Theory of dipolar relaxation in lamellar system: Application to lyotropic liquid crystals

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We propose a theory of dipolar spin relaxation for lamellar geometry where one of the spin species diffuses on an infinite plane while the other diffuses within an infinite layer of finite thickness. Analytical expressions of the frequency dependence of the spectral densities and spin relaxation rates are given. The theoretical frequency variation of the longitudinal relaxation rate appears to be drastically dependent of the anisotropic diffusion ratio and on the thickness of the layer. An application of this theory to lamellar lyotropic liquid crystal gives the spatial distribution of an organic counterion solute in the bilayer from the frequency variation of the $^{31}$P longitudinal relaxation rates of the surfactant. This gives some information about the surfactant-organic counterion interaction and the hydration degree of the phosphate group.

I. INTRODUCTION

Nuclear spin relaxation has proven useful to obtain structural and dynamical informations on quasi two-dimensional (2D) systems. This requires spin relaxation models particularly adapted to this low dimensional geometry. For instance to measure the lateral diffusion of nuclei in membrane-bound paramagnetic spin labels a 2D theory is needed. Other nuclear relaxation problems involving bounded diffusion in restricted 2D geometries demands also some specific models. This is the case for diffusion of fluids at the surface of graphitized carbon blacks or inside intercalation materials.

It is well known that in a nuclear spin relaxation experiment the structural and dynamical informations generally come from the frequency and temperature dependences of the spin relaxation rates. The question of the specificity of the relaxation process responsible of these dependences is then of particular importance. When dealing with translational diffusion of spins 1/2 like protons or phosphorus the dipolar relaxation gives the major contribution. An other question appears about the possible separation of the intramolecular and intermolecular processes. This is done usually by an isotopic dilution method, measuring the spin-lattice relaxation rate $1/T_1$ at different values of the proton/deuterium isotopic ratio. In order to decrease the number of parameters in the theory, it is also tempting to use a complementary technique such as pulse gradient spin echo to measure the self-diffusion coefficient at a given temperature. Now the structural information on these quasi 2D systems, at a given temperature, can be easily extracted from a comparison of experimental and theoretical frequency dependences of $1/T_1$. $^*$

We propose in this paper a theory of dipolar spin relaxation for lamellar geometry more general than our previous analysis where we have considered that the two different spin species diffuse only in parallel planes. Here one spin species diffuses on an infinite plane while the other diffuses within an infinite layer of finite thickness $d$. We give analytical expressions of the frequency dependence of the spectral densities and spin relaxation rates contrary to a recent calculation only valid in the extreme narrowing limit. We found that the theoretical frequency variation of $1/T_1$ is drastically dependent of the anisotropic diffusion ratio and on the thickness of the layer.

The present work provides a theoretical foundation for the analysis of spin-lattice relaxation in lyotropic lamellar mesophases. An application of this theory allows to define the spatial distribution of a ionic solute in the interstitial water of a bilayer from the frequency variation of the $^{31}$P longitudinal relaxation rates of the polar head of the surfactant. This gives some information about the surfactant organic counterion interaction and the hydration number of the phosphate group.

II. THEORY

We consider the spin relaxation by intermolecular dipolar interactions between a nuclear spin species ($I$) diffusing in the infinite plane of a layer component and an other spin species ($S$) diffusing within an infinite layer of finite thickness $d$ (Fig. 1). Here we emphasize the case of an anisotropic diffusion of the spin $S$ described by an unbounded diffusion perpendicular to the normal axis $z$ and a bounded diffusion parallel to $z$ axis ($-d/2 < z < d/2$). The standard theory of dipolar relaxation for a heteronuclear translational diffusion gives the following expression for the spin-lattice relaxation rate of the nuclei $I$ (Ref. 9)
FIG. 1. Schematic diagram of the lamellar system. The spin $l$ belonging to the polar head diffuses laterally in an infinite plane while the spin $S$ (proton of the pyridine) diffuses within an infinite layer of finite thickness $d$, whose middle is situated at distance $Z$ from the plane. The $M$ axes are fixed to the lamellar system. The $L$ axes are fixed in the laboratory system, with the $Z_L$ axis parallel to the applied constant magnetic field $B_0$. The diffusion coefficients of the two spins are written on the diagram.

