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Coupling of Hydrogen Bonding to Orientational Fluctuation Modes in the Liquid Crystal PHBA

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Abstract—In the liquid state, the molecules of the carboxylic acids are associated in pairs by hydrogen bonds connecting their acid groups. If these dimers are long and rigid, they can form a nematic phase.

The dimer molecules of the liquid crystal *p*-hexyloxybenzoic acid have been deuterated on the hydrogen bonds, and the nuclear quadrupolar spin-lattice relaxation rate $1/T_1$ of these deuterons has been studied. In the nematic phase, $1/T_1$ is frequency dependent between 2.7 and 13.8 MHz; its temperature behavior is identical with that of the parameter S describing the orientational order of the nematic phase. In the isotropic phase, $1/T_1$ behaves in the same way as in conventional nematics: at high nuclear frequencies, it is still frequency dependent, and rather unsensitive to temperature in the vicinity of the nematic–isotropic transition; at low frequencies, it has no frequency dependence, but diverges when the transition temperature T_c is approached from above:

$$\frac{1}{T_1} \propto 1/\sqrt{T - T^*} \text{ with } T_c - T^* = 3\,°\mathrm{K}.$$

The " critical frequency " which separates these two regimes is on the order of 14 MHz near T_c.

These results are interpreted in the following way. Two processes may contribute to $1/T_1$: the formation and destruction of the hydrogen bonds, and the orientational motions of the molecules. It is proposed here that these two processes are strongly coupled, i.e., that the lifetimes of the various hydrogen-bonding configurations are controlled by the collective fluctuations of the molecular orientations. Assuming that the local orientations and local concentrations of broken bonds are the only slowly relaxing quantities in the system, the decay in time of their fluctuations is described by a system of coupled transport equations. The resulting spectral density for the fluctuations of the concentration of broken bonds reproduces the main features of the observed behavior.

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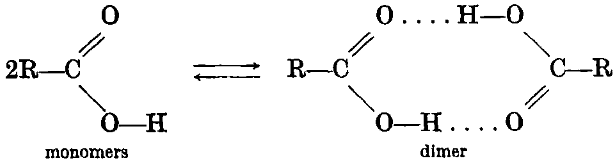
Introduction

(A) The molecules of the carboxylic acids tend to associate in pairs (" dimers "), with hydrogen bonds connecting their respective acid groups(1,2,3,4):



These hydrogen bonds are rather strong (~ 5 kcal/mole for the benzoic acids). Consequently, in the pure liquid, the relative concentration of non-associated molecules is very small (on the order of 10^{-3}). This is evidenced by IR and Raman studies of the O—H vibrations.(2)

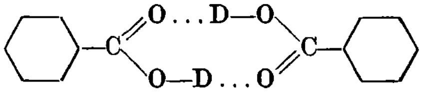
The dynamics of such dimer$\rightleftarrows$monomer equilibria has been extensively studied by ultrasonic absorption(1); this technique permits a measurement of the relaxation time of the equilibrium, which is found to lie in the megaherz (MHz) range. That frequency range is also the usual NMR range; thus, it is tempting to try to observe the dynamics of these processes through the measurement of NMR relaxation times. A convenient way to study these effects is to replace the protons of the hydrogen bonds by deuterons, and measure the spin-lattice relaxation rate $1/T_1$ of these deuterons.

Clearly, the quadrupolar interaction of the deuteron with its local electronic environment will change abruptly when a hydrogen bond is built or broken. Because that quadrupolar interaction is much larger than the dipole–dipole interactions for the deuterons, its modulation by the association–dissociation processes can dominate the spin-lattice relaxation of the deuterons.

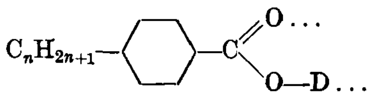
However, the orientational motions of the molecules do also modulate that quadrupolar interaction. Their contribution to $1/T_1$ has to be evaluated, and then separated from that of the association–dissociation processes.

Finally, the hydrogen bonds might be broken or built in relation with the orientational motions of the molecules. This situation is more complex because its investigation requires a knowledge of the microscopic details of the hydrogen bond formation processes.

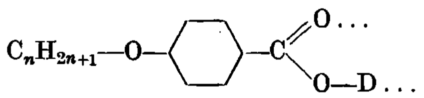
(B) In order to test these possibilities in a simple case, we have investigated first the spin-lattice relaxation of the acid deuterons in pure benzoic acid:



These molecules do not form a nematic phase; however, they do not differ much from the alkyl- or alkyloxy benzoic acid molecules:



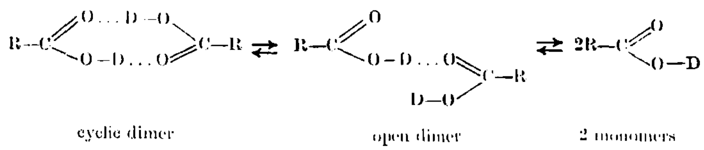
or



which do form an observable nematic phase if the length of the aliphatic chain is greater than C_3; in particular, the energy of the hydrogen bonds should be more or less the same in all these materials.

Our results are shown in Fig. 1; the relaxation rate $1/T_1$ appears to be proportional to $\exp(E/RT)$ (Arrhenius behavior) over most of our temperature range (i.e., from 125 °C to 200 °C). The activation energy E is 4.8 kcal/mole, which is close to the admitted value for the bond-breaking reaction in benzoic acid.(2,3)

This could suggest that the spin-lattice relaxation is produced by the formation and destruction of the hydrogen bonds. It is usually admitted(1) that the reaction scheme is of the type



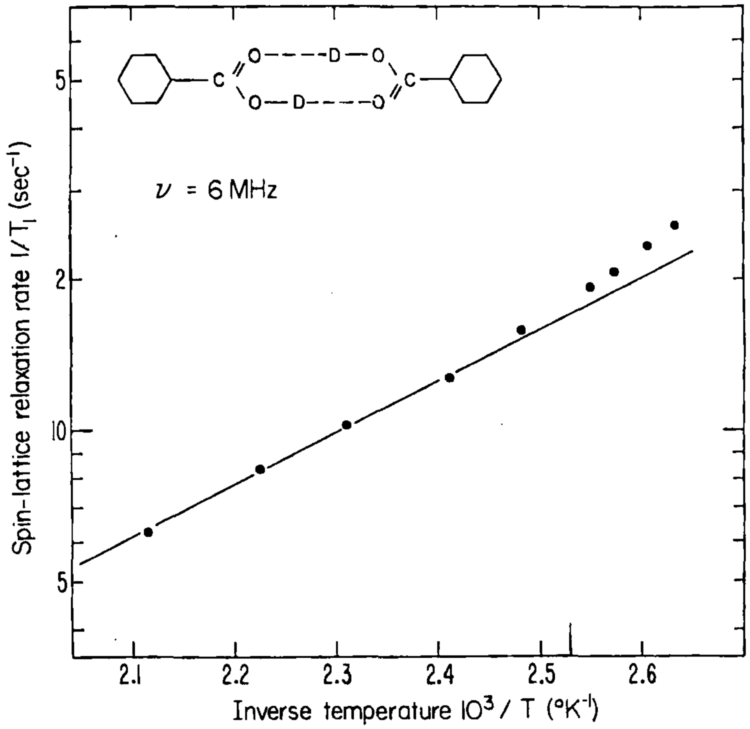


Figure 1. Deuteron spin-lattice relaxation rate versus $1/T$ in benzoic acid. The slope of the straight line is related to the activation energy of the H-bonding reactions. The low temperature data, deviating from this Arrhenius behavior, are remains of a virtual isotropic-nematic transition well below the freeezing temperature T_m.

However, that " activation energy evidence " is not decisive. At this stage, it could also be argued that $1/T_1$ is controlled by the orientational motions (tumbling) of the dimer molecule (although, for such large molecules, the tumbling rate is not expected to be controlled by an activation energy; the orientational motions are usually too complex for that⁽⁵⁾).

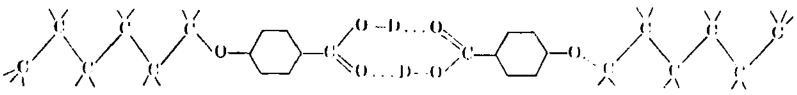
By the lower temperatures (mainly in the supercooling range), the data deviate from the Arrhenius plot, the rise of $1/T_1$ with decreasing temperature being faster than predicted by the $\exp(E/RT)$ law. Apparently, at these temperatures, the processes responsible for the nuclear relaxation are more complex than simply going over the energy barriers of the hydrogen bonds (" one molecule processes "). For example, the association–dissociation processes might involve many molecules at the same time. Or, alternatively, the orientational motions of the molecules might be collective motions. At this point, we remember that the benzoic acid molecule is not terribly different from the somewhat longer molecules which do form a nematic phase, and that, in nematic liquids, the orientational motions of the molecules are strongly collective even at temperatures well above the nematic phase.

Accordingly, that preliminary experiment on benzoic acid suggests the existence of a virtual nematic phase at temperatures well below the melting point. However, it does not permit us to decide whether the nuclear relaxation is produced:

—either directly by the orientational motions of the molecules

—or directly by the association–dissociation processes, with, at low temperatures, an indirect coupling to the orientational motions.

(C) Our main study was made on the acid deuterons of para-hexyloxybenzoic acid (PHBA): this way we hoped to investigate further these eventual collective processes.



This material shows the following phases:

$$\text{Solid} \xrightarrow[T_m = 110\,^\circ\text{C}]{} \text{nematic liquid} \xrightarrow[T_c = 150.5\,^\circ\text{C}]{} \text{isotropic liquid.}$$

As in the case of conventional nematics,(6,7,8) we expect the collective orientational fluctuations to show dramatic effects (critical slowing down and divergence of the correlation length) in the vicinity of the nematic-to-isotropic transition temperature T_c. These effects have been discussed by de Gennes,(9) and the reader is referred to that paper for a discussion of the orientational fluctuation modes in the isotropic phase of nematic liquids; the relevant NMR experiments have been discussed in Ref. 10.

