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Surface forces, undulating bilayers, and nuclear-spin relaxation

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Nuclear-spin relaxation due to bilayer undulations in amphiphile-water systems has previously been interpreted in terms of the elastic bending modes of a freely fluctuating bilayer. Generalizing the relaxation theory to include the effect of the compressional stiffness of a multibilayer system, we show that the spin relaxation depends on, and hence provides information about, the interactions between the bilayers.

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Out-of-plane fluctuations of amphiphilic bilayers in the lamellar phase of surfactant-water systems and in multilamellar phospholipid-water systems have recently attracted considerable interest [1–3]. Since these fluctuations are controlled by the bilayer bending rigidity and the interactions between the bilayers, their study can provide information that is vital to the understanding of microstructure and phase behavior in these complex fluids. Experimental data on bilayer fluctuations have come mainly from studies of scattering and nuclear-spin relaxation. Spin relaxation rates from lamellar systems have been determined over a wide frequency range using field-cycling [4,5] or pulse-train [6–9] techniques, and at zero frequency using the transverse relaxation rate [10,11]. The existing theory [12] relating spin relaxation rates to bilayer fluctuations is valid only in the high-frequency regime where bilayer interactions can be ignored. We present here a more general theory, based on the full Landau–Peierls–de Gennes Hamiltonian, showing that the independent-bilayer theory is not applicable under typical experimental conditions. Spin relaxation rates can thus provide information on bilayer interactions.

Within the regime of the conventional Bloch-Wangsness-Redfield perturbation theory of spin relaxation [13], the effect of bilayer fluctuations on the spin relaxation is described, to second order in the bilayer deformation, by the time correlation function

$$G(\tau)=\langle \mathbf{n}_\perp(0)\cdot\mathbf{n}_\perp(\tau)\rangle. \tag{1}$$

Here $\mathbf{n}_\perp$ is the projection of the bilayer normal (director) on the lateral base plane, related (to leading order) to the vertical (along the optic axis) bilayer displacement, u, as $\mathbf{n}_\perp=-\nabla_\perp u$. After a spatial Fourier transform of u, one obtains

$$G(\tau)=\sum_{\mathbf{q}} q_\perp^2\langle|\hat{u}(\mathbf{q})|^2\rangle\exp(-\tau/\tau_{\mathbf{q}}). \tag{2}$$

The time constant for the dissipative decay of the independent fluctuation modes is $\tau_{\mathbf{q}}=-(q_\perp^2 D)^{-1}$, with an effective "diffusion coefficient" $D=D_u+D_t$ accounting for viscoelastic bilayer fluctuations (D_u) and molecular translational diffusion in the bilayer plane (D_t). Although D_u depends on $\mathbf{q}$ in general [14], we consider here only the pure undulation mode ($q_z=0$), for which $D_u=K_1/\eta$ with K_1 the curvature-elastic splay modulus and η the solvent viscosity. The frequency-dependent spin relaxation rates are determined by a spectral density function $J(\omega)$, which is the cosine transform of $G(\tau)$, i.e.,

$$J(\omega)=\sum_{\mathbf{q}} q_\perp^2\langle|\hat{u}(\mathbf{q})|^2\rangle\frac{\tau_{\mathbf{q}}}{1+(\omega\tau_{\mathbf{q}})^2}. \tag{3}$$

The phenomenological static description of thermally excited elastic distortions in the smectic A phase, as developed by Landau, Peierls, and de Gennes, is based on the Hamiltonian [15]

$$\mathscr{H}=\tfrac{1}{2}\int_V d\mathbf{r}\left[\bar{B}\left(\frac{\partial u}{\partial z}\right)^2+K_1(\nabla_\perp^2 u)^2\right], \tag{4}$$

where $\bar{B}$ and K_1 are the macroscopic elastic constants associated with longitudinal compression (at constant chemical potential) and director splay, respectively. In the presence of a magnetic field, as in an NMR experiment, Eq. (4) must be supplemented with a magnetic Hamiltonian [16]. If the magnetic interaction is neglected (cf. below), a Fourier decomposition of Eq. (4) yields with the equipartition theorem [15]

