

ELECTRON-SPIN RELAXATION IN ISOTROPIC  
AND ORDERED FLUIDS

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Abstract

Recent experimental and theoretical studies of spin probes in isotropic and liquid crystalline media are discussed. It is shown how ESR studies of the pressure and temperature dependence of the nematic ordering of the probe can be used to test equations of state of this phase and to obtain information on the nature of the orienting potential of the probe. The Freed, Bruno, Polnaszek theory appropriately generalized, is utilized to interpret ESR line shapes and relaxation in the motional narrowing and slow tumbling regions. The nature of reorientational motion under orienting potentials is discussed in terms of anisotropic diffusion and viscosity. It is shown that the effects of the slowly relaxing local structure (SRLS) about the spin probe must be included to explain observed results in both isotropic and nematic solvents. Such mechanisms can affect the diffusion coefficient, rendering it frequency dependent, and/or the mean orienting potential rendering it time-dependent. The properties of the isotropic-nematic phase

transitions as probed by ESR is discussed. A general theory combining effects of localized motions and of co-operativity on the spin relaxation is outlined. Recent studies of Heisenberg spin-exchange and relaxation by intermolecular dipolar interactions modulated by translational diffusion are also discussed.

## I) ISOTROPIC FLUIDS

### A) Rotational Motions

We review here our studies of molecular dynamics in liquids by the use of spin probes<sup>1-9</sup> in a variety of solvent utilizing the PD-TEMPONE (perdeuterated 2, 2,6,6-tetramethyl-4-piperidone-N-oxide) radical, which yields well resolved hyperfine lines with a minimum of inhomogeneous broadening as well as the PADS (peroxylamine disulfonate) radical. One is able to study motional dynamics for rotational correlation times  $\tau_R$  over the very wide range  $10^{-12}$  sec. through  $10^{-6}$  sec., and this yields considerable insights as a result of inter-comparing the relaxation information obtained in these different regions.<sup>1-9</sup>

In our slow tumbling work we have shown the excellent agreement between experiment and theory provided a model of random jumps of moderate angle (ca.  $50^\circ$ ) is used in the predictions<sup>1,6,4,5</sup>. This is perhaps the only current type of experiment wherein a single experimental spectrum contains sufficient information to distinguish between different molecular models for reorientation.

In the extensive motional narrowing studies on the PD-TEMPONE systems that were performed in conjunction with the slow motional work, it was usually found that the PD-TEMPONE radical undergoes isotropic rotation, but there were some deviations (e.g. for ethanol solvent) which could be interpreted in terms of specific hydrogen-bonding effects. PADS, on the other hand, typically undergoes anisotropic diffusion.<sup>4,5</sup>

Other information is obtained from the frequency dependence of the relaxation results, i.e. by comparing non-secular (and pseudo-secular) spectral densities with secular spectral densities. We have carefully demonstrated the existence of anomalies in the behavior of the non-secular spectral densities.<sup>1,5</sup>

We have theorized on the possibility that these results may relate to the relatively slowly relaxing fluctuating intermolecular torques, which should be present when solvent molecules are comparable in size to the solute molecules, so their rotational correlation times should be comparable.<sup>1,10</sup> It is in this limit that Brownian motion models are breaking down, and the exciting possibility exists that one is able to probe such microscopic details. In particular, we have found that, instead of the usual Debye-type spectral densities:  $j(\omega) = \tau_R / (1 + \omega^2 \tau_R^2)$  where  $\tau_R$  is the rotational correlation time of the probe molecule, our results consistently require the use of a modified form  $j(\omega) = \tau_R / (1 + \epsilon \omega^2 \tau_R^2)$  with the adjustable parameter  $\epsilon \sim 4$  or  $5$ . This result was confirmed by performing experiments both at X-band and 35-GHz.<sup>1,5</sup> Our theoretical models, while based on fundamental statistical mechanical analysis, are still relatively crude in an effort to obtain results that are fairly simple to analyze. Thus, if we assign a single relaxation time  $\tau_M$  to the fluctuating torques seen by the probe molecule, and if we assume the validity of a coarse graining-in-time approach [i. e. we examine times  $t$  where  $\tau_J \ll t \ll \tau_R$  such that angular momentum has relaxed (with correlation time  $\tau_J$ ) while the molecule has not significantly reoriented], then our experimental results are consistent with having  $\tau_M \sim \tau_R$ .