The organization of the following sections of this paper is as follows:

—In (1), the measurements of $1/T_1$ in the isotropic phase of PHBA are presented; the low frequency data show a divergent behavior similar to the critical behaviour observed in conventional nematics, while the high frequency data appear to deviate from that regime;

—These results are discussed in (2): the critical regime is related to the critical slowing down of long wavelength fluctuations of the magnitude of the local alignment of the molecules, while the high frequency regime is attributed to short wavelength spatial variations of that local alignment;

—The experiments in the nematic phase are presented in (3). They show another divergent behavior on the low temperature side of T_c, in contrast with all previous data on conventional nematics;

—The interpretation of these data requires a discussion of the microscopic behavior of the nematic systems made of dimer molecules like PHBA. A simplified description of this behavior, based on a " static coupling " between the fluctuations of the molecular alignment and the H–bonding equilibrium, is presented in Sec. 4.

—The dynamical aspects of this coupling are studied in Sec. 5, assuming that the local orientations and local concentrations of broken bonds are the only slowly relaxing quantities in the system, and writing a system of coupled transport equations for the decay in time of their fluctuations.

1. Experiments in the Isotropic Phase

First, the main differences between the behaviors of $1/T_1$ in PHBA and BA (benzoic acid) are evident when the PHBA data are plotted in the same way as the BA data. Figure 2 shows a Log. plot of $1/T_1$ versus inverse temperature $1/T$, in PHBA, for a nuclear frequency of 6 MHz. Clearly, the variation of that relaxation rate with temperature is much faster than in the case of BA, and it can no longer be described by an activation energy. When the nematic–isotropic transition temperature T_c is approached from above, the relaxation rate nearly diverges; however, the transition occurs shortly before this divergence is reached (Fig. 3). The law of the divergence is similar to that observed at 3 MHz in PAA.(7) Figure 4 shows that, within 15 °C of the transition, it can be fitted to the law:

$$\frac{1}{T_1} \propto 1/\sqrt{T-T^*}$$

where T^* is, as in PAA, a temperature slightly below T_c:

$$T_c - T^* = 3 \pm 0.5\,°\mathrm{K}.$$

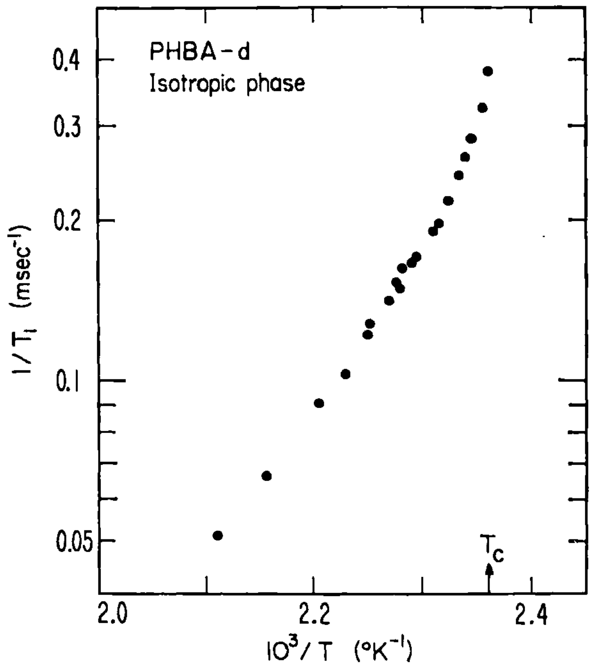


Figure 2. Deuteron spin-lattice relaxation rate versus $1/T$ in para-hexyloxybenzoic acid. The scales are the same as for benzoic acid (Fig. 1). The non-Arrhenius behavior and the very rapid temperature dependence are controlled by the collective orientational fluctuation modes. These modes are slowing down critically in the vicinity of the nematic–isotropic transition temperature T_c.

No frequency dependence of T_1 is observed by going to lower frequencies (Fig. 3). However, at the highest frequency of our experiment (13.8 MHz), the behavior of T_1 appears to change, 3 °K above T_c, from the frequency independent, critically divergent in T regime to a frequency dependent regime where no divergence of

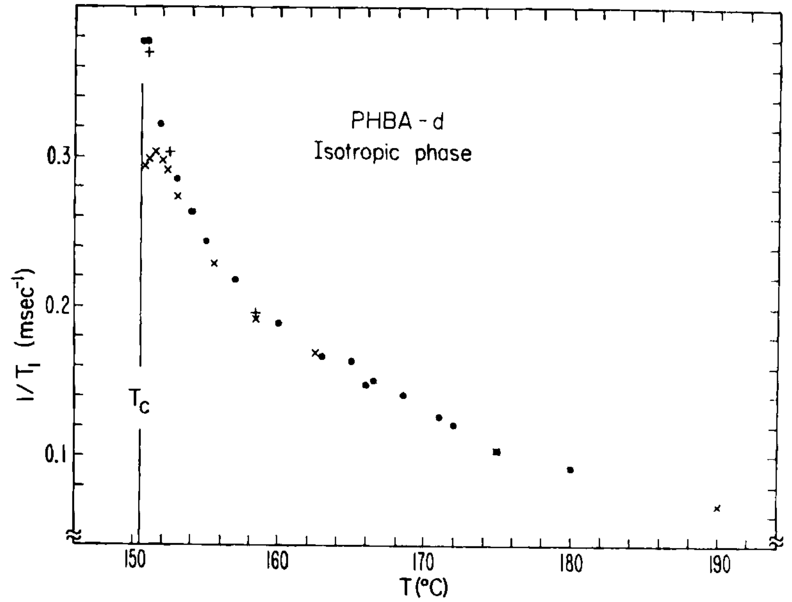


Figure 3. Deuteron spin-lattice relaxation rate $1/T_1$ versus temperature T_1 in the isotropic phase of *p*-hexyloxybenzoic acid. ● = measurements at $\omega = 6.53$ MHz, + = 4 MHz, × = 13.8 MHz.

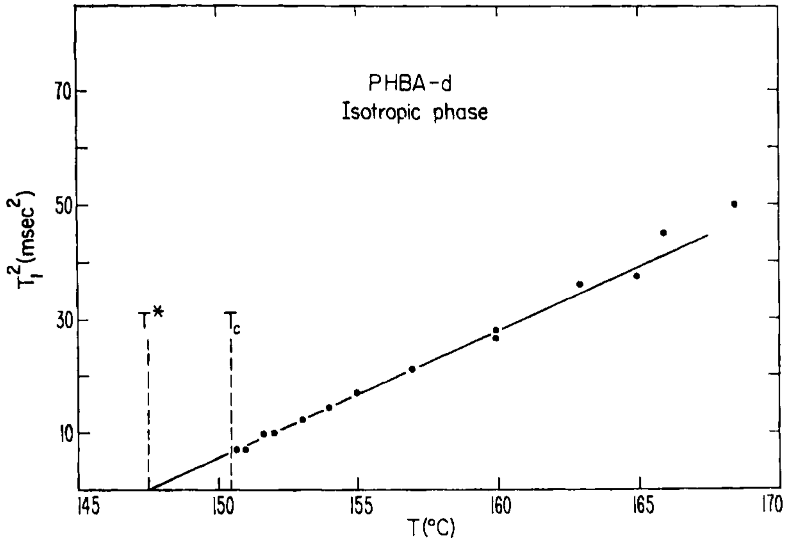


Figure 4. Square of deuteron spin-lattice relaxation times T_1 versus temperature T; T^* is interpreted as being the temperature where the relaxation time τ of the long wavelength orientational modes would diverge.

$1/T_1$ in the vicinity of T_c is observed (see Fig. 5). Doubtless, this change of regime occurs because, at this temperature, some characteristic relaxation frequency of the liquid becomes comparable with the NMR frequency ($\omega_n\tau \sim 1$).

In the next section, we will see that this characteristic frequency may be interpreted as the frequency of the long wavelength fluctuations of the alignment of the molecules. In that case, our experi-

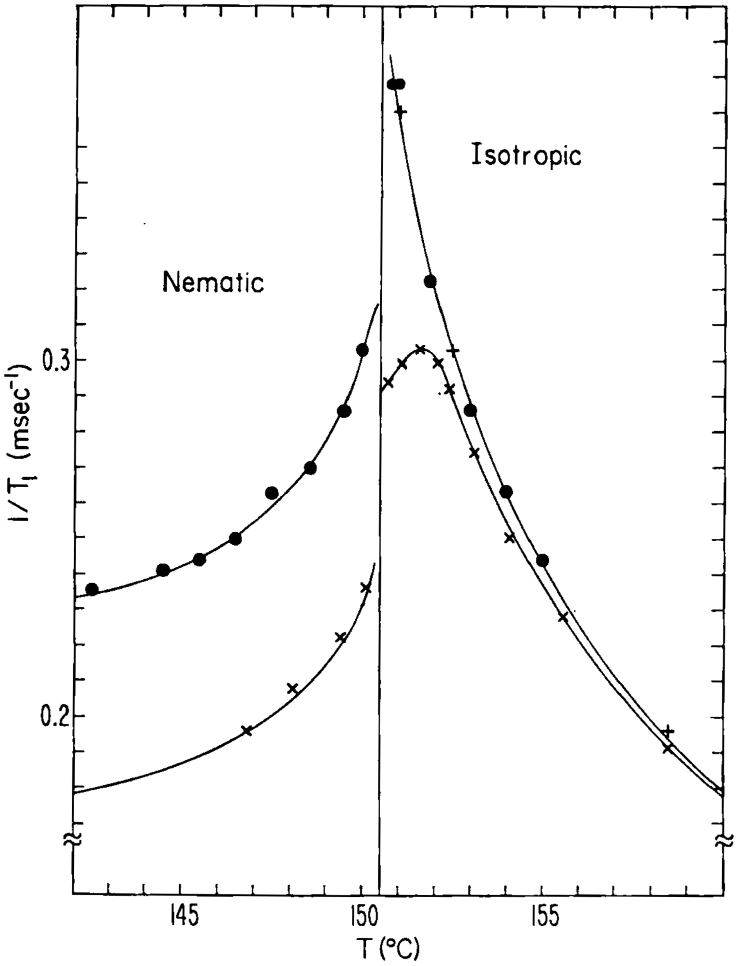


Figure 5. Magnified display of the $1/T_1$ data in the vicinity of T_c. ● = 6.53 MHz, + = 4 MHz, × = 13.8 MHz.

ment permits also a determination of this frequency at all temperatures.

