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NMR Transverse Relaxation Function Calculated for Constrained Polymer Chains: Application to Entanglements and Networks

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ABSTRACT: A general method is presented for calculating the NMR transverse relaxation function due to dipolar interactions between a spin pair, rigidly attatched to a constrained polymer chain. The constraints considered are those restricting the dynamics of the end-to-end vector of an arbitrary group of consecutive polymer segments. A direct application is made to the motion of polymer chains, as perceived by NMR, in deformed cross-linked systems. The ability to handle this type of constraint enables a more general hierarchical chain structure to be created, where the dynamics on one scale can be quite different from those operating on another scale, so that entanglements as well as cross-links can be included. General results are given for the relaxation function in a form that is shown to be dynamically scale invariant. The methods presented and in particular the incorporation of the constraints are entirely novel and lead to an exact calculation of the transverse NMR relaxation function. As a result the conditions under which the NMR relaxation is exponential or otherwise are clearly shown. The general results are explicitly illustrated by the case of a chain, consisting of two levels of structure, i.e., a small-scale structure with relatively fast (with respect to the NMR time) relaxation and a larger scale structure subjected to deformation and governed by slower dynamics.

1. Introduction

1.1. Measurement of the adiabatic relaxation of the transverse magnetization of nuclear spins fixed to a polymer chain is an important source of information about the semilocal and long-time relaxation processes of polymer molecules. Using this technique the dynamics of polymer chains in a variety of environments and under a range of controlled physical conditions have been investigated. Of immediate relevance for this paper are situations where the NMR active chains are constrained, as, for example, in a melt of entangled molecules[1–9] or for molecules cross-linked into a rubber network or gel,[10–21] and then subjected to a state of deformation.

It is the object of this paper to present a new and systematic calculation of the transverse relaxation function that is capable of embracing a wide class of models for the chain dynamics as well as a variety of physical constraints on the chain configurations. The basic theory underlying NMR[22–24] and its application to polymers[25–27] is well-known and in this section only the results relevant to the rest of the paper are introduced.

Since most polymer molecules are composed of proton pairs or methyl groups, this case will be used as the basic model. In a magnetic field **B**, directed along the z axis, the transverse components of the nuclear magnetization m_x, m_y of one of the protons can be considered to precess with an angular frequency ω_0 (the Larmor frequency); i.e., $m_x(t) \sim \cos \omega_0 t$ and $m_y(t) \sim \sin \omega_0 t$. The time evolution of the complex combination $m(t) = m_x(t) + im_y(t)$ can be described by the oscillator equation

$$\mathrm{d}m(t)/\mathrm{d}t = i\omega_0 m(t) \tag{1.1}$$

However, the relaxation of the transverse magnetization is not tied to the frequency ω_0, as in most polymer systems the relaxation is induced by dipolar interactions. If we consider only a proton pair, then the presence of the second spin contributes a dipolar magnetic field at the site of the first spin, which in turn leads to an additional interaction energy of $\hbar\Delta\omega(\mathbf{d})$, with

$$\Delta\omega(\mathbf{d}) = \delta(3\cos^2\alpha - 1) \tag{1.2}$$

where

$$\delta = 3\gamma^2\hbar/4d^3$$

γ is the gyromagnetic ratio, **d** is the vector distance between the two spins, and α is the angle that this vector makes with the magnetic field **B**. Within a proton pair the distance between the two spins is constant and only the angle $\alpha = \alpha(t)$ varies with time in a manner determined by the dynamics of the main-chain bonds to which the proton pair is fixed. The system can now be regarded as an oscillator with a natural frequency $\omega_0 + \Delta\omega(\alpha)$ and the oscillator equation can be integrated to give

$$m(t) = m(0)\exp(i\omega_0 t)\exp\left(\int_0^t i\Delta\omega(\alpha(t'))\,\mathrm{d}t'\right) \tag{1.3}$$

The dephasing of the transverse components of the magnetization or equivalently the broadening of the resonant line at ω_0 due to the dipole interaction is described by the second exponential term of (1.3). More precisely the transverse relaxation function $G(t)$ is defined as

$$G(t) = \left\langle\cos\left(\int_0^t \Delta\omega(\alpha(t'))\,\mathrm{d}t'\right)\right\rangle \tag{1.4}$$

where the averaging is done over all the dynamic configurations of the bond angle $\alpha(t')$ in the time interval from 0 to t.

It is entirely through the term $G(t)$ that the NMR technique is sensitive to angular anisotropic reorientation, caused by slow relaxation processes, entanglements, cross-linking, or any other process that would lead to a nonzero averaging of the dipole interaction in the time interval t.

1.2. The Second Moment Approximation and T_2. The experimental results obtained for the relaxation of the transverse nuclear magnetism are invariably analyzed in terms of a relaxation time T_2,[22] notwithstanding the fact that in a great many cases the relaxation is far from exponential. In such cases an ad hoc operational definition is employed,[7,9,25,28] leaving the experimental results open to ambiguous physical interpretations. This has been considered in a previous paper,[29] which will be referred to as paper 1. Simple exponential behavior is seen for relatively short chains and is char-

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acteristic of liquidlike behavior where the relaxation time of the chain is much shorter than a characteristic NMR time (set by the dipole interactions, to be discussed later). However, in physical situations involving temporary constraints such as entanglements or permanent constraints such as cross-links, a complete reorientation of the bond carrying the spin pair will not be possible. The persistence of angular correlations in these systems leads in the appropriate time interval to an observed nonexponential relaxation behavior, the shape of which is clearly a source of extra information about the dynamical influence of these constraints. The conditions under which a simple exponential relaxation would be obtained can be readily seen by expanding the cosine term in (1.4) as

$$G(t) \simeq 1 - \int_0^t \int \langle \Delta\omega(\alpha(t_1))\Delta\omega(\alpha(t_2)) \rangle \, dt_1 \, dt_2 + \ldots \quad (1.5)$$

In order for the second term to be at least linear in t the angular reorientational process must be sufficiently fast for the dipole field produced by the second proton in the pair to be uncorrelated at different times. That is, we must set

$$\langle \Delta\omega(\alpha(t_1))\Delta\omega(\alpha(t_2)) \rangle = T_2^{-1}\delta(t_1 - t_2) \quad (1.6)$$

then

$$G(t) \simeq 1 - t/T_2 \simeq \exp(-t/T_2)$$

Clearly for entangled and cross-linked polymer chains, which by their nature show long configurational correlation times, the replacement of the angular correlation function (1.6) by a δ function is clearly not appropriate. The corresponding experimental results on these systems, not surprisingly, show highly nonexponential behavior for the relaxation of the transverse magnetization.

