for translational diffusion in a static director field.

D. High-frequency-director-fluctuation contribution

The bulk of the literature on spin relaxation by director fluctuations is concerned with longitudinal relaxation rates and hence with the *second-order* director-fluctuation contribution to the spectral density function $J_1^D(\omega)$ [4–6]. For the purpose of estimating the director-fluctuation contribution to $J_1^L(\omega_0)$ and $J_2^L(2\omega_0)$ in our lyotropic nematic phases, we summarize here the necessary relations.

Under the conditions stipulated in Sec. II A, we have for the N_C^+ phase

$$J_{1,\mathrm{dir}}^L(\omega_0) = c_R(\pi\chi_{\mathrm{loc}})^2 j_1^{\mathrm{dir}}(\omega_0) \ , \tag{2.42a}$$

and for the N_D^- phase ($k=1$ or 2)

$$J_{k,\mathrm{dir}}^L(k\omega_0) = \tfrac{1}{2} c_R(\pi\chi_{\mathrm{loc}})^2 j_1^{\mathrm{dir}}(k\omega_0) \ . \tag{2.42b}$$

Here we have only included the leading (second-order) director-fluctuation contribution. The reduced spectral density function in (2.42) is given by [4,5]

$$\begin{aligned} j_1^{\mathrm{dir}}(\omega) &= (1-S_{\mathrm{dir}})\frac{1}{\omega_c}\int_0^1 dx \frac{x^4}{(x^2+\epsilon^2)[x^4+(\omega/\omega_c)^2]} \\ &= (1-S_{\mathrm{dir}})\frac{\pi U(\omega_c/\omega)}{(8\omega_c\omega)^{1/2}} \ , \end{aligned} \tag{2.43}$$

where

$$U(x) = H(x-1) + \frac{1}{\pi}\left[\arctan\frac{\sqrt{2x}}{1-x} - \arctan\frac{\sqrt{2x}}{1+x}\right] . \tag{2.44}$$

$H(z)$ is the unit step function and the cutoff frequency ω_c is defined as

$$\omega_c = q_c^2\left[D+\frac{\kappa}{\eta}\right] . \tag{2.45}$$

(In the derivation of these results, terms of order ϵ have been neglected.)

For thermotropic nematic liquid crystals it is commonly assumed that $\omega_0 \ll \omega_c$ so that the cutoff function $U(\omega_c/\omega_0)$ has attained its low-ω_0 limit of unity. In this limit one obtains the celebrated $\omega_0^{-1/2}$ relaxation dispersion [6]. For lyotropic nematic liquid crystals, however, the cutoff frequency ω_c is much lower and one has instead $\omega_0 \gg \omega_c$ at conventional magnetic fields (cf. Sec. IV D). The cutoff function then reduces to

$$U(x) = \frac{(2x)^{3/2}}{3\pi} \ . \tag{2.46}$$

(This form is accurate to within a few percent for $x<0.3$.) Consequently,

$$j_1^{\mathrm{dir}}(\omega_0) = (1-S_{\mathrm{dir}})\frac{\omega_c}{3\omega_0^2} \ , \tag{2.47a}$$

which is of the same form as the high-frequency tail of a Lorentzian dispersion with correlation time $3/\omega_c$. Since $1/\omega_c$ should exceed the longest single-micelle tumbling correlation time [12,17], director fluctuations are not expected to contribute significantly to the high-frequency spectral densities (cf. Sec. IV D). With (2.18) and (2.45) inserted into (2.47a), we obtain

$$j_1^{\mathrm{dir}}(\omega_0) = \frac{4\pi k_B T(1+\eta D/\kappa)}{\lambda_c^3 \eta \omega_0^2} \ . \tag{2.47b}$$

Note that the dependence on the viscoelastic constants is overshadowed by the strong dependence on the ill-defined cutoff wavelength λ_c, and that, in the immobile spin limit ($D \ll \kappa/\eta$), the director-fluctuation contribution does not depend on the elastic constant κ.

E. Incomplete motional averaging

In the preceding analysis it was tacitly assumed that director-fluctuation modes of all wave vectors down to the low-q cutoff $2\pi/\xi_m$ are fast on the NMR time scale so that all modes in the range $2\pi/\xi_m < q < q_c$ contribute to motional averaging of the quadrupole splitting ν_Q (via S_{dir}) and to the zero-frequency spectral density $j_{\mathrm{dir}}(0)$ (which was treated within the restrictions of motional-narrowing theory). The condition for motional averaging by a director-fluctuation mode of wave vector q is roughly

$$\omega_Q(q) \ll q^2\left[\frac{\kappa}{\eta}+D\right] , \tag{2.48}$$

where the frequency $\omega_Q(q)$ is the part of the quadrupole coupling that is modulated by the director-fluctuation mode of wave vector q. While there is some uncertainty about how to define $\omega_Q(q)$, previous estimates [4,21] suggest that the motional-averaging condition (2.48) is indeed satisfied for *thermotropic* nematics.

For our lyotropic nematic liquid crystals, however, the observation of a significant inhomogeneous broadening (not due to the B_0 field or to static dipolar couplings) in the ^{2}H spectrum demonstrates that the inequality (2.48) is not satisfied over the whole q range (cf. Sec. IV A). Since the effect is rather small, it is analyzed in a simple approximate manner rather than by invoking the full machinery of the stochastic Liouville equation.

We thus define a wave vector q^* such that modes with $q > q^*$ are completely motionally averaged [i.e., (2.48) is obeyed], while modes with $q < q^*$ can be treated as static on the NMR time scale. Since the variance of the (Gaussian) local director orientation θ_{Dd} may be expanded in q modes as (cf. Sec. II B)

$$\sigma^2 = \langle \theta_{Dd}^2 \rangle = \sum_{\mathbf{q}} \langle |\hat{\theta}_{Dd}(\mathbf{q})|^2 \rangle \ , \tag{2.49}$$

it follows that

$$\sigma^2=\sigma_f^2+\sigma_s^2 \ , \tag{2.50}$$

where the subscripts refer to the fast (motionally averaged) and slow (static) q modes. Incomplete motional averaging thus leads to an order parameter $S_{\mathrm{dir}}^*=1-\frac{3}{2}\sigma_f^2$ that is larger than the value $S_{\mathrm{dir}}=1-\frac{3}{2}\sigma^2$ for complete motional narrowing;

$$S_{\mathrm{dir}}^*=S_{\mathrm{dir}}+\tfrac{3}{2}\sigma_s^2 \ . \tag{2.51}$$

To (approximately) account for the effects of incomplete motional averaging on the quadrupole splitting ν_Q and the spectral density $j_{\mathrm{dir}}(0)$ we simply replace S_{dir} by S_{dir}^* in (2.9) and (2.22). Proceeding as in the derivation of (2.18), the static variance may be related to the motional averaging wavelength λ^* as

$$\sigma_s^2=\frac{2k_BT}{\pi\kappa\lambda^*}[1-\epsilon^*\arctan(1/\epsilon^*)] \ , \tag{2.52}$$

with $\epsilon^*=(q^*\xi_m)^{-1}$.

