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NMR spin-lattice relaxation from molecular defects in nematic polymer liquid crystals

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Abstract. — We calculate the contributions $J_1(\omega_0)$ and $J_2(2\omega_0)$ to the NMR relaxation rate $T_1^{-1}(\omega_0)$ caused by the motion of proposed molecular defects in polymer liquid crystals. The results are $J_1 \propto \omega_0^{1/2}$ and $J_2 \propto \omega_0^{-1/2}$ for low Larmor frequencies $\omega_0$. The scaling of the $J$ functions with chain length is also given. It is hoped that NMR may offer a way of determining the contribution of molecular defects to dynamical processes in well ordered polymer liquid crystal melts.

1. Introduction.

In a series of papers [1-3] etc., we described the molecular dynamics of polymer liquid crystals (PLCs) in their well-ordered phases by the motion of their molecular defects. For comb polymer liquid crystals these defects were torsional [1] - a region of upward pointing teeth along the backbone being separated from a downward region by a twist through 180°. For main chain polymers the defects were [2, 3] de Gennes' hairpins [4], that is, changes in direction from up to down of the chain backbone. In each case the constraint of a nematic field makes the defect-mediated dynamics of nematic polymers radically different from that met in conventional isotropic flexible polymers. Our purpose here is to calculate the signature in dynamical NMR experiments of these dynamical processes in PLCs. NMR offers possibly the most direct test of how realistic these models are and we hope to stimulate with this paper tests of the foregoing theory.

The dynamics of teeth in a comb or side chain PLC (SC PLC) is relatively straightforward and we thus start with this example. In contrast, main chain polymers (MC PLCs) have exceptionally complicated motion, the inextensibility of a worm making the equations of motion highly non-linear and non-local. A model that would appear to capture the essence of this

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motion is the "diffusing pulley" [2, 3]. In both the SC and MC cases we give expressions for the correlation functions $J_1$ and $J_2$ that determine $T_1^{-1}(\omega_0)$, the longitudinal relaxation rate in NMR.

We shall find that $T_1^{-1} \approx \omega_0^{-1/2}$ holds for times (\approx \omega_0^{-1} ) long compared with that needed for a defect to diffuse through its own length and for times short compared with that needed for a defect to diffuse completely along a chain. These times will be quantified below. This result is that expected for a simple diffuser. The complicated diffusional mechanism for MC PLC defects does not seem to influence the characteristic exponent of $-1/2$. It instead manifests itself in the length dependence ($L$) of the prefactors of the $\omega_0^{-1/2}$ result for the rate.

The $-1/2$ exponent is also that which one expects from the director fluctuation modes in 3-D [5] and hence the molecular mechanism we discuss must be distinguished from the director effects by supplementary experiments possibly by using the $L$ dependence or by varying the angle between the NMR field and the director. In a concluding section we discuss experiments already carried out by Kothe et al. [6].

The $\omega_0^{-1/2}$ result is that for the dominant relaxation mechanism at low frequencies. We shall find, as a consequence of orientational localisation to the director that there is another contribution of the form $\omega_0^{1/2}$ arising from the $J_1$ term. By the use of appropriate pulse sequences [7], these two relaxation mechanisms are experimentally separately discernible [8].

2. Nature of the defects and NMR correlation functions.

For concreteness imagine a pair of interacting protons with a separation vector anchored rigidly in a mesogenic unit of the chain, that is, either in a tooth of a comb polymer or in a rigid section of the backbone of a MC polymer. Corrections for the separation vector not being parallel to the chain axis may easily be applied. Equally one can imagine a deuteron in the electric field gradient of a chemical bond, that is a system with an electric quadrupole moment instead of a proton pair.

In a nematic environment the dipolar interaction between the proton spins gives a splitting proportional to the nematic order and the coupling strength - see for example de Gennes [9]. The nematic environment is locally very mobile and these lines suffer motional narrowing associated with the dipole pairs seeing an averaged environment. However non secular (off diagonal) parts of the interaction induce transitions between the states of different $z$-spin and hence, since the lifetime is now finite, a line broadening is produced. Such transitions contribute to the spin lattice relaxation rate $T_1^{-1}(\omega_0)$ thus:

$$\frac{1}{T_1(\omega_0)} = \omega_D^2 \int_{-\infty}^{\infty} dt \{ \exp(i\omega_0 t) \langle F_1(t)F_1^*(0) \rangle + \exp(2i\omega_0 t) \langle F_2(t)F_2^*(0) \rangle \},$$

(1)

where $\omega_D = \hbar \gamma^2/d^3$, $\gamma$ is the proton gyromagnetic ratio and $d$ the distance between the protons in a pair. As we note above, this is a homonuclear dipole-dipole relaxation mechanism. The first part of (1) is conventionally called $J_1(\omega_0)$ and the second part $J_2(2\omega_0)$. Here the $F$ functions are given by:

$$F_1(t) = \frac{3}{2\sqrt{2}} \sin \theta(t) \cos \theta(t) \exp[i\phi(t)],$$

(2)

$$F_2(t) = -\frac{3}{4} \sin^2 \theta(t) \exp[2i\phi(t)].$$

(3)

The averages of the $F$ functions are taken over all proton pairs and all chains. Using the fact that the correlation functions are stationary we have $\langle g(t)g^*(0) \rangle = \langle g^*(-t)g(0) \rangle$. It is easy to
show that $T_1$ is real and that an alternative expression is:

$$\frac{1}{T_1(\omega)} = 2\Re\left(\omega_0^2 \int_0^\infty dt\{\exp(i\omega t)(F_1(t)F_1^*(0)) + \exp(2i\omega t)(F_2(t)F_2^*(0))\}\right)$$  (4)

where $\Re$ denotes the real part. See [5] for a discussion and [10] for a derivation. These results are discussed in the context of monomeric liquid crystals in [11].