A working definition for T_2, which is used independently of whether the NMR relaxations are exponential or not, is given from (1.6) as

$$T_2^{-1} = \int_0^\infty \langle \Delta\omega(0)\Delta\omega(t) \rangle \, dt \quad (1.7)$$

The use of this expression is closely allied to the second moment approximation.[7,24,30] This can be stated in the form, for a stochastic process $\chi(t)$

$$\langle \exp(i\chi(t)) \rangle \simeq \exp((-1/2)\langle \chi^2(t) \rangle) \quad (1.8)$$

In the present case the stochastic process is given by

$$\chi(t) = \int_0^t \Delta\omega(\alpha(t')) \, dt'$$

and (1.8) approximates the relaxation function as

$$G(t) \simeq \exp(-1/2 \int_0^t (t - t') \langle \Delta\omega(0)\Delta\omega(t') \rangle \, dt') \quad (1.9)$$

The second moment approximation is widely used in NMR work, but its validity is limited to molecular motions that relax faster than a time scale set by the dipolar interactions. This has been discussed in detail in paper 1,[29] using the Rouse model of polymer chain motion. For slow relaxation processes the approximation (1.8) was shown to be inadequate. A well-known example is provided by the limiting case of a chain of frozen bonds, for which an exact result is available[3] that is in total disagreement with (1.9). Consequently, its use in physical systems with permanent constraints (networks) or slow relaxations (entanglements) must be suspect.

1.3. Overview of the Paper. Several interrelated problems are posed by a systematic evaluation of the relaxation function $G(t)$ for a constrained polymer molecule. First, a choice must be made of a model for the dynamic properties of the local bond carrying the proton pair. Second, a means must be found of imposing constraints, such as cross-links, which influence the dynamical behavior of the polymer chain in a global manner. Third, a systematic method is required to perform the statistical averaging of the cosine term in (1.4) without making uncontrolled approximations. These three problems are addressed in this paper.

For the choice of a suitable model, it should be noted that the dipole interaction (1.2), which determines the relaxation function, involves the orientation $\alpha(t)$ of the proton pair with the applied magnetic field **B**. The proton pair is assumed to be rigidly attatched to the main-chain bond vector and consequently reorientates in step with the molecular motion of the chain. General theories of NMR relaxation do exist[22,31] that directly deal with the angle $\alpha(t)$ as a stochastic (Brownian motion) process; however, for polymer molecules the complexity of the local connectivity in terms of bond angles, steric hinderances, etc. renders this local bond approach unworkable from an analytic point of view. On the other hand the connectivity of the monomer units comprising the polymer chain enables the powerful and simplifying notion of scale invariance[32] to be used. This renders many of the details at the atomic level irrelevant and is particularily suited to a treatment of the dynamics of chain molecules at times considerably longer than local atomic relaxation times.

The scale-invariant approach for NMR has been successfully pioneered by Cohen-Addad in a series of papers[3-5] and the essential features will be outlined in the section 2. The immediate advantage of this model, which was demonstrated in paper 1,[29] is that a method exists enabling the statistical average of the cosine function in (1.4) to be calculated without resorting to the second moment or any similar approximation. Paper 1 was concerned with unrestricted Rouse chains; however, the main purpose of this paper is to generalize the method to a wider class of dynamical models and, in particular, to show how readily the method can accommodate the inclusion of dynamical constaints into NMR calculations. The main results are reported in section 3 and further analyzed to obtain analytic expressions in section 4. In section 5 the full problem of a chain with both a dynamic and configurational hierarchical structure is considered and applications to network and entanglement problems are made in section 6. In the Appendix various mathematical results are proved concerning Gaussian random variables together with a new method of handling dynamical constraints by using a "path integral" method. This technique has already been considered elsewhere to describe the dynamic effects of topological entanglements.[33] Adaptation to the present NMR problem is fully developed in the Appendix.

2. A Scale-Invariant Model for the NMR Transverse Relaxation Function

Scale-invariant polymer models are produced by subdividing the polymer chain into groups of sequential monomer units. The specifically local conformational details are then partially averaged so as to produce an effective coarse-scale structural unit. The statistical properties of the rescaled polymer chain, consisting of the coarse-scale units, are then considerably simplified in comparison with those of the original molecular chain. This idea has been adapted to the NMR properties of polymers, in particular the dipole interaction between spin pairs, by Cohen-Addad et al.[3-5] The original dipolar interaction (1.2), associated with a particular proton pair, is

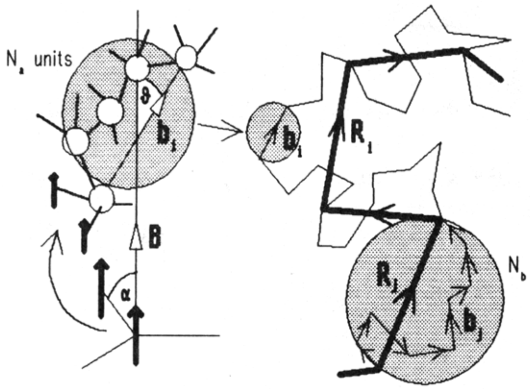

Figure 1. Left-hand side represents the Cohen-Addad model where N_a atomic bonds containing the spin pair are rescaled to form a $\{\mathbf{b}\}$ chain vector. A futher rescaling is considered with N_b of the $\{\mathbf{b}\}$ chain bond vectors forming an $\{\mathbf{R}\}$ chain vector. The dynamics of the $\{\mathbf{R}\}$ and $\{\mathbf{b}\}$ chains are considered to be quite different.

expressed in terms of the local variables d and the angle α. These are determined by the atomic structure of the particular monomer units comprising the polymer chain. Cohen-Addad showed how these could be partially averaged to give a rescaled dipole interaction that is less specific with regard to the atomic details and more appropriate for the description of NMR properties associated with slow relaxation processes.