$$\langle|\hat{u}(\mathbf{q})|^2\rangle=\frac{k_B T}{V\kappa d(q_z^2/\xi_p^4+q_\perp^4/d^2)}, \tag{5}$$

where we have introduced the (average) bilayer repeat distance d, the bilayer bending rigidity $\kappa=dK_1$, and the transverse orientational correlation length (or patch length) $\xi_p=(d^2K_1/\bar{B})^{1/4}$, which defines the crossover from a short-wavelength regime ($q_\perp\xi_p\gg1$) with independent bilayer fluctuations to a long-wavelength regime ($q_\perp\xi_p\ll1$) with coupled bilayer fluctuations [17].

The theoretical description of bilayer fluctuations presents some subtleties due to the many length scales involved in the problem: the sample dimensions L_z and $L_\perp$, the bilayer period d, the lateral continuum cutoff length a (with a^2 of the order of the amphiphile cross-sectional area), the patch length ξ_p (a measure of the relative importance of bilayer rigidity and compressional stiffness), and the magnetic coherence length [15] $\xi_m=(\mu_0K_1/|\Delta\chi|B^2)^{1/2}$ (a measure of the relative importance of bilayer rigidity and magnetic

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torque). Whereas a completely general treatment entails considerable mathematical complexity, simple analytical results can be obtained by noting that only a small fraction of the six-dimensional parameter space is experimentally relevant. Thus, for example, the magnetic interaction adds to the denominator of Eq. (5) a term $q_\perp^2/\xi_m^2$, which can be neglected if $\xi_p^2 \ll 2\pi\xi_m^2/N$, with $N=L_z/d$ the number of bilayers in the stack.

An interesting result follows directly from Eq. (3): the zero-frequency spectral density $J(0)$ is directly proportional to the mean-square bilayer displacement,

$$J(0)=\langle u^2\rangle/D. \tag{6}$$

Provided that $a^2/\pi \ll \xi_p^2 \ll L_\perp^2/N$, we obtain from Eqs. (5) and (6)

$$J(0)=\frac{k_BT}{8\kappa\omega_p}\ln N, \tag{7}$$

where we have introduced the "patch frequency" $\omega_p=\pi D/\xi_p^2$, which is essentially the inverse of the time taken to "diffuse" one orientational correlation length. It should be noted that $J(0)$ does *not* diverge in the thermodynamic limit (as one might expect for diffusion in two dimensions); when the sample thickness $L_z=Nd$ is sufficiently large the inequality $\xi_p^2 \ll 2\pi\xi_m^2/N$ is no longer valid and the magnetic interaction, which then limits the layer fluctuations, must be included. For all practical purposes, however, Eq. (7) is valid.

Inserting Eq. (5) into Eq. (3) and converting the sum to a three-dimensional integral, we obtain for the spectral density function

$$J(\omega)=\frac{k_BT}{8\kappa\omega_p}\ln\left|\frac{1+\omega/\omega_p}{1/N+\omega/\omega_p}\right|. \tag{8}$$

This result, like its $\omega=0$ limit in Eq. (7), is valid provided that

$$a^2/\pi \ll \xi_p^2 \ll \min(2\pi\xi_m^2, L_\perp^2)/N, \tag{9}$$

which is true in virtually all cases of interest. In addition, we have assumed that $\omega \ll \pi^2 D/a^2$, since at higher frequencies [where $J(\omega)\propto\omega^{-2}$] bilayer fluctuations do not contribute significantly to spin relaxation. The patch frequency ω_p defines the crossover from a low-frequency regime ($\omega \ll \omega_p$) with coupled bilayer fluctuations to a high-frequency regime ($\omega \gg \omega_p$) with independent bilayer fluctuations. In the high-frequency regime, Eq. (8) takes the remarkably simple form

$$J(\omega)=\frac{k_BT}{8\kappa\omega}, \tag{10}$$

showing that, in this regime, $J(\omega)$ is not only independent of the bilayer coupling but also independent of the rate of bilayer fluctuations and lateral molecular diffusion.