The inhomogeneous satellite line shape is obtained as

$$L(\omega)=\int_0^\pi d\theta_{LS}\sin\theta_{LS}f(\theta_{LS})L_S(\omega,\theta_{LS}) \ , \tag{2.53}$$

where θ_{LS} is the angle between the B_0 field and the static (partially averaged) director and $L_S(\omega,\theta_{LS})$ is the homogeneous satellite line shape corresponding to a given static director orientation:

$$L_S(\omega,\theta_{LS})=\frac{R_2}{(R_2)^2+[\omega-\omega_Q^0P_2(\cos\theta_{LS})]^2} \ , \tag{2.54}$$

where R_2 is the transverse relaxation rate and ω_Q^0 is the angular frequency of the satellite (relative to the center of the spectrum) for the (hypothetical for the N_D^- phase) case of the phase director along the B_0 field ($\theta_{LD}=0$) and with no static broadening of the satellites.

We must now relate the distribution $f(\theta_{LS})$ in (2.53) to the Gaussian static director distribution $f(\theta_{DS})$ with variance σ_s^2. For the N_C^+ phase, $\theta_{LD}=0$ and $\theta_{LS}=\theta_{DS}$, so that

$$f(\theta_{LS})\sim\exp(-\theta_{LS}^2/\sigma_s^2) \ . \tag{2.55a}$$

For the N_D^- phase, $\theta_{LD}=\pi/2$ and $\cos\theta_{LS}=\sin\theta_{DS}\cos\phi_D$, so that

$$\begin{aligned} f(\theta_{LS})\sim&\int_0^{2\pi}d\phi_D\int_0^\pi d\theta_{DS}\sin\theta_{DS}\exp(-\theta_{DS}^2/\sigma_s^2)\\ &\times\delta[\cos\theta_{LS}-\sin\theta_{DS}\cos\phi_D]\\ \sim&\exp(-\cos^2\theta_{LS}/\sigma_s^2) \ . \end{aligned} \tag{2.55b}$$

By analytically transforming the distribution function rather than the Euler angles, one avoids a time-consuming numerical double integral [22].

III. EXPERIMENT

A. Materials and sample preparation

SDS (sodium dodecyl sulphate), selectively deuterated at the α position (next to the sulphate headgroup), from Synthelec (Lund, Sweden) was purified by repeated recrystallization from aqueous solution. Decanol (n-decanol, specially pure) from BDH Chemicals and deuterium-depleted water from Sigma were used as supplied. The composition of the investigated nematic $N_C^+(N_D^-)$ phase sample was 24.5 (24.9):4.4(5.4):71.1 (69.7) weight % of SDS-decanol-water, corresponding to molar ratios $n_w/(n_{\mathrm{dec}}+n_{\mathrm{SDS}})=35.2$ (32.2) and $n_{\mathrm{dec}}/(n_{\mathrm{dec}}+n_{\mathrm{SDS}})=0.25$ (0.29). The volume fraction micelles (SDS + decanol) was $\phi=0.27$ (0.28). These compositions are the same as used for the ^{2}H relaxation studies in Ref. [12], where the relevant part of the ternary phase diagram can be found.

The sample preparation started by mixing appropriate amounts of SDS and water yielding an isotropic micellar (L_1) phase. This micellar phase and decanol were weighed into a 7-mm i.d. Pyrex tube (filled to approximately 15 mm height) which was immediately flame sealed. Upon mixing at 20 °C a clear, viscous, birefringent nematic (N_C^+ or N_D^-) phase was obtained.

The samples were nematic from approximately 15 °C (where the SDS precipitates) to about 25.4 °C for the N_C^+ phase and to approximately 28.5 °C for the N_D^- phase. At higher temperatures the samples entered two-phase regions (two superimposed signals in the NMR spectra) with the nematic N_C^+ (N_D^-) phase in equilibrium with an L_1 (N_C^+) phase. The $N_C^+-L_1$ two-phase region is narrow, approximately 1 °C, while the $N_D^--N_C^+$ two-phase region is much wider.

B. Spin-relaxation experiments and results

The ^{2}H and ^{23}Na NMR experiments were performed on a Bruker MSL-100 spectrometer (resonance frequencies 15.371 MHz and 26.487 MHz for ^{2}H and ^{23}Na), equipped with a 10-mm vertical saddle-coil probe and a 2.35-T superconducting magnet.

The sample volume was centered in the saddle coil yielding a spatial rf (B_1) inhomogeneity of less than ±10%. The magnetic field inhomogeneity was less than 20 (10) Hz for ^{2}H (^{23}Na). The temperature was regulated by a Stelar VTC87 regulator with a high air flow (1.5 m^3/h), reducing temporal and spatial temperature fluctuations to within ±0.03 °C. Typically, the length of the 180° pulse was 20 (13) μs for ^{2}H (^{23}Na). Since the resonant 180° pulses (applied at the center of the spectra) showed less than 6% attenuation at the ^{2}H and ^{23}Na satellites, the pulses were considered nonselective. Considerable care was taken to avoid systematic errors [12,22].

While, in general, a 2D quadrupolar echo (2D QE) experiment [23,24] is required to obtain the homogeneous satellite linewidth for ^{23}Na, the homogeneous ^{2}H linewidth is usually obtained from a single-exponential fit to the decay of the quadrupolar echo amplitude with increasing τ [25]. The relatively large B_1 inhomogeneity, however, then introduces a small systematic error (by giving rise to a small-amplitude modulation of the decay). To eliminate this artifact, we used 2D QE experiments to determine the homogeneous ^{2}H satellite linewidth $\Delta\nu_s^{\rm hom}$ from a Lorentzian fit to the central line in the $F1$ cross-section spectrum derived from the satellite position in $F2$. The experimental uncertainty ($\pm 2\sigma$, due to noise) in $\Delta\nu_s^{\rm hom}$ is estimated to ± 20 Hz for ^{2}H.

For ^{23}Na it was found that, in all investigated cases, the satellite lines in the conventional 1D spectrum were Lorentzian, cf. Fig. 1, and their width was the same (within the experimental uncertainty) as the homogeneous satellite linewidth $\Delta\nu_s^{\rm hom}$ obtained from a 2D QE experiment (correcting for the reduction of the small magnetic field inhomogeneity broadening in the 2D QE experiment [24]). In other words, static quadrupolar inhomogeneity did not contribute to the ^{23}Na satellite linewidth. Therefore, the ^{23}Na zero-frequency spectral density $J_0^L(0)$ could be obtained from the linewidths in the 1D quadrupolar echo spectrum, using $\tau = 1/\nu_Q$ so that all three peaks in the spectrum are in phase [23,24], according to [24]

$$J_0^L(0)=\pi(\Delta\nu_s^{\rm inhom}-\Delta\nu_c^{\rm inhom}) \quad (I=\tfrac{3}{2},{}^{23}\mathrm{Na}) \, , \qquad (3.1)$$

where $\Delta\nu_s^{\rm inhom}$ and $\Delta\nu_c^{\rm inhom}$ are the full linewidths (including a small magnetic field inhomogeneity broadening) of the satellite (s) and central (c) lines as obtained from Lorentzian fits.