We have based our treatment on the construction of a generalized Fokker-Planck equation along well established theoretical lines, and then we "collapse it" to a generalized Smoluchowski equation by using the coarse-graining-in-time such that angular momentum is equilibrated and only orientational degrees of freedom and (their coupling to the surroundings) need to be considered. Our simplified model comes about by assuming a simple "memory function" for the fluctuating torque correlation function (which is rigorously a complex many-body

function).

Another theoretical method, not yet fully developed, is one we call the "augmented stochastic Liouville" approach.<sup>1</sup> In this approach one augments the conventional formalism of the stochastic-Liouville equation, which is based on Brownian motion models, by adding extra degrees of freedom for the fluctuating torques treated stochastically, so that the composite process, including the various degrees of freedom (reorientation, angular momentum, fluctuating torques) may again be treated by a Markovian operator. Our preliminary analysis of this approach indicates that it can be a very useful one, provided stochastic models are carefully chosen and provided the extensive computations called for can be effectively carried out.<sup>1</sup>

Note that in both the generalized Fokker-Planck and the augmented Stochastic-Liouville approaches the spin degrees of freedom are explicitly included. In particular, using the former method, it was possible to derive the very important stochastic-Liouville method<sup>11</sup> from first principles.<sup>10</sup> It is found to be the correct "semi-classical" limit for a spin-bearing Brownian particle (and furthermore it indicates starting points for considering non-Brownian effects). In this derivation we explicitly obtain an additional term representing the back-reaction of the spins on the molecular reorientational degrees of freedom. This is the term which guarantees relaxation of spins to thermal equilibrium, thereby removing the usual flaw in semi-classical spin-relaxation theory.<sup>11</sup>

ESR saturation experiments are also of considerable importance because they relate directly to spin-rotational relaxation, which reflects  $\tau_J$ . Here, one is exploring the effects of a very fast process, for which only the very fast fluctuating components of the intermolecular torques can contribute most effectively.

We have demonstrated in our experiments that in some cases there is a very significant break-down of the Hubbard-Einstein relations,<sup>12</sup> which are appropriate for Brownian motion, and which interrelate  $\tau_J$  and  $\tau_R$ .<sup>13</sup> Our tentative explanation is that this is due to the existence of a range of fluctuating torque components with different characteristic relaxation times, so that these components contribute differently to  $\tau_R$  and  $\tau_J$ . Also we observe that in these experiments both  $\tau_R$  and  $\tau_J$  still appear to be characterized by activation processes with substantially the same activation energies as that for the viscosity even when the Hubbard-Einstein relations break-down.<sup>13</sup>

The theory of slow-tumbling ESR spectra has now been extended to the use of vanadyl probes.<sup>14, 15</sup>

#### B). Translational Diffusion

Over the past few years we have been studying in detail the phenomenon of Heisenberg spin exchange (HE) which leads to concentration-dependent broadening of the ESR lines. Most ESR results are consistent with strong exchange (i. e. the radicals exchange their spins at each encounter)<sup>16</sup>. This is a diffusion controlled process and the observed Heisenberg-exchange frequency,  $\omega_{HE}$  is directly proportional to the translational diffusion coefficient of the radicals in the solvent, which determines  $\tau_2^{-1}$ , the bimolecular collision frequency. As such, these measurements can provide translational diffusion coefficients for the identical radicals. More interesting however, are studies on those cases where the simple picture breaks down. Thus, there are some cases where the exchange is not strong (i. e. there is not exchange of spin upon each bimolecular collision); then  $\omega_{HE}$  is dependent upon the lifetime of the collision pair,  $\tau_1$ . The latter is a parameter which relates more specifically to the microscopic details of motion in liquids than does

the overall diffusion rate for encounters between radicals. This is also a parameter of considerable significance in the study of chemical reactions in the liquid phase especially for cage reactions. We have been particularly successful in achieving intermediate-to-weak diffusion by utilizing charged radicals with significant inter-radical repulsive effects.<sup>13,17</sup>

In our more recent experiments we have performed Heisenberg spin exchange measurements on PADS [peroxyl-amine disulfonate] solutions of low ionic strength, and these have been analyzed in terms of our newer more refined models of Heisenberg spin exchange modulated by translational diffusion.<sup>17b</sup> These models explicitly include the finite range of the exchange interaction as well as the effects of the (shielded)-Coulombic repulsions. The earlier analyses were based on a simple contact exchange model (i. e. the exchange interaction  $J(r)$  is non-zero and constant only while the radicals are "in contact").<sup>17</sup> The predictions including the finite range of  $J(r)$  are quite different and appear to be in better agreement with experiment.<sup>18</sup>