$\theta$ and $\phi$ are the polar and azimuthal angles of the chain element containing the proton pair. They are measured with respect to the director which we take as being parallel to the NMR field. In highly ordered phases $\theta \simeq 0$ or $\pi$, except in the region of a defect. For uniaxial phases $\phi$ is random. The defects we envisage are sketched in figure 1. In each case one can show [1, 2, 4] that for long chains:

$$\tan[\theta(s)/2] = \exp(s/\lambda)$$  (5)

where $s$ is the arc length along the chain and where the defect is located at $s = 0$. The characteristic length $\lambda$ is given by $\lambda = \sqrt{\epsilon/(3aS)}$ where $\epsilon$ is the torsional (for combs) or bend (for MC polymers) stiffness, $a$ is the nematic coupling constant, and $S$ is the order parameter. The latter must be close to 1 for well defined hairpins to exist. The form (5) and the geometric quotient $\lambda$ are a consequence of the compromise between two competing effects, elastic and nematic. The former requires that the transition up to down be as slow as possible, the latter as fast as possible, as one changes arc position long the chain.

We now introduce two simplifying assumptions: (a) we are in a regime of temperature $T$ and length $L$ such that there is only one hairpin per chain (we later see how this can be relaxed). (b) The nematic melt is dense enough that $\phi$ motion of the portion of the chain with a hairpin is suppressed by the steric obstruction of the neighbouring chains, at least on timescales where $\theta$ motion is still important. For MC hairpins this may be a good assumption: $\phi$ values are relevant whenever $\theta \neq 0$, that is when the protons pass over the hairpin. What is in question is whether or not the $\phi$ direction of the chain at a particular proton pair changes between visits of the hairpins. For $\phi$ to change the chain has to rotate about an axis through the hairpin and parallel to $\hat{n}$. The smaller scale thermal undulations (shown in Fig. 1b but supressed in Eq. (5) - see [12] for a discussion of why (5) is still useful for discussing thermal effects) in fact give the chain a transverse dimension greater than $\lambda$. This means that the arms of the hairpin are hindered from rotating because they are in conflict with the arms of many other chains. We expect this hinderance to make $\phi$ rotational motion of the hairpin extremely slow. If the $\phi$ motion were totally free then it would provide a rapid relaxation process which would totally dominate the $\theta$ motion(1). For side chain polymers the static nature of $\phi$ is much more questionable since the backbone can move at least locally, and hence the angle, $\phi$, of the plane of $\theta$-rotation can change. In the simplified picture of figure 1a this plane swept out by the $\theta$ motion is perpendicular to the backbone axis and hence it (and $\phi$) move as the backbone does.

Having, by assumption (b), frozen $\phi$ it drops out of (1) and can hence be neglected in (2), (3) and (4). Consider a hairpinned chain which has one arm of length $s_1(t)$, that is $s_1(t)$ is the position at time $t$ of the hairpin measured from the end of the chain, as shown in figure

(1) For an unobstructed hairpinned chain one can see that the two timescales are comparable. The time for a proton pair to diffuse through a hairpin length $\lambda$ is $r_\lambda \sim \lambda^2/D \sim \lambda^2 L/D_0$ where the curvilinear diffusion constant $D$ scales like $D_0/L$. For rigid angular diffusion the drag is also proportional to $L$ in the absence of wiggles that increase the lateral extent. Hence $\langle \phi^2 \rangle \sim 1 = D_\phi r_\phi \rightarrow r_\phi \sim 1/D_\phi \sim L$ as in the curvilinear case.
Fig. 1. — (a) A typical side chain polymer liquid crystal in the oblate phase $N_I$. The teeth point up or down with respect to the director $\hat{n}$. A torsional defect between up and down teeth is shown. (b) A main chain liquid crystal polymer with one hairpin defect. The proton pair at arc position $s$ has its principal axis parallel to the chain axis. The extent $\lambda$ (the hairpin length) is also shown. (c) The angles $\theta$ and $\phi$ of a tooth or backbone with respect to the director $\hat{n}$.

2. $s_p$ is the distance of the proton pair from the end of the chain. Then the angle $\theta_p$ that the proton pair axis has with respect to the director (also taken to be the NMR field direction) is:

$$\theta_p(t) = 2 \tan^{-1}[\exp\left(\frac{s_p - s_1(t)}{\lambda}\right)],$$

that is, it depends on the distance between the pair and the current position of the hairpin. The $F's$ are then functions of $y = (s_p - s_1(t))/\lambda$ since we put $\theta_p(t)$ from (6) into (2) and (3) respectively:

$$F_1(y) = -\frac{3}{2\sqrt{2}} \tanh y \cosh y$$
Fig. 2. — The coordinate system used in the evaluation of $f_1(t)$ and $f_2(t)$ for a hairpin defect in a main chain PLC via the diffusing pulley model. The length $s_1$ is the length of one of the arms at time $t$, and $s_p$ (a constant in time) is the arc length position of the proton pair in question. The transverse size $d$ of the hairpin is set equal to zero for the purposes of dynamics but is shown as finite here for clarity.