The model of Cohen-Addad is schematically summarized on the left-hand side of Figure 1. (The full figure is used in section 5). This model considers a concurrent sequence of $s = 1, 2, ..., N_a$ atomic bonds, at a time t, each carrying an NMR spin pair (described by the interspin vector $\mathbf{d}_s(t)$), which are then treated as part of a larger submolecule. The dipole interaction energy $\hbar\Delta\omega(\alpha)$ of a particular spin pair is then average over all configurations of this submolecule, subject only to the constraint that the end-to-end vector of this submolecule is held fixed. Since the spin pairs are assumed to be rigidly attached to the structural bond vectors, the averaging over the dipole interaction (1.2) is subject to the condition that the sum over the spin pair vectors $\mathbf{d}_s(t)$ of the submolecule is also fixed, i.e.

$$\sum_{s=1}^{N_a}\mathbf{d}_s(t) = \mathbf{b}_j(t) \tag{2.1}$$

where $\mathbf{b}_j(t)$ is a given (constrained) vector. The rescaled dipole interaction $\hbar\Delta\omega^*(\mathbf{b}_j)$ to be associated with this semilocal, submolecule vector $\mathbf{b}_j$ is then calculated as the constrained average:

$$\Delta\omega^*(\mathbf{b}_j) = \delta\langle(3\cos^2\alpha - 1)\rangle_{\{\sum\mathbf{d}_s=\mathbf{b}_j\}} \tag{2.2}$$

From a dynamic point of view it is assumed that at the atomic level the rate of configurational change of the spin-pair vectors $\{\mathbf{d}(t)\}$ is much faster than the time scale $\delta^{-1} = (3\gamma^2\hbar 4d^3)^{-1}$ set by the dipole interaction. For a sufficiently large number N_a of spin-pair vectors eq 2.2 can be evaluated[34] and the leading term is

$$\Delta\omega^*(\mathbf{b}_j) = \frac{\delta\{2z_j^2(t) - x_j^2(t) - y_j^2(t)\}}{N_a^2d^2} \tag{2.3}$$

where (x_j, y_j, z_j) are the coordinates of the sub-molecule vector $\mathbf{b}_j$, with $b_j^2 = x_j^2 + y_j^2 + z_j^2$.

As a cosmetic exercise the expression (2.3) for $\Delta\omega^*(\mathbf{b}_j)$ can also be written as

$$\Delta\omega^*(\mathbf{b}_j) = \frac{\delta}{N_a}\left(\frac{b_j^2}{N_a d^2}\right)\{3\cos^2(\vartheta_j(t)) - 1\} \tag{2.4}$$

where ϑ_j is the angle between $\mathbf{b}_j$ and the magnetic field $\mathbf{B}$, as shown in Figure 1. For a sufficiently large number N_a of bonds in the submolecule, the average value of $\mathbf{b}_j$ is given by $\langle\mathbf{b}_j^2\rangle = N_a^2$ and consequently $\Delta\omega^*$ as given by (2.4) is similar in form to the original expression (1.2) but scaled by the factor N_a^{-1}. However, this form conceals the important and simplifying feature that rescaling has done more than simply to reduce the strength of the interaction by N_a^{-1}. The dynamics governing the local angular variables $\alpha(t)$ are determined by molecular conformational details, whereas for the rescaled chain they can be adequately described by a Gaussian random process. This, as was shown in paper 1, is crucial to the problem of performing the dynamical averaging involved in calculating the transverse relaxation function.

In this paper the effect of additional constraints imposed on the chain will be considered. More specifically the effect of restricting the dynamics of the end-to-end vector of the $\{\mathbf{b}\}$ chain to be an experimentally controlled function $\mathbf{R}(t)$ will be considered; i.e., the constraint

$$\mathbf{r}_N(t) = \sum_{j=1}^{N}\mathbf{b}_j(t) = \mathbf{R}(t) \tag{2.5}$$

will be imposed on the $\{\mathbf{b}\}$ chain configuration at all times t. This is the first step in constructing a hierarchical chain structure with which the effects of entanglements, cross-links, and time-dependent deformations on the NMR properties of the chain can be accounted for. In fact the constraint vector $\mathbf{R}(t)$ bears the same relationship to the entire $\{\mathbf{b}\}$ chain as the semilocal vector $\mathbf{b}_j$ does to the submolecule, built from atomic bonds. This relationship is schematically shown in Figure 1 by the two shaded circles, spanned by the vectors $\mathbf{b}_i$ and $\mathbf{R}_j$. In this way we can also demonstrate and retrospectively justify the dynamical scale invariance of the proposed model.