When the Heisenberg spin exchange is weak, then intermolecular dipolar interactions can become an important concentration-dependent relaxation mechanism in ESR. We have shown in an ENDOR study on semi-quinones how it is possible to separate the two components as a result of their differing effects on ESR and ENDOR linewidths.<sup>13</sup>

The earlier theories of spin relaxation by dipolar interactions modulated by translational diffusion have uniformly ignored the existence of a distance of minimum approach in the relative diffusion of the molecules. We were able to obtain analytic solutions for the proper boundary-value problem including the distance of minimum

approach.<sup>19</sup> The most significant corrections are for the higher frequency spectral densities. Also, we have shown<sup>19</sup> how the equilibrium pair correlation function between spin-bearing molecules in liquids may be incorporated as an effective force in the relative diffusion expressions. Good agreement between our theory and experiments of Harmon and Muller<sup>20</sup> on dipolar relaxation in liquid ethane is obtained. We also obtained theoretical solutions for the effects of ionic interactions in electrolyte solutions on the intermolecular dipolar relaxation.

## II) Liquid Crystals

The main feature that characterizes the nematic phase over the isotropic is the existence of long-range ordering. The simplest way to incorporate its effects into the molecular dynamics is in terms of a Smoluchowski equation for Brownian motion which includes the potential of mean torque. The resulting diffusion equation has been solved by Nordio and by us.<sup>21-23, 2, 6</sup> The potential of mean torque is an equilibrium property, which is derivable from measurements of the hyperfine line shifts.<sup>24, 25, 2, 8</sup> That is, one first obtains the ordering tensor for the molecule in the nematic phase, which is fully specified in terms of its principal molecular axes, usually chosen on the basis of molecular symmetry considerations and the two order parameters:  $S \equiv \frac{1}{2} \langle 3\cos^2\beta - 1 \rangle$  and  $\delta \equiv \frac{\sqrt{6}}{2} \langle \sin^2\beta \cos^2\alpha \rangle$ . [Here  $\beta$  is the angle between  $\hat{n}$  the director, and the principal symmetry axis of the molecule, and  $\alpha$  is the azimuthal angle for the projection of the director in the molecular x-y plane.] These two order parameters are directly obtained from observed hyperfine and g-shifts. Then  $U(\beta, \alpha)$ , the potential of mean torque, is estimated by interpreting the angular brackets as an average over the equilibrium distribution in orientation given by  $P_0(\beta, \alpha)$



$$P_0(\beta, \alpha) = \exp[-U(\beta, \alpha)/KT] / \int d\Omega \exp[-U(\beta, \alpha)/KT]$$

This experimentally determined potential is then inserted into the Smoluchowski equation enabling the prediction of line shapes.

We showed,<sup>2</sup> in a careful lineshape study on PD-TEMPONE dissolved in several nematics, that reasonable agreement with such a theory could be achieved; but as the molecular motions slow down with reduced temperature, large discrepancies develop. Reasonable success in dealing with these anomalies was achieved by introducing a model of slowly relaxing local structure-SRLS.<sup>2</sup> The basic idea here is that the large liquid crystal molecules will be reorienting significantly slower than a smaller probe molecule. In this case, it is suggested by the general theory,<sup>10</sup> that it is necessary to augment the potential of mean torque by an additional component  $U(\beta, \alpha, t)$  which is slowly varying in time, but with a time average  $\langle U'(\beta, \alpha) \rangle = 0$ . In this SRLS model each spin probe sees a net local potential given by  $U + U'(t)$ , which remains essentially constant during the time-scale  $\tau_R$ , required for it to reorient. Then, over a longer time-scale, the local potential  $U'(\beta, \alpha, t)$  relaxes. Our approximate analysis for PD-TEMPONE yielded rough estimates of the "order parameter" relative to the local structure, of  $S_l^2 \sim 1/16$  and  $\tau_x/\tau_R \sim 10$ , where  $\tau_x$  is the relaxation-time of the local structure.<sup>2,3</sup> This observation has been supported by our combined pressure and temperature dependent study<sup>3</sup> (cf. next section). We have recently obtained additional evidence for this SRLS mechanism from experiments using as solvents, long-chain molecules which do not exhibit liquid crystalline phases.<sup>26</sup>

Another important feature of liquid crystalline solvents is their high viscosity, which results in larger values of  $\tau_R$ . In particular, for larger spin probes that more nearly approximate the size and shape of the solvent molecules, the observed

spectra must be subjected to a slow-tumbling analysis if meaningful assignments of ordering and relaxation are to be made.<sup>2,6,8,9,23</sup> This was clearly demonstrated in our recent study on a large cholestane (CSL) spin label.<sup>9</sup> Consistent and sensible behavior of the ordering and of  $\tau_R$  with temperature could only be obtained from the rigorous slow-tumbling analysis. Unfortunately, much of the previous work in this area was based on simplified motional-narrowing analyses, and thus much of it must be regarded as unreliable.

