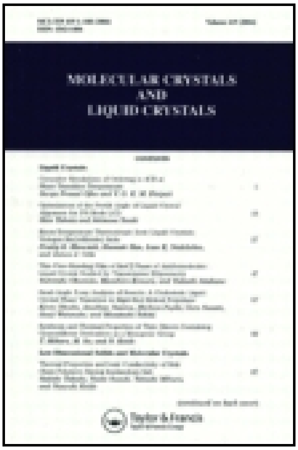

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A Study of the Angular Dependence of NMR Relaxation Times in Macroscopically Oriented Lyotropic Liquid Crystal Lamellar Phases

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The angular dependence of ^1H and ^2H NMR relaxation rates has been investigated for macroscopically oriented multi-bilayers of egg yolk lecithin and dimyristoyl lecithin in the Lα phase. Proton $T_{1\rho}$ values show a strong dependence on the orientation of the bilayer normals to the magnetic field, while deuterium $T_{1\rho}$ and T_1 values and proton T_1's show little or no orientation dependence. The results are interpreted on the basis of a simple modification of the theory of Ukleja, Pirs and Doane for relaxation in oriented thermotropic phases. The results confirm the presence of collective fluctuations in the density of lipid packing in the plane of the bilayer which dominate proton relaxation at low frequencies. There is no evidence of a significant contribution from collective order fluctuations.

INTRODUCTION

Nuclear magnetic resonance (NMR) has been utilized extensively in the study of molecular ordering and motion in lyotropic liquid crystals.[1–4]

The molecular order parameter *S* which characterizes the degree of reorientational restriction experienced by the molecules in the liquid crystal environment[5,6] can be determined by the technique of deuterium NMR labelling.[2] Similar information averaged over a longer time scale can be obtained in suitable cases from studies of the ^{13}C or ^{31}P chemical shift anisotropy.[7,8] NMR relaxation times on the other hand are sensitive to the rates of molecular motion. In this context it is important to emphasize that molecular order parameters are relatively insensitive to the time scale of molecular motion. They provide information only about the time averaged molecular orientations and conformation which may be present in the system, although the appropriate time scale for this averaging will depend on the measuring technique, being much shorter for ESR (spin labels) than for NMR methods where the time scale is 10^{-3}–10^{-5}s. Thus measurements of NMR relaxation times as a function of both frequency and sample orientation can provide much useful information for developing detailed models of molecular motion in such systems.[9]

Although the lipid bilayer or lamellar ($L\alpha$) phase has been most extensively investigated, the majority of NMR relaxation studies have employed coarse lipid dispersions in which the bilayers are randomly oriented with respect to the magnetic field. In such cases, where the relaxation is dependent on sample orientation, the measured relaxation times reflect a weighted average of the values for all orientations of the liquid crystal axes with respect to the magnetic field and in general the corresponding relaxation functions can be expected to be non-exponential. Orientation dependent relaxation times have been reported for aligned samples in a number of thermotropic phases,[10–12] but only very limited data is available for lyotropics[13,14] which are generally more difficult to orient macroscopically. In this paper we present results for the orientation dependence of ^1H spin-lattice relaxation times in the rotating frame ($T_{1\rho}$) in samples of egg yolk lecithin (EYL) and dimyristoyl lecithin (DML) bilayers oriented between glass slides. The form of the orientation dependence differs markedly from that found in thermotropic phases where the relaxation is dominated at low frequencies by collective order fluctuations. However it is shown that the theory of Ukleja, Pirs and Doane[15] for such phases can be adapted to the present case and gives good agreement with the observed results. This is surprising in view of the greater complexity of molecular motion that can be anticipated for lipid bilayers which comprise flexible molecules and in which reorientation of both the whole molecule and individual segments (conformational motion) can take place. In contrast proton T_1's and deuterium T_{1_ρ}'s are expected to exhibit only a weak angular dependence. Experimentally these parameters exhibit little or no variation with sample orientation.