2. Discussion of Isotropic Phase Data

This section is based on de Gennes's description of the isotropic phase of liquid crystals.(9) We will first summarize the points of this theory which are essential for the interpretation of our results, and then discuss more specifically the NMR aspects. As the temperature and frequency behaviors of T_1 appear to be quite similar to those observed in the conventional liquid crystal PAA,(7,10) this discussion will follow closely that given in Ref. 10.

(A) COLLECTIVE VARIABLES

In the isotropic phase of a liquid crystal, packing conditions and van der Waals attractions impose a substantial alignment of neighboring molecules.(9,10) The fluctuations of the molecular orientations are essentially collective excitations (Fig. 6). They can be represented by a collective variable (a second rank tensor $\overline{\overline{Q}}$), describing both the magnitude and the orientation of the local alignment.(9) Some of these collective molecular reorientations result essentially in a uniform variation of the magnitude of the local alignment (i.e., of the magnitude of $\overline{\overline{Q}}$); they contribute to the free energy of the liquid by terms of the type $(Q_{\beta\gamma})^2$. The other fluctuations produce spatial variations of the local alignment (for example, non-uniform

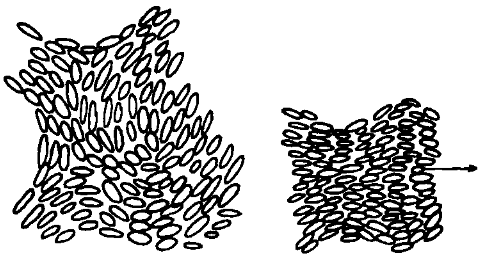


Figure 6. Schematic representation of a collective fluctuation of the molecular orientations in a nematic phase (right) and in an isotropic phase (left).

variations of its orientation, or of its magnitude). They contribute to the free energy by terms involving spatial derivatives of $\bar{\bar{Q}}$. Collecting all these terms yields the free energy associated with a general fluctuation of $\bar{\bar{Q}}$(9)

$$F = \sum_{\alpha\beta\gamma} A(Q_{\beta\gamma})^2 + L(\partial_\alpha Q_{\beta\gamma})^2$$

As the nematic–isotropic transition is approached from above, A goes to 0:

$$A = a(T - T^*)^\gamma$$

This way the system can produce large fluctuations in Q at low cost in free energy. On the other hand, L is a constant describing the elastic coupling between two neighboring molecules, and should have a rather weak temperature dependence. T^* is the temperature where the system would have a second order phase transition to a nematic phase. Actually, the transition occurs at a temperature T_c slightly above T^*.(7,9)

(B) COLLECTIVE MODES

The orientational disorder expressed by F is then analyzed into fluctuation modes. The free energy associated with a fluctuation of wave number q is:

$$F_q = AQ_q^2 + Lq^2Q_q^2.$$

That fluctuation relaxes exponentially in time:

$$\frac{dQ_q}{dt} = -\Gamma_q Q_q.$$

The damping constant Γ_q is related to the free energy F_q by the dispersion relation:

$$\Gamma_q = \frac{1}{\tau_q} = \frac{1}{\nu}(A + Lq^2)$$

where ν is a viscosity coefficient. Two types of modes can then be distinguished. At long wavelengths, the modes are q independent, and their temperature behavior in the vicinity of the transition (critical slowing down) is related to that of A:

$$\Gamma = \frac{1}{\tau} = \frac{A}{\nu} \propto (T - T^*)^\gamma.$$

At short wavelengths, the dispersion relation of the modes is q-dependent, but temperature independent:

$$\Gamma_q = \frac{L}{\nu} q^2.$$

The dispersion relation for all the modes can also be rewritten with the correlation length $\xi = (L/A)^{1/2}$:

$$\Gamma_q = \frac{L}{\nu}\left(q^2 + \frac{1}{\xi^2}\right).$$

For long wavelengths ($q\xi \ll 1$), the liquid looks disordered, and the modes describe fluctuations of the magnitude of the orientational order, whose amplitude diverges at T^*. At short wavelengths ($q\xi \gg 1$), the system looks ordered, and the modes are quite similar to the collective fluctuations of the orientation of the local alignment

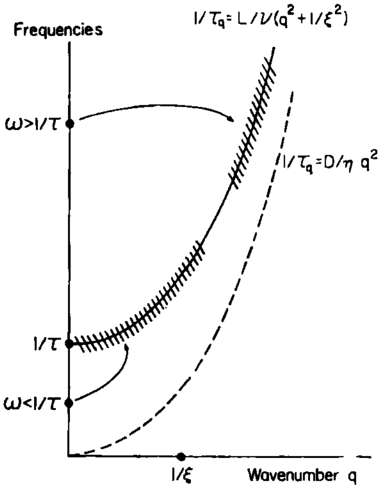


Figure 7. Dispersion relations of the orientational fluctuation modes in the isotropic and nematic phase of a liquid crystal. Full line = isotropic phase, broken line = nematic phase. τ = relaxation time of the modes with infinite wavelength, ξ = orientational correlation length, ω = nuclear frequency • τ and ξ are also connected by the dispersion relation $1/\tau = (L/\nu)1/\xi^2$.

in the nematic phase. ξ^2 and τ diverge as $(T-T^*)^{-\gamma}$ when the transition is approached from above.

(C) Spin-lattice Relaxation in the Low Frequency Range $\omega \ll 1/\tau$

The contribution of mode q to $1/T_1$ is proportional to its spectral density $J_q(\omega)$ at the nuclear frequency ω:

$$J_q(\omega) = \langle a_q^2 \rangle \frac{\tau_q}{1+\omega^2\tau_q^2}$$

From the equipartition theorem and the expression of F_q, the mean square amplitude $\langle a_q^2 \rangle$ is equal to: $k_B T/L(q^2+1/\xi^2)$. The total nuclear relaxation rate is then obtained by summing all these contributions:

$$\frac{1}{T_1} = \int d^3q J_q(\omega).$$

For nuclear frequencies smaller than the width of the narrowest Lorentzian $J_0(\omega)$, $1/T_1$ is independent of ω (see Fig. 8). However, it does depend strongly upon the widths $1/\tau_q$ of these spectral densities. In the $\omega \ll 1/\tau$ regime, the dominant contributions to $1/T_1$ come

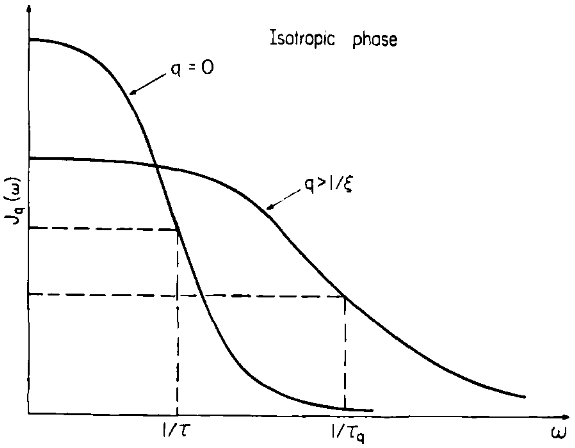


Figure 8. Spectral densities $J_q(\omega)$ for orientational modes of different wavelengths $\lambda = 2\pi/q$. For $q \ll 1/\xi$, all the modes have the same spectrum, of width $1/\tau$ (see the dispersion relations in Fig. 7). For $q \gg 1/\xi$, the spectrum is very flat, and has a very small density $J_q(0)$ at $\omega = 0$.

from the modes of wavelengths comparable with ξ ($q\xi \sim 1$); summing up their contributions yields(7,10):

$$1/T_1 \propto \sqrt{\tau\tau'}$$

where τ is the lifetime of the long wavelength orientational fluctuation modes, and τ' is a molecular time, $\sim 10^{-10}$ sec. τ' is largely temperature independent, but τ diverges at T^*; thus, $1/T_1$ should also diverge:

$$1/T_1 \propto (T - T^*)^{-\gamma/2}.$$

This is indeed observed (see Fig. 4); the value of the exponent γ is found to be equal to the mean field exponent $\gamma = 1$.

In summary, when looking at the liquid on time scales longer than the relaxation times of its orientational order, one sees essentially the critical slowing down of order fluctuations in a disordered system.

(D) High Frequency Range $\omega \gg 1/\tau$

For $\omega > 1/\tau$, the relaxation rate $1/T_1$ gets frequency dependent; the dominant contribution comes from the modes for which $L/\nu q^2 \sim \omega$, which are very similar to the modes of the ordered phase (see Fig. 7). The calculation of $1/T_1$ yields the same frequency dependence as in the nematic phase(14):

$$\frac{1}{T_1} \propto \sqrt{\frac{\tau'}{\omega}}$$

This behavior is indeed observed at 13.8 MHz: when the temperature is lowered below $T = T_c + 3$ °C, the relaxation time τ gets larger than $1/\omega$; T_1 becomes frequency dependent and looses its critically divergent temperature behavior. This permits a determination of τ at $T = T_c(2\pi/\tau \sim 13.8$ MHz), and also at all temperatures, as the temperature law of τ is known ($\gamma = 1$).

In summary, when the liquid is observed on time scales shorter than the relaxation times of its orientational order, it appears to behave as an ordered system.

(E) The main results which we have been able to get in this section concern the semi-macroscopic behavior of the system (i.e., spatial scales ξ and time scales τ much larger than the molecular ones a and τ'). Apparently, this behavior does not depend much upon the microscopic processes; for example, the critical behavior of the relaxation rate of the acid deuterons in PHBA is quite similar to that of the N^{14} in PAA,(7) although the microscopic processes involved in the nuclear relaxation can be very different. This is not a surprise; it is well known that such critical order fluctuations, as soon as $\xi \gg a$ and $\tau \gg \tau'$, are no longer very sensitive to the microscopic details of the system.(12) Consequently, it is, at this stage, still not possible to decide between the various possible mechanisms for spin-lattice relaxation in PHBA (i.e., molecular associations or molecular reorientations).