In contrast to the ^{23}Na case, the satellites in the ^{2}H spectrum were slightly asymmetric (cf. Fig. 1), suggesting a contribution from quadrupolar inhomogeneous broadening. This was more clearly seen in the large difference between the inhomogeneous and homogeneous ^{2}H linewidths. The spectral density $J_0^L(0)$ was thus obtained from the *homogeneous* satellite linewidth as [25]

$$J_0^L(0)=\tfrac{2}{3}(\pi\Delta\nu_s^{\rm hom}-\tfrac{3}{2}J_1^L-J_2^L) \quad (I=1,{}^2\mathrm{H}) \, . \qquad (3.2)$$

J_1^L and J_2^L have previously been determined [12] to be about 10 s^{-1} each (independently of sample and temperature), so the correction in (3.2) amounts to less than 1%. For convenience, the lab-frame spectral densities $J_k^L = J_k^L(k\omega_0)$ in (3.1) and (3.2) are defined so as to include spin-dependent numerical factors and coupling constants.

The static broadening of the ^{2}H satellites also includes contributions from unresolved ^{2}H-^{2}H and ^{2}H-^{1}H static dipolar couplings. As the quadrupolar echo pulse sequence only partly refocuses these dipolar couplings [26,27], the experimental quantities $\Delta\nu_s^{\rm hom}$ and $\Delta\nu_s^{\rm inhom}-\Delta\nu_s^{\rm hom}$ tend

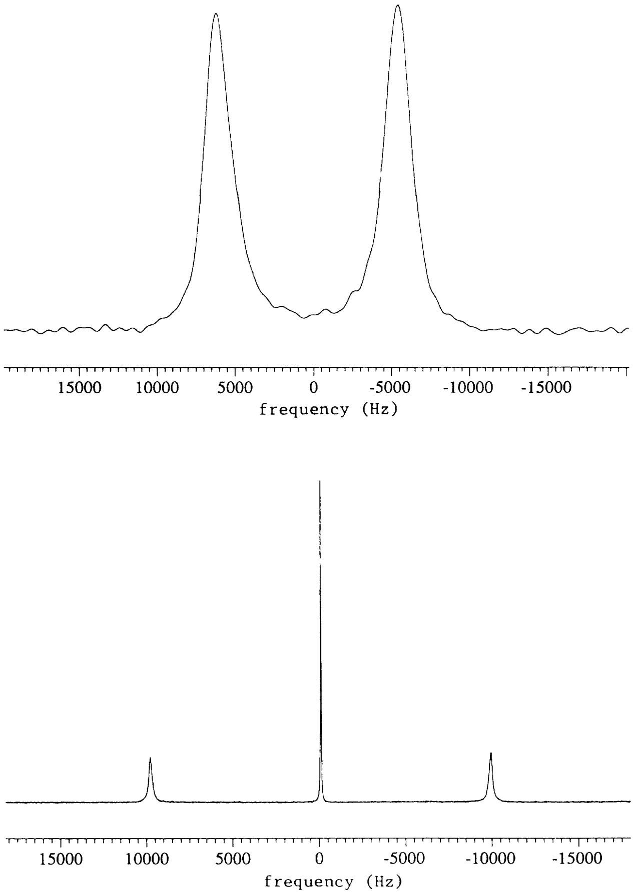

FIG. 1. ^{2}H (top) and ^{23}Na (bottom) 1D quadrupolar echo spectra from the N_C^+ sample at 24.9 °C.

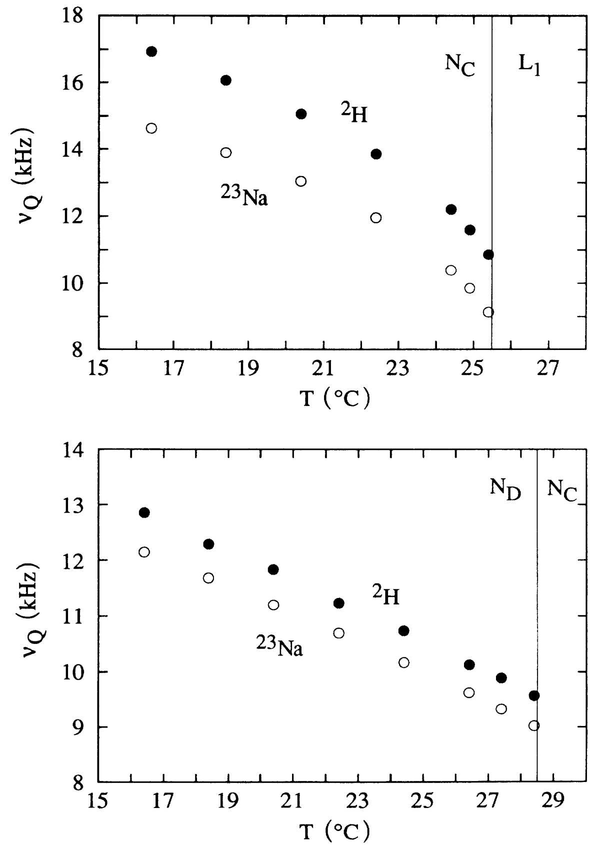

FIG. 2. Temperature variation of ^{2}H and ^{23}Na quadrupole splittings from the N_C^+ (top) and N_D^- (bottom) phases. The experimental uncertainties are smaller than the size of the symbols. The vertical lines indicate the N_C^+-L_1 and $N_D^- - N_C^+$ transition temperatures.

TABLE I. Lab-frame spectral densities $J_0^L(0)$[a] and director-fluctuation contributions $J_{0,\mathrm{dir}}^D(0)$[b] for ^{2}H (SDS) and ^{23}Na (Na$^+$) in the N_C^+ and N_D^- phases.

		^{2}H		^{23}Na	
T (°C)	Phase	$J_0^L(0)$ (s^{-1})	$J_{0,\mathrm{dir}}^D(0)$ (s^{-1})	$J_0^L(0)$ (s^{-1})	$J_{0,\mathrm{dir}}^D(0)$ (s^{-1})
16.4	N_C^+	1885	1870	202	149
18.4				216	166
20.4		2220	2205	239	191
22.4		2555	2540	327	281
24.4		3225	3210	480	436
24.9		3415	3400	572	528
25.4		3775	3760	702	659
16.4	N_D^-	3075	6090	392	556
18.4				355	498
20.4		2755	5450	345	490
22.4				346	506
24.4				362	550
26.4				374	584
27.4				394	630
28.4		2800	5540	401	648

[a] Obtained from measured linewidths according to (3.1) or (3.2).

[b] Obtained from $J_0^L(0)$ using (2.1)–(2.3) and estimates of the local contributions (cf. Sec. IV B).

to overestimate the *quadrupolar* homogeneous linewidth and the *quadrupolar* static broadening, respectively. However, the effect (estimated from dipolar effects seen in the hexagonal phase of the present system [28]) is small: <40 Hz in $\Delta\nu_s^{\mathrm{hom}}$ and $\leq 1°$ in the static orientational spread σ_s (cf. Secs. II E and IV A). The propagation of these small systematic errors causes the parameter $(\kappa/\eta+D_{\mathrm{SDS}})$ to be underestimated by at most 15% (cf. Sec. IV D).