THEORY

Expressions for spin-lattice relaxation times in the laboratory (T_1) and rotating (T_{1_ρ}) frames take the general form[16,17]

$$\frac{1}{T_1} = K[J_1(\omega_0) + J_2(2\omega_0)] \tag{1}$$

$$\frac{1}{T_{1_\rho}} = K\left[\frac{1}{4}J_0(2\omega_1) + \frac{5}{2}J_1(\omega_0) + \frac{1}{4}J_2(2\omega_0)\right] \tag{2}$$

where for relaxation due to magnetic dipolar couplings between proton pairs $K = (9/8)\,(\mu_0/4\pi)^2\,(\gamma^4\hbar^2/r^6)$, while for relaxation via the interaction of a spin 1 quadrupole such as deuterium with an axially symmetric electric field gradient (E.F.G.), $K = (9/32)\,(e^2qQ/\hbar)^2$. The spectral intensity functions $J(\omega)$ are Fourier transforms of correlation functions describing the molecular motion which gives rise to the relaxation

$$J_p(\omega) = \int_{-\infty}^{\infty} G_p(\tau)e^{i\omega\tau}d\tau \tag{3}$$

$$G_p(\tau) = \langle F_p^*(t+\tau)\,F_p(t)\rangle. \tag{4}$$

The $F_p(t)$ are functions of the position coordinates of the interaction vector $\mathbf{R}(\alpha,\phi)$ with respect to the magnetic field $\mathbf{B}_0$ which is assumed to lie along the Z axis in the laboratory frame (Figure 1)

$$\begin{aligned} F_0 &= (1\text{-}3\cos^2\alpha) \\ F_1 &= \sin\alpha\cos\alpha\, e^{i\phi} \\ F_2 &= \sin^2\alpha\, e^{2i\phi}. \end{aligned} \tag{5}$$

For the case of protons the interaction vector is the H—H vector **r**, while for deuterons it is the symmetry axis of the E.F.G., which lies along the C—D bond.[2]

Bloembergen, Purcell and Pound[18] treated the case of an isotropic liquid by assuming the correlation functions $G_p(\tau)$ to be exponential, characterized by a single correlation time τ_c such that

$$G_p(\tau) = \langle|F_p(t)|^2\rangle\, e^{-\tau/\tau_c}. \tag{6}$$

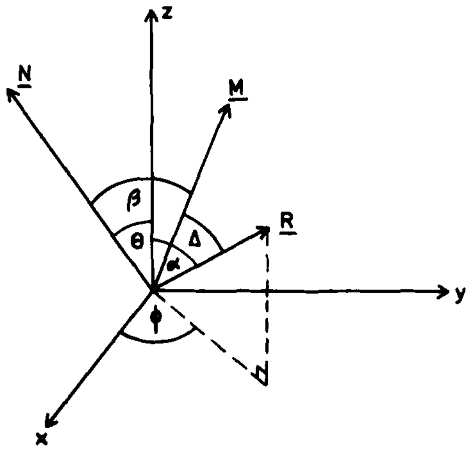

FIGURE 1 Angles used to define the relative orientations of the applied magnetic field B_0, liquid crystal director (bilayer normal) N, molecular (segmental) axis M and interaction vector R.

The theory was subsequently extended by Woessner[19,20] to the case of anisotropic rotational diffusion in which the molecules reorient rapidly about a preferred axis which itself reorients more slowly and *isotropically*. However Seiter and Chan[21] have pointed out that for the case of lipid bilayers, *restricted* anisotropic motion applies. The axis of the lipid chains (or of a particular chain segment) **M** has a preferred orientation parallel to the liquid crystal director **N**, which for the Lα phase is the bilayer normal (Figure 1). In such a case the molecular or segmental order parameter

$$S = \left\langle \frac{3\cos^2\beta - 1}{2} \right\rangle \tag{7}$$

is non zero ($0 \leqslant S \leqslant 1$) and in general the ensemble averages $\langle |F_p(t)|^2 \rangle$ in Eq. (6) must be evaluated numerically.