The constrained relaxation function for the rescaled chain can be written in the form

$$G(\Delta,t;\mathbf{R}) = \langle\cos\left(\int_0^t\Delta\omega^*(\mathbf{b}_j(t'))\,\mathrm{d}t'\right)\rangle_{\{\mathbf{r}_N(t)=\mathbf{R}(t)\}} \tag{2.6}$$

Using (2.3) for $\Delta\omega^*$ gives

$$G(\Delta,t;\mathbf{R}) = \text{real part:}\ \left\langle\exp\left(\frac{3i\Delta}{2b^2}\int_0^t\{2z_j^2(t') - x_j^2(t') - y_j^2(t')\}\,\mathrm{d}t'\right)\right\rangle_{\{\mathbf{r}_N(t)=\mathbf{R}(t)\}} \tag{2.7}$$

where

$$b^2 = N_s d^2 \quad\text{and}\quad \Delta \equiv \frac{\delta}{N_a} = \frac{\gamma^2\hbar}{2N_a d^3} = 3.77\times10^5/(N_a d^3)s^{-1} \tag{2.8}$$

for a proton pair with the distance between them d measured in angstroms. If we consider the dynamics of the submolecule bond coordinates to be independent, then the statistical problem is completely contained in the term

$$g(\Delta,t{:}X) = \left\langle\exp\left(\frac{3i\Delta}{2b^2}\int_0^t x_j^2(t')\,\mathrm{d}t'\right)\right\rangle_{\{x_N(t)=X(t)\}} \tag{2.9}$$

where $x_N(t)$ and $X(t)$ are the x components of $\mathbf{r}_N(t)$ and

$\mathbf{R}(t)$, respectively, so that

$$G(\Delta,t;\mathbf{R}) = \text{real part: } \{g(2\Delta,t{:}Z)g(-\Delta,t{:}X)g(-\Delta,t{:}Y)\} \tag{2.10}$$

To evaluate $g(\Delta,t;X)$ given by (2.9) we need a dynamicalmodel of the chain constructed from the coarse-grained submolecule vectors $\{\mathbf{b}_j\}$ and a systematic method of averaging over all the dynamical configurations of this scale-invariant chain. These topics are considered in the next section.

3. Calculation of the Constrained Transverse Relaxation Function

3.1. Some Exact Results Involving Gaussian Variables. The principal theoretical problem to be considered in this section is the evaluation of the component $g(\Delta,t;X)$, given by (2.9), of the full relaxation function $G(\Delta,t;\mathbf{R})$. To maintain as much generality as possible a minimum of modeling will be used to describe the dynamics of the chain. In particular it is assumed that the dynamics of the submolecule vectors $\{\mathbf{b}_j(t)\}$ are "driven" by Gaussian random forces $\{\xi_j(t)\}$ through linear equations of the form

$$\mathbf{b}_j(t) = \sum_{k=1}^{N} \int_{-\infty}^{t} G_{jk}(t-t')\xi_j(t')\,\mathrm{d}t' \tag{3.1}$$

Both the Rouse[35] and the tube model of Edwards[36] can be expressed in this form by an appropriate choice of "Green's" function $G_{jk}(t-t')$. The linearity of eq 3.1 ensures that the time evolution of $\mathbf{b}_j(t)$ also forms a Gaussian random process, which in turn determines that the statistical dynamic properties are completely described by the bond correlation function

$$\gamma_{jk}(t-t') = \langle \mathbf{b}_j(t)\cdot\mathbf{b}_k(t')\rangle \tag{3.2}$$

In order to evaluate $g(\Delta,t{:}X)$ given by (2.9), two exact results for Gaussian random variables are used together with a "path integral" method of handling dynamic constraints. These are essentially mathematical in content and are discussed and proven in the Appendix.

To introduce the results into the discussion at this point it is most convenient to state them in a matrix form. Consider $\mathbf{b}_j$ as a column matrix of T elements:

$$\mathbf{b}_j \equiv \{b_j(1), b_j(2), ..., b_j(n), ..., b_j(T)\} \qquad \text{for } j = 1\text{–}N$$

In other words the time is treated as a discrete variable and the interval from 0 to t is divided up into T intervals. The elements $\{b_k(n)\}$ are considered as Gaussian random variables described by the correlation matrix γ_{ij}

$$\gamma_{ij} = \{\gamma_{ij}(n,m)\} = \{\langle b_i(n)b_j(m)\rangle\}$$

Then for any nonsingular $T \times T$ matrix $\mathbf{M}$, the following result is proven in the Appendix:

$$[\det(\mathbf{M})]^{1/2}\langle \exp((1/2)\mathbf{b}_j\cdot\mathbf{M}\cdot\mathbf{b}_j)\rangle_0 = [\det[\mathbf{M}\cdot(1-\gamma_{jj}\cdot\mathbf{M})^{-1}]]^{1/2} \tag{3.3}$$

where the averaging is not subject to any constraint. The terms det ($\mathbf{M}$) and $\mathbf{M}^{-1}$ refer to the determinant and inverse of $\mathbf{M}$, respectively, and terms such as $\mathbf{b}_j\cdot\mathbf{M}\cdot\mathbf{b}_j$ are matrix products, i.e.

$$\mathbf{b}_j\cdot\mathbf{M}\cdot\mathbf{b}_j = \sum_{nm=1}^{T} b_j(n)M(n,m)b_j(m)$$

When the elements $\{b_j(n)\}$ are subjected to the constraint

$$\sum_{k=1}^{N} b_k(n) = R(n) \qquad \text{for each } n = 1\text{–}T \tag{3.4}$$

where $\{R(n)\}$ forms the column matrix

$$\mathbf{R} = \{R(1), R(2), ..., R(T)\}$$

then the following result, also proven in the Appendix, holds

$$[\det(\mathbf{M})]^{1/2}\langle \exp((1/2)\mathbf{b}_j\cdot\mathbf{M}\cdot\mathbf{b}_j)\rangle_{\text{constraint},\sum\mathbf{b}_j=\mathbf{R}} = [\det(\mathbf{Q})]^{1/2}\exp\left(\frac{1}{2}\mathbf{R}\cdot\frac{\mathbf{Q}}{N^2}\cdot\mathbf{R}\right) \tag{3.5}$$

where

$$\mathbf{Q}^{-1} = \mathbf{M}^{-1} - \Gamma \tag{3.6a}$$

and

$$\Gamma = \gamma_{jj} - N^{-1}\sum_{i=1}^{N}\gamma_{ij} \tag{3.6b}$$

The application of the mathematical result (3.5) to the physical problem can be made if the time is treated as a discrete variable and the interval from 0 to t is divided up into T intervals of duration ϵ, with $t = \epsilon T$, $t' \to t_n = n\epsilon$, and $\int_0^t \mathrm{d}t' = \epsilon\sum_{n=0}^{n=T}$. Ultimately the limit $\epsilon \to 0$ will always be used to recover the continuous time result, but this imagined discretization of the time interval is a conceptual help.