3. Experiments in the Nematic Phase

The nematic phase has a long range order of the molecular orientations; the orientations of all the molecules fluctuate around the macroscopic direction of alignment $\mathbf{n}_z$. The magnitude of that orientational order is described by an ensemble average over the angular deviations θ with respect to $\mathbf{n}_z$ of all the molecules in the sample:

$$S = \tfrac{1}{2}(3\cos^2\theta - 1).$$

The larger the amplitude of the fluctuations of the molecular orientations around $\mathbf{n}_z$, the smaller the value of S. At the nematic–isotropic transition S drops sharply to zero: the system can no longer maintain a long range order; the alignment of the molecules is preserved only on a local scale (short range order),(9) and is described by the parameter $\bar{\bar{Q}}$, as discussed in Sec. 2. A consequence of the existence of that orientational long range order is that the NMR spectrum of the acid deuterons in PHBA is a doublet, and that the splitting of that doublet is directly proportional to S (see Refs. 7, 13 for a discussion of NMR spectra in nematic phases). We have measured that splitting in the whole nematic phase; the corresponding values of S are plotted in Fig. 9.

The measurements of the deuteron relaxation rates $1/T_1$ in the nematic phase at four different frequencies are presented in Fig. 10. They indicate that $1/T_1$ tends to diverge in the vicinity of T_c. Furthermore, the overall shape of these curves reminds strongly that of the order parameter S. Indeed, a plot of T_1 versus S shows that,

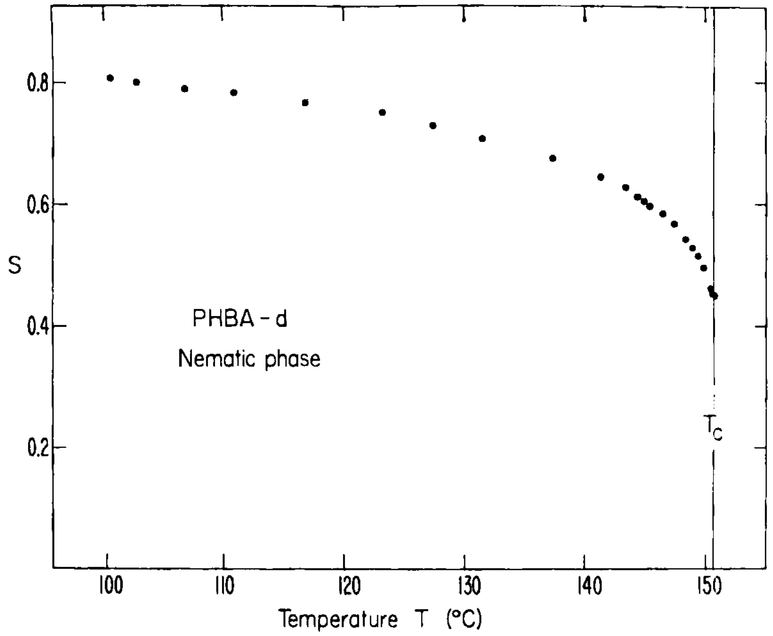


Figure 9. Orientational order parameter S versus temperature in the nematic phase of PHBA. These values have been deduced from the quadrupolar splitting of the deuteron resonance line in the nematic phase.

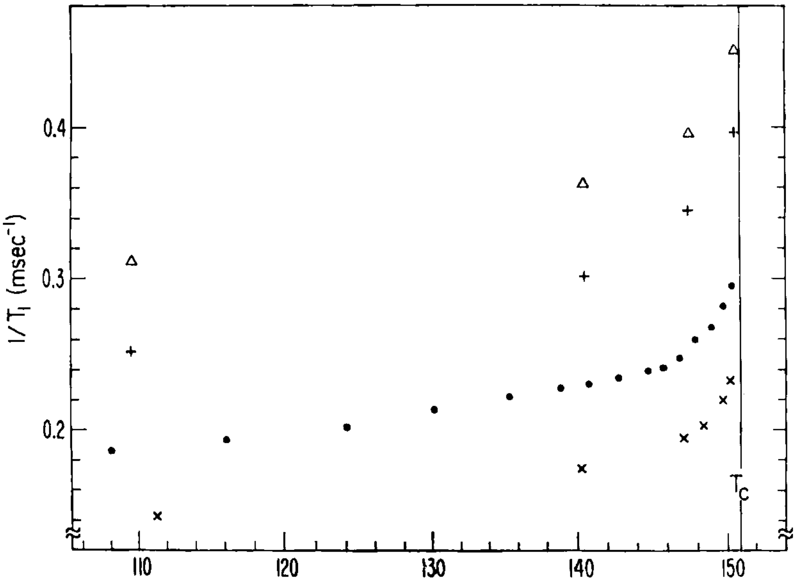


Figure 10. Deuteron $1/T_1$ versus T in the nematic phase of PHBA △ = 2.7 MHz, + = 4 MHz, ● = 6.53 MHz, × = 13.8 MHz.

within experimental errors (see Fig. 11),

$$1/T_1 \propto 1/S.$$

This law fits the data particularly well at the highest frequencies where our precision is the best.

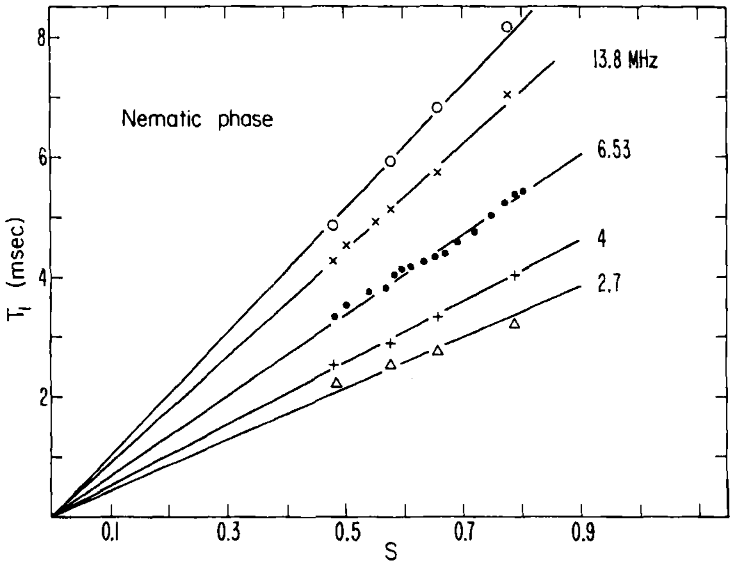


Figure 11. Deuteron T_1 versus orientational order parameter S in the nematic phase. The circles correspond to the high frequency limit of T_1 (see Fig. 15).

On the other hand, the frequency dependence of $1/T_1$ is not nearly as simple: we were unable to fit it to any simple law, either $1/\sqrt{\omega}$, which is the law observed in conventional nematics, or $1/\omega^2$, which is the law observed in viscous liquids (Fig. 12).

Finally, we also measured the transverse spin-lattice relaxation time T_2. From the measured values of T_2, we have calculated $1/T_2' = 1/T_1$ $(\omega = 0)$ (see Appendix B). The values of $1/T_2'$ are plotted as zero-frequency measurements of $1/T_1$ in Fig. 12; they appear to diverge much faster than $1/T_1$ when the nematic–isotropic transition is approached from below. Figure 13 shows that this divergence obeys the law:

$$1/T_2' \propto 1/S^3$$

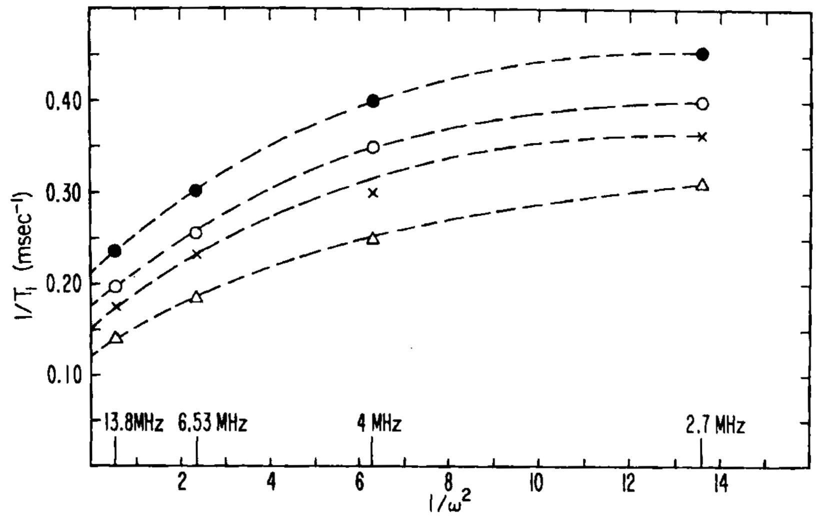


Figure 12. $1/T_1(\omega)$ versus $1/\omega^2$ in the nematic phase. For a perfect Lorentzian spectral density, the high frequency points ($\omega > 4$ MHz) corresponding to each temperature should be aligned.

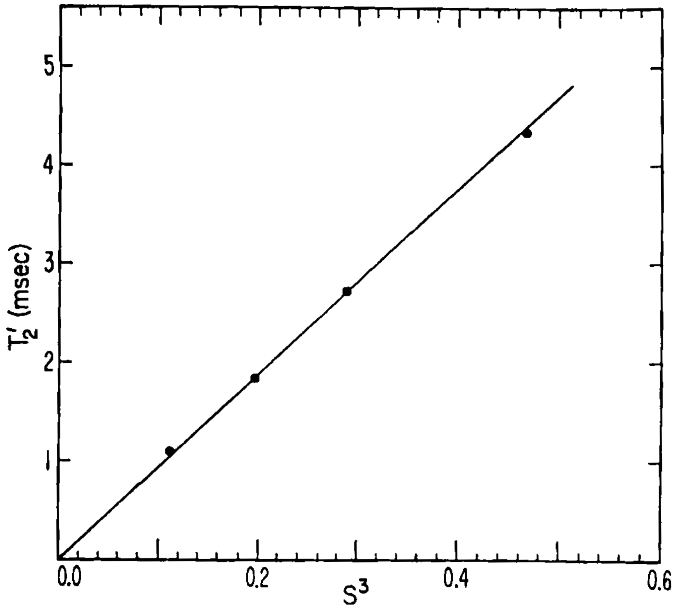


Figure 13. $T_2' = T_1(\omega = 0)$ versus S^3 in the nematic phase. T_2' has been calculated from T_2 and T_1 measured at 13.8 Mc, as explained in Appendix B.