The model of Ukleja, Pirs and Doane[15] for relaxation in thermotropic nematics evaluates the averages analytically by making use of the identity $\langle \cos^2\beta \rangle = \frac{1}{3}(2S + 1)$ from the definition of S, and the approximate relation $\langle \cos^4\beta \rangle = \frac{1}{5}(4S + 1)$ which is strictly true only for $S = 0$ and $S = 1$. As well as contributions to relaxation from the reorientation of individual molecules, characterized by a single correlation time τ_c, these authors were able to incorporate contributions from collective modes of reorientation (order fluctuations) and for the case of relaxation via magnetic dipolar couplings, from modulation of the inter-molecular interactions by relative translational motion of the molecules, described by a second correlation time τ_D. (The quadrupolar interaction which dominates ^{2}H relaxation is entirely intra-molecular in origin.) The model has been extended by Blinc *et al.*[11] to the case of thermotropic smectic phases and we have adapted it to describe relaxation in lipid bilayers on the basis of the following assumptions.

(i) Rapid reorientation of the lipid alkyl chains about their long axes in the Lα phase[1,6,22,23] averages the intra-molecular interactions onto the molecular axis **M**. Thus the model utilizes a reduced static interaction strength K in Eqs. (1) and (2) and the angle between the interaction vector **R** and **M**, $\Delta = 0$ for both dipolar (^{1}H) and quadrupolar (^{2}H) cases.

(ii) Rapid lateral diffusion of the molecules in the plane of the lamellae similarly greatly reduces the time averaged inter-molecular dipolar interactions and projects then onto the bilayer normal.

(iii) A single correlation time τ_c is used to characterize the reorientation of individual chain segment axes which modulates the intra-molecular couplings. This may be associated with conformational flexing of the chains or tilt of the molecule as a whole. It is assumed that $\tau_c \lesssim 10^{-9}$s consistent with the known increase of T_1 with temperature above the gel–liquid crystal transition,[24,25] which corresponds to the limit $\omega_0\tau_c < 1$.

(iv) Collective density fluctuations which modulate the inter-molecular couplings at rates lower than those associated with translational diffusion[14] are characterized by a correlation time τ_D.

Thus the model treats explicitly only the lower frequency modes of molecular motion which modulate the intra and inter-molecular couplings respectively. It is these modes which can be expected to dominate NMR relaxation behavior, particularly T_{1_ρ}. In addition comparison of ^{1}H and ^{2}H relaxation rates allows a separation of inter and intra-molecular contributions. The general expressions for the relaxation rates $(T_1)^{-1}$ and $(T_{1_\rho})^{-1}$ as a function of both frequency and sample orientation (defined by the angle θ between the director **N** and the magnetic field $\mathbf{B}_0$) are very complex. However if we exclude contributions from collective order fluctuations (see below) results for the mean square values of the orientation functions can be expressed compactly in matrix form:

$$\begin{pmatrix} \langle|F_0(t)|^2\rangle \\ \langle|F_1(t)|^2\rangle \\ \langle|F_2(t)|^2\rangle \end{pmatrix} = \begin{pmatrix} 4(4S+1)/5, & -12S, & 9S \\ 2(1-S)/15, & S\ , & -S \\ 8(1-S)/15, & 0\ , & S \end{pmatrix} \begin{pmatrix} 1 \\ \sin^2\theta \\ \sin^4\theta \end{pmatrix} \tag{8}$$

For $S \rightarrow 0$ these reduce to the BPP results.[18]

In an earlier paper[14] we reported a low frequency dispersion in $T_{1\rho}$ for the protons in EYL bilayers, which we tentatively ascribed to modulation of the inter-molecular interactions by fluctuations in the packing density of lipid molecules in the plane of the bilayer. For the case of $T_{1\rho}$ the term in $J_0(2\omega_1)$ will dominate, where $\omega_1 = \gamma B_1$ is determined by the strength B_1 of the "spin locking" *RF* field. Thus we can write for the inter-molecular contribution to the proton relaxation rate in the rotating frame

$$\left(\frac{1}{T_{1\rho}}\right)_{\text{inter}} \approx K_{\text{inter}}\left[\frac{4(4S+1)}{5} - 12S\sin^2\theta + 9S\sin^4\theta\right]\cdot \frac{2\tau_D}{1+4\omega_1^2\tau_D^2} \tag{9}$$

which in the limit of perfect molecular order ($S \rightarrow 1$) reduces to

$$\left(\frac{1}{T_{1\rho}}\right)_{\text{inter}} \approx K_{\text{inter}}\,[(3\cos^2\theta-1)^2]\cdot\frac{2\tau_D}{1+4\omega_1^2\tau_D^2}$$