\[
\frac{1}{T_{1l}} = (\gamma_1 \gamma_S \tilde{h})^2 S(S + 1) \left[ \frac{1}{3} J_L^{(0)}(\omega_l - \omega_S) + J_L^{(1)}(\omega_l) + 2J_L^{(2)}(\omega_l + \omega_S) \right],
\]

where the $J_L^{(q)}(\omega)$ are the spectral densities $(q = 0, \pm 1, \pm 2)$ in the laboratory frame $L$, whose $Z_L$ axis is parallel to the field $B_0$. Introducing the Eulerian angles $\alpha, \beta, \gamma$ such as $\alpha = \gamma = 0$, such spectral densities can be expressed from those $J_M^{(q)}(\omega)$ in the lamellar fixed frame $M(x,y,z \text{ in } \text{Fig. } 1)$ by the well-known Wigner matrices $d^{(2)}_{m\nu}$ (Ref. 10)

\[
J_L^{(q)}(\omega) = \frac{4\pi \sigma_S \alpha_m}{D_I Z^2} \left\{ \frac{1}{d_R^2} \left[ I(\mu = 2 - d_R, \Omega_R) + I(\mu = 2 + d_R, \Omega_R) - 2I(\mu = 2, \Omega_R) \right] + \sum_{\nu = -1}^{2} \frac{2}{d_R^2} \left[ K_\nu(\mu = 2 - d_R, \Omega_R) + K_\nu(\mu = 2 + d_R, \Omega_R) - 2(-1)^\nu K_\nu(\mu = 2, \Omega_R) \right] \right\},
\]

where $\alpha_0 = 1/2, \alpha_{\pm 1} = 1/3$ and $\alpha_{\pm 2} = 1/12$ and with the two following integrals:

\[
I(\mu, \Omega_R) = \int_0^\infty \frac{du}{u^3} \frac{u^2 e^{-\mu u}}{\Omega_R},
\]

\[
K_\nu(\mu, \Omega_R) = \int_0^\infty \frac{du}{(u^2 + b_1^2)^2 + \Omega_R^2},
\]

where $b_1 = (\pi l/d_R)^2$. The function $I$ represents the contribution of the unbounded 2D diffusion while the superposition of the functions $K_\nu$ expresses mainly the contribution induced by the bounded diffusion. The integral $I$ has been evaluated in Appendix A

\[
I(\mu, \Omega_R) = \frac{1}{2} \Re \left[ e^{\mu u} E_1(\mu u) + e^{-\mu u} E_1(-\mu u) \right],
\]

where $E_1$ is the exponential integral function of the complex variable

\[
u_1 = -\sqrt{2\Omega_R / (1 - i)}.
\]
The single-valued function \( E_1 \) has been evaluated by a truncated power series for small enough \(|u_1|\) and by a Laguerre integration along a contour which does not cross the negative real axis for other \(|u_1|\) values.\(^{12}\) The integral \( K_1 \) has been evaluated in Appendix B using Ref. 13

$$
\begin{align*}
K_1(\mu, \Omega_R) &= \frac{1}{\left[ b_1^2 (1-D_R)^2 + \Omega_R^2 \right]^2} \left[ \frac{b_1^2}{2} (1-D_R) \left[ b_1^2 (1-D_R)^2 - \Omega_R^2 (1+3D_R) \right] - \frac{\Omega_R^2}{2} (b_1^2 D_R^2 - \Omega_R^2) \right] \\
&\times \text{Re}[e^{\mu u_2} E_1(\mu u_2) + e^{-\mu u_2} E_1(-\mu u_2)] \\
&+ \left[ b_1 (1-D_R) \Omega_R \left[ b_1^2 D_R^2 - \Omega_R^2 \right] - b_1 D_R \Omega_R^2 \right] \text{Im}[e^{\mu u_2} E_1(\mu u_2) + e^{-\mu u_2} E_1(-\mu u_2)] \\
&+ \left[ b_1^2 (1-D_R)^2 \left( 1-2D_R \right) + b_1^2 \Omega_R^2 \left( 3-2D_R \right) \right] \text{Re}[e^{\mu u_2} E_1(\mu u_2)] \\
&- \mu \frac{b_1^2}{2} (1-D_R) \left[ b_1^2 (1-D_R)^2 + \Omega_R^2 \right] \text{Im}[e^{\mu u_2} E_1(\mu u_3)]
\end{align*}
$$

with the two complex variables

$$
\begin{align*}
u_2 &= \frac{\sqrt{2}}{2} \left[ \sqrt{b_1^2 D_R^2 + \Omega_R^2} - b_1 D_R \right] + i \sqrt{b_1^2 D_R^2 + \Omega_R^2} - b_1 D_R, \\
u_3 &= i b_1.
\end{align*}
$$

In order to provide a comparison with experimental data, we give the calculated variations of \( 1/T_{1I} \) with \( d_R \), the frequency \( v_1 \), and the anisotropic diffusion ratio \( D_R \) in Figs. 2-4, respectively. Here \( I \) stands for a phosphorus nuclei diffusing laterally and \( S \) represents a proton diffusing within an infinite layer of finite thickness \( d \) (Fig. 1). These calculations use the parameters described in the experimental section, namely, \( Z = 12 \text{ Å} \) and \( \beta = \pi/2 \).