and

$$F_2(y) = -\frac{3}{4} \frac{1}{\cosh^2 y}$$

The two contributions to $T_1^{-1}$ are then obtained by Fourier transforming time correlation functions $f(t)$:

$$f(t) = \left( \int ds_1 G(s_1, s_0; t) F\left(\frac{s_p - s_1}{\lambda}\right) F\left(\frac{s_p - s_0}{\lambda}\right)\right)_{s_p, s_0}$$

where $G(s_1, s_0; t)$ is the probability that if the defect is at $s_0$ at $t = 0$ then it is at $s_1$ at a time $t$. This Green's function thus contains the information on the molecular dynamics. In addition one should average over starting points $s_0$ of the defect and over choices $s_p$ for the proton pair so that one obtains:

$$f(t) = \frac{1}{L^2} \int_0^L ds_p \int_0^L ds_0 \int_0^L ds_1 G(s_1, s_0; t) F\left(\frac{s_p - s_1}{\lambda}\right) F\left(\frac{s_p - s_0}{\lambda}\right).$$

In proceeding from (9) to (10) we have assumed that the proton pairs are distributed uniformly along the chain and that the distribution of arm lengths of the chain is uniform. It now remains to calculate $f(t)$ for various dynamical evolutions $G$, that is for the various models applicable to SC and MC PLCs.

3. Molecular dynamics.

3.1 SIDE CHAIN PLCs. — In [1] a stereo regular comb polymer was envisaged. This meant that in addition to being nematically ordered ($N_I$ in the nomenclature of [13]) the teeth are positioned on the same side of the chain, unless a torsional defect (costing torsional and nematic energy) intervenes. Such a defect can move without the cost of further energy by the flipping of teeth adjacent to the defect [1]. We re-adopt this model, with the relaxation of the stereochemical requirement that for NMR we are not concerned with a regularity of attachment. In dielectric response [1] we wanted a defect to delineate regions of up and down teeth and hence a reversal of dipole direction to be associated with a defect. Here it is a Hamiltonian of
quadrupolar symmetry that gives the broadening and hence no distinction is drawn between up and down. Hence from the point of view of NMR dynamics, the regularity with which side teeth are attached to the backbone is unimportant. Of the essence here is that to turn a tooth over requires torsional energy, except where the tooth lies next to a defect between sequences of teeth otherwise in their natural position. Flipping the tooth in question then causes the defect to move 1 unit (in the direction of the tooth). Thus for this aspect of SC dynamics careful stereoregular synthesis is not vital and we hope that our present model will be relevant for currently available SC systems in nematic and smectic phases.

In this situation a defect takes \( \alpha \) steps of length \( l \) (of random direction along the chain) per unit time. Standard walk statistics yields \( \langle h^2 \rangle = \alpha l^2 t \), whence by identification the diffusion constant for such motion is \( D = \alpha l^2 \). One can immediately write down the propagator \( G \) as the Gaussian form since we are dealing with a simple random walker:

\[
G(s_1 - s_0; t) = \left( \frac{1}{2\pi Dt} \right)^{1/2} \exp \left( -\frac{(s_1 - s_0)^2}{2Dt} \right). \tag{11}
\]

This is for times short enough that a defect does not explore the whole chain, i.e., \( t < L^2/D \).

A qualitative analysis of (10) is most informative. The functions \( F_1 \) and \( F_2 \) are highly localised (to within \( \lambda \)) of \( s_p \), and \( G \) is finite for values of \( s_1 \) within \( Dt \) of \( s_0 \) (see Fig. 3). For appreciable contributions to (10) one must evidently have \( s_0 \) and \( s_1 \) both within \( \lambda \) of \( s_p \). If \( Dt \gg \lambda^2 \) (that is a defect has time to diffuse through a distance much greater than its own length), then \( G \) is broad compared with \( \lambda \) and doesn’t distinguish between different values of \((s_1 - s_0)\) in the range \((-\lambda, \lambda)\) and one can effectively set \( s_1 = s_0 \) in \( G \). The result is just the return probability \( G(0; t) = \left( \frac{1}{2\pi Dt} \right)^{1/2} \) There remains \( \int ds_1 F_2[(s_p - s_1)/\lambda] = 3\lambda/2 \) and then similarly the \( \int ds_0 \) whence:

\[
f_2(t) \approx \frac{1}{L} \left( \frac{1}{2\pi Dt} \right)^{1/2} \left[ \int_{-\infty}^{\infty} ds_1 F_2 \left( \frac{s_1}{\lambda} \right) \right]^2 = \frac{9}{4} \frac{\lambda^2}{L} \left( \frac{1}{2\pi Dt} \right)^{1/2} \tag{12}
\]

The same analysis for \( f_1(t) \) requires more care as \( F_1 \) is anti-symmetric about the origin. Then \( \int dx F_1(x) = 0 \) and the above method yields zero. More accurate analysis may be found in appendix A. The result is:

\[
f_1(t) = \frac{\lambda^2}{2L} \left( \frac{3}{2} \right)^2 \frac{1}{\sqrt{2}} \left( \frac{\pi \lambda^2}{D} \right) \frac{3}{2} \tag{13}
\]

The difference between the \( f_1 \) and \( f_2 \) results arises from the different symmetry of the \( F \) functions and the rigid orientational constraint of the nematic field which has \( F = 0 \) everywhere except in the defect.