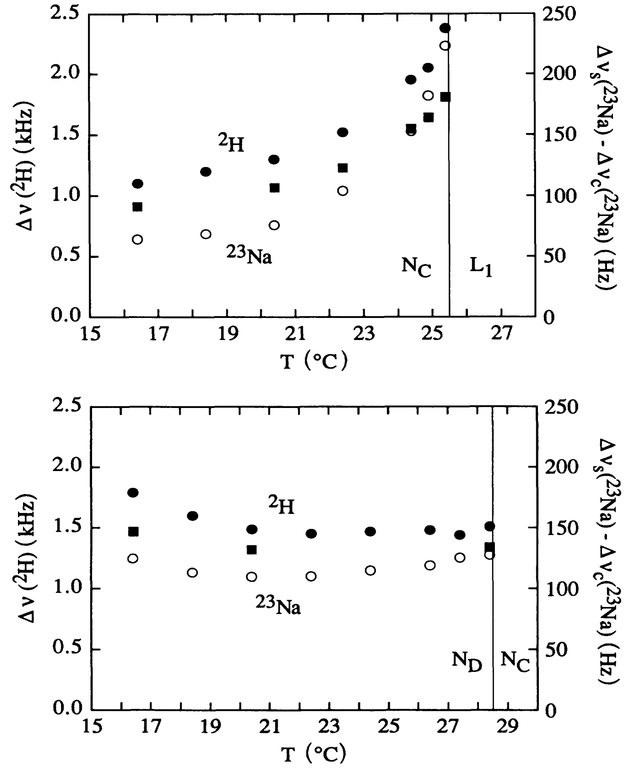

FIG. 3. Temperature variation of inhomogeneous (●) and homogeneous (■) ^{2}H linewidths and of ^{23}Na satellite-central linewidth difference (○) in the N_C^+ (top) and N_D^- (bottom) phases. The experimental uncertainties are smaller than the size of the symbols. The vertical lines indicate the $N_C^+-L_1$ and $N_D^- - N_C^+$ transition temperatures.

The measured quadrupole splittings ν_Q are shown in Fig. 2. The ^{23}Na splitting was obtained from the frequency-offset difference between the central line and the satellites as provided by the line-shape fits, and the ^{2}H splitting was measured directly as the peak separation. (The true splitting is deduced in Sec. IV A by including the static quadrupolar broadening in the analysis). The measured linewidths are shown in Fig. 3. The inhomogeneous ^{2}H linewidth is the width at half-height of the satellites. The zero-frequency spectral density $J_0^L(0)$, as obtained from (3.1) or (3.2) and the data in Fig. 3, is given in Table I. The linewidth data in Fig. 3, reflecting mainly temperature variation of $J_0^L(0)$, is similar for the two nuclei but is qualitatively different for the two nematic phases.

IV. DATA ANALYSIS

The ^{2}H and ^{23}Na quadrupole splittings and relaxation data presented in Sec. III will now be analyzed in terms of director fluctuations using the theoretical results of Sec. II. First, however, we must address the issues of incomplete motional averaging (^{2}H data) and relaxation contributions from local motions (^{23}Na data). In addition, we need to estimate the translational diffusion coefficients for the SDS surfactant and the Na$^+$ counterion in the nematic phases.

A. Static broadening of ^{2}H spectrum

As noted above (Secs. II E and III B), the ^{2}H spectrum from the α-deuterated SDS surfactant in the nematic samples exhibits asymmetrically broadened satellites. We ascribe this broadening to incomplete motional averaging of the quadrupole coupling by the long-wavelength-director-fluctuation modes (cf. Sec. II E). Magnetic field inhomogeneity and temperature gradients can account for neither the magnitude nor the asymmetry of this static broadening, which is absent from the ^{23}Na spectra.

The static director spread σ_s was obtained from line-shape analysis according to (2.53)–(2.55). The least-squares fit (using the Levenberg-Marquardt algorithm [29]) involved four adjustable parameters: the static-director spread σ_s, the true quadrupole frequency ω_Q^0, a frequency offset, and a factor accounting for the slightly unequal peak amplitudes. A minor baseline correction (the offset) was performed manually. A fifth parameter, the homogeneous linewidth $\Delta\nu_s^{\mathrm{hom}}$, was taken from the 2D QE experiments (cf. Sec. III B) and was not adjusted in the fit. The result of a typical fit is shown in Fig. 4. The minor discrepancy between experimental and fitted spectra is ascribed to a small first-order phase error (due to the problem of compensating for the pulse duration).

The fitted parameters of primary concern, σ_s and the homogeneous (peak-to-peak) splitting ν_Q^0 (equal to ω_Q^0/π for the N_C^+ phase and to $\omega_Q^0/2\pi$ for the N_D^- phase), are given in Table II. The remaining parameters, the frequency offset and the satellite amplitude ratio, showed only small deviations (less than 150 Hz and 6%, respectively) from their nominal values (0 and 1, respectively).

B. Local motions and continuum cutoff

To obtain the director-fluctuation contribution, $J_{0,\mathrm{dir}}^D(0)$, to the measured spectral density $J_0^L(0)$, we must subtract the contribution from local motions. According to (2.1)–(2.3), we have for the N_C^+ phase

$$J_{0,\mathrm{dir}}^D(0)=J_0^L(0)-J_{0,\mathrm{loc}}^D(0)\ , \tag{4.1a}$$

and for the N_D^- phase

$$J_{0,\mathrm{dir}}^D(0)=2[J_0^L(0)-\tfrac{1}{4}J_{0,\mathrm{loc}}^D(0)-\tfrac{3}{4}J_{2,\mathrm{loc}}^D(0)]\ . \tag{4.1b}$$

We consider first the case of surfactant ^{2}H relaxation.

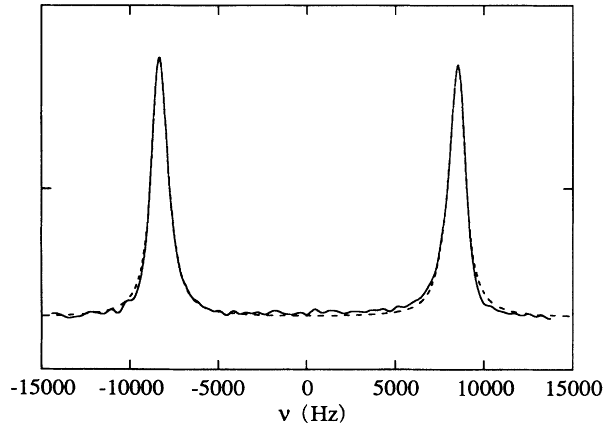

FIG. 4. Experimental (solid) and fitted (dashed) ^{2}H spectrum from the N_C^+ phase at 16.4 °C. The fitting procedure is described in Sec. IV A.

TABLE II. Static director spread σ_s and homogeneous quadrupole splitting ν_Q^0 deduced from the ^{2}H line-shape analysis.

T (°C)	Phase	σ_s (deg)	ν_Q^0 (kHz)	ν_Q (kHz)[a]
16.4	N_C^+	8.0	17.25	16.93
20.4		8.9	15.48	15.06
22.4		10.3	14.29	13.85
24.4		13.4	12.74	12.21
24.9		13.9	12.22	11.60
25.4		15.7	11.61	10.86
16.4	N_D^-	10.4	13.20	12.86
20.4		7.8	11.95	11.83
28.4		9.1	9.89	9.56
uncertainty		±0.4	±0.04	±0.05

[a] Peak-to-peak separation in inhomogeneously broadened spectrum.

As discussed in detail elsewhere [12,18], three kinds of motion contribute to $J_{0,\mathrm{loc}}^D(0)$: (i) "internal" motions, (ii) diffusion of the SDS molecule over the curved micelle surface, and (iii) local reorientation of the micelle. On the basis of our previous NMR studies of the hexagonal [22] and nematic [12] phases in the present system, we can estimate the contribution to $J_0^L(0)$ from "internal" motions to 2 s^{-1} and from surface diffusion to 10 s^{-1} (N_C^+ phase) or 25–40 s^{-1} (N_D^- phase). This is merely about 1% of the total $J_0^L(0)$ (cf. Table I).