One notes in Fig. 2 the large sensitivity of \( 1/T_{1I} \) with the thickness of the layer \( d \). The divergence observed when \( d_R = 2(d = 2Z) \) is logarithmic as shown in Appendix C in the particular case of the low frequency limit (\( \omega \rightarrow 0 \))

$$
J_{M}^{\text{spin}}(v_1 = 0) = \frac{4 \pi \sigma_S \sigma_M}{D_z Z^2} \left[ -\frac{1}{d_R^2} \ln \left( 1 - \frac{d_R^2}{4} \right) + \frac{2}{d_R^2} C(d_R, D_R) \right]
$$

FIG. 2. Calculated variations with the geometric factor \( d_R \) of the nuclear spin-lattice relaxation rate of spin \( I \). Here \( Z = 6 \text{ Å}, D_z = 2 \times 10^{-6} \text{ cm}^2/\text{s}, D_1 = 2 \times 10^{-6} \text{ cm}^2/\text{s}, \) \( v_1 = 121 \text{ MHz} \).

Here \( C \) is a function of \( D_R \) and \( d_R \) independent of the frequency. Such frequency dependence close to \( \omega \rightarrow 0 \) stands between the usual forms: \( -1/\sqrt{v_1} \) (Ref. 14) and \( -\ln v_1 \) (Ref. 4) found for a translational diffusion in a 3D and 2D systems, respectively.

The influence of the finite thickness \( d \) on \( 1/T_{1I} \) is particularly evident on the frequency dependences shown in Fig. 3. One notes a large frequency dependence (one order of magnitude between 0 and 200 MHz for \( d_R = 0.2 \) (quasi 2D case) and almost no variation for \( d_R = 1.97 \) (quasi 3D case). The intermediate cases shown on this figure point out

FIG. 3. Calculated variations with the frequency \( v_1 \) of the nuclear spin-lattice relaxation rate of spin \( I \) for different values of the geometric factor \( d_R \) from 0.2 (quasi-2D case) to 1.97 (quasi-3D case). The other parameters are the same than in Fig. 2.
the usefulness of the theory for the comparison with experimental data. The influence of the restricted geometry on $1/T_1\beta$ is also visible on the variation with the anisotropic diffusion ratio $D_R$ (Fig. 4). The calculations have been made in fixing $D_L \sim 2 \times 10^{-8}$ cm$^2$/s and varying $D_R$. At the limit of a fast lateral diffusion $1/D_R \gg 1$ and for $d_R = 0.17$ one reaches asymptotically the result $1/T_1\beta \sim -D_R$ in $1/(\Omega_R D_R)$ characteristic of a quasi 2D system. There is also in this latter case a significant frequency effect not visible in the case where $d_R = 1.75$ (Fig. 4). For a very slow lateral diffusion $1/D_R \sim 1$, one notes the usual large frequency effect either for small or large $d_R$ (Fig. 4).

**III. EXPERIMENT**

**A. Materials**

The octylphosphoric acid (OCTP) was synthetized by addition of phosphorus oxichloride to $n$ octylalcohol. The octylphosphoryl dichloride was hydrolyzed by a concentrated sodium hydroxide aqueous solution. The octylphosphoric acid was recovered by hydrochloric acid addition to the pyridine-water solution and purified by recrystallisation in $n$ hexane. The perdeuterated pyridine (deuterium content $\sim 99\%$) and heavy water (deuterium content $\sim 99.8\%$) were purchased from the "Service des molécules marquées (C.E.A., Saclay)."

The phase diagram of the OCTP/pyridine/water system was determined by $^{31}$P NMR, the mesophases being characterized by x-ray scattering in the laboratory of Dr. B. Gallot (Centre de Biophysique Moléculaire, CNRS, Orléans). For a 1:1 OCTP/pyridine molar ratio (pyridinium octylhydrogen phosphate, denoted hereafter as surfactant) one obtains successively on raising the water concentration and changing the molar fraction $x$ of the surfactant: a lamellar phase ($0.1 < x < 0.85$), a hexagonal phase ($0.06 < x < 0.1$) and a micellar solution ($x < 0.06$). The experiments reported here have been done on a lamellar phase with $x = 0.26$, whose melting point is 350 K. For this composition, the thickness of the hydrocarbon and polar layers are 14.3 and 15.7 Å, respectively. The area per polar head is 33 Å$^2$ as shown by x-ray scattering using the procedure described in Ref. 16. The polar layers are constituted by water and phosphate groups, the average distance between the phosphorus layers, measured by x-ray scattering, being ca. 12.5 Å.