4. Interpretation of Nematic Phase Results

The temperature and frequency behaviors of $1/T_1$ in the nematic phase of PHBA appear to differ widely from those observed in conventional nematics. Indeed, pure orientational processes (i.e., molecular reorientations) are known to give, in nematic liquids, no dependence of T_1 on S, and a different frequency law $T_1(\omega)$.(14) The origin of our new behavior lies presumably in the nature of the PHBA molecules (dimers); in other words, the association–dissociation processes must come in somehow. However, these processes alone yield a temperature dependence similar to that observed in benzoic acid at high temperatures ($1/T_1 \propto e^{E/kT}$), and not a temperature dependence controlled by the orientational order parameter S or by the critical fluctuations (in the isotropic phase). Again, as in benzoic acid at lower temperatures, we have to assume that the association–dissociation processes are coupled to the collective orientational motions of the molecules. So we will first study that coupling slightly more carefully, and then attempt to calculate the corresponding spin-lattice relaxation rate.

(A) COUPLING OF ASSOCIATION–DISSOCIATION PROCESSES WITH ORIENTATIONAL ORDER

(i) *No coupling*: We first describe the simplest case where the hydrogen bonding reactions involve only independent molecules (no orientational correlations between molecules, no collective processes). Also, in a first step, we will consider only the [cyclic dimer ⇄ open dimer] equilibrium. Such an equilibrium:

$$Y_1 \underset{K_2}{\overset{K_1}{\rightleftarrows}} Y_2$$

is entirely described by the rate constants K_1 and K_2 : K_1 is the rate of conversion of Y_1 into Y_2, and K_2 is the reverse rate. Alternatively, one could describe it by the lifetimes $\tau_1 = 1/K_1$ and $\tau_2 = 1/K_2$ of the two species. The time evolution of the system, when shifted away from equilibrium, obeys the rate equation:

$$\frac{dc_1}{dt} = -K_1c_1 + K_2c_2$$

where c_1 and c_2 are the relevant concentrations. Accordingly, the system relaxes towards equilibrium with the time constant τ:

$$\frac{1}{\tau} = K_1 + K_2 = \frac{1}{\tau_1} + \frac{1}{\tau_2}.$$

In our case, Y_1 may represent a molecule with a broken H bond, and Y_2 the same molecule with the H bond formed: then $K_1 \gg K_2$, $\tau_1 \ll \tau_2$, and $1/\tau \sim 1/\tau_1$, i.e., the relaxation time of the equilibrium is the lifetime of the unstable species.

(ii) *Static coupling*: That there must be a coupling between the formation or rupture of H bonds between molecules and their orientational motions is rather evident. Indeed, the lifetimes of the dimers and monomers should depend on the magnitude of the orientational order. For example, if the degree of local orientational order is high, neighboring molecules are nearly parallel, and most of the collisions between molecules would not break the dimers. On the other hand, if the local orientational order is poor, a large number of the collisions between molecules can break their H bonds. Let us put this in a more quantitative form, and discuss more precisely the rupture of an H bond belonging to a cyclic dimer. We assume that the two constituent molecules of the dimer tend to follow separately the local order, and that the H bond breaks when its angle gets too large (see Fig. 14). Thus we have to estimate the average value of the angles β imposed to the H bonds by the orientational disorder of the liquid.

The direction of the local alignment in a nematic liquid is usually described by a vector $\mathbf{n}$ (the " director ").(15) The deviations $\mathbf{n}_\perp$ of $\mathbf{n}$ with respect to the macroscopic direction of alignment $\mathbf{n}_z$ describe the collective fluctuations of the orientations of the molecules. It is then possible to express the angle β imposed to the H bond by the local distortions of the orientational order as:

$$\beta = \frac{\partial n_\perp}{\partial z}.$$

The orientational disorder can be analyzed in modes (these are again the collective modes for the fluctuations of the molecular orientations). The Fourier component β_q corresponding to a mode of wavelength $2\pi/q$ is:

$$\beta_q = q n_q.$$

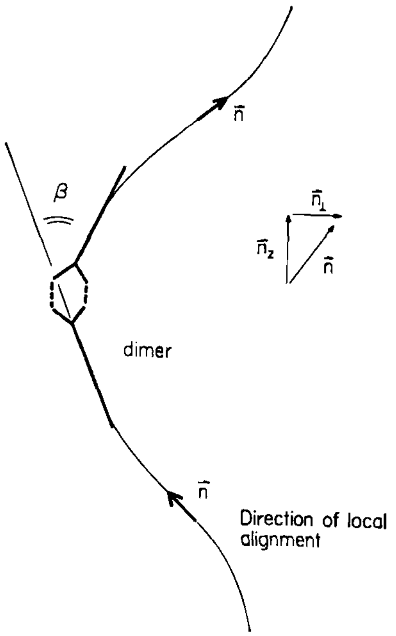


Figure 14. Effect of an orientational fluctuation on the hydrogen bonds of a dimer, assuming that the two components of the dimer tend to follow independently the local alignment.

Thus the mean square amplitude of the angles β associated with that mode is:

$$\langle \beta_q^2 \rangle = q^2 \langle n_q^2 \rangle .$$

In the nematic phase, the free energy associated with a mode of wavenumber q is proportional to q^{2}(11):

$$F_q = Dq^2$$

D being an elastic constant (this could be guessed from the discussion of Sec. 2, taking an infinite correlation length ξ—but the elastic constants of the nematic phase are temperature dependent). The average thermal amplitude n_q^2 can then be calculated through the equipartition theorem:

$$\langle n_q^2 \rangle = \frac{k_B T}{Dq^2} .$$

Summing over all the modes yields the total mean square amplitude of β:

$$\langle\beta^2\rangle = \int_0^{q\,\max} q^2 \frac{k_BT}{Dq^2} d^3q = \frac{k_BT}{D} q^3 \max.$$

It is generally admitted that the elastic constants D vary like the square of the order parameter S.[16] This yields:

$$\langle\beta^2\rangle \propto 1/S^2.$$

We assume that the distribution of the angles β is a gaussian, and that the possibility of breaking an H bond is proportional to $\sqrt{\langle\beta^2\rangle}$. The lifetime of the H bond is then given by:

$$1/\tau_2 \propto \sqrt{\langle\beta^2\rangle} \propto 1/S.$$

The reverse reaction can be treated in the same way: it is likely that the H bond can be formed again if the two constituent molecules are reasonably parallel to each other. So we assume that the probability of forming the H bond goes like the proportion of open dimers which have a small angle β:

$$\frac{1}{\tau_1} \propto \frac{1}{\sqrt{\langle\beta^2\rangle}} \propto S.$$

Of course, these results are valid only if S is not too small (it is a small angle approximation).

(B) Effect on Nuclear Spin-Lattice Relaxation

The correlation function for the fluctuations of the local concentration of broken H bonds is controlled by the lifetime τ_1 of these broken bonds (see Sec. A (i)):

$$G_1(t) \propto \mathrm{e}^{-t/\tau_1}.$$

These fluctuations modulate the nuclear quadrupolar interaction of the deuterons. The relevant correlation function is (see Appendix A for details):

$$F(t) = \frac{\tau_1}{\tau_2} \mathrm{e}^{-t/\tau_1}.$$

The induced nuclear spin-lattice relaxation rate is:

$$\frac{1}{T_1} \propto \int F(t)\,\mathrm{e}^{i\omega t}\,\mathrm{d}t = \frac{\tau_1}{\tau_2}\frac{1/\tau_1}{\omega^2+(1/\tau_1)^2}.$$

Our data show that $1/T_1$ is frequency dependent between 2.7 and 13.8 MHz. This suggests that we are in the high frequency situation $\omega \gg 1/\tau_1$. Then:

$$\frac{1}{T_1} \propto \frac{1}{\tau_2} \frac{1}{\omega^2}.$$

Accordingly, the nuclear relaxation rate should vary as $1/S$ when the temperature is changed within the nematic phase. This is observed, with a good precision for all our frequencies except the lowest one where the experimental uncertainties are larger (Fig. 11).

When the nuclear frequency ω is changed at fixed temperature, $1/T_1$ should go like $1/\omega^2$. It appears that the observed frequency dependence is smaller, and also more complex (Fig. 12).

That the " static coupling " description fails to account for the experimental frequency dependence of T_1 is not a surprise. Indeed, that description takes properly into account the effect of the amplitude of the orientational modes, but not that of their time dependence; so it was expected to predict correctly the temperature dependence of T, and to fail for its frequency dependence.

Finally, the zero frequency limit of $1/T_1$ is in this model:

$$\frac{1}{T_1}(\omega = 0) \propto \frac{\tau_1^2}{\tau_2} \propto \frac{1}{S^3}$$

The values of $1/T_2' = 1/T_1\ (\omega = 0)$ which have been deduced from our measurements of the transverse spin-lattice relaxation time T_2 follow this law with a good accuracy (Fig. 13).

In conclusion, the " static coupling " model relates the temperature dependences of T_1 and T_2 to the temperature dependence of the amplitude of the orientational fluctuations, through the coupling of these fluctuations with the H bonding processes. The resulting temperature dependences of T_1 and T_2 are, in this model:

$$1/T_1 \propto 1/S; \quad 1/T_2 \propto 1/S^3$$

They are identical with the observed ones.

(C) Higher Order Reactions

The reactions involving monomers:

$$\text{open dimer} \rightleftarrows 2 \text{ monomers}$$

$$\text{cyclic dimer} \rightleftarrows 2 \text{ monomers}$$

have a different statistics from those of the type $Y_1 \rightleftarrows Y_2$. Indeed, the relaxation time of an equilibrium of the type:

$$2Y_1 \underset{K_2}{\overset{K_1}{\rightleftarrows}} Y_2$$

is, in the limit where $K_1 \gg K_2$, and for a pure liquid (no solvent):

$$\frac{1}{\tau} = \sqrt{2K_1K_2}\,.$$

The correlation function for the corresponding fluctuations of the quadrupolar interaction of the deuteron is:

$$F(t) = \sqrt{\frac{K_2}{K_1}}\,e^{-t/\tau}.$$

The induced spin-lattice relaxation rate is:

$$\frac{1}{T_1} = \sqrt{\frac{K_2}{K_1}}\,\frac{1/\tau}{\omega^2 + (1/\tau)^2}$$

or, in the limit $\omega\tau \gg 1$:

$$\frac{1}{T_1} \propto K_2 \frac{1}{\omega^2} = \frac{1}{\tau_2}\frac{1}{\omega^2}$$

which is identical with the behavior expected for the [cyclic dimer $\rightleftarrows$ open dimer] equilibrium.