The contribution from local micelle reorientation is more difficult to estimate since it brings up the vexed issue of the physical significance of the cutoff wavelength λ_c and, indeed, of the local director field. We are facing here the general statistical-mechanical problem of merging continuum and particle concepts into a self-consistent description.

To be useful, the cutoff wavelength must be sufficiently large that we can use the macroscopic ($q=0$ limit) elastic constant and nematic viscosity in the continuum description of director fluctuations. The local director may be defined with reference to a group of N micelles enclosed in a volume of linear dimension λ_c and the ordering tensor for the instantaneous orientation of these micelles with respect to an external frame. The orthogonal transformation that diagonalizes this tensor defines the orientation of the (instantaneous) local director and the largest eigenvalue defines the local order parameter S_{loc}. The nematic order parameter S_{nem}, describing the orientational order of the micelle with respect to the macroscopic phase director, is then

$$S_{\mathrm{nem}}=S_{\mathrm{loc}}S_{\mathrm{dir}}\ , \tag{4.2}$$

where S_{dir} is the director-fluctuation order parameter introduced in Sec. II A, and we have assumed that the *local* director, like the mean director, is at least a threefold symmetry axis.

If the averaging volume is taken to be of the same spheroidal shape as the micelle and if the cutoff wavelength is identified with the longest dimension of this volume, then

$$\lambda_c = 2a(N/\phi)^{1/3} , \tag{4.3}$$

where a is the major semiaxis of the micelle and ϕ is the volume fraction micelles in the nematic fluid. For the nematic samples studied here $\phi = 0.27$ and, on the basis of our previous NMR study [12] of micelle size and order, $a \approx 7$ nm in both N_C^+ and N_D^- phases at all investigated temperatures. Values for λ_c of 30, 40, and 50 nm thus correspond to 2.7, 6.3, and 12.3 micelles in the local averaging volume. In the following calculations we shall set $\lambda_c = 40$ nm. Note that this value is much larger than the typical cutoff wavelengths of 2–3 nm used for thermotropic nematics [7,13,14]. There are three reasons for this difference. First, the surfactant micelles are larger than the thermotropic nematic molecules. Second, the relevant length scale for assessing the validity of continuum theory is the separation between the molecules or aggregates rather than their length. This distinction is unimportant for one-component fluids such as thermotropic nematic liquid crystals, but accounts for the factor $\phi^{-1/3}$ in (4.3). Third, we argue that several micelles should be included in the averaging volume used to define the local director, i.e., $N > 1$ in (4.3).

The partitioning of reorientational modes into local and continuum modes, as reflected in the factorization of the nematic order parameter in (4.2), also applies to the reorientational contributions to the spectral densities $J_m^D(0)$. To avoid double counting, $J_{m,\mathrm{loc}}^D(0)$ should reflect only those reorientational modes that are confined to the averaging volume of dimension λ_c. With $\lambda_c = 40$ nm, this leaves little room for anything but noncooperative single-micelle reorientation modes. Adopting a model of restricted rotational diffusion in an even uniaxial restoring potential of the mean torque [30] one can show that the dominant tumbling-mode contribution to $J_0^D(0)$ takes the form [17]

$$J_{0,\mathrm{rot}}^D(0) = c_R(\pi\chi_{\mathrm{loc}})^2 \frac{(1-S_{\mathrm{loc}})^3}{2S_{\mathrm{loc}}^2(4S_{\mathrm{loc}}-1)D_\perp} , \tag{4.4a}$$

where $D_\perp$ is the tumbling rotational diffusion coefficient of the micelle. This simple high-order approximation is accurate to within a few percent for $S_{\mathrm{loc}} \geq 0.7$. Using S_{loc} values as deduced below and calculating $D_\perp$ for a spheroid of axial ratio $\rho = 3.5$ [12] with the viscosity of water, we thus estimate the contribution to $J_0^L(0)$ from single-micelle reorientation to $< 1\ \mathrm{s}^{-1}$ for the N_C^+ phase and $< 40\ \mathrm{s}^{-1}$ for the N_D^- phase, i.e., at most approximately 1% of the total $J_0^L(0)$ (cf. Table I).

Next we consider the case of counterion ^{23}Na relaxation. As compared to the ^{2}H case, the contribution from local motions is larger (mainly because of the larger ^{23}Na quadrupole coupling constant), while the contribution from director fluctuations is much smaller (because the counterions diffuse much faster than the surfactants). Consequently, the local motions contribute significantly to $J_0^L(0)$ in the ^{23}Na case. The contribution to $J_0^L(0)$ from "internal" motions (mainly picosecond dynamics in the counterion hydration shell [31,32]) and surface diffusion can be estimated from our previous work [12,22]: 30–40 s^{-1} from "internal" motions and 10 s^{-1} (50–70 s^{-1}) from surface diffusion in the N_C^+ (N_D^-) phase.

Because of the larger χ_{loc} for ^{23}Na, the contribution from local reorientation predicted by (4.4a) is about five times larger than for ^{2}H. This contribution would then account for as much as half of $J_0^L(0)$ (at the highest temperature for the N_D^- phase). The actual contribution, however, is considerably smaller since, for counterions, (4.4a) should be replaced by

$$J_{0,\mathrm{rot}}^D(0) = c_R(\pi\chi_{\mathrm{loc}})^2 \frac{(1-S_{\mathrm{loc}})^2}{S_{\mathrm{loc}}^2} \times \left[\frac{2(4S_{\mathrm{loc}}-1)D_\perp}{1-S_{\mathrm{loc}}} + \frac{1}{\tau_{\mathrm{ex}}} \right]^{-1} , \tag{4.4b}$$

where τ_{ex} is the intermicellar exchange time for the counterions. We estimate [12] that $\tau_{\mathrm{ex}} \approx 10$ (20) ns for the N_C^+ (N_D^-) phase. Using the S_{loc} values deduced below, we thus find that the local-reorientation contribution is negligible for the N_C^+ phase, while it amounts to 4–10 % of $J_0^L(0)$ for the N_D^- phase. As the deduced S_{loc} value depends on the local-reorientation correction, the calculation was performed self-consistently.

In Table I we give the director-fluctuation contributions $J_{0,\mathrm{dir}}^D(0)$ obtained from (4.1) and corrected for local motions (except single-micelle reorientation) as described above.

C. Translational diffusion coefficients

For the analysis of $J_{0,\mathrm{dir}}^D(0)$ we need the diffusion coefficients for translational motion over distances large compared to the continuum cutoff wavelength λ_c of the Na$^+$ counterion and the SDS surfactant molecule. Since macroscopic diffusion measurements have not been carried out on lyotropic nematic phases, we have to rely on estimates based on related sources of information.