In general the overall proton relaxation rate will be a sum of inter and intra-molecular contributions

$$\frac{1}{T_R} = \left(\frac{1}{T_R}\right)_{\text{intra}} + \left(\frac{1}{T_R}\right)_{\text{inter}}. \tag{10}$$

MATERIALS AND METHODS

Egg yolk lecithin in chloroform/methanol solution and synthetic L-α-dimyristoyl phosphatidylcholine (DML) were obtained from Sigma chemicals and used without further purification. A sample of DML with perdeuterated alkyl chains was obtained from Serdary Research Laboratories. The synthetic lecithins were dissolved in chloroform (~0.1 gm/ml) and the solutions pipetted onto thin glass slides (20 mm × 6 mm × 0.1 mm). Once the majority of the solvent had evaporated, the slides were placed in a vacuum dessicator which was evacuated by means of a diffusion pump to remove final traces of solvent. The slides were then hydrated by exposing to a D_2O saturated nitrogen atmosphere for ~24 hours and then stacked (above the chain melting temperature in the case of DML) to form a sample of 20–30 such slides. After transferring to NMR sample tubes, the samples were further equilibrated in a D_2O atmosphere for several days during which the alignment gradually improved.[13,14] Sample hydration was checked by observation of the ^2H splittings from D_2O which had been previously studied for such samples[13,26] and checked by subsequent weight analysis. Samples used in this study contained ~9 D_2O/lipid.

^1H NMR measurements were performed on a Bruker SXP spectrometer operating at 60 MHz. ^2H measurements were performed on a Bruker CXP 100 spectrometer at 13.82 MHz. Both machines were fitted with Bruker temperature controllers. Samples were placed in a specially designed sample holder which allowed the orientation θ to be set to $\pm 0.1°$. T_1 measurements were made by the inversion-recovery technique, while $T_{1\rho}$ data were obtained by the standard "spin-locking" method. Relaxation times were determined by least squares fitting of the data. Theoretical values of the relaxation rates were calculated on the modified Ukleja *et al.* theory by means of a computer program (BASIC) on an Apple II micro-computer. The results were manually fitted to the corresponding experimental data.

RESULTS AND DISCUSSION

Results for the orientation dependence of ^1H relaxation in EYL and DML bilayers are shown in Figures 2 and 3 respectively. $T_{1\rho}$ values show a strong orientation dependence with a maximum relaxation time at the "magic angle" $\theta = \cos^{-1} 1/\sqrt{3} = 54.7°$, while within experimental error T_1 values show little or no orientation dependence. The $T_{1\rho}$ values for EYL were measured at two different frequencies $\omega_1 = \gamma B_1$ corresponding to values of the spin-locking *RF* of $B_1 = 0.35$ mT and 1.19 mT respectively, and show the frequency dispersion as reported earlier.[14] Similar results are also obtained for oriented DML multilayers [Figure 4(a), where the relaxation times are plotted directly]. A comparison of $T_{1\rho}$ values for protons in DML—D_2O oriented multilayers and the corresponding deuterium signal from the sample with perdeuterated chains is shown in Figure 4. The absence of an orientation dependence in the latter case confirms that the motion dominating