The spectral density function in Eq. (8) governs the spin relaxation probed in a field-cycling experiment. The quadrupolar echo train experiment (as applied to nuclei of spin $I=1$) yields a slightly different (effective) spectral density function [18]

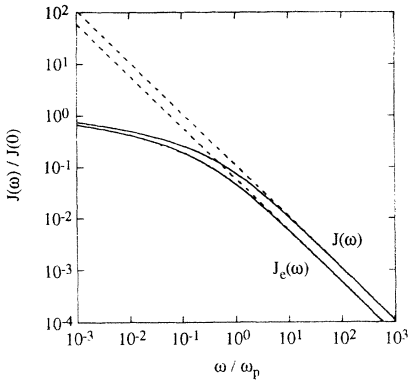

FIG. 1. Field-cycling, $J(\omega)$, and pulse-train, $J_e(\omega)$, spectral density dispersion in lamellar phase with $N=10^4$ bilayers in the stack. The dashed lines correspond to the $1/\omega$ limiting law, which is obeyed at frequencies ω much larger than the patch frequency ω_p.

$$J_e(\omega)=\frac{8}{\pi^2}\sum_{n=0}^{\infty}(2n+1)^{-2}J((2n+1)\pi\omega/2), \tag{11}$$

where ω now refers to the pulse train frequency. Combination with Eq. (8) yields

$$J_e(\omega)=\frac{k_BT\xi_p^2}{\pi^3\kappa D}\sum_{n=0}^{\infty}(2n+1)^{-2}\ln\left(\frac{1+\Omega_n}{1/N+\Omega_n}\right), \tag{12}$$

with $\Omega_n=(2n+1)\pi\omega/(2\omega_p)$. In the $\omega=0$ limit Eq. (12) coincides with Eq. (7), as expected. In the high-frequency ($\omega \gg \omega_p$) regime, Eq. (12) reduces to

$$J_e(\omega)=\frac{\alpha k_BT}{8\kappa\omega}, \tag{13}$$

which differs from Eq. (10) by a factor

$$\alpha=\frac{16}{\pi^3}\sum_{n=0}^{\infty}(2n+1)^{-3}\approx 0.5428.$$

Figure 1 shows the dispersion of $J(\omega)$ and $J_e(\omega)$ as described by Eqs. (8) and (12), along with the corresponding high-frequency limiting forms, Eqs. (10) and (13).

In all reported studies of nuclear-spin relaxation due to bilayer fluctuations the coupling between adjacent bilayers was ignored. If the compressional term $\bar{B}(\partial u/\partial z)^2$ in the Hamiltonian, Eq. (4), is omitted one obtains a fluctuation spectrum $\langle|\hat{u}(\mathbf{q})|^2\rangle$ of the $q_\perp^{-4}$ form characteristic of a freely fluctuating membrane [1]. Inserting this into Eq. (3) we obtain (for $\omega \ll \pi^2 D/a^2$) the spectral density function

$$J(\omega)=\frac{k_BT}{4\pi\kappa\omega}\arctan(\omega/\omega_L), \tag{14}$$

with $\omega_L=\pi^2 D/L_\perp^2$. For $\omega \gg \omega_L$ this reduces to Eq. (10), which is the result obtained by Marqusee, Warner, and Dill [12]. The $\omega=0$ limit of Eq. (14) is

$$J(0)=\frac{k_BTL_\perp^2}{4\pi^3\kappa D}. \tag{15}$$

The spectral density function in Eq. (14), or the corresponding pulse-train version obtained from Eqs. (11) and (14), has been used in all recent relaxation dispersion studies of bilayer fluctuations, [4–8] and its limiting form, Eq. (15), has been used to interpret transverse relaxation [6,7,9,19]. In these studies, however, $L_\perp$ was not identified with the lateral sample dimension but was instead regarded as a (physically obscure) "long-wavelength cutoff of the elastic modes" [20]. To interpret the relaxation dispersion, previous authors have used either [4,5] the high-frequency limit of Eq. (14), i.e., Eq. (10), or a numerical finite-difference algorithm [6–8] which, under the conditions of interest, is equivalent to Eqs. (11) and (14). As is evident from Eq. (14), the relaxation dispersion is fully determined by two parameters (κ/k_BT and ω_L) in the decoupled-bilayer theory. Hence, it is not possible to separately determine D and $L_\perp$ (or the "cutoff length"), as some authors claim to have done [6–8].