The original problem of calculating $g(\Delta,t{:}X)$, posed by (2.9), is obtained by setting

$$\mathbf{M} = \frac{3i}{b^2}\Delta\epsilon 1 \quad \text{i.e.,} \quad M(n,m) = \frac{3i}{b^2}\Delta\epsilon\delta_{\mathrm{nm}}$$

and by using (3.6a) to give

$$\mathbf{Q} = \frac{3i}{b^2}\Delta\epsilon\left(1 - \frac{3i}{b^2}\Delta\epsilon\mathbf{\Gamma}\right)^{-1} \tag{3.7}$$

With this choice for $M(t_n,t_m)$ eq 3.5 gives

$$g(\Delta,t;\mathbf{R}) = \left\langle \exp\left[\frac{3i}{2b^2}\Delta\epsilon\sum_{n}^{T} b(n)^2\right]\right\rangle_{\text{constraint}} = \frac{1}{\left[\det\left(1-\frac{3i}{b^2}\Delta\mathbf{\Gamma}\right)\right]^{1/2}}\exp\left[\frac{3i}{2Nb^2}\times \frac{\Delta}{N}\epsilon^2\sum_{n}^{T}\sum_{m}^{T}R(n)\mathbf{S}(n,m)R(m)\right] \tag{3.8}$$

where

$$\epsilon\mathbf{S}^{-1} = 1 - \frac{3i}{b^2}\Delta\epsilon\mathbf{\Gamma}$$

Although (3.8) represents an exact solution of the problem set by (2.9), it is still of little practical use unless a prescription is given of how the determinant and inverse of $\mathbf{S}^{-1} = (1 - 3i\Delta\epsilon\mathbf{\Gamma})$ are to be calculated. This problem is tackled by means of a Fourier transform on the finite time interval 0–t. Some attention is given to this in the next section, because it is an unusual application of the Fourier transform technique. Normally this transform is used to change from a functional dependence on time to one on frequency; however, in this case the interval over which the transform is defined itself depends on t. The resulting transform retains a dependence on t, which will be exploited.

3.2. Fourier Representation on a Finite Time Interval. The fundamental matrix in this work is the $\{\mathbf{b}\}$ chain bond vector correlation function $\gamma(n,m) \equiv \gamma(t_n,t_m)$, which is only a function of $(t_n - t_m)$ or $(n - m)$. Normally such matrix forms are "diagonalized" by a Fourier transform taken over the entire time interval $-\infty < t_n, t_m < \infty$; e.g.,

$$\gamma(\omega) = \int_{-\infty}^{\infty} \mathrm{d}\tau\, \gamma(\tau) \exp(i\omega\tau) \tag{3.9}$$

In a diagonal representation the inverse and determinant of a matrix are then trivial. However, the problem at hand, i.e., (2.9) in continuous time or (3.8) in discrete time, is expressed only over the finite interval (0–t), for which the required diagonalization no longer occurs. Instead a discrete Fourier transform can be defined on the interval (0–t), whereby, for example, the column matrix $\mathbf{b} \equiv \{b(1), b(2), ..., b(T)\}$ can be transformed to $\mathbf{b}_\alpha \equiv \{b_{\alpha 1}, b_{\alpha 2}, ..., b_{\alpha T}\}$, where

$$b_\alpha = T^{-1} \sum_{m=0}^{T} b(m) \exp(2\pi i(\alpha m)/T) \tag{3.10}$$

The index α is an integer also chosen in the range 0 to T. In the continuous time notation, (3.10) becomes

$$b_{\alpha;t} = \frac{1}{t} \int_0^t \mathrm{d}t'\, b(t') \exp\left(2\pi i \frac{\alpha t'}{t}\right) \tag{3.11}$$

The notation $b_{\alpha;t}$ emphasizes that the transform is based on a finite interval (0–t). Essentially $b_{\alpha;t}$ represents the configurational dynamics of the $\{\mathbf{b}\}$ chain expressed as normal modes; however, over a finite interval they are not strictly independent. For example, the correlation function of these modes $\gamma_{\alpha,\beta;t}$ or the derived quantity $\boldsymbol{\Gamma}_{\alpha,\beta;t}$ can be defined as

$$\boldsymbol{\Gamma}_{\alpha,\beta;t} = T^{-2} \sum_{n,m=0}^{T} \boldsymbol{\Gamma}(t_n - t_m) \exp[2\pi i(\alpha t_n + \beta t_m)/T] = \frac{1}{t^2} \int \int_0^t \mathrm{d}t'\, \mathrm{d}t''\, \boldsymbol{\Gamma}(t' - t'') \exp\left[2\pi i \frac{(\alpha t' + \beta t'')}{t}\right] \tag{3.12}$$

This does not appear to achieve anything, since $\boldsymbol{\Gamma}_{\alpha,\beta;t}$ is now a function of three variables, α, β, and t. It is only when the variables t', t'' extend over the infinite range $-\infty < t',t'' < \infty$ does $\boldsymbol{\Gamma}_{\alpha,\beta;t}$ become strictly diagonal, i.e., $\boldsymbol{\Gamma}_{\alpha,\beta;t} = \boldsymbol{\Gamma}_\alpha \delta_{\alpha,-\beta}$. Nevertheless the transform (3.10) is useful as a source of systematic approximations. To make this clear the substitutions $x = t' - t''$ and $y = t' - t''$ are made in the integral of (3.12), so that $\boldsymbol{\Gamma}_{\alpha,\beta;t}$ can be written as

$$\boldsymbol{\Gamma}_{\alpha,\beta;t} = \frac{1}{2t^2} \int_{-t}^{t} \mathrm{d}x \int_{|x|/2}^{t-|x|/2} \mathrm{d}y\, \boldsymbol{\Gamma}(x) \times \exp\left[\pi i x \frac{(\alpha - \beta)}{2t}\right] \exp\left[\pi i y \frac{(\alpha + \beta)}{2t}\right] \tag{3.13}$$