For counterions we assume that

$$D_{\mathrm{Na}}(T) = \alpha D_{\mathrm{Na}}^0(T) , \tag{4.5}$$

where $D_{\mathrm{Na}}^0(T)$ is the known [33] limiting self-diffusion coefficient of Na$^+$ in H_2O. The temperature-independent factor α accounts for the obstruction effect and for the effect of the local electrostatic field. In principle, α could be calculated by solving the steady-state Smoluchowski-Poisson-Boltzmann equation in a spheroidal cell, as previously done for spherical [34] and cylindrical [35] geometry. With the surface charge density and volume fraction of our N_C^+ sample, the cylindrical model yields $\alpha_\perp = 0.58$. Accounting for the difference in geometry, we take $\alpha = 0.65$ for the N_C^+ phase. This estimate should not be off by more than 10%. For the N_D^- phase, α should be smaller because of the stronger local electric field surrounding the oblate spheroidal micelle; we use the value $\alpha = 0.3$. The greater uncertainty in this value propagates to the viscoelastic constants deduced for the N_D^- phase (cf. Sec. IV D). The D_{Na} values obtained in this way, in the range $(3\text{–}9) \times 10^{-10}\ \mathrm{m}^2\,\mathrm{s}^{-1}$, are much larger than the "diffusion coefficient" κ/η for viscoelastic director fluctuations (cf. Sec. IV D). Consequently, the ^{23}Na data can be analyzed using the static director limit of the theory in Sec. II C.

Two processes may contribute to the translational motion of the SDS molecules: (i) molecular migration of individual SDS molecules from one micelle to another, and (ii) displacement of the entire micelle. For the first process we may write

$$D_{\mathrm{SDS}}(T)=\frac{d^2}{6\tau_{\mathrm{res}}(T)}\ , \tag{4.6}$$

where d is the average nearest-neighbor intermicellar separation and τ_{res} is the mean residence time of a SDS molecule in a micelle. The latter quantity has been determined from kinetic studies on micelle solutions [36]: $\tau_{\mathrm{res}}=6\ \mu\mathrm{s}$ at 25 °C with an activation energy of 40 $\mathrm{kJ\,mol^{-1}}$ in the range 10–25 °C. Since the fraction of nonmicellized surfactant is very small (about 10^{-3}), an escaped SDS molecule is reabsorbed within a few nanoseconds so that only nearest-neighbor micelles can be reached. We thus identify d with the average cell diameter, $d=2b(\rho^n/\phi)^{1/3}$ with $n=1$ (2) for the N_C^+ (N_D^-) phase. With the minor semiaxis of the micelle $b=2.0$ nm, the micellar axial ratio $\rho=3.5$, and the micelle volume fraction $\phi=0.27$, we thus obtain D_{SDS} values in the range $(2\text{–}7)\times10^{-12}\ \mathrm{m^2\,s^{-1}}$, i.e., two orders of magnitude smaller than D_{Na}.

As regards the second process, the diffusion coefficient for a single micelle at infinite dilution is calculated to be approximately $5\times10^{-11}\ \mathrm{m^2\,s^{-1}}$. Although this is an order of magnitude larger than D_{SDS} due to molecular migration, the high micelle density and strong intermicellar electrostatic repulsion should make micelle translation a highly cooperative process that may be too slow to contribute to D_{SDS}.

Since the D_{SDS} values obtained from (4.6) are of the same order of magnitude as $(\kappa/\eta+D_{\mathrm{SDS}})$ (cf. Sec. IV D), we cannot use the immobile spin limit of the theory in Sec. II C to analyze the ^{2}H data. Rather we must consider the more general case where both translational diffusion and viscoelastic fluctuations contribute to $J^D_{0,\mathrm{dir}}(0)$. Treating the general case along the lines of Sec. II C, we find that the resulting effective correlation time τ_{dir} agrees to within a few percent with (2.41) modified by the substitution $\kappa/\eta\rightarrow\kappa/\eta+D$, provided that D is not much larger than κ/η.

D. Director fluctuations

In order to eliminate the local quadrupole coupling constant χ_{loc} from the analysis, we form the quotient

$$Q=J^D_{0,\mathrm{dir}}(0)/\nu_Q^2\ , \tag{4.7}$$

which, according to the results in Sec. II, is given by

$$Q(^{23}\mathrm{Na})=\frac{\pi^2}{4}\left[\frac{(1-S_{\mathrm{dir}})}{P_2(\cos\theta_{LD})S_{\mathrm{dir}}}\right]^2\frac{\lambda_c^2}{D_{\mathrm{Na}}}\times\left[\ln\left[\frac{2\pi\xi_m}{\lambda_c}\right]-1.12\right]\ , \tag{4.8a}$$

$$Q(^2\mathrm{H})=\frac{\pi}{12}\left[\frac{(1-S_{\mathrm{dir}}-\frac{3}{2}\sigma_s^2)}{P_2(\cos\theta_{LD})(S_{\mathrm{dir}}+\frac{3}{2}\sigma_s^2)}\right]^2\times\frac{\lambda_c^2}{\left[\dfrac{\kappa}{\eta}+D_{\mathrm{SDS}}\right]}\left[\ln\left[\frac{2\pi\xi_m}{\lambda_c}\right]-1.52\right]\ . \tag{4.8b}$$

Among the parameters appearing in (4.8), θ_{LD} and σ_s are known experimentally, D_{SDS} and D_{Na} are obtained from (4.5) and (4.6), and λ_c is set to 40 nm (cf. Sec. IV B). The magnetic coherence length ξ_m, which only weakly affects Q, is not known for the nematic phases studied here. It has been determined, however, for the N_C^+ phase of the closely related system sodium *decyl* sulphate-decanol-water [37]. With the reported values of $\kappa/\Delta\chi_D$ and our magnetic field ($B_0=2.35$ T), we obtain from (2.12) $\xi_m=18\text{–}22\ \mu\mathrm{m}$ in the 20 °C temperature interval investigated [37]. Assuming that $(\kappa/\Delta\chi_D)^{1/2}$ does not vary significantly between the two systems, we take $\xi_m=20\ \mu\mathrm{m}$ for our N_C^+ phase (at all temperatures). Further, we assume that $(\kappa/\Delta\chi_D)^{1/2}$ has essentially the same value in the N_D^- phase, so that $\xi_m=20\sqrt{2}\approx28\ \mu\mathrm{m}$ according to (2.12). [The factor $S_{\mathrm{dir}}^{1/2}$ in (2.12) is approximated by unity here.]

Substituting S_{dir} from (2.18) into (4.8a), we see that $Q(^{23}\mathrm{Na})$ now involves only one unknown, the elastic constant κ. Furthermore, for large S_{dir}, $Q(^{23}\mathrm{Na})$ is essentially proportional to κ^{-2} and depends only logarithmically on λ_c. Consequently, κ can be determined rather accurately despite some uncertainty in λ_c and D_{Na}.

The temperature variation of κ in the two phases is shown in Fig. 5; as expected κ decreases with increasing temperature. The dependence of κ on the estimated parameters λ_c, ξ_m, and D_{Na} is weak; if ξ_m is changed to 10 (40) μm, then κ decreases (increases) by 4%; changing λ_c to 30 (50) nm increases (decreases) κ by 8 (6) %; and if D_{Na} is varied by ±10%, then κ varies by only ±5%.

Figure 6 shows the order parameter S_{dir} obtained from κ and λ_c through (2.18). In both phases S_{dir} is in the range 0.8–0.9, except a few degrees within the N_C^+-L_1 transition, at which $S_{\mathrm{dir}}\approx0.65$ (for $\lambda_c=40$ nm).