**B. Measurements of spin-lattice relaxation rates**

The $^{31}$P longitudinal relaxation rates were determined with a mean standard deviation of $\pm 8\%$ at least for three values of the ratio $C_{D_2N}/C_{H_2N}$ between 0 and 1 (Table I). These measurements were performed by inversion recovery at 24.3, 36.4, 81.0, 121.5, and 202.5 MHz by means of Bruker WP 60, WH 90, AC 200, MSL 300 and WH 500 spectrometers. The samples were heated above 350 K and slowly cooled down to 300 K in the probe, the measurements being done at this temperature. Under these conditions the director (optical axis) of the lamellar phase is aligned perpendicular to the magnetic field ($\beta = \pi/2$). The $^{31}$P longitudinal relaxation rates induced by the pyridine protons are then determined from a linear least-square fit of $1/T_{1\beta}(^{31}$P$)$ vs the ratio $C_{D_2N}/C_{H_2N}$ between 0 and 1 by taking the difference between the extreme points at zero and complete dilution (Table I). This method allows to separate properly the intermolecular and intramolecular relaxation processes, however due to the differences the precision on the data decreases.

**C. Measurements of the self-diffusion coefficients**

The self-diffusion coefficients of the octylphosphate $D_{OCTP}$ and pyridinium $D_{Pyr}$ ions were measured by the pulsed field gradient spin-echo method (PGSE). These ex-

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**TABLE I.** Spin-lattice relaxation rates of $^{31}$P at various frequencies for different isotopic dilution ratio $C_{D_2N}/C_{H_2N}$.

<table>
<thead>
<tr>
<th>Systems</th>
<th>24.3 MHz</th>
<th>36.4 MHz</th>
<th>81.0 MHz</th>
<th>121.5 MHz</th>
<th>202.5 MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{D_2N} + D_{O}$</td>
<td>0.863</td>
<td>0.8</td>
<td>0.613</td>
<td>0.621</td>
<td>0.719</td>
</tr>
<tr>
<td>0.75$C_{D_2N} + 0.25C_{H_2N} + D_{O}$</td>
<td>0.82</td>
<td>0.645</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5$C_{D_2N} + 0.5C_{H_2N} + D_{O}$</td>
<td>1.124</td>
<td>0.909</td>
<td>0.702</td>
<td>0.676</td>
<td>0.84</td>
</tr>
<tr>
<td>0.25$C_{D_2N} + 0.75C_{H_2N} + D_{O}$</td>
<td>1.136</td>
<td>0.77</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{H_2N} + D_{O}$</td>
<td>1.281</td>
<td>1.149</td>
<td>0.83</td>
<td>0.82</td>
<td>0.893</td>
</tr>
<tr>
<td>$1/T_{1\beta}(^{31}$P$)$ due to the pyridine</td>
<td>0.418</td>
<td>0.349</td>
<td>0.223</td>
<td>0.199</td>
<td>0.15</td>
</tr>
</tbody>
</table>
periments were performed on a home built spectrometer equipped with a 2.1 T electromagnet (Bruker). The magnetic field was locked with an external probe, using the $P$ resonance in trifluoroacetic acid doped with copper acetate. During field gradient pulses the lock was disabled. The temperature was controlled at 298 ± 0.2 K by a fluid thermostat using Fluorinert FC-43 (3M Co). The PGSE experiments were performed using a steady background gradient to minimize the effects of the heterogeneity of the system. The magnitude of the pulsed field gradient is based on a calibration using pure water as a reference with a diffusion constant of $2.3 \times 10^{-5}$ cm$^2$/s at 298 K. The magnitude of the steady background gradient $G_b$ was obtained by fitting the spin-echo without the presence of a pulsed field gradient and was typically 1 G/cm. The magnitude of the pulsed field gradient $G$ was in the range 0–160 G/cm. The length of the gradient pulses was $\delta = 2$ ms whereas the diffusion time $\Delta$ between gradient pulses ranged from 5 to 83 ms (see the sequence in Fig. 5). Usually 50 echo amplitudes $A(G)$ were collected in which the pulsed field gradient intensity was incremented. Spin–spin relaxation measurements were obtained by the spin echo method with an estimated accuracy of 2%. The FID were accumulated while the relative phase of the $\pi$ and $\pi/2$ pulses was alternated. One hundred data points are collected.

In the PGSE experiments, the temperature of the probe cannot be raised up to 350 K so the director alignment procedure was not feasible and the samples were randomly oriented. The attenuation of the echo $A(G)/A(0)$ as a function of the strength of the field gradient and for different values of the delay $\Delta$ between gradient pulses, was fitted by the expression $A(G)/A(0) = \int_0^\pi \exp \left[ -k (D^1 \sin^2 \theta + D^2 \cos^2 \theta) \right] \sin \theta d\theta$, $\theta$ being the angle between the director and the magnetic field. In Eq. (10), the lateral diffusion coefficient $D_{\mathrm{OCTP}}^l$ (or $D_{\mathrm{pyr}}^l$) and the diffusion coefficient along the director $D_{\mathrm{OCTP}}^l$ (or $D_{\mathrm{pyr}}^l$) were taken as adjustable parameters in the fitting procedure, using the Simplex method. The coefficient $k$ is given by

$$k = \gamma^2 \left( G^2 \delta \left( \Delta - \delta - \frac{\delta^2}{3} \right) - G_b \delta \right) \left[ \delta (d_1 + d_2) + d_1^2 + d_2^2 + \frac{2}{3} \delta^2 - 2 \tau^2 \right] + \frac{2}{3} G_b^2 \tau^2.$$