The y integral can be done, but the cases $\alpha + \beta = 0$ and $\alpha + \beta \neq 0$ should be treated separately as they crucially affect the relative magnitudes of the diagonal ($\beta = -\alpha$) and off-diagonal ($\beta \neq \alpha$) terms. For the "diagonal" term $\beta = -\alpha$ the y integral gives $(t - x)$ and $\boldsymbol{\Gamma}_{\alpha;t} \equiv \boldsymbol{\Gamma}_{\alpha,-\alpha;t}$ can be written as

$$\boldsymbol{\Gamma}_{\alpha;t} = \frac{1}{t^2} \int_0^t \mathrm{d}x\, (t - x) \boldsymbol{\Gamma}(x) \cos(2\pi x \alpha/t) \tag{3.14}$$

Since $\Gamma(t')$ is defined in (3.6b) in terms of the bond correlation function, then for times t' greater than the longest dynamical relaxation time, the integration in (3.14) can be extended to ∞ and $\boldsymbol{\Gamma}_{\alpha;t}$ has as its leading term the scaled form

$$\boldsymbol{\Gamma}_{\alpha;t} \sim \frac{1}{t} \int_0^\infty \mathrm{d}t'\, \Gamma(t') \cos(2\pi t' \alpha/t) \sim t^{-1} \int_0^\infty \mathrm{d}t'\, \boldsymbol{\Gamma}(t') \sim t^{-1} \quad \text{for large } t \tag{3.15}$$

Whereas for the off-diagonal terms $\alpha + \beta \neq 0$, the y integral in (3.13) can be done and $\boldsymbol{\Gamma}_{\alpha,\beta;t}$ written in the form

$$\boldsymbol{\Gamma}_{\alpha,\beta;t} = \frac{1}{t^2} \int_0^t \mathrm{d}x\, \Gamma(x) \times \cos\left[\frac{2\pi x}{t} \frac{(\alpha - \beta)}{2}\right] \left\{\sin\left[\frac{2\pi x}{t} \frac{(\alpha + \beta)}{2}\right]\right\} \frac{t}{\pi(\alpha + \beta)} \sim t^{-2} \int_0^t \mathrm{d}x\, \boldsymbol{\Gamma}(x) x \sim t^{-2} \quad \text{for large } t \tag{3.16}$$

Thus for times greater than the characteristic time of the chain dynamics the diagonal terms are dominant.

In the other limit of $t \rightarrow 0$, it can be seen from (3.14) that the single diagonal term $\alpha = -\beta = 0$ gives the dominant contribution, since the other diagonal terms and all the off-diagonal terms involve cosine and sine factors that are rapidly oscillating in this limit. In section 6 an expression, (6.3), is given for $\boldsymbol{\Gamma}_{\alpha,\beta;t}$, evaluated for a single relaxation time process, which explicitly illustrates these general features.

The advantage of this representation is that the use of the diagonal term, given by (3.14), will give the correct result in the two limits $t \rightarrow 0$ and $t \rightarrow \infty$. In paper 1 it was shown how the off-diagonal terms can be treated in a perturbation expansion to give systematic corrections for times on the order of the bond correlation relaxation times. Experience showed that they were small and that the use of the diagonal terms gave a good result for the range of times for which the relaxation function was measurable. In the remainder of this paper only the diagonal terms are used, in which case explicit expressions can be given for the formal terms in (3.8); e.g.

$$\det\left(1 - \frac{3i}{b^2}\Delta\boldsymbol{\Gamma}\right) = \prod_\alpha \left(1 - \frac{3i}{b^2}\Delta t \boldsymbol{\Gamma}_{\alpha;t}\right) \tag{3.17a}$$

and

$$S(t',t'') = \sum_{\alpha=-\infty}^{\infty} S_{\alpha;t} \exp\left[-2\pi i \alpha \frac{(t' - t'')}{t}\right] \tag{3.17b}$$

where

$$S_{\alpha;t} = \frac{1}{t} \frac{1}{1 - \frac{3i}{b^2}\Delta t \boldsymbol{\Gamma}_{\alpha;t}} \tag{3.17c}$$

The full result can be written in the continuous time notation as

$$g(\Delta,t{:}X) = \left\langle \exp\left[\frac{3i}{2b^2}\Delta \int_0^t x^2(t')\, \mathrm{d}t'\right] \right\rangle_{\text{constraint}} = \left\{\prod_\alpha \left(1 - \frac{3i}{b^2}\Delta t \boldsymbol{\Gamma}_{\alpha;t}\right)^{-1/2}\right\} \times \exp\left(\frac{3i}{2Nb^2}\frac{\Delta}{N}\right) \int_0^t \int_0^t X(t') S(t' - t'') X(t'')\, \mathrm{d}t'\, \mathrm{d}t'' \tag{3.18}$$

and for the unconstrained chain, using (3.3)

$$g(\Delta,t{:}X) = \left\langle \exp\left[\frac{3i}{2b^2}\Delta \int_0^t x^2(t')\, \mathrm{d}t'\right] \right\rangle_0 = \left\{\prod_\alpha \left(1 - \frac{3i}{b^2}\Delta t \gamma_{\alpha;t}\right)^{-1/2}\right\} \tag{3.19}$$