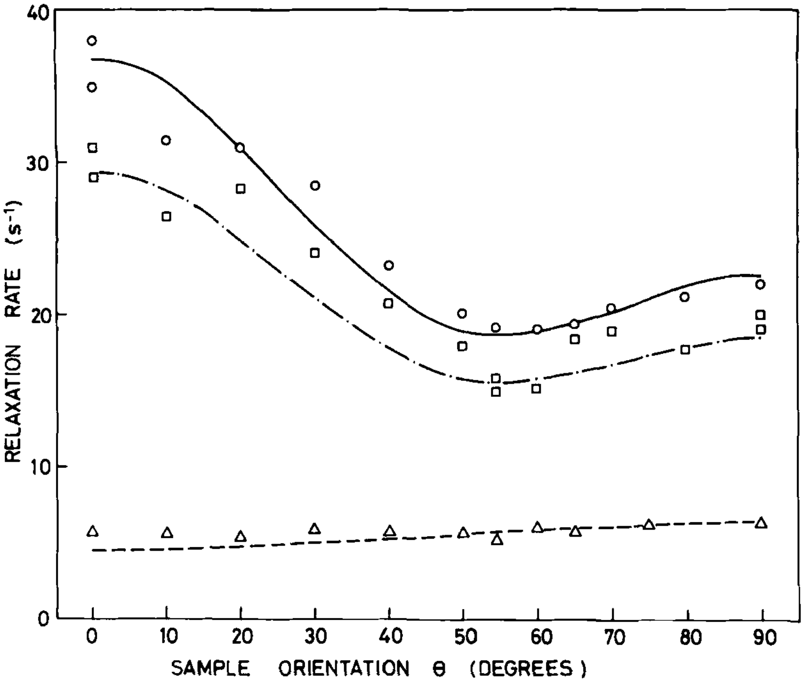

FIGURE 2 Experimental proton relaxation rates $T_{1\rho}^{-1}$ and T_1^{-1} (discrete points) and corresponding theoretical curves for EYL—D_2O multilayers at 298 K as a function of sample orientation θ. ○ $T_{1\rho}^{-1}$, $B_1 = 0.35$ mT; □ $T_{1\rho}^{-1}$, $B_1 = 1.19$ mT; △ T_1^{-1} data (60 MHz).

proton $T_{1\rho}$ values is inter-molecular in origin and therefore inoperative in affecting ^{2}H relaxation. In fitting the theory to our results we have selected a correlation time $\tau_D = 10^{-6}$s consistent with the observed dispersion in proton $T_{1\rho}$ values. With τ_c subject to the condition in (iii) above, the ^{1}H $T_{1\rho}$ data were then determined almost exclusively by the parameters K(inter) and S which were selected to fit the magnitude and orientation dependence of the relaxation times respectively. Values of K(intra) and τ_c were then chosen to fit the T_1 data. It should be noted here that ^{1}H spin-lattice relaxation rates are affected by spin diffusion and therefore represent a weighted average of the values for all protons in the sample which contribute to the observed signal. For this reason the order parameter and interaction strengths which we obtain can be expected to reflect a similar averaging. Optimum parameters for all the samples are presented in Table I.

In the case of the ^{2}H $T_{1\rho}$ data for perdeuterated DML chains [Figure 4(b)] only the intra-molecular interactions need be considered. In fit-