Thus, in principle, the temperature dependence of T_1 in liquid PHBA does not permit to distinguish between the reactions involving only dimers (open $\rightleftarrows$ cyclic) and those involving monomers. However, we may use the frequency dependence of T_1 for this purpose. Indeed, ultrasonic absorption data in acetic acid (1) indicate that the relaxation frequencies of the (dimer $\rightleftarrows$ 2 monomers) reactions are much higher. For such high frequencies $1/\tau$, it is the limit $\omega\tau \ll 1$ which is appropriate. In that regime, the deuteron spin-lattice relaxation rate should be:

$$\frac{1}{T_1} \propto \frac{1}{K_1} \begin{cases} \text{independent of } \omega \\ \text{proportional to } 1/S \end{cases}$$

Such a high frequency contribution to $1/T_1$ does appear into the plots of $1/T_1$ versus ω (see Figs. 12 and 15). Taking that high frequency

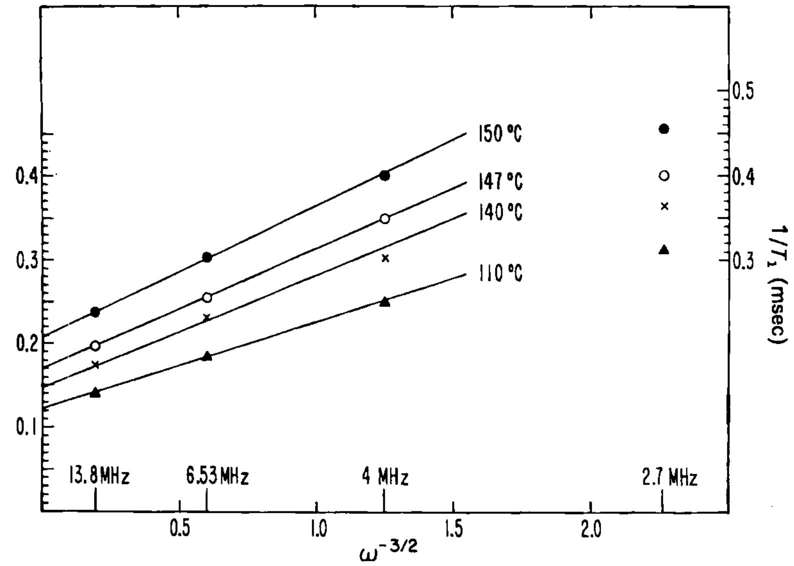


Figure 15. $1/T_1(\omega)$ versus $\omega^{-3/2}$ in the nematic phase. The $\omega^{-3/2}$ law is believed, within our description, to be a mere coincidence.

limit of T_1 and plotting it against S (dots in Fig. 11) shows that this contribution has the correct behavior $1/T_1 \propto 1/S$. The same argument shows that our zero frequency data ($1/T_1$ $(\omega = 0) \propto 1/S^3$) cannot be produced by these processes. In summary, the relaxation of the higher order reactions of the type (dimer $\rightleftarrows$ 2 monomers) must be fast compared to the NMR frequencies, so that its frequency independent contribution to $1/T_1$, while relatively unimportant at low frequencies (T_2), becomes significant in the high frequency limit. Our data permit an estimation of the two relaxation frequencies: $f_1 \sim 5$ MHz for the first relaxation, and $f_2 = 20$ MHz for the second relaxation.

5. Dynamic Coupling

The preceding section described the coupling of the H-bonding equilibrium with the static part of the orientational fluctuations (" frozen disorder ") only. Consequently, that treatment failed to account for the observed frequency dependence of T_1. Accordingly, we have to study the coupling between the dynamics of both processes.

More precisely, when the fluctuations of the orientational variable are much slower than the fluctuations of all the other variables describing the liquid, their decay in time obeys the relaxation equation:

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = -\Gamma Q$$

where the frequency independent damping constant $\Gamma = 1/\tau$ summarizes the effect of all the other fluctuations.

Similarly, if the fluctuations of the concentration of broken bonds were much slower than all other fluctuations, they would decay exponentially in time:

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -k_1 c.$$

Whenever there are slow variables, their fluctuations may be coupled; their relaxation is then described by a system of coupled transport equations:

$$(1)\quad \begin{cases} \dfrac{\mathrm{d}Q}{\mathrm{d}t} = -\Gamma Q - mc \\[2ex] \dfrac{\mathrm{d}c}{\mathrm{d}t} = -m'Q - k_1 c. \end{cases}$$

The solutions $Q(t)$ and $c(t)$ are then linear combinations of exponential decays, and the spectral densities of the corresponding correlation functions $\langle Q(0)Q(t)\rangle$ and $\langle c(0)c(t)\rangle$ are superpositions of Lorentzians. Thus it is not suprising that the observed spectral density cannot be fitted to a single Lorentzian.

(A) CHOICE OF THE COUPLED VARIABLES

(i) *Orientational variable*: The local alignment of the molecules is described by a second rank tensor $\bar{\bar{Q}}$(9) (see Sec. 2). The fluctuations of $\bar{\bar{Q}}$ can be divided into two groups: uniform fluctuations of the magnitude of the local alignment, corresponding to terms $(Q_{\alpha\beta})^2$ in de Gennes's free energy, and fluctuations involving spatial derivatives of $\bar{\bar{Q}}$ (terms $(\partial_\alpha Q_{\beta\gamma})^2$ or $\partial_\alpha Q_{\alpha\gamma}\delta_\beta Q_{\beta\gamma}$) which describe non-uniform variations of the orientation and magnitude of the local alignment.

In the nematic phase, the fluctuations of the magnitude of the local alignment are small compared to the fluctuations of its orientation (just because the magnitude of that alignment is large)(11); the good orientational variables are then the spatial derivatives $\partial_\alpha Q_{\beta\gamma}$ (or, alternatively, the spatial derivatives of the director **n**, which have been used in Sec. 4). In the isotropic phase, depending on the nuclear frequency, it is possible to sample either type of fluctuation (see the discussion of Sec. 2, and Ref. 10); the good variable for the critical regime is of course the magnitude $Q_{\beta\gamma}$ of the local alignment.

(ii) *Concentration variable.* The fluctuations of the concentration of broken H bonds can be described by the magnitude C of that concentration, and by its rate of change $\dot{C} = \mathrm{d}C/\mathrm{d}t$. Our previous discussion of the nematic phase (Sec. 4) indicates that the equilibrium concentration C_{eql} is small ($C_{\mathrm{eql}} = k_2/k_1$, where $k_1 \gg k_2$: very few bonds are broken in the nematic phase), while $\dot{C}$ is much larger ($\dot{C} = -k_1 C$). Accordingly, the fluctuations of $\dot{C}$ might be dominant in the nematic phase. On the other hand, k_1 is much smaller in the isotropic phase (it is proportional to the magnitude of the local alignment, which is small in the isotropic phase), while C gets significantly larger; thus the fluctuations of C should be dominant in the isotropic phase), while C gets significantly larger; thus the fluctuations of C should be dominant in the isotropic phase.

(iii) *Coupled variables.* The preceding discussions suggest that the dominant fluctuation modes of the system can be described, in the nematic phase by $\dot{C}$ and $\partial_\alpha Q_{\beta\gamma}$, and in the isotropic phase by C and $Q_{\beta\gamma}$. Our choice of variables in the nematic phase is consistent with the analysis of Sec. 4. Indeed, it is the probability of breaking or forming one bond which has been related to the angle β between the two components of a dimer, β being in turn related to the spatial derivatives of the orientation variable ($\beta = n_\perp/\partial z$, or $\partial Q_{xz}/\partial z$ in the geometry of Fig. 14). None of these arguments, however, has much value as a proof. Indeed, the details of the couplings are probably much more complex. The following discussion should be regarded only as an attempt to show the complexity of this problem, even in the simplest case of two variables.(19)

(B) GENERAL EQUATIONS

The decay of a large fluctuation of the 2 coupled variables, say Q

and C, obeys a system of linear transport equations of the type (I), i.e.:

$$\frac{d}{dt}\begin{pmatrix} Q \\ C \end{pmatrix} = I^{-1}\begin{pmatrix} Q \\ C \end{pmatrix}$$

where I^{-1} is the " transport matrix ".

The decay of the correlation functions of the fluctuations of Q and C around their equilibrium values is governed by a similar equation:

$$\frac{d}{dt}\begin{pmatrix} QQ & QC \\ CQ & CC \end{pmatrix} = I^{-1}\begin{pmatrix} QQ & QC \\ CQ & CC \end{pmatrix} \tag{II}$$

where the notation $QQ = \langle Q(0)Q(t)\rangle$ has been used.

The coefficients of the transport matrix I^{-1} are related to the correlation functions of the corresponding " fluctuating forces " by the linear response theory.⁽²⁰⁾ They include:

$$\Gamma = \frac{(\dot{Q}^{+}\dot{Q}^{+})}{\langle Q^2\rangle}, \; k = \frac{(\dot{C}^{+}\dot{C}^{+})}{\langle C^2\rangle}, \; h = \frac{\langle \dot{Q}C\rangle}{\langle Q^2\rangle^{1/2}\langle C^2\rangle^{1/2}},$$

$$\dot{f} = \frac{(\dot{Q}^{+}\dot{C}^{+})}{\langle Q^2\rangle^{1/2}\langle C^2\rangle^{1/2}}, \; f = \frac{\langle QC\rangle}{\langle Q^2\rangle^{1/2}\langle C^2\rangle^{1/2}}$$

where $\dot{Q}^{+}$ is the " fluctuating force " associated with the variable Q, and $(\dot{Q}^{+}\dot{Q}^{+})$ the time integral of its correlation function.⁽²⁰⁾

According to the time reversal symmetry of the variables, h is identical to zero for a coupling of Q to C, while f is identical to zero for a coupling of Q (or $\partial_\alpha Q$) to $\dot{C}$ (i.e. if C is replaced by $\dot{C}$ in the preceding expressions.)