From the definitions (7) and (8) one sees that \( F_2 \) is smaller than \( F_1 \) when \( \theta \approx 0 \), but since the main contributions to \( T_{1}^{\perp} \) comes when the proton pairs are in a defect, then the \( \theta \gg 0 \) values dominate. The fact that the two halves of the \( F_1 \) function cancel and those of the \( F_2 \) do not, means \( F_2 \) is much more efficient in broadening the lines.

The final result for \( T_{1}^{\perp}(\omega) \) for SC PLCs is, at the most divergent order,

\[
T_{1}^{\perp}(\omega) \approx \lambda^2 \frac{1}{L} \left( \frac{1}{D \omega} \right)^{1/2} + \lambda^3 \frac{\omega}{L} D^{3/2} + . \tag{14}
\]
3.2 MAIN CHAIN DYNAMICS. — After considerable analysis we have suggested in previous work [2, 3] that a reasonable and tractible model for hairpin dynamics is that of the “diffusing pulley”. A hairpin can move by the diffusional motion of either one or both of its arms. The drag on an arm is proportional to its length. Its mobility is therefore proportional to the inverse of its length. It turns out [2] that one must add the mobilities of the two arms to get the overall mobility for a hairpin. The probability function for the length, \( \Psi(s_1, t) \) then satisfies the diffusion equation:

\[
\frac{\partial \Psi}{\partial t} = \frac{k_B T}{4\mu} \frac{\partial}{\partial s_1} \left\{ \frac{1}{s_1} + \frac{1}{L - s_1} \frac{\partial \Psi}{\partial s_1} \right\},
\]

where \( \mu \) is the drag per unit length. Considering diffusion along the line \((0, L)\) inspection of equation (15) shows that the hairpin has a position-dependent diffusion constant. The diffusional rate is large if \( s_1 \) or \( L - s_1 \) is small. That is, when one the arms is short and thus little drag is exerted, it moves quickly and hence contributes effectively to the motion of the hairpin. It is clear that although a hairpin is a localised defect its motion is highly non-local and requires the rest of the chain to move.

There are two main timescales in this problem. The longest is the time it takes a hairpin to diffuse along the length of the chain and be destroyed at the ends. This is roughly [3]

\[
\tau_L = \frac{\mu L^3}{k_B T}.
\]

One can see this by scaling \( s_1 \) by \( L \) in (15) and extracting \( L^3 \) on the right hand side which then sets the scale of \( t \) on the left hand side as is explicitly done in appendix B. More qualitatively one sees that most of the time the hairpin arms have length scaling like \( L \), actually being \( \sim L/2 \), and hence the diffusion constant is effectively \( D \sim k_B T/\mu L \). A time can then be extracted from the diffusion law \( L^2 = D\tau_L \). Thus the characteristic time scale is \( \tau_L \sim L^2/D \sim L^3\mu/k_B T \).
The second timescale is that taken by a hairpin to diffuse through its own characteristic width $\lambda$, and is approximately:

$$\tau_\lambda = \frac{\mu L \lambda^2}{k_B T}. \quad (17)$$

These timescales are widely separated because $L \gg \lambda$. We are interested in times $t$ such that $\tau_\lambda < t < \tau_L$. At shorter times than this one is looking at molecular details and the motion of thermal fluctuations or wiggles on the chain. At times longer than $\tau_L$ one needs to account for hairpin creation and destruction.

The diffusion equation (15) allows us in principle to calculate the propagator for hairpin motion:

$$G(s_1, s_0; t) = \sum_{n=0}^{\infty} \Psi_n(s_1) \Psi_n(s_0) e^{-\epsilon_n t}, \quad (18)$$

where $\epsilon_n$ and $\Psi_n$ are the eigenvalues and eigenfunctions of:

$$-\epsilon_n \Psi_n(s_1) = \frac{k_B T}{4\mu} \frac{d}{ds_1} \left\{ \frac{1}{s_1} + \frac{1}{L - s_1} \right\} \Psi_n, \quad s_1 \in (0, L), \quad (19)$$

and the eigenfunctions are orthonormal:

$$\int_0^L ds_1 \Psi_n(s_1) \Psi_m(s_1) = \delta_{nm}. \quad (20)$$

Putting the $G$ of (18) into equation (10) for $f(t)$ we obtain:

$$f(t) = \frac{1}{L^2} \sum_{n=0}^{\infty} e^{-\epsilon_n t} \int_0^L ds_p q_n^2(s_p) = \frac{1}{L^2} \sum_{n=0}^{\infty} e^{-\epsilon_n t} p(n) \quad (21)$$

where the functions $q_n(s)$ are given by

$$q_n(s_p) = \int_0^L ds_0 \Psi_n(s_0) P\left( \frac{s_p - s_0}{\lambda} \right) \quad (22)$$

and $p(n)$ by

$$p_2(n) = \frac{1}{L^2} \int_0^L ds_p q_n^2(s_p). \quad (23)$$

For the $F_2$ case one can make straightforward progress. One expects that the $\Psi_n(s_0)$ for small $n$ and for $L \gg \lambda$ not to vary rapidly on the length scale $\lambda$. Under these conditions, over the range of $s_0$ for which $F_2$ is finite (i.e. within roughly $\lambda$ of $s$) one can take $\Psi_n(s_0)$ to be constant, namely $\Psi_n(s_p)$, and $q_n(s_p)$ then becomes:

$$q_n(s_p) = \Psi_n(s_p) \int_0^L ds_0 F_2\left( \frac{s_p - s_0}{\lambda} \right) = 2\lambda \Psi_n(s_p). \quad (24)$$