FIG. 5. Pulsed gradient field spin echo sequence: $\delta = 2$ ms, $\Delta$ varies in the range (5–43 ms), $d_1 = 1$ ms, $d_2$ variable, $\tau = d_1 + d_2 + \delta$, the steady background gradient $G_b = 1$ G/cm, the pulsed field gradient $G$ varies in the range (0–160 G/cm).

The meanings of the parameters appearing in this expression are displayed in Fig. 5. The self-diffusion coefficients of the octylphosphate anion was measured on the OCTP/C$_6$H$_5$N/D$_2$O system, yielding $D_{\mathrm{OCTP}}^l = 8.9 \times 10^{-7}$ cm$^2$/s and $D_{\mathrm{pyr}}^l < 10^{-8}$ cm$^2$/s [Figure 6(a)]. The perdeuterated OCTP being not available, the pyridinium self-diffusion coefficients were measured on the OCTP/C$_6$H$_5$N/D$_2$O system. In this case the echo attenuation $A(G)/A(0)$ may be considered as the sum of two functions weighted by the number of nonexchangeable protons, i.e., 17 and 5 for OCTP and the pyridinium cation, respectively. The best fit of the echo attenuation was achieved for $D_{\mathrm{pyr}} = 1.2 \times 10^{-6}$ cm$^2$/s and $D_{\mathrm{pyr}}^l < 10^{-8}$ cm$^2$/s for this cation [Figure 6(b)].

This procedure implies that the $T_2$ relaxation times of pyridinium and OCTP protons are of comparable magnitude. In order to examine this point, we have performed proton spin-echo experiments at 300 MHz under high resolution conditions. The pyridinium gives a very complex pattern with many lines superimposed to a barely resolved spectrum of OCTP protons. These two spectra are spread over 2 and 10 kHz, respectively, so that the corresponding $T_2$ cannot be measured. It might be said however that their echo signals decay roughly at the same rate. A measurement of the $M_{xy}$ decay has been done at the apex of the OCTP proton signal, which corresponds to C$_2$ through C$_7$ methylene groups. Owing to the flexibility of the octyl chain, this decay is multiexponential with $T_2$ varying from 0.7 to 20 ms as shown by the limiting slopes of log $M_{xy}$ vs $2\tau$. A third component of the spectrum is the residual of labile protons exchanging among heavy water, pyridinium cation, and OCTP, whose $T_2 = 28$ ms. Even after repetitive exchange against D$_2$O, they still correspond to 8%-10% of the OCTP protons. The lateral diffusion coefficient of these labile protons, estimated from pulsed field gradient experiments on the OCTP/C$_6$H$_5$N/D$_2$O lamellar phase is $3.5 \times 10^{-6}$ cm$^2$/s. They contribute most likely to the diffusion coefficients given above for pyridinium and OCTP which must be considered as upper limits.

IV. DISCUSSION

In Fig. 7 we have displayed the best fit obtained of the $^{31}$P longitudinal relaxation rates induced by the pyridine protons. This is achieved for $d_R = 1.67, D_i = 1.21 \times 10^{-6}$ cm$^2$/s, and $D_j = 2.0 \times 10^{-6}$ cm$^2$/s. The average distance between the phosphorus layers measured by x-ray scattering being ca. 12.5 Å, one then finds for the accessible layer thickness of the pyridinium $d = Zd_R = 10.44$ Å. The average distance between the oxygens of two different layers being ~11 Å, one concludes that there is an homogeneous distribution of the pyridinium cation in almost the whole accessible volume. Owing to the value found for $d$, the accessible volume for the two pyridinium on a 33 Å$^2$ area is 344.5 Å$^3$. The molecular volume for each pyridine being ~135.5 Å$^3$, this left 74.5 Å$^3$ available for the water in the polar layers, i.e., an average of 2.5 water molecules (each of which being in a volume of 30 Å$^3$). Because the layered phase associates potentially three water
molecules for each OCTP surfactant, one then concludes that the hydration degree of the phosphate group is 1.75, i.e., less than two water molecules are fixed on the polar head surfactant.