By combining the S_{dir} values in Fig. 6 with the measured quadrupole splittings ν_Q in Fig. 2, we can obtain the local quadrupole coupling constant χ_{loc} from (2.9). We then make use of the relation [12]

$$\chi_{\mathrm{loc}}=S_{\mathrm{loc}}|S_{shp}(\rho)|\bar{\chi}\ , \tag{4.9}$$

where S_{loc} is the local order parameter, related to the orientation of a micelle with respect to the local director (cf. Sec. IV B), S_{shp} is a known function of the micellar axial ratio ρ accounting for orientational averaging by surface diffusion [12,17], and $\bar{\chi}$ is the residual quadrupole coupling constant (motionally averaged by "internal" motions only). Taking ρ and $\bar{\chi}$ from our previous work [12,22], we thus obtain the local order parameters shown in Fig. 6. The (asymmetric) error bars include the propagation of the uncertainty in axial ratio $\rho=3.5\pm0.5$ [12]. It is interesting to note that the local orientational order is substantially lower for the oblate micelles in the N_D^- phase than for the prolate micelles in the N_C^+ phase.

Having determined κ, we can then use $Q(^2\text{H})$ to obtain the nematic viscosity η from (4.8b). However, as the resulting $(\kappa/\eta+D_{\text{SDS}})$ is close in value to the estimated D_{SDS} (even smaller for the N_D^- phase) it is clear that we cannot obtain reliable results for η. In Fig. 5 we, therefore, show the quantity $(\kappa/\eta+D_{\text{SDS}})$, which provides an upper bound on D_{SDS} (corresponding to $\eta\rightarrow\infty$) and a lower bound on η (corresponding to $D_{\text{SDS}}=0$). In the N_C^+ phase, the minimum nematic viscosity obtained in this way decreases from 2.0 poise (16.4 °C) to 0.4 poise (25.4 °C). If we use our estimate for D_{SDS} (cf. Sec. IV C), these figures are instead 3.2 and 0.5 poise. In contrast, for the N_D^- phase a more accurate estimate of D_{SDS} is needed to deduce η. As compared to κ and S_{dir}, $(\kappa/\eta+D_{\text{SDS}})$ is somewhat more sensitive to the values of the estimated parameters; a variation in λ_c by 10 nm or a 10% variation in D_{Na} changes $(\kappa/\eta+D_{\text{SDS}})$ by 12%. Due to cancellation, $(\kappa/\eta+D_{\text{SDS}})$ is insensitive to ξ_m.

In a recent study [12], where we interpreted the ^{2}H and ^{23}Na *longitudinal* relaxation rates essentially in terms of "internal" motions and molecular diffusion over the curved micelle surface, we tacitly neglected any contribution from director fluctuations to the high-frequency lab-frame spectral densities $J_1^J(\omega_0)$ and $J_2^L(2\omega_0)$. We are now in a position to check this assumption.

Inserting $(\kappa/\eta+D_{\text{SDS}})$ or D_{Na} into (2.45), we obtain for $\lambda_c=40$ nm cutoff frequencies ω_c of $(0.2-2.0)\times10^5$ s^{-1} and $(0.8-2.0)\times10^7$ s^{-1} for ^{2}H and ^{23}Na, respectively, in the two samples. Since, therefore, $\omega_c\ll\omega_0$ it follows that (2.47) is an accurate approximation. Calculating χ_{loc} from the splitting ν_Q and S_{dir} via (2.9), we obtain from (2.42) and (2.47) the director-fluctuation contributions to $J_1^L(\omega_0)$ (N_C^+) and to $J_1^L(\omega_0)$ and $J_2^L(2\omega_0)$ (N_D^-) of 0.05 s^{-1} for ^{2}H and 0.3 s^{-1} for ^{23}Na in the N_C^+ phase (and even less in the N_D^- phase). If we decrease the cutoff wavelength λ_c to the largest dimension of the micelles (approximately 14 nm) then these contributions increase by a factor 8. Even then, however, the director-fluctuation contribution is negligible compared to the local-motion contribution to $J_1^L(\omega_0)$ and $J_2^L(2\omega_0)$ (approximately 10 s^{-1} for ^{2}H and approximately 50 s^{-1} for ^{23}Na) [12].

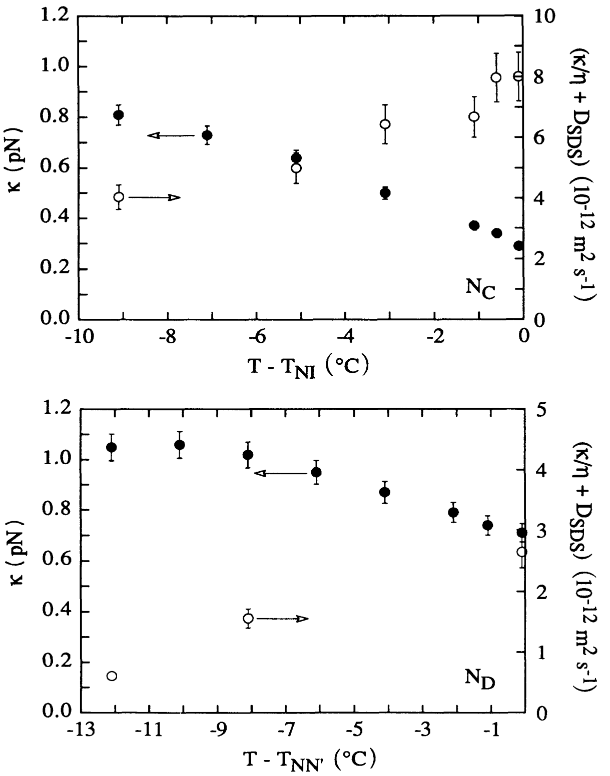

FIG. 5. Temperature variation of the elastic constant κ (solid symbols, left scale) and of the effective "diffusion coefficient" $(\kappa/\eta+D_{\text{SDS}})$ (open symbols, right scale) in the N_C^+ (top) and N_D^- (bottom) phases. The error bars correspond to the propagated random errors in the experimental data. The transition temperatures are $T_{NI}=25.5$ °C and $T_{NN'}=28.5$ °C.

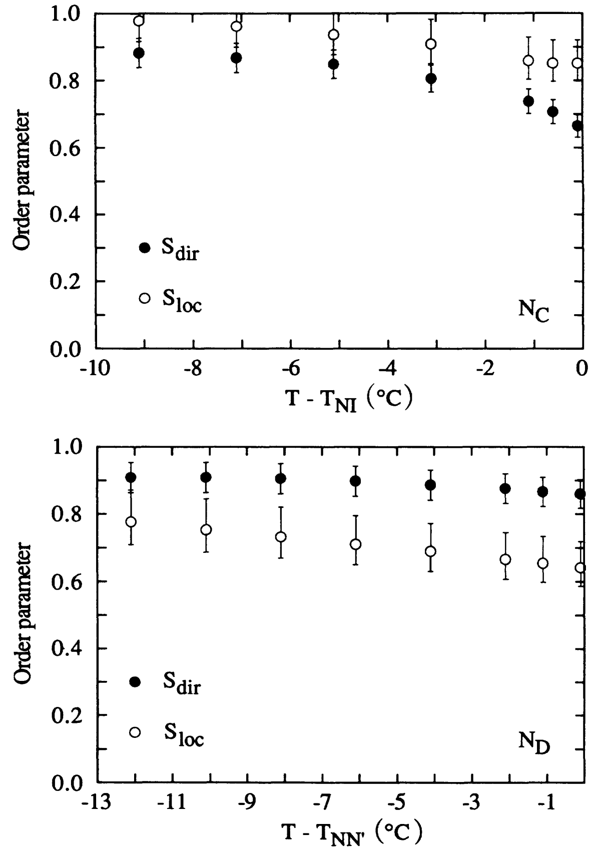

FIG. 6. Temperature variation of the director-fluctuation order parameter S_{dir} and the local order parameter S_{loc} in the N_C^+ (top) and N_D^- (bottom) phases. The error bars for S_{dir} correspond to the propagated random errors in the ^{23}Na data, while for S_{loc} they also account for the propagated uncertainty in micelle size (cf. text). The transition temperatures are $T_{NI}=25.5$ °C and $T_{NN'}=28.5$ °C.