The the $p(n)$ part of the summand in (21) becomes $p(n) = 4\lambda^2 \int_0^L ds_p q_n^2(s_p)$ which by orthonormality can then be evaluated trivially and there remains

$$f_2(t) = \left( \frac{3}{4} \right)^2 \left( \frac{2\lambda}{L} \right)^2 \sum_{n=0}^{\infty} e^{-\epsilon_n t}. \quad (25)$$
Fig. 4. — A log-log plot (‘s) of the scaled eigenvalues \( \lambda_n = \varepsilon_n (4\mu L^3)/(k_B T) \) of the eigenequation (19) using (59) and (60) of appendix B. We have chosen to use absorbing boundary conditions here, although the scaling of the eigenvalues is independent of the boundary conditions. Here \( L/\lambda = 20 \). Also shown is the line \( \lambda_n = 4n^2 \).

Fig. 5. — A log-log plot of \( p_2(n) \) using \( L/\lambda = 50 \) and absorbing boundary conditions. This was obtained using (51). Note that \( p_2(n) \) is approximately constant out to \( n \approx L/\lambda \).

The form of the summand is valid up to values of \( n \) where the assumption of slow variation of \( \Psi_n \), breaks down, that is for \( n < L/\lambda \). This condition can be qualitatively understood by considering the eigenfunctions to be close to sin and cos for most of their range, that is where equation (19) is insensitive to the spatial variation of the diffusion constant. Figure 5 shows \( p_2(n) \) versus \( n \) and indeed indicates a region of \( n \) small where \( p_2(n) \) is a constant.

The problem is now reduced to finding the \( n \) dependence of \( \lambda_n \). To do this precisely one
Fig. 6. — A log-log plot of $p_1(n)$ (•’s) using $L/\lambda = 50$ and absorbing boundary conditions. This was obtained using (55). Also shown is a line of the form constant $\times n^2$.

needs to solve (19). This is done in appendix B where the eigenfunctions are shown to be parabolic cylinder functions. However, the eigenvalues $\epsilon_n$ can be calculated quite accurately by ignoring the spatial dependence of the diffusion constant. It can then be seen that the eigenvalues scale as

$$\epsilon_n \sim \zeta \frac{k_B T}{4\mu L^3} n^2,$$

where $\zeta$ is a constant, in our case $\zeta = 4$. This result can be compared with the exact numerical scaling of the eigenvalues shown in figure 4 where one sees that (26) is very closely followed. For $t$ sufficiently large one can assume that the summand in (25) is valid to $n = \infty$ (since where it is invalid the exponential factor kills any contribution) and hence extract the analytic behaviour of $f_2(t)$ by converting the sum to an integral. The result is:

$$f_2(t) = \left(\frac{3}{4}\right)^2 \frac{(2\lambda)^2}{L^2} \sqrt{\frac{2}{2}} \frac{4\mu L^3}{k_B T \zeta t}.$$

As before, the $f_1(t)$ correlation function is more subtle since $F_1$ is odd and hence in $\int F_1 \Psi_n$ the gradient of $\Psi_n$ is sensed. If we express $f_1(t)$ as:

$$f_1(t) = \sum_{n=0}^{\infty} \exp(-\epsilon_n t)p_1(n)$$

then the results of appendix B tell us that $p_1(n) \sim n^2$ up to $n \approx L/\lambda$ (see Fig. 6). One can understand these numerical results qualitatively. The diffusion constant $D(s)$ is slowly varying in the middle of the chain ($s = L/2$) and for much of the chain a defect diffuses simply with constant $D$. Under these circumstances the eigenfunctions are well approximated by $\sin\left(\frac{n\pi s}{L}\right)$ or $\cos\left(\frac{n\pi s}{L}\right)$ (depending on the boundary conditions) and hence $\frac{\partial \Psi_n}{\partial s}$ introduces a factor of
\[ n/L, \text{ whereupon} \]
\[ p_1(n) \approx \left( \frac{3}{2\sqrt{2}} \right)^2 \frac{\pi \lambda}{L} n^2. \]  
(29)

We can then extract the analytic behaviour by again converting the sum to an integral to obtain:
\[ f_1(t) \approx \left( \frac{3}{2\sqrt{2}} \right)^2 \frac{\pi \lambda}{4} \frac{(4\mu L^3)}{k_B T \zeta t}^{3/2} \]  
(30)

The overall result for \( T_{1}^{-1}(\omega_0) \) for the main chain system due to hairpin motion is then:
\[ T_{1}^{-1}(\omega_0) = 2\omega_0^2 \left\{ \left( \frac{3}{4} \right)^2 \frac{(2\lambda)^2}{L^2} \frac{\sqrt{\pi}}{2} \frac{4\mu L^3}{k_B T \zeta} (2\omega_0)^{-1/2} A + \left( \frac{3}{2\sqrt{2}} \right)^2 \frac{\sqrt{\pi \lambda}}{4} \frac{(4\mu L^3)}{k_B T \zeta} \omega_0^{1/2} B \right\} \]  
(31)

where \( A \) and \( B \) are positive constants of order unity. This result is valid for frequencies \( 1/\tau_L < \omega_0 < 1/\tau_\lambda \), and may be written more simply as:
\[ T_{1}^{-1}(\omega_0) = 2\omega_0^2 \left\{ \left( \frac{\lambda}{L} \right)^2 \tau_L^{1/2} \{ A' \omega_0^{-1/2} + B' \left( \frac{\lambda}{L} \right)^2 \omega_0^{1/2} \tau_L \} \right\} \]  
(32)

If \( L/\lambda \) is large then there is a region \( 1/\tau_L < \omega_0 < \left. \frac{1}{\tau_L} \frac{L}{\lambda} \right. \) where the behaviour at low frequencies is dominated by the \( J_2(2\omega_0) \) term with a dependence \( \omega_0^{-1/2} \). The \( J_1(\omega_0) \) behaviour is quite different, scaling like \( \omega_0^{1/2} \).