This spatial distribution for the pyridine and the close values found for the self-diffusion lateral coefficients of the octylphosphate \( D_\text{OCTP} \) and pyridinium \( D_\text{pyr} \) ions could indicate that these ions are not completely independent. Some ion-counterion pairs could then participate dynamically to the relaxation process. This could explain why the relative lateral diffusion \( D_r = 1.2 \times 10^{-6} \text{ cm}^2/\text{s} \) found through our independent-particles theory is not quite equal to the sum of the two self-diffusion coefficients, \( D_r = D_\text{pyr} + D_\text{OCTP} = 2.1 \times 10^{-6} \text{ cm}^2/\text{s} \), measured by the PGSE method.

Though these values of \( D_r \) are not very different, it is interesting to estimate the influence of such pairs in the relaxation process. Firstly, it is necessary to obtain an average distance between the ion and the counterion in solution using the main result of the Debye–Hückel theory. The pyridine is dissolved in water whose relative permittivity \( K_r \) is very high \((K_r \sim 78.5)\), thus reducing the Coulomb field from the vacuum by almost two orders of magnitude. Owing to the shielding counterion effect the ionic potential in solutions falls off more steeply with distance than the coulombic interaction. The Coulombic potential (divided by the relative permittivity) is then replaced by the shielded Coulomb potential \(-\exp(-r/r_D)/(K_r r)\), where \( r_D \) is the shielding distance at \( K_r \) and \( r_D \) is the Debye length. This distance can be interpreted as an average charge separation. It is well known that this Debye length is inversely proportional to the ionic concentration, in other words the higher the ionic concentration the more effective the shielding. Here one has a very high ionic concentration (ca. 3 molar), so that we expect a relatively small value of \( r_D \) (<3 Å) and a relatively large shielding effect favoring the existence of close pairs of ion-counterion species in the layer plane at distance \( r > r_D \).

Let us consider now the influence of such pairs in the relaxation process. From the results given above, one has two pyridine ions in a cylinder of 33 Å² area and 10.44 Å length corresponding to the diffusion thickness. This gives an average distance of 3.4 Å between the phosphorus and the center of one of the pyridine. This distance found from geometric arguments is consistent with the Debye length \( r_D \) given above. Assuming that the \( ^{31}\text{P} \) atom remains in the same
lamellar plane, independently of the surfactant wobbling motion, the expression of the longitudinal relaxation rate given by Lipari and Szabo\textsuperscript{21} for a time dependent $I$-$S$ distance ($^1$H-$^31P$) becomes

$$\frac{1}{T_{1I}} = \gamma_1^2 \gamma_3^2 R^2_0 \tau_1 \left[ \left( \frac{1}{r_{1S}^2} \right) - \sum_{n=2}^{\infty} \left( \frac{C_{2n} m \gamma_3}{r_{1S}^2} \right)^2 \right].$$

(A12)

Here $C_{2n}$ is a spherical harmonic of rank two. The measurements of the pyridine $^2$H splittings and $^{13}$C chemical shift anisotropy show that the order parameter of the $z$ axis, perpendicular to the pyridine plane is $S_{2z} = 0.12\pm 0.02$ Adopting the simple "wobbling in a cone" model, this corresponds to a restricted motion of the $z$ axis within a cone of half angle $78^\circ$ whose axis is the director of the lamellar phase. We have then estimated from Eq. (12) the $^31P$ spin relaxation rate due to the motions of pyridine protons on a spherical sector centered at the vertical to the $^31P$ atom. The motional correlation time $\tau_c = 1.12 \times 10^{-10}$ s was estimated from the average of the pyridine rotational diffusion coefficients given by $^{13}$C and $^2$H relaxations. A calculation of the angular integrals present in the rhs of Eq. (12) leads to a spin relaxation rate $1/T_{1I} = 0.05$ s$^{-1}$ when considering that only one proton at a time effectively contributes. This contribution of the pair is then an half order of magnitude smaller than the one found with our translational diffusion independent-particle theory. Moreover the very small value of $\tau_c$ indicates that this motion is in the extreme motional narrowing regime and consequently there will be no frequency dependence expected from this motion contrary to what we observe in Fig. 7. In fact this value of $1/T_{1I}$ should be multiplied by the molar fraction of the condensed solute. This latter fraction being certainly much lower than the bulk solute, the actual value of $1/T_{1I}$ for the pairs must be lowered significantly. The major contribution to the relaxation, which depends on the frequency, then comes mainly from the lateral translation of the two independent particles $^1$H-$^31P$ (Fig.7).

V. CONCLUSION

The present work has provided a theoretical foundation for the analysis of spin-lattice relaxation in lyotropic lamellar mesophases. We have proposed a theory of dipolar spin relaxation for lamellar geometry where one of the spin species diffuses on an infinite plane while the otherdiffuses within an infinite layer of finite thickness. Analytical expressions of the frequency dependence of the spectral densities and spin relaxation rates are given. We found that the theoretical frequency variation of the longitudinal relaxation rate is drastically dependent of the anisotropic diffusion ratio and on the thickness of the layer. An application of this theory allows to define the spatial distribution of a ionic solute in the interstitial water of a bilayer from the frequency variation of the $^31P$ longitudinal relaxation rates of the polar head of the surfactant. This gives some information about the surfactant organic counterion interaction and the hydration degree of the phosphate group. This theory could be easily applied when one of the spin species is a paramagnetic ion with a long electron spin-lattice relaxation time compared with the one coming from the diffusion. This might be useful to investigate the localization and diffusion of any solute in the hydrocarbon layer.