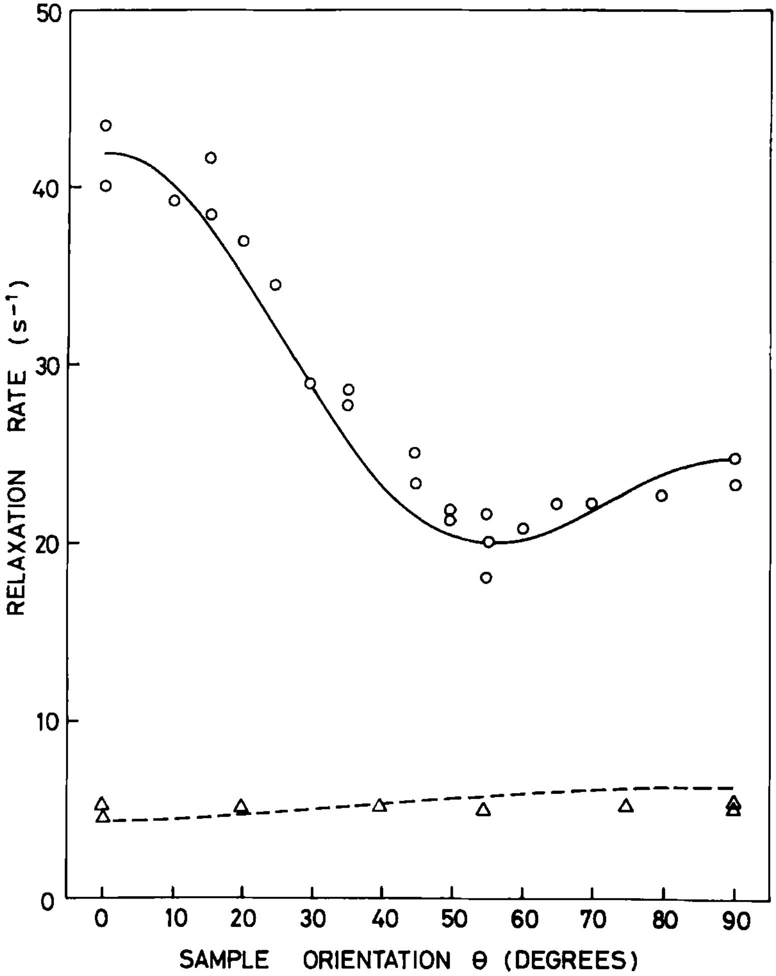

FIGURE 3 Experimental proton relaxation rates $T_{1\rho}^{-1}$ and T_1^{-1} (discrete points) and corresponding theoretical curves for DML—D$_2$O bilayers at 304 K as a function of sample orientation θ. ○ $T_{1\rho}^{-1}$, $B_1 = 0.35$ mT; △ T_1^{-1} data (60 MHz).

ting these data, the same values of S and τ_c have been used as for the corresponding ^{1}H data [Figure 4(a) and Table I], while an interaction strength K(intra) = 5×10^{10}s^{-2} was employed. This compares with a rigid lattice value of 3.2×10^{11}s^{-2} based on a value for the quadrupole coupling content appropriate to a C—D bond (e^2qQ/h) = 170 kHz.[27] In our model the interaction strength is reduced relative to this value by rapid long axis chain reorientation and other high frequency con-