4. Discussion.

We have evaluated the NMR spin lattice relaxation rates, \( T_{1}^{-1}(\omega_0) \), in highly ordered comb and main chain polymer liquid crystals. Transitions between the triplet levels of a proton pair in an external field are induced by the motion of the rigid axis that connects the protons. We have assumed that the motion in the highly ordered case is due to the random passage of molecular defects along the chain and past the proton pair in question.

Torsional defects in a comb polymer obey a simple diffusion equation where the diffusion constant does not depend on position along the chain. This reflects the local character of the dynamics. The two contributions to \( T_{1}^{-1}(\omega_0) \) are \( J_2(2\omega_0) \sim \omega_0^{-1/2} \) and \( J_1(\omega_0) \sim \omega_0^{1/2} \).

Hairpin defects in main chain systems are predicted to have a position-dependent diffusion constant, reflecting the non-local character of their dynamical evolution. The propagator for this motion has been evaluated in terms of parabolic cylinder functions which allow the numerical evaluation of the correlation functions needed to determine \( T_{1}^{-1}(\omega_0) \). For times long compared with that needed for a hairpin to diffuse through its own length, but short compared with that needed for the hairpin to explore the entire length length of the chain, the motion reflected in the \( J_1 \) and \( J_2 \) functions is apparently that of simple diffusion, \( J_1(\omega_0) \sim \omega_0^{1/2} \) and \( J_2(2\omega_0) \sim \omega_0^{-1/2} \). The results \( J_2 \) and \( J_1 \) in this limit reflect the return probability and its time derivative, \( \partial G(s_0, s_0; t) / \partial t \) respectively. \( G \) scales like \( t^{-1/2} \) for both simple diffusion and the more complicated diffusive pulley motion.

We reiterate that in the current problem the chain is moving (by diffusing along its own length in a complicated manner so that a particular arc point passes through the defect (a hairpin). This is unconnected with the quite different problem of the motion in conventional.
(non-nematic, flexible) polymers. Involved motion can be envisaged in such systems, for instance the motion of a chain as the result of diffusion of defects themselves along the chain, as in for instance de Gennes' reptation model [14] where the defects are packets of chain slack. de Gennes obtains \( G(s_0, s_0; t) \sim t^{-1/4} \) and \( J \sim \omega_0^{-3/4} \). The form of these results, depending as they do on the diffusive motions of a gas of defects, are not surprisingly qualitatively different from ours. Other models for polymer motion mediated by defect diffusion are available but they are unrelated to the current problem. We find that for our basically diffusive motion, whatever complications arise, that we retain \( t^{-1/2} \) for the return probability.

Experiment in a main chain system [6] finds \( T^{-1}_1(\omega_0) \sim \omega^{-0.65} \) (without differentiating between the \( J_1(\omega_0) \) and \( J_2(2\omega_0) \) contributions). This has been successfully fitted [6] over a wide frequency range by assuming hindered Brownian rotational motion of the rigid units considered to move independently of each other. The range of frequencies in which the results have been obtained appears to be outside the frequency range of that expected for director fluctuations. The latter have a \( \omega^{-1/2} \) signature in \( T^{-1}_1 \) which is a characteristic only of 3-D and is independent of, for instance, the extreme disparity between the different Frank nematic elastic constants which occurs in polymer liquid crystals.

We have calculated \( T^{-1}_1(\omega_0) \) in the hope that there might be a clear signature of defect motion in it. The results are partly disappointing in that the dominant form is akin to that of director fluctuations and not in agreement with the \( T^{-1}_1 \) found thus far by experiment on MC PLCS. Possible interest still remains in (i) the difference in the \( J_1 \) and \( J_2 \) contributions; (ii) the differing \( L \) dependence of the broadening due to the two components; (iii) the angular dependence of \( J_1 \) and \( J_2 \) and (iv) the form of \( T^{-1}_1 \) for side chain PLCS. Above all it is hoped that experiments will now tell us whether the models of dynamics so far considered retain the essence of polymer molecular motion in nematic environments.

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Appendix

A: The \( f_1(t) \) function for a comb.