APPENDIX A: CALCULATION OF $\kappa(\mu, \Omega_R)$

In order to evaluate the integral

$$I(\mu, \Omega_R) = \int_0^\infty du \frac{u^3 e^{-\mu u}}{u + \Omega_R},$$

(A1)

one expands the integrand of Eq. (A1) in rational functions of lower degree

$$I(\mu, \Omega_R) = \frac{i}{40\sqrt{2O}} \left[ (1 + iO) \left( \int_0^\infty du \frac{u^3 e^{-\mu u}}{u + u_1} \right) - (1 - iO) \right. \left. \times \left( \int_0^\infty du \frac{u^3 e^{-\mu u}}{u + u_1} - \int_0^\infty du \frac{u^3 e^{-\mu u}}{u - u_1^*} \right) \right],$$

(A2)

where $u_1 = \sqrt{\Omega} \exp(3i\pi/4)$ and $u_1^*$ is the complex conjugate of $u_1$. Each of the integrals in Eq. (A2) can be expressed in terms of the complex exponential integral function $Ei$ (Ref. 13)

$$\int_0^\infty du \frac{u^3 e^{-\mu u}}{u + u_1} = u_1^2 e^{\mu u_1} Ei(-\mu u_1) + \frac{u_1}{\mu} - \frac{u_1^2}{\mu^2} + \frac{2}{\mu^3},$$

(A3)

with $|\arg(u_1)| < \pi$ and $\text{Re}(\mu) > 0$. Substituting Eq. (A3) in Eq. (A2) yields

$$I(\mu, \Omega_R) = -\frac{1}{4} \left[ e^{\mu u_1} Ei(-\mu u_1) + e^{-\mu u_1} Ei(\mu u_1) + e^{\mu u_1^*} Ei(-\mu u_1^*) + e^{-\mu u_1^*} Ei(\mu u_1^*) \right].$$

(A4)

In the calculation it is much more convenient to use an other exponential integral function related to $Ei(z)$ by

$$E_i(z) = \frac{\text{sign}(-z)}{z} \int_z^\infty \frac{e^{-t}}{t} dt.$$

This single-valued function has been evaluated by a truncated power series for small enough $|z|$ and by a Laguerre integration along a contour which does not cross the negative real axis for other $|z|$ values.\textsuperscript{12} Substituting the following properties in Eq. (A4)

$$E_i(-z) = -E_i(z) = -e^{-z} E_i(z),$$

(A6)

one obtains finally the analytical expression given in Eq. (6a)

$$I(\mu, \Omega_R) = 2 \text{Re} \left[ e^{\mu u_1} E_i(\mu u_1) + e^{-\mu u_1^*} E_i(-\mu u_1^*) \right].$$

(A7)

APPENDIX B: CALCULATION OF $K(\mu, \Omega_R)$

Here we outline the main steps allowing the evaluation of the integral
One expands the integrand of Eq. (B1) in a sum of rational functions of lower degree. This gives after some elementary calculations

\[ K_i(\mu, \Omega_R) = \int_0^\infty du \frac{u^5(u^2 + b_i D_R)e^{-\mu u}}{(u^2 + b_i)^2[(u^2 + b_i D_R)^2 + \Omega_R^2]} \cdot \]

where the two functions \(k_{1i}\) and \(k_{2i}\) are given by

\[ k_{1i}(\mu, \Omega_R) = \int_0^\infty du \frac{a_i u^9 + (g_i - \Omega_R^2) u^7 + (c_i - b_i D_R \Omega_R^2) u^5}{[u^2 + b_i D_R]^2 + \Omega_R^2} e^{-\mu u}, \]

\[ k_{2i}(\mu, \Omega_R) = \int_0^\infty du \frac{[-a_i u^9 + (e_i + \Omega_R^2) u^7 + (f_i + b_i D_R \Omega_R^2) u^5]}{[u^2 + b_i]^2} e^{-\mu u}, \]

with the notations

\[ a_i = -2b_i(1 - D_R), \]
\[ g_i = b_i^2 D_R (1 - 5D_R), \]
\[ c_i = b_i^2 D_R (1 - 3D_R), \]
\[ e_i = b_i^2 (1 - D_R), \]
\[ f_i = b_i^2 D_R (1 - D_R)(3 - D_R), \]

(\text{B4})

and \( D_R \) being defined in the text.