In deriving Eqs. (14) and (15) we neglected the interaction of the anisotropic diamagnetic susceptibility of the lamellar phase with the external magnetic field. Including this magnetic interaction [16] in the Hamiltonian, we obtain in place of Eq. (15)

$$J(0)=\frac{k_BTL_\perp\xi_m}{2\pi^2\kappa D} \tag{16a}$$

for a diamagnetically negative phase oriented perpendicular to the magnetic field, and

$$J(0)=\frac{k_BT\xi_m^2}{2\pi\kappa D}\ln\left(\frac{L_\perp}{\pi\xi_m}\right) \tag{16b}$$

for a diamagnetically positive phase oriented parallel to the field. The zero-frequency spectral density thus depends on the strength (and orientation) of the magnetic field.

If bilayer coupling cannot be neglected, the spin relaxation should be described by Eqs. (7) and (8) rather than by Eqs. (14)–(16). As we have shown, the spectral density function $J(\omega)$ is unaffected by bilayer coupling only at frequencies ω much larger than the patch frequency ω_p. It is thus imperative to estimate the magnitude of ω_p for the systems of interest.

Using the expressions for ω_p and ξ_p given above and expressing the compression modulus $\bar{B}$ in terms of the bilayer interaction per unit area, $V(s)$, we obtain

$$\omega_p=\pi(D_u+D_t)\left(\frac{1}{\kappa}\frac{d^2V}{ds^2}\bigg|_{s=d}\right)^{1/2}. \tag{17}$$

If V includes several interactions, ω_p is dominated by the "stiffest" interaction, having the largest curvature at the equilibrium separation d.

In dilute lamellar phases built from electroneutral (or salt-screened) bilayers, the steric repulsion [21] $V(s)=(3\pi^2/128)(k_BT)^2/[\kappa(s-\delta)^2]$ dominates, and

$$\omega_p=\frac{3\pi^2k_BT(D_u+D_t)}{8\kappa(d-\delta)^2}, \tag{18}$$

with δ the bilayer thickness. With parameters typical for dilute lamellar surfactant systems [3,16], $\kappa=2.5k_BT$, $d=200$ Å, $\delta=35$ Å, and $D_u\approx D_t\approx5\times10^{-10}$ m^2s^{-1}, we obtain $\omega_p\approx5\times10^6$ rad s^{-1}.

For neutral phospholipids [such as di-myristoyl-phosphatidyl-choline (DMPC)] under typical conditions ($\delta=35$ Å, $d=60$ Å, $\kappa\approx20k_BT$) it appears that the compressional stiffness is due mainly to the so-called hydration repulsion [22] $V(s)=V_0\exp[-(s-\delta)/\lambda_h]$, whence

$$\omega_p=\frac{\pi(D_u+D_t)}{\lambda_h}\left(\frac{V_0}{\kappa}\right)^{1/2}\exp\left[-\frac{(d-\delta)}{2\lambda_h}\right]. \tag{19}$$

Adopting the typical values [22] $V_0=5k_BT$ Å^{-2}, $\lambda_h=2$ Å, and $D_u\approx3\times10^{-9}$ $m^2s^{-1}\gg D_t$, we obtain $\omega_p\approx5\times10^8$ rad s^{-1}.

In both of these examples, the patch frequency ω_p is well above the frequency range ($\omega<10^5$ rad s^{-1}), where bilayer fluctuations contribute significantly to spin relaxation. It appears, therefore, that bilayer coupling is important for the spin relaxation under all experimentally relevant conditions.

Finally, we note that Blinc *et al.* [23] have presented an expression for the spectral density function in a smectic A phase, which in our notation reads

$$J(\omega)=\frac{k_BT}{8\kappa\omega_p}\ln[1+(\omega_a/\omega)^2], \tag{20}$$

with $\omega_a=\pi^2D/a^2$ the high-frequency cutoff. This expression differs qualitatively from our result, Eq. (8); in particular, it diverges for $\omega=0$. Although Eq. (20) was apparently derived on the basis of the same Hamiltonian that is used here, Eq. (4), no details of the derivation were given.

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