These expressions, (3.18) and (3.19), are major results of this paper, as they provide calculable explicit expressions for the relaxation function $g(\Delta,t{:}X)$, from which the full relaxation function $G(\Delta,t;\mathbf{R})$ of the transverse magnetization can be found, using (2.10). The only input to this result, which depends on a physical model for the dynamics of the chain, is the bond vector correlation function $\gamma_{ij}(t) = \langle x_i(0) x_j(t) \rangle$. This determines the function

$\mathbf{\Gamma}_{\alpha;t}$ by means of (3.6b) and the transform (3.14); i.e.

$$\mathbf{\Gamma}_{\alpha;t} = \frac{2}{t}\int_0^t \mathrm{d}t'\,(t-t')\cos\left[\frac{2\pi t'}{t}\mathbf{\Gamma}(t')\right] = \frac{2}{t}\int_0^t \mathrm{d}t'\,(t-t')\cos\left(\frac{2\pi t'}{t}\right)\{\langle x_j(0)x_j(t')\rangle - N^{-1}\sum_{i=1}^{N}\langle x_i(0)x_j(t')\rangle\} \quad (3.20)$$

and $S(t'-t'')$ from (3.17b) and (3.17c).

For a one-bond chain ($N = 1$) the result is readily checked since the term in brackets in (3.20) cancels and $\mathbf{\Gamma}_{\alpha,t} = 0$. It then follows from (3.17b,c) that

$$S_{\alpha;t} = t^{-1} \quad \text{and} \quad S(t_1 - t_2) = \delta(t_1 - t_2)$$

so that

$$g(\Delta,t) = \exp\left[\frac{3i\Delta}{2b^2}\int_0^t \mathrm{d}t'\,X(t')^2\right]$$

which is in agreement with starting expression (2.9) when the bond vector $\mathbf{b}_j(t)$ is set equal to the constraint $\mathbf{R}(t)$.

4. Scale Invariance and Long-Time Behavior

4.1. Dynamical Scale Invariance. An immediate application of this result is to confirm the original scaling procedure introduced by Cohen-Addad and used in section 2 to define the scaled NMR submolecule. In this initial rescaling no account was taken of the dynamics of the original atomic bonds, essentially they were considered as being much faster than the time scale set by the dipolar interaction. In the main part of this paper a rescaling at a larger scale has been considered where a chain consisting of N of these submolecule bonds has been constrained so that the chain end-to-end vector, at a time t, is fixed at the value $\mathbf{R}(t)$. In the limit that the relaxation times of the chain between the constrained ends are very fast, a rescaled version of the original submolecule model should be obtained. That this is the case can be seen by examining the behavior of the bond correlation function $\gamma_{ij}(t)$ in the α representation

$$\gamma_{ij\ \alpha;t} = \frac{1}{t^2}\int_0^t \mathrm{d}t_1\,(t-t_1)\langle x_i(0)x_j(t_1)\rangle \cos(2\pi x\alpha/t) \quad (4.1)$$

The limit of very fast dynamics for the bond vectors $\{x_j(t)\}$ is obtained by letting the slowest relaxation time $\tau \to 0$. Both the transformed correlation functions $\gamma_{ij\ \alpha;t}$ and $\mathbf{\Gamma}_{\alpha;t} \approx \tau$ and consequently for $t \gg \tau$ tend to zero as $\tau \to 0$. In this limit the functions $S_{\alpha;t}$ and $S(t_1 - t_2)$ are determined from (3.17c,b) once again as

$$S_{\alpha;t} = t^{-1} \quad \text{and} \quad S(t_1 - t_2) = \delta(t_1 - t_2)$$

and therefore the relaxation function (3.18) can be written as

$$g(\Delta\tau) = \exp\left[\frac{3i\Delta^*}{2b^{*2}}\int_0^t \mathrm{d}t_1\,X^2(t_1)\right] \quad (4.2)$$

where $\Delta^* = \Delta/N$ and $b^{*2} = Nb^2$ This has exactly the same form as the unconstrained starting expression (2.9) except for the rescaling of the dipole interaction strength $\Delta \to \Delta^*$ and the size of the bond vector $b \to b^*$ and demonstrates the dynamical scale invariance of the original model.

4.2. Analytic Long-Time Results. When the time t over which the relaxation of the transverse components of the nuclear magnetization is measured is larger than the longest relaxation time of the bond correlation function $\gamma_{ij}(t)$, the infinite product of factors occurring in (3.18) and (3.19) for $g(\Delta,t;X)$ and $g(\Delta,t)$ can be usefully simplified. The unrestricted result (3.19) for $g(\Delta,t)$ will be used, i.e.

$$g(\Delta,t) = \prod_\alpha\left\{1 - \frac{3i\Delta t}{b^2}\gamma_{\alpha;t}\right\}^{-1/2} \quad (4.3)$$

In the large time limit $\gamma_{\alpha;t}$ can be written in the scaled form $\gamma^*(\alpha/t)$, given by

$$\gamma^*(\alpha/t) \equiv t\gamma_{\alpha;t} = 2\int_0^\infty \mathrm{d}t'\,\gamma(t')\cos\left(\frac{2\pi t'\alpha}{t}\right)$$

The infinite product of factors in (4.3) then becomes

$$\prod_\alpha\left\{1 - \frac{3i\Delta t}{b^2}\gamma_{\alpha;t}\right\}^{-1/2} = \exp\left[-\frac{1}{2}\sum_\alpha \ln\left\{1 - \frac{3i\Delta}{b^2}\gamma^*(\alpha/t)\right\}\right] \quad (4.4)$$

For large times the sum over α can be converted to an integral over the variable $\omega = 2\pi\alpha/t$ according to

$$\sum_\alpha = \frac{t}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}\omega$$

and (4.4) can be written as the exponential

$$g(\Delta,t) = \exp[-\beta(\Delta,N)t] \quad (4.5)$$

where

$$-\beta(\Delta,N) = \int_0^\infty \frac{\mathrm{d}\omega}{2\pi}\ln\left\{1 - \frac{3i\Delta}{b^2}\gamma^*(\omega)\right\} \quad (4.6a)$$

and

$$\gamma_{ij}^*(\omega) = \int_0^\infty \mathrm{d}t_1\,\langle x_i(0)x_j(t_1)\rangle\cos(\omega t_1) \quad (4.6b)$$

In principle $\beta(\Delta,N)$ is a complex quantity so that the complete relaxation function $G(\Delta,t)$, given by (2.10), has the form

$$G(\Delta,t) = \exp(-\lambda t)\cos(\Omega t) \quad (4.7)$$

where the real part $\lambda = \{\beta(2\Delta,N) + 2\beta(-\Delta,N)\}$ and the imaginary part $\Omega = \{\beta(2\Delta,N) + 2\beta(-\Delta,N)\}$.