We have also performed careful experiments at the isotropic-nematic phase transition utilizing careful temperature control.<sup>7</sup> We found that the ESR linewidth parameters behave anomalously as the phase transition at temperature  $T_c$  is approached from either side. In fact, the width parameters appear to diverge. We have successfully analyzed the anomalous contributions in terms of Landau-de Gennes mean-field theory<sup>27</sup> for the weak first order transition, as applied to ESR relaxation.<sup>7,28</sup> That is, both the magnitude of the effect, and the critical exponent, are in close agreement with theory. Most importantly, these observations display a symmetry about  $T_c$  for spin-relaxation due to critical fluctuations, which is expected from simple theory, but had not previously been demonstrated experimentally. In fact, the usual light scattering and NMR studies had only successfully dealt with order fluctuations above  $T_c$ . We feel these results demonstrate the considerable value of ESR studies of phase transitions in liquid crystals.

Recently, we have presented a unified treatment of the theory of spin relaxation in liquid crystals that is applicable to both NMR and ESR.<sup>28</sup> This theory takes into account the statistical inter dependence of the faster rotational

reorientation of the individual spin-bearing molecules and the slower director or order parameter fluctuations. The analysis is in terms of a composite Markov process including both types of motions. That is, one must solve for the rotational reorientation governed by a Smoluchowski equation, but with a time-dependent  $U(\beta, \alpha, t)$  (see above). The time dependence of  $U(\beta, \alpha, t)$  is due to 1) director fluctuations in the nematic phase; 2) quasi-critical order fluctuations at phase transitions; and/or 3) slow fluctuations in the local structure (SRLS), and these may be regarded as multi-dimensional Markov processes. Our analysis has enabled us to remove some weaknesses in previous treatments that typically were presumed to be based on an assumption of the statistical independence of the different motional processes. Wade<sup>29</sup> in a current review of NMR relaxation in liquid crystals has already applied our analysis to a discussion of NMR results.

### III) Pressure-Dependent Studies

We were able to show in an extensive study on PD-TEMPONE in a nematic liquid-crystal solvent<sup>3</sup> that the motional narrowing relaxation results, as well as the "pressure-induced" slow-tumbling results, yield anomalies virtually identical to those seen in the previous studies<sup>2</sup> as a function only of temperature. The close relationship between our observed anomalies and the  $\tau_R$ -values, independent of whether these  $\tau_R$ -values are achieved by reduced temperature or increased pressure, appear to confirm that they are due to fluctuating intermolecular interactions (e.g. the SRLS mechanism) rather than any intramolecular processes.

We have also shown<sup>3</sup> that pressure-dependent ESR studies are very useful for obtaining thermodynamic data associated with the ordering of the spin probe. This data may be utilized to test equations of state for the liquid crystalline phase as well as to test the nature of the orienting potential. The relevant thermodynamic derivatives one wishes to measure are  $(\partial \ln S^{(i)} / \partial \ln T)_V$  and  $(\partial \ln T / \partial \ln V)_S^{(i)}$  (where  $S^{(i)}$  for  $i = p$  represents the order parameter of the probe). Actually one may obtain the derivatives  $(\partial \ln S^{(i)} / \partial \ln T)_p$  and  $(\partial \ln T / \partial \ln P)_S^{(i)}$  from the pressure-dependent ESR studies. Then one uses PVT data to obtain the desired derivatives. In particular,  $(\partial \ln S^{(i)} / \partial \ln T)_V$  represents a good test of the applicability of simple theories of the equation of state of the nematic phase. We have found in our initial work on PD-TEMPONE in Phase V solvent,<sup>3</sup> discrepancies between simple Maier-Saupe-type mean-field theories and the experimental results. These discrepancies are similar to those found earlier by McColl and Shih in an NMR study on a different nematic (PAA).<sup>30</sup> Our results for  $(\partial \ln T / \partial \ln V)_S^{(i)}$  enabled us to show that the orienting potential of the PD-TEMPONE is essentially independent of molar volume  $V$ , although recent PVT work indicates a  $V^{-3.5}$  dependence for the liquid crystalline phase. Our result is consistent with our model of the probe in a "cavity" in the liquid-crystalline structure.<sup>3</sup>

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