V. CONCLUDING DISCUSSION

In this work we have demonstrated that director fluctuations dominate the transverse spin-relaxation rates from lyotropic nematic liquid crystals, which thus contain valuable information about the viscoelastic properties of these phases. Counterion nuclei (such as ^{23}Na) see an effectively static director field, whence the local director orientation is modulated exclusively by translational diffusion. Consequently, the zero-frequency spectral density $J_0^L(0)$ provides access to the elastic constant of the nematic fluid (if the macroscopic counterion diffusion coefficient is known and if the corrections for local motions can be estimated). Surfactant-bound nuclei (such as ^{2}H), by virtue of their slower diffusion, experience the viscoelastic director-fluctuation (collective reorientation) modes, thus providing access to the nematic viscosity (if κ is known, e.g., from counterion relaxation data, and if the surfactant diffusion coefficient can be estimated).

As shown in our previous NMR study of the present nematic phases [12], the strong temperature dependence of the ^{2}H and ^{23}Na quadrupole splittings (cf. Fig. 2) is due mainly to a reduction of the nematic order parameter $S_{\mathrm{nem}} = S_{\mathrm{dir}} S_{\mathrm{loc}}$ with increasing temperature. On the basis of the present analysis, the qualitatively different temperature dependence of the linewidths (cf. Fig. 3) from the two phases can be rationalized in terms of the director-fluctuation spectral density $J_{0,\mathrm{dir}}^D(0)$ (cf. Table I) as follows. The temperature dependence of $J_{0,\mathrm{dir}}^D(0)$ derives essentially from the two factors $(1-S_{\mathrm{dir}})^2 S_{\mathrm{loc}}^2 \sim S_{\mathrm{loc}}^2/\kappa^2$ and $1/D_{\mathrm{Na}}$ or $1/(\kappa/\eta + D_{\mathrm{SDS}})$; the former is a measure of the amplitude of the fluctuations and the latter is a measure of the fluctuation time scale. As can be seen from Figs. 5 and 6, the amplitude increases while the fluctuation time decreases with increasing temperature. In the N_C^+ phase the amplitude factor has the strongest temperature dependence, thus accounting for the monotonic linewidth increase in Fig. 3. In the N_D^- phase the temperature variation in the two factors nearly cancel, thus accounting for the nearly temperature-invariant linewidth in Fig. 3.

As far as we know, the only previous spin-relaxation study of a lyotropic nematic phase is that of Wong and Jeffrey [38], who reported ^{2}H $R_2(=\pi\Delta\nu_s^{\mathrm{hom}})$ data from the α-deuterated surfactant in the N_D^- phase of the system potassium laurate-decanol-potassium chloride-water. The temperature variation of R_2 from this phase is qualitatively similar to the results (Fig. 3) from our N_D^- phase: a high-temperature plateau and an increase (although much stronger than in our case) of the transverse relaxation rate at lower temperatures. Wong and Jeffrey attributed the high-temperature plateau to ^{2}H-^{1}H dipolar relaxation and the low-temperature increase to extremely slow *trans*-gauche isomerization. In light of the present work, we propose a different interpretation in terms of director fluctuations. Neglecting surfactant diffusion, the temperature dependence of R_2 should then derive essentially from the viscoelastic constants in the combination η/κ^3. The strong increase in R_2 as the low-temperature phase boundary is approached can thus be ascribed largely to an increasing nematic viscosity, the elastic constant being less temperature dependent (cf. Fig. 5). On the other hand, Wong and Jeffrey did invoke director fluctuations to account for the *high-frequency* spectral densities $J_1^L(\omega_0)$ and $J_2^L(2\omega_0)$, basing their conclusion on the assumed $1/\sqrt{\omega}$ form of the director-fluctuation dispersion. As shown in Secs. II D and IV D, however, the appropriate frequency dependence for lyotropic nematic liquid crystals is of the form $1/\omega^2$. As discussed elsewhere [12], it appears that the high-frequency spectral densities can be adequately accounted for in terms of diffusion of the surfactant molecule over the curved micelle surface.

Finally, we briefly compare the viscoelastic constants and order parameters deduced here with the rather limited amount of published data, obtained by other methods, for related lyotropic nematic phases. In making such comparisons, it should be borne in mind that our nematic samples, with a micelle volume fraction of 0.27, are unusually dilute.

The nematic order parameters derived from x-ray and neutron scattering are typically in the range 0.8–0.9 [39–42]. As it has been suggested [40] that the order parameter derived from scattering data is due mainly to long-wavelength orientational fluctuations, we identify it with our S_{dir}. As can be seen from Fig. 6, our S_{dir} values are indeed consistent with this interpretation.

Next we consider the elastic constant κ. For the N_D^- phase of the system decylammonium chloride-ammonium chloride-water Zhou, Stefanov, and Saupe [43], from measurements of magnetic-field-induced deformations, obtained $\kappa_1 = 2.6$ pN and $\kappa_3 = 4.7$ pN for the splay and bend elastic constants at a temperature of 48 °C (7 °C below the nematic-isotropic transition). According to mean field theory [44,45] the elastic constants should scale as $(\phi S_{\mathrm{loc}})^2$. Taking into account the higher micelle volume fraction ($\phi \approx 0.44$) in the sample studied by Zhou, Stefanov, and Saupe, their elastic constants are close to those obtained here (cf. Fig. 5). More sophisticated theories [46,47] suggest that the elastic constants also should depend sensitively on the micelle size and the intermicellar interaction. Electron microscopy studies [48] suggest, however, that the micelles in the phase investigated by Zhou, Stefanov, and Saupe are of a size comparable to that in the present phases [12].

The "diffusion coefficient" κ/η for director fluctuations has been obtained by Lacerda Santos, Galerne, and Durand [49] for the N_D^- phase of the system potassium laurate-decanol-water using Rayleigh scattering. (X-ray scattering studies [39] indicate that the oblate micelles in this phase have an axial ratio of approximately 2.8, i.e., not far from the value 3–4 obtained [12] for our N_D^- phase.) At 19 °C, about 20 °C below the nematic-isotropic transition, these authors report $D_{\mathrm{splay}} = \kappa_1/\eta_{\mathrm{splay}} = 11.5 \times 10^{-12}$ m^2 s^{-1} and $D_{\mathrm{twist}} = \kappa_2/\eta_{\mathrm{twist}} = 1.6 \times 10^{-12}$ m^2 s^{-1}. Referring to Fig. 5, we note that these values are in the same range as those obtained here (assuming that D_{SDS} does not make a dominant contribution).

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