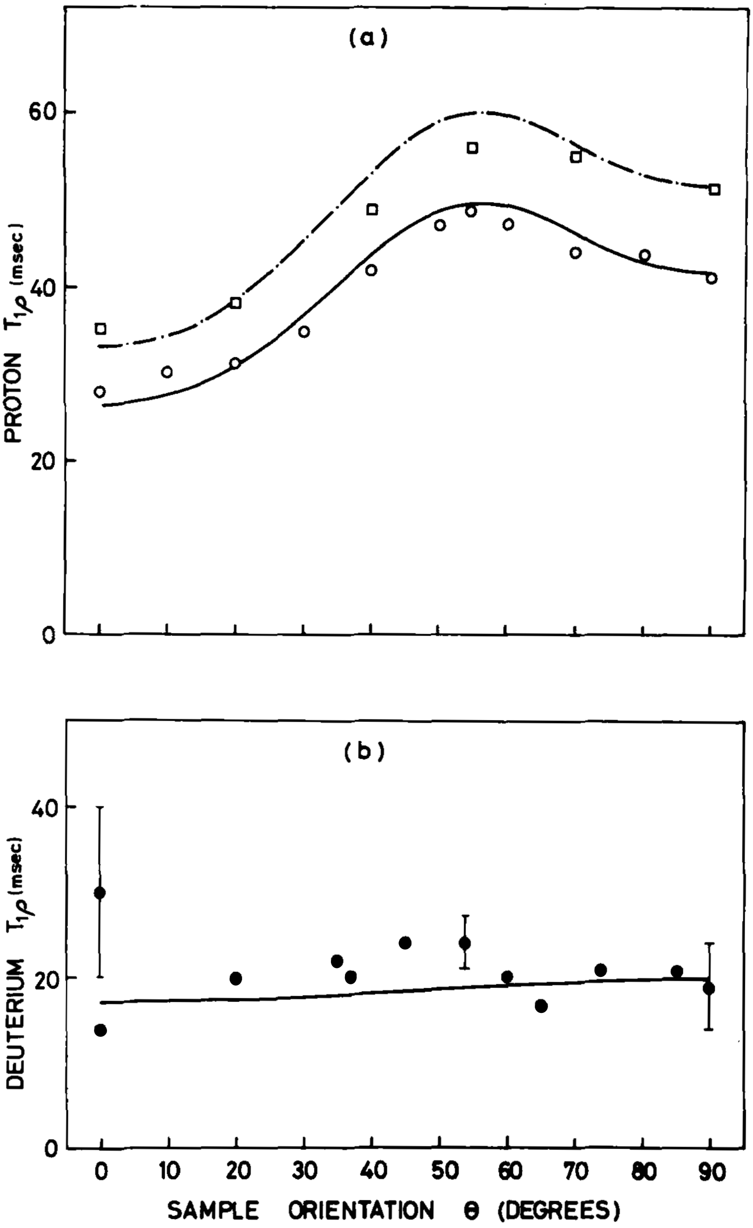

FIGURE 4 Comparison of the orientation dependence of (a) proton and (b) deuterium $T_{1\rho}$ values for DML—D_2O multilayers at 315 K. ○ proton $T_{1\rho}$, $B_1 = 0.35$ mT, □ proton $T_{1\rho}$, $B_1 = 1.19$ mT, ● deuterium $T_{1\rho}$, $B_1 = 4.6$ mT.

TABLE I

Parameters used in fitting the experimental data

Sample	EYL—D_2O	DML—D_2O	DML—D_2O	DML(d_{54})—D_2O
Temperature (K)	298	304	315	315
S	0.22	0.24	0.20	0.20
τ_D(s)	10^{-6}	10^{-6}	10^{-6}	—
Kinter (s^{-2})	4×10^7	4.5×10^7	4.3×10^7	—
τ_c (s)	8×10^{-10}	8×10^{-10}	8×10^{-10}	8×10^{-10}
Kintra (s^{-2})	7×10^9	7×10^9	7×10^9	5×10^{10}

formational modes. The model also predicts a value for deuterium spin lattice relaxation in the laboratory frame T_1 which is relatively insensitive to sample orientation and compares well with values ~25 ms obtained experimentally. Errors in the deuterium relaxation data are rather large however [Figure 4(b)], particularly at sample orientations around $\theta = 0°$ where the splittings are broad and a wide receiver bandwidth must be employed. In addition in the absence of spin diffusion the relaxation can be expected to be non exponential, reflecting a superposition of relaxation functions for different sites with varying segmental S values. Note that the suggestion of Brown and Davis[28] that the orientation independence of deuterium spin lattice relaxation times results from rapid translational diffusion around vesicles cannot apply in the case of macroscopically oriented samples.

The value chosen for K(intra) in the case of proton relaxation ($7 \times 10^9 s^{-2}$) also reflects a reduction from the rigid lattice value ($\sim 2.8 \times 10^{10} s^{-2}$ for a CH_2 group in an alkyl chain with separation $r = 1.7$ Å) but here, although the interaction between geminal pairs will experience a similar motional averaging, that between protons along the chain axis will be unaffected by long axis reorientations and therefore makes a comparable contribution to the total interaction strength.[29] The value selected to fit the ^{1}H T_1 data is consistent with estimates made on this basis. The strength of the residual inter-molecular interaction (K(inter) $\sim 4.0 \times 10^7 - 4.5 \times 10^7 s^{-2}$), some two orders of magnitude smaller than the intra-molecular value, reflects previous findings that this interaction is averaged to a very small value by rapid translational diffusion on the Lα phase.[30,31] However as the theory shows it is still capable of dominating relaxation at low frequencies owing to the presence of the long correlation time τ_D describing density fluctuations in the lipid packing.

Overall, in spite of the relative simplicity of the model, (only two correlation times are employed explicitly), it is capable of explaining