(C) DYNAMIC COUPLING IN THE NEMATIC PHASE

In the case of a coupling of $\dot{C}$ to the spatial derivatives of Q (denoted $\partial_\alpha Q$), the transport matrix is:

$$I^{-1} = \begin{bmatrix} \Gamma & -h\,\dfrac{\langle \partial_\alpha Q^2\rangle^{1/2}}{\langle C^2\rangle^{1/2}} \\[2ex] +h^{*}\,\dfrac{\langle \dot{C}^2\rangle^{1/2}}{\langle \partial_\alpha Q^2\rangle^{1/2}} & k_1 \end{bmatrix}$$

It has the following eigenvalues:

$$2\lambda \pm \ = \Gamma + k_1 \pm \sqrt{(\Gamma - k_1)^2 - 4hh^*}\ .$$

The solutions of the transport equations (II) are then[(20)]:

$$\begin{aligned}\langle \dot{C}\dot{C} \rangle &= \frac{\langle \dot{C}^2 \rangle}{\lambda_+ - \lambda_-}\{(\lambda_+ - k_1)\,\mathrm{e}^{-\lambda_- t} - (\lambda_- - k_1)\,\mathrm{e}^{-\lambda_+ t}\} \\ \langle \partial_\alpha Q\,\partial_\alpha Q \rangle &= \frac{\langle \partial_\alpha Q^2 \rangle}{\lambda_+ - \lambda_-}\{(\lambda_+ - \Gamma)\,\mathrm{e}^{-\lambda_- t} - (\lambda_- \Gamma)\,\mathrm{e}^{-\lambda_+ t}\}\end{aligned} \qquad \text{(III)}$$

The respective signs of the two exponential decays of each correlation functions are always opposite; for example, it is easy to check that

$$(\lambda_+ - k_1)(\lambda_- - k_1) = hh^* > 0$$

This would produce a dip (negative Lorentzian) in the spectral density of the fast variable, and depresses the high frequency background of the slow one. It can also be verified that the spectral densities are always positive.

Next, the couplings of $\dot{C}$ to each orientational mode can be analyzed separately, taking spatial Fourier transforms of the transport equations. The intrinsic damping rate of the orientational mode with wavenumber (q) is then (see Fig. 7 and Ref. 11):

$$\Gamma_q = \frac{1}{\tau_q} = \frac{D}{\eta}\,q^2.$$

On the other hand, as far as intramolecular bonds only are considered (see Sec. 4), no spatial dependence should come into the intrinsic relaxation rate k_1 of the concentration fluctuations. Finally, the coupling coefficient h_q is pure imaginary and q dependent (stability conditions imply $h_q \propto q$).

Our experience of nuclear relaxation in the nematic phases of other materials suggests that the dominant orientational modes are those for which Γ_q is on the order of the nuclear frequency ω[10,14]. This permits to break up our discussion into a low frequency situation (ω and $\Gamma_q \ll k_1$) and a high frequency situation (ω and $\Gamma_q \gg k_1$).

Finally, following our analysis of Sec. 4, we will assume that the spin-lattice relaxation is produced by the concentration fluctuations,[(21)] so that:

$$\frac{1}{T_1}(\omega) = \frac{k_2}{k_1}\langle CC \rangle_\omega .$$

Low frequency behavior—The observed spectral density should be the Fourier transform of:

$$\langle CC\rangle = \langle C^2\rangle \left[e^{-k_1 t} - \frac{hh^*}{k_1^2} e^{-\Gamma t} \right].$$

The first term gives rise to the main Lorentzian, while the second is responsible for the dip. The ratio of the amplitudes of the main Lorentzian and the dip is temperature independent if h is dependent on the orientational order parameter S, as k_1 is. In particular, the value of the total density at zero frequency determines the temperature dependence of $1/T_1(\omega = 0)$. The experimental behavior $1/T_1(\omega = 0) \propto 1/S^3$ is recovered by taking $k_1 \propto S$ and $k_2 \propto 1/S$, as in Sec. 4.

High frequency behavior—The relevant correlation function is:

$$\langle CC\rangle = \langle C^2\rangle \left[e^{-k_1 t} - \frac{hh^*}{\Gamma^2} e^{-\Gamma t} \right].$$

The contribution of the second term, integrated over all the modes is negligible. Thus the induced spin-lattice relaxation rate is essentially

$$\frac{1}{T_1} \propto \frac{k_2}{k_1} \langle CC\rangle_\omega \propto \frac{k_2}{\omega^2}.$$

The corresponding temperature dependence of T_1 is of course $1/T_1 \propto 1/S$, as in Sec. 4. This result also implies that ultimately, at very high frequencies, $1/T_1$ has to go like $1/\omega^2$; the fact that it does not is due to the depression of the low frequency points by the broad wings of the dip. Accordingly, it seems that the $\omega^{-3/2}$ behavior which appears in Fig. 16 is a mere coincidence, but the extension of our frequency range is anyway too small to decide on this point.

Spectrum of the orientational fluctuations—We may finally comment on the spectrum of $\langle QQ\rangle$,, which should be made of a positive component proportional to $1/\sqrt{\omega}$, as in conventional nematics, and a negative Lorentzian of width k_1: such a spectrum would be completely different from the observed one; this is an additional justification of our assumption that $1/T_1$ is controlled by $\langle CC\rangle$.

(D) Dynamic Coupling in the Isotropic Phase of PHBA

In the case of a coupling of the concentration C to the magnitude Q

of the local alignment, the transport matrix is (20):

$$I^{-1}\begin{bmatrix} \Gamma - f\dot{f} & (f - \Gamma f)\dfrac{\langle Q^2\rangle^{1/2}}{\langle C^2\rangle^{1/2}} \\ (f - k_1 f)\dfrac{\langle C^2\rangle^{1/2}}{\langle Q^2\rangle^{1/2}} & k_1 - f\dot{f} \end{bmatrix} \frac{1}{1-f^2}\cdot$$

Again, the solutions of the transport equations can be put in the form III, but the eigenvalues λ_+ and λ_- are more complicated:

$$(1-f^2)2\lambda\pm\ = (\Gamma+k_1)(1-fg) \pm \sqrt{(\Gamma+k_1)^2(1-fg)^2 - 4(\Gamma k - \dot{f}^2)(1-f^2)}$$

with $g = 2\dot{f}/(\Gamma+k_1)$, the coupling coefficients f and $\dot{f}$ being real and positive.

The respective signs of the two exponential decays in $\langle CC\rangle$ are always the same; indeed:

$$(\lambda_+ - k_1)(\lambda_- - k_1) = -(k_1 f - \dot{f})^2 < 0.$$

Accordingly, the spectral density of $\langle CC\rangle$ should be made of a narrow positive component, of width k_1, and a broad background, of width Γ. The same holds for $\langle QQ\rangle$.

The broad components of both correlation functions can be responsible for the (frequency independent) critical divergence of $1/T_1$ in the vicinity of the transition. Indeed, as shown in Sec. 2, the high frequency component of the spectrum of $\langle QQ\rangle$ is, after integration over all orientational modes:

$$\int \langle Q_q{}^2\rangle \frac{\Gamma_q}{\omega^2+\Gamma_q{}^2}\, d_q{}^3$$

which, for $\omega > \Gamma$, yields $1/T_1 \propto 1/\sqrt{\Gamma} = \sqrt{\tau}$ as observed experimentally. The high frequency component of the spectrum of $\langle CC\rangle$ yields a similar result too. This can easily be shown when either f or $\dot{f}$ is neglected; for $\dot{f} = 0$, we get:

$$\int \langle C^2\rangle \frac{k_1 f^2}{\omega^2+\Gamma_q{}^2}\, d_q{}^3$$

which gives the same result $1/T_1 \propto \sqrt{\tau}$ (f is q independent). In the same way, $f = 0$ yields:

$$\int \langle C^2\rangle \frac{f_q{}^2}{\Gamma_q}\frac{1}{\omega^2+\Gamma_q{}^2}\, d_q{}^3.$$

The experimental law is then recovered if $\dot{f}_q^2$ is proportional to either Γ_q (which is most likely) or q^2.

In summary, we get $1/T_1 \propto \sqrt{\tau}$ independently of whether the spin-lattice relaxation is produced by $\langle CC \rangle$ or by $\langle QQ \rangle$. In fact, it is presumably a mixture of both. Indeed, while $\langle CC \rangle$ dominates the spin-lattice relaxation in the nematic phase, the width k_1 of its main component becomes so narrow in the isotropic phase that it does no longer contribute much to $1/T_1$ for nuclear frequencies of a few MHz; the contribution of $\langle QQ \rangle$ then becomes significant. On the other hand, that narrow component of width k_1 does contribute to the zero frequency value of T_1. Indeed, while T_1 was observed to be frequency independent between 2.7 and 6.53 MHz, T_2 was found to be definitely shorter than T_1, by about a factor of 2.

(E) ISOTROPIC PHASE OF BENZOIC ACID

The situation in benzoic acid is just reverse of that in the isotropic phase of PHBA. Indeed, the orientational width Γ is now so large that the corresponding spectral densities do no longer contribute much to the spin-lattice relaxation; on the other hand, k_1 is much faster than in PHBA (because the molecules are shorter). The spin-lattice relaxation at nuclear frequencies is then produced by the narrow component (k_1), and its temperature dependence controlled by k_1 and k_2. For temperatures for above the virtual nematic–isotropic transition of benzoic acid, the hydrogen-bonding processes are poorly coupled to the orientational fluctuations; the temperature dependences of k_1 and k_2 are then controlled by the activation energies of the forward and backward reactions. This gives rise to the observed " Arrhenius " behavior of the spin-lattice relaxation rate ($1/T_1 \propto \exp(+E/kT)$).