Here we write down the analysis leading to (13). We need to evaluate:

\[
    f_1(t) = \frac{1}{L^2} \left( \frac{1}{2\pi Dt} \right)^{1/2} \int_0^L ds_p \int_0^L ds_0 \int_0^L ds_1 \exp \left( -\frac{(s_1 - s_0)^2}{2Dt} \right) F_1(\frac{s_p - s_1}{\lambda}) F_1(\frac{s_p - s_0}{\lambda}).
\]

(33)

We first calculate the \( \int_0^L ds_0 \) which may be done by changing variables to \( x = (s_p - s_0)/\lambda \) whence:

\[
    \int_{-\infty}^{\infty} \exp \left( -\frac{(s_1 - s_p + \lambda x)^2}{2Dt} \right) F(x),
\]

(34)

and where, with little error, the limits have been expanded to \( \pm \infty \). Taylor expanding the exponential to first order in \( x \) yields:

\[
    \lambda \int_{-\infty}^{\infty} dx F_1(x) \left\{ 1 - \lambda x \frac{(s_1 - s_p)}{Dt} \right\} \exp \left( -\frac{(s_1 - s_p)^2}{2Dt} \right).
\]
The first term is zero, and the second term is

\[
\frac{3\pi}{2\sqrt{2}} \lambda^2 \frac{D}{2t} \exp \left( -\frac{(s_1 - s_p)^2}{2Dt} \right). \tag{35}
\]

Substituting this into (33) and letting \( y = (s_p - s_1)/\lambda \) allows us to write the integral over \( s_1 \) as

\[
\frac{\lambda^4}{Dt \left( \frac{3}{2\sqrt{2}} \right)^2} \pi \int_{-\infty}^{\infty} dy \ y \ \text{sech} \ y \ \text{tanh} \ y \exp \left( -\frac{\lambda^2 y^2}{2Dt} \right). \tag{36}
\]

Since the \( \text{sech} \ \text{tanh} \) part of the integrand is peaked about \( y \in (-1, +1) \) and \( \lambda^2 \ll Dt \) we can replace the exponential by 1 leaving the result:

\[
\frac{\lambda^4}{Dt \left( \frac{3}{2\sqrt{2}} \right)^2} \pi^2
\]

Upon trivially integrating over \( s_p \) in (33) (13) is obtained.

A similar analysis for \( f_2 \) yields the result (12) of the text plus corrections at higher order in \( \frac{4}{t} \).

B: Solution of the hairpin diffusion equation.

In this section we solve exactly the eigenmode equation (19) for hairpins undergoing "diffusing pulley" motion. This allows us to calculate the correlation functions \( \langle F(t)F(0) \rangle \) needed in the evaluation of \( T_1^{-1}(\omega_0) \).

To do this we first change variables to \( T = tk_T/4\mu L^3 \) and \( x = 2s_1/L - 1 \), so we need to solve:

\[
-\lambda_n \psi_n(x) = \frac{d}{dx} \left\{ \left( \frac{1}{1-x^2} \right) \frac{d\psi_n(x)}{dx} \right\} \quad x \in (-1, 1). \tag{37}
\]

so that the eigenfunctions \( \Psi \) of (19) can be expressed as \( \Psi(s,t) = \psi(2s/L-1,t/T) \). The scaled eigenvalue is \( \lambda_n = \epsilon_n 4\mu L^5/k_T \). In the case where \( \lambda_n = 0 \) we have \( \psi(x) = A(x - x^3/3) + C \) where \( A \) and \( C \) are constants. To examine the cases where \( \lambda_n \neq 0 \) we define a new function \( h(x) \) via

\[
h(x) = \left( \frac{1}{1-x^2} \right) \frac{d\psi_n(x)}{dx} \tag{38}
\]

This function is effectively the flux and satisfies (from (37))

\[
-\lambda_n \psi(x) = \frac{dh(x)}{dx} \tag{39}
\]

Differentiating this, and using (38) yields the following differential equation for the flux:

\[
\frac{d^2 h}{dx^2} + \lambda_n (1-x^2) h(x) = 0. \tag{40}
\]

This may be put into a standard form by letting \( x = \gamma u \) where \( \gamma = (4\lambda_n)^{-1/4} \) so that:

\[
\frac{d^2 h}{du^2} - \left( \frac{u^2}{4} - \frac{\sqrt{\lambda_n}}{2} \right) h = 0 \tag{41}
\]
The solutions may then be expressed in terms of parabolic cylinder functions \[15\] \( M \):

\[
h(x) = \exp\left(-\frac{x^2}{2}\sqrt{\lambda_n}\right)M\left(\frac{1 - \sqrt{\lambda_n}}{4}, \frac{1}{2}, x^2\sqrt{\lambda_n}\right)
\]

(42)

and

\[
h(x) = x\exp\left(-\frac{x^2}{2}\sqrt{\lambda_n}\right)M\left(\frac{3 - \sqrt{\lambda_n}}{4}, \frac{3}{2}, x^2\sqrt{\lambda_n}\right)
\]

(43)

so that from (39) the eigenfunctions are (provided \( \lambda_n \neq 0 \)):

\[
\psi_n(x) = -x\exp\left(-\frac{x^2}{2}\sqrt{\lambda_n}\right)M\left(\frac{1 - \sqrt{\lambda_n}}{4}, \frac{1}{2}, x^2\sqrt{\lambda_n}\right)
\]

(44)

\[
+ x(1 - \sqrt{\lambda_n})\exp\left(-\frac{x^2}{2}\sqrt{\lambda_n}\right)M\left(\frac{5 - \sqrt{\lambda_n}}{4}, \frac{3}{2}, x^2\sqrt{\lambda_n}\right)
\]

and

\[
\psi_n(x) = (1 - x^2\sqrt{\lambda_n})\exp\left(-\frac{x^2}{2}\sqrt{\lambda_n}\right)M\left(\frac{3 - \sqrt{\lambda_n}}{4}, \frac{3}{2}, x^2\sqrt{\lambda_n}\right)
\]

(45)

\[
+ x^2\sqrt{\lambda_n}(1 - \sqrt{\lambda_n})\exp\left(-\frac{x^2}{2}\sqrt{\lambda_n}\right)M\left(\frac{7 - \sqrt{\lambda_n}}{4}, \frac{5}{2}, x^2\sqrt{\lambda_n}\right)
\]