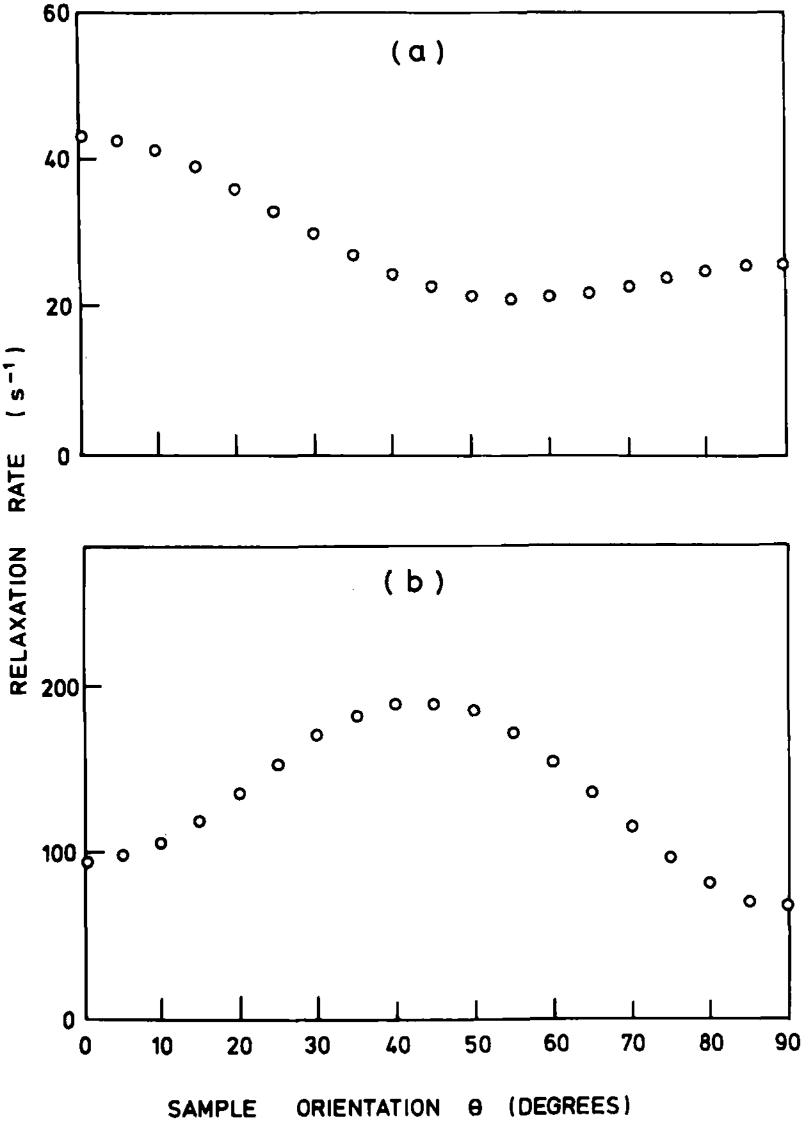

FIGURE 5 Effect of collective order fluctuations on the orientation dependence of proton relaxation rates $T_{1\rho}^{-1}$. (a) Theoretical values for DML-D_2O at 304 K in the absence of order fluctuations. (b) Relaxation dominated by collective order fluctuations.

both qualitatively and quantitatively the broad features of the results, notably the orientation dependence of proton $T_{1\rho}$'s and the relative independence of both deuterium $T_{1\rho}$'s and proton T_1's to sample orientation. Values of S are somewhat lower than those obtained for un-oriented bilayers,[1,2] although it should be remembered that our value represents an average over all segments of the molecule. However in view of the approximation employed by Ukleja *et al.*, absolute values of S are only likely to be reliable for the limits $S \rightarrow 0$ or $S \rightarrow 1$. There is some variation in "best fit" parameters between different samples (notably S, reflecting different degrees of sample alignment, and K(intra) which is higher for the less fluid synthetic lipid with saturated chains, particularly close to the chain melting transition), but in general a fairly consistent picture emerges. The model is capable of explaining the broad features of the spectrum of molecular motions in lipid bilayers, at least at low frequencies. It confirms the presence of significant density fluctuations at low frequencies which dominate proton $T_{1\rho}$'s. The higher frequency motions with correlation times around 10^{-9}s comprise chain tilting, kink formation and other conformational modes.[6] In view of the complexity of the system these would better be described in terms of a range of correlation times centered around the above value. Failure to account for such features may account for the residual orientation dependence of T_1 values predicted by the model which is larger than that observed in practice. The fact that collective order fluctuations do not make a significant contribution to relaxation in these lipid bilayers is illustrated in Figure 5. Here the calculated orientation dependence of $(T_{1\rho})^{-1}$ (using parameters similar to those in Table I) is compared with that obtained when order fluctuations are included, using the same parameters and a value of the viscous/elastic parameter[15] $d = (2\sqrt{2}\pi/kT)(K^3/\eta)^{1/2} = 10^4\text{s}^{-1/2}$ chosen such that the order fluctuations dominate relaxation at low frequencies. Clearly the orientation dependence is qualitatively different from that observed in practice (Figures 2 and 3).

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