6. Conclusions

The critical behaviors of $1/T_1$ on both sides of the nematic–isotropic transition indicate that T_1 is **ultimately** controlled by the orientational fluctuation modes of the liquid. However, the shape and the temperature dependence of the observed frequency spectrum $1/T_1(\omega)$ in the nematic phase indicate that $1/T_1$ is in fact **produced** by fluctuations of the local concentrations of broken H bonds, these fluctuations being coupled with the orientational modes, and controlled by them. This coupling can be analyzed in two steps. In a first step, one considers the dynamical mixing of the two types of modes produced by the existence of off-diagonal coefficients in the transport matrix (i.e., by the crossed correlation functions). This yields a good description of the shape of the observed spectral densities (Sec. 5). In a second step (Sec. 4), we have seen that the diagonal coefficients Γ and k_1 of the transport matrix are connected by a very simple relation ($\Gamma \propto S^2$ and $k_1 \propto S$). This is similar to the Debye relation which connects the diagonal coefficients Γ and η in the coupling of orientation to flow for normal molecular liquids.(18)

Two types of informations on the dynamics of PHBA can be extracted from our experiments. The first group concerns the " semi-macroscopic " behavior of the fluctuations of the molecular orientations, rather independently from the microscopic details of the system. In the isotropic phase, our data are consistent with the predicted dispersion relation for the orientational modes:

$$\Gamma_q = \frac{1}{\tau_q} = \frac{L}{\nu}\left(q^2 + \frac{1}{\xi^2}\right) = \frac{1}{\tau} + \frac{L}{\nu}q^2.$$

They also provide a determination of the relaxation frequency $\Gamma = 1/\tau$ of the long wavelength modes; finally, they specify the critical exponent of τ, and the temperature T^* where the corresponding modes would diverge. In the nematic phase, we have measured the orientational long range order parameter S; our data are also in agreement with the theoretical law for the dependence on S of the amplitude of the orientational modes:

$$\langle n_q^2 \rangle = \frac{k_B T}{D q^2} \propto \frac{1}{S^2}.$$

The second group of informations concerns the microscopic details of the fluctuations of the concentration of broken bonds. First we have been able to identify separately the two reaction steps of the hydrogen bonding equilibrium. The first step (cyclic dimer $\rightleftarrows$ open dimer) is responsible for the spin-lattice relaxation of the deuterons at low frequencies, while the second one (open dimer $\rightleftarrows$ 2 monomers) is responsible for our high frequency limit. Next, the main features of the coupling of these reactions to the orientational fluctuations have been precised. In particular, the rate constants k_1 and k_2 of the bond forming and bond breaking reactions have been related to the orientational order parameter S.

Finally, it would be tempting to construct a model for the mechanism of that coupling,(22) so that one could ascertain the way in which the variables are coupled. However, we believe that this requires the accumulation of additional experimental data; in particular we encourage direct measurements of the spectral densities $\langle QQ \rangle_\omega$ (by Rayleigh scattering) and $\langle CC \rangle_\omega$ (by ultrasonic absorption), as well as static determinations of the equilibrium concentrations (through IR spectra).

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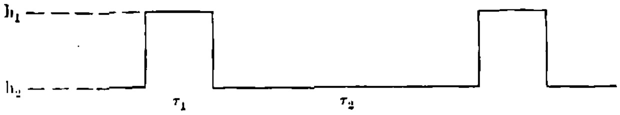
Appendix A

Time Correlation Function for the Modulation of the Deuteron's Quadrupolar Interaction by H-bonding Processes

The spin-lattice relaxation of the deuteron is induced by fluctuations of the molecular electric field gradient (E.F.G.) at the site of the deuteron.(7) That EFG is significantly larger in a non-bonded configuration, with respect to a bonded configuration. This appendix presents a computation of the correlation function for such fluctuations of the EFG produced by H–bonding reactions of the type:

$$y_1 \underset{k_2}{\overset{k_1}{\rightleftarrows}} y_2 .$$

In this reaction, $\tau_1 = 1/k_1$ is the average lifetime of the non-bonded configuration y_1, where the EFG experienced by the deuteron is h_1; τ_2, k_2, y_2, and h_2 are similar notations for the bonded species. The succession in time of the values of the EFG experienced by the deuteron can be represented in the following way:



The time correlation function of the EFG is the thermal average:

$$G(t) = \langle h(0)h(t)\rangle$$

We will use the following notations:

Π_1 = probability of the EFG h_1 for the deuteron
= relative concentration of deuterons with EFG h_1

or:

$$\Pi_1 = \frac{\tau_1}{\tau_1+\tau_2} \text{ and } \Pi_2 = \frac{\tau_2}{\tau_1+\tau_2}$$

and:

$$\frac{1}{\tau} = \frac{1}{\tau_1}+\frac{1}{\tau_2} = \text{relaxation time of the equilibrium.}$$

The correlation function can then be written:

$$G(t) = \underbrace{h_1\Pi_1}_{\substack{\text{deuter-}\\ \text{ons in}\\ h_1 \text{ at}\\ t=0}} \times \{\underbrace{h_1\Pi_1 + h_1\Pi_2 e^{-t/\tau}}_{\text{fractions of these deuterons in } h_1 \text{ at } t} + \underbrace{h_2\Pi_2 - h_2\Pi_2 e^{-t/\tau}}_{\text{fractions of these deuterons in } h_2 \text{ at } t}\}$$

$$+ \text{ symmetrical terms}$$

or, keeping the time dependent part only:

$$G(t) = (h_1 - h_2)^2\Pi_1\Pi_2 e^{-t/\tau}$$

In the limit where $\tau_2 \gg \tau_1$ (H bonds stable), this yields:

$$G(t) = (h_1 - h_2)^2 \frac{\tau_1}{\tau_2} e^{-t/\tau_1}$$

APPENDIX B

CONNECTION BETWEEN T_2 AND $T_2' = T_1(\omega = 0)$ IN THE NEMATIC PHASE

The relaxation rates $1/T_1$ and $1/T_2$ produced by fluctuations of quadrupolar interactions are related to the spectral density of these fluctuations:(23)

$$1/T_1(\omega) = 3R[J(\omega)+4J(2\omega)]$$

$$1/T_2(\omega) = \frac{3}{2}R[3J(0)+5J(\omega)+2J(2\omega)]$$

R being a constant measuring the magnitude of the quadrupolar interaction of the deuteron with the associated EFG.

Assuming that $J(\omega) \propto 1/\omega^2$ (high frequency limit of a Lorentzian), we get:

$$\frac{1}{T_2'} = \frac{5}{12}\left(\frac{8}{T_2(\omega)} - \frac{11}{T_1(\omega)}\right).$$

REFERENCES

1. Corsar, R. D. and Atkinson, G., *J. Chem. Phys.* **54**, 4090 (1971); Tatsumoto, N., *J. Chem. Phys.* **47**, 4561 (1967).
2. Allen, G. and Caldin, E. F., *Trans. Farad. Soc.* **49**, 895 (1953); Ito, M., *J. Molec. Spectroscopy* **4**, 144 (1960); Pimentel and McClellan, *The Hydrogen Bond*, Freeman.
3. Muller, N. and Hughes, O. R., *J. Phys. Chem.* **70**, 3975 (1966); Davis, J. C. and Pitzer, K. S., *J. Phys. Chem.* **64**, 886 (1960).
4. Blinc, M. and Blinc, R., *J. Polym. Sci.* **32**, 506 (1958).
5. Davies, D. B. and Matheson, A. J., *J. Chem. Phys.* **45**, 1000 (1966).
6. Lister, J. D. and Stinson, T. W., *J. Appl. Phys.* **41**, 996 (1970); Stinson, T. W. and Lister, J. D., *Phys. Rev. Letters* **25**, 503 (1970).
7. Cabane, B. and Clark, W. G., *Phys. Rev. Letters* **25**, 91 (1970).
8. Zadoc Kahn, J., *Annales de Physique* **6**, 31 (1936); Zvetkof, V., *Acta Physiochemica USSR* **19**, 86 (1944); Martinoty, P., Landau, S. and Debeauvais, F., *Phys. Rev. Letters* **27**, 1123 (1971).
9. de Gennes, P. G., *Mol. Cryst. and Liq. Cryst.* **12**, 193 (1971).
10. Cabane, B., Adv. Mol. Rel. Proc. (1972).
11. Orsay group on liquid crystals, *J. Chem. Phys.* **51**, 816 (1969).
12. Kadanoff, L. P., *et al.*, *Rev. Mod. Phys.* **39**, 395 (1967).
13. Rowell, J. C., Phillips, W. D., Melby, L. R. and Panar, E. M., *J. Chem. Phys.* **43**, 3442 (1965).
14. Pincus, P., *Solid State Comm.* **7**, 415 (1969); Weger, M. and Cabane, B., *Journal de Physique* (Paris) **30**, *Supplement C4*, 72 (1969); Blinc, R., Hogenboom, D. L., O'Reilly, D. E. and Peterson, E. M., *Phys. Rev. Letters*, **23**, 969 (1969); Doane, J. W. and Visintainer, J. J., *Phys. Rev. Letters*, **23**, 1421 (1969).
15. We might also use for this purpose the tensor $\underline{\underline{Q}}$ defined in Section 2. This would be more correct, but also more complicated than a discussion based on **n**. Indeed, in the nematic phase, small deviations of the local orienta-

tion with respect to n_z can be described very simply through the use of $\mathbf{n}_\perp$. For a definition of **n**, see Ref. 11.

16. Saupe, A., *Z. Naturforschg.* **15A,** 810 (1960).
17. Stegeman, G. I. A. and Stoicheff, B. P., *Phys. Rev. Letters* **21,** 202 (1968).
18. Keyes, T. and Kivelson, D., *J. Chem. Phys.* **54,** 1786 (1971); Reuven, A. B. and Gershon, N. D., *J. Chem. Phys.* **54,** 1049 (1971).
19. A better way to treat this problem is to consider the three coupled variables C, $\dot{C}$, and $\partial_\alpha Q_{\alpha\beta}$. Furthermore, symmetry arguments imply that the correct variables involve also spatial derivatives of the original ones.
20. Mori, H., *Progr. Theor. Phys.* **33,** 423 (1965); Keyes, T. and Kivelson, D., *J. Chem. Phys.* **56,** 1057 (1972).
21. For exponential correlation functions, one can switch from $\langle CC \rangle$ to $\langle \dot{C}\dot{C} \rangle$ by adding or subtracting a δ function. $1/T_1$ being controlled by $\langle CC \rangle$, and the coupling being dominated by $\langle \dot{C}\dot{C} \rangle$, this transformation is made in both directions, so that the total effect is nil.
22. For example, the coupling of $\dot{C}$ to $\partial_\alpha Q_{\beta\gamma}$ in the nematic phase could be represented in the following way. Each molecule rotates very quickly around its long axis. Whenever it is bent by the distortions of the local alignment, it suffers many collisions from its neighbors: thus a hydrogen bond may be broken.
23. Abragam, A., *The Principles of Nuclear Magnetism*, Oxford University Press, 1961.