We wish to calculate the functions \( q_n(s_p) \) and \( p(n) \) using the eigensolutions \( \Psi_n \) derived from the \( \psi_n \). For the \( F_2 \) case the \( q_n \) is explicitly

\[
q_n(s_p) = \int_0^L ds_0 \Psi_n(s_0) \text{sech}^2 \frac{s_p - s_0}{\lambda_h}
\]

(46)

To proceed further we need to introduce boundary conditions for the problem. On average the number of hairpins is conserved. We model this by taking zero flux boundary conditions, that is hairpins are reflected at the ends of the chain. In reality they are annihilated and recreated at the ends (in the regime where there are few hairpins and we don’t consider pair creation within the chain). The inadequacy of modelling this by reflection will not be great if we limit ourselves to times less than \( \tau_L \), the time discussed around equation (16). Thus we have:

\[
h(x) = \left(\frac{1}{1 - x^2}\right)\frac{d\psi_n(x)}{dx} = 0 \text{ at } x = \pm 1.
\]

(47)

Setting \( h(x = \pm 1) = 0 \) yields conditions for the eigenvalues \( \lambda_n \) using (42) and (43):

\[
M\left(\frac{1 - \sqrt{\lambda_n}}{4}, \frac{1}{2}, \sqrt{\lambda_n}\right) = 0
\]

(48)

and

\[
M\left(\frac{3 - \sqrt{\lambda_n}}{4}, \frac{3}{2}, \sqrt{\lambda_n}\right) = 0.
\]

(49)

With these boundary conditions and by judicious integrations by parts we need only calculate the flux for use in (22) and hence in (23). To correctly normalise the flux according to (20) we introduce a normalised flux \( H_n(x) \) which depends on the solutions (42) and (43):

\[
H_n(x) = h_n(x) \left(\frac{L}{2\lambda_n} \int_{-1}^{+1} dz (1 - z^2) h_n^2(z)\right)^{-\frac{1}{2}}
\]

(50)
Then considering first the $F_2$ case:

\[ p_2(n) = \frac{1}{2L} \int_{-1}^{+1} dyQ_n^2(y), \]

where

\[ Q_0(y) = \frac{\lambda_h}{\sqrt{L}} \left( \tanh \frac{(y+1)L}{2\lambda_h} - \tanh \frac{(y-1)L}{2\lambda_h} \right) \]

and

\[ Q_n(y) = \frac{L^2}{2\lambda_h \lambda_n} \int_{-1}^{+1} dx H_n(x) \sech^2 \left( \frac{y-x}{2\lambda_h} \right) \tanh \left( \frac{(y-x)L}{2\lambda_h} \right) \quad n > 0. \]

A similar calculation can be carried out for the $f_1$ correlation function the result being:

\[ \langle \sin \theta(t) \cos \theta(t) \sin \theta(0) \cos \theta(0) \rangle = \sum_{n=0}^{\infty} \exp(-\lambda_n t k_B T/(4\mu L^3))p_1(n) \]

where

\[ p_1(n) = \frac{1}{2L} \int_{-1}^{+1} dyR_n^2(y), \]

and

\[ R_0(y) = \frac{\lambda_h}{\sqrt{L}} \left( \sech \frac{(y-1)L}{2\lambda_h} - \sech \frac{(y+1)L}{2\lambda_h} \right), \]

\[ R_n(y) = \frac{L^2}{4\lambda_h \lambda_n} \int_{-1}^{+1} dx H_n(x) \sech \left( \frac{y-x}{2\lambda_h} \right) \left( 2 \tanh^2 \frac{(y-x)L}{2\lambda_h} - 1 \right). \quad n > 0 \]

It is also possible to do the calculation for the boundary conditions such that the hairpins fall off the end of the chain

\[ \psi(z) = 0 \quad \text{at} \quad z = \pm 1. \]

From (44) and (45) these give the following equations to be solved for the eigenvalues:

\[ -M\left( \frac{1 - \sqrt{\lambda_n}}{4}, \frac{1}{2}, \sqrt{\lambda_n} \right) + \left( 1 - \sqrt{\lambda_n} \right) M\left( \frac{5 - \sqrt{\lambda_n}}{4}, \frac{3}{2}, \sqrt{\lambda_n} \right) = 0 \]

and

\[ (1 - \sqrt{\lambda_n}) M\left( \frac{3 - \sqrt{\lambda_n}}{4}, \frac{3}{2}, \sqrt{\lambda_n} \right) + \sqrt{\lambda_n} \left( 1 - \sqrt{\lambda_n} \right) M\left( \frac{7 - \sqrt{\lambda_n}}{4}, \frac{5}{2}, \sqrt{\lambda_n} \right) = 0. \]

In this case the $Q_n(y)$ function is changed to:

\[ Q_n(y) = \lambda_h \int_{-1}^{+1} dx (1 - x^2) H(x) \tanh \left( \frac{y-x}{2\lambda_h} \right) \]

and the $R_n(y)$ function to

\[ R_n(y) = \lambda_h \int_{-1}^{+1} dx (1 - x^2) H(x) \sech \left( \frac{y-x}{2\lambda_h} \right) \]

The dependence on $n$ of $\lambda_n$, $p_2(n)$ and $p_1(n)$ for particular cases described in the captions can be seen in figures (4), (5) and (6).
References