The function \( k_{1i} \) is easily transformed as

\[ k_{1i}(\mu, \Omega_R) = \frac{1}{2|u_2|^2[|u_2|^2 - |u_2|^2]} \int_0^\infty du \left[ a_i u^9 + (g_i - \Omega_R^2) u^7 \right] \]
\[ \times \left[ \frac{u_2^7}{u - u_2} + \frac{u_2^7}{u + u_2} \right] e^{-\mu u}, \]

(\text{B5})

where \( u_2 \) is a complex variable defined by

\[ u_2 = \frac{\sqrt{2}}{2} \left[ \sqrt{\frac{b_i^2 D_R \Omega_R^2}{D_R}} + i \sqrt{\frac{b_i^2 D_R \Omega_R^2}{D_R} + b_i D_R} \right]. \]

Each of the integrals of the rhs of Eq. (B5) can be estimated in terms of the exponential integral function \( Ei \) by using the relation

\[ \int_0^\infty \frac{u^e - \mu u}{u + u_2} du = (-1)^{e-1}(u_2)^e Ei(-\mu u_2) \]
\[ + \sum_{k=1}^\infty \frac{(k-1)!(-u_2)^{e-k}}{k!} \mu^{-k} \]

with \(|\arg u_2| < \pi\) and \(\Re \mu > 0\). \hspace{1cm} (\text{B7})

The function \( k_{2i} \) is easily transformed as

\[ k_{2i}(\mu, \Omega_R) = \frac{1}{2b_i^2} \int_0^\infty du \left[ a_i u^9 - (e_i + \Omega_R^2) u^7 \right] \]
\[ \times \left[ \frac{1 + u/2u_3 + \frac{1 - u/2u_3}{(u + u_3)^2} + \frac{1 - u/2u_3}{(u - u_3)^2}}{e^{-\mu u}}, \]

(\text{B8})

where the complex variable \( u_3 \) is defined by

\[ u_3 = \frac{i}{b_i} \]

(\text{B9})

The integral in Eq. (B8) can be estimated after some changes of variables and using repetitively the relation

\[ \int_0^\infty ds s^e e^{-\mu u} = e^{-\mu u}, \sum_{k=0}^{\infty} \frac{n!}{k! \mu^{e-k+1}}. \]

(\text{B10})

The remaining steps, leading to Eq. (7) of the text, only consists of long but straightforward algebraic manipulations.

When \( D_R = 0 \) and \( \Omega_R = 0 \), the integral \( K_i \) becomes simpler

\[ K_i(\mu, \Omega_R) = \left[ \frac{3}{4} + \frac{1 + \mu^2 b_i}{8} \right] \Re(e^{u_2} \mu u_3) \]
\[ - \frac{7}{8} \mu \sqrt{b_i} \operatorname{Im}(e^{u_2} \mu u_3). \]

(\text{B12})

This simple result in comparison to the one of Eq. (7) allows to check such equation. Taking in this latter \( D_R = 0 \), a limiting development in \( \Omega_R/b_i \ll 1 \) leads to Eq. (B12) after using the properties of derivation of the exponential integral function.\(^{11}\)

APPENDIX C: LOW FREQUENCY LIMIT OF \( J_R^0(\alpha) \)

A limiting development in \( \Omega_R^2/b_i \) of Eqs. (6a) and (7) gives after using the properties of derivation of the exponential integral function \( E_1(x) \) (Ref. 11)
$J_m^{(m)}(\omega) = \frac{4\pi\sigma_2\alpha_m}{D_1 Z^2} \left\{ -\frac{1}{d_R^2} \ln\left(1 - \frac{d_R^2}{4}\right) \right. \\
+ \frac{2}{d_R^2} \sum_{\mu=1}^{\infty} \left[ X_i(\mu = 2 - d_R, 0) + X_i(\mu = 2, 0) \right] \\\n- \frac{\pi}{4} \frac{\Omega_R}{\Omega_R^2 + \phi(\Omega_R^2)} \right\}, \quad (C1)$

where the function $X_i$ is given by

$X_i(\mu, 0) = \left\{ \frac{1}{2} \frac{2D_R}{(1 - D_R)^2} - \text{Re}\left\{ e^{\mu b_i}E_i(j\mu b_i) \right\} \right. \\
+ \left( D_R \frac{1}{(1 - D_R)^2} \left( \frac{\mu b_i}{2(1 - D_R)} \right) \right) \text{Re}\left\{ e^{\mu b_i}E_i(j\mu b_i) \right\} \right. \\
- \left( \frac{1}{2} \frac{2D_R}{(1 - D_R)^2} \right) \left( \frac{\mu b_i}{2(1 - D_R)} \right) \text{Im}\left\{ e^{\mu b_i}E_i(j\mu b_i) \right\} \right\}. \quad (C2)$