The phenomenological transverse relaxation time T_2 and the status of the widely used second moment approximation can be discussed in the context of this result. Briefly, if the bond vector correlation function satisfies

$$\langle x(0)_i x_j(t_1)\rangle \sim 0 \quad \text{for} \quad t > \tau_{\max}$$

then from (4.6b) it follows that $\gamma_{ij}(\omega) < b^2\tau_{\max}$. In which case, for $\Delta\tau_{\max} < 1$ the logarithm in (4.6a) can be expanded to give

$$\beta(\Delta,N) = \frac{3i\Delta}{b^2}\int_0^\infty \frac{d\omega}{2\pi}\gamma^*(\omega) + \frac{1}{2}\left\{\frac{3\Delta}{b^2}\right\}^2\int_0^\infty \frac{\mathrm{d}\omega}{2\pi}[\gamma^*(\omega)]^2 + \ldots$$

and $\Omega = \text{imag}\ \{\beta(2\Delta,N) + 2\beta(-\Delta,N)\} = 0$ to order $(\Delta\tau_{\max})^2$ because of the cancellation of the linear terms. Hence the relaxation function $G(\Delta,t)$ is purely exponential and the decay rate λ can be identified with the transverse relaxation time T_2^{-1}; i.e.

$$\lambda \equiv T_2^{-1} = 27\frac{\Delta^2}{b^2}\int_0^\infty \frac{\mathrm{d}\omega}{2\pi}[\gamma^*(\omega)]^2$$

Using (4.6b) for $\gamma^*(\omega)$ gives

$$T_2^{-1} = 27\frac{\Delta^2}{b^2}\int_0^\infty \mathrm{d}t\,[\langle x_j(0)x_j(t)\rangle]^2$$

This is just the result of the second moment approximation. The calculation of T_2 for the Rouse model of polymer dynamics, its dependence on molecular weight, and its relaxation spectra are described in detail in paper

1,[29] where the effect of the cosine factor in (4.7) is also discussed.

5. Constrained Hierarchical Systems

Networks and entanglements introduce into polymer systems additional structures at large scales and long times, which can also be probed by using the relaxation of transverse magnetization. To investigate these aspects within the framework proposed in this paper the hierarchical system shown schematically in Figure 1 will be used.

As was discussed in section 2, the original atomic bond vectors constituting the polymer chain are rescaled into groups of containing N_a consecutive atomic bonds. Each individual group **j** is spanned by an end-to-end vector $\mathbf{b}_j$. The dynamics of the $\{\mathbf{b}_i\}$ vectors is described, as before, by the correlation function

$$\gamma_{ij}^{(b)}(t) = \langle \mathbf{b}_i(0)\cdot\mathbf{b}_j(t)\rangle$$

A new grouping of N_b consecutive $\{\mathbf{b}_i\rangle$ $(i = 1, ..., N_b)$ vectors is considered, spanned by an end-to-end vector $\mathbf{R}_J$. The $\{\mathbf{R}_J\}$ $(J = 1, ..., N_R)$ is now considered to form at an even larger scale chain consisting of N_R large-scale segments based on the $\{\mathbf{R}_J\}$ vectors and governed by dynamics quite different from that operating on the $\{\mathbf{b}_i\}$ vector subchains. The dynamics of the $\{\mathbf{R}_J\}$ vector chain is described by a new correlation function $\gamma_{IJ}^{(R)}$:

$$\gamma_{IJ}^{(R)}(t) = \langle \mathbf{R}_I(0)\cdot\mathbf{R}_J(t)\rangle \qquad (5.1)$$

For example, in entangled systems the $\{\mathbf{R}_J\}$ chain could be used to describe large-scale and long-time reptation dynamics, while the $\{\mathbf{b}_j\}$ subchains would still be governed by relatively fast Rouse dynamics. Alternatively, in network systems the $\{\mathbf{R}_J\}$ chain could be used to label the network junction points. Again the dynamics of these points will be different from that of the subchains. This hierachy could be indefinitely extended, however, if no further restrictions are placed on the $\{\mathbf{R}_J\}$ vectors, then the relaxation function for the hierarchical chain is, in matrix notation

$$g(\Delta,t;\mathbf{b},\mathbf{R}) = \langle\langle \exp[(1/2)\mathbf{b}\cdot\mathbf{M}\cdot\mathbf{b}]\rangle_{\sum\mathbf{b}=\mathbf{R}}\rangle_{\{\mathbf{R}\}} \qquad (5.2)$$

The nested averages are readily evaluated. First, from (3.5), the constrained inner average is obtained as

$$g(\Delta,t;\mathbf{b},\mathbf{R}) = \langle\langle \exp[(1/2)\mathbf{b}\cdot\mathbf{M}\cdot\mathbf{b}]\rangle_{\sum\mathbf{b}=\mathbf{R}}\rangle_{\{\mathbf{R}\}} = \frac{[\det[\mathbf{M}\cdot(1-\boldsymbol{\Gamma}^{(b)}\cdot\mathbf{M})^{-1}]]^{1/2}}{(\det\mathbf{M})^{1/2}}\left\langle \exp\left[\frac{1}{2}\mathbf{R}\cdot\frac{\mathbf{M}}{N^2}\cdot(1-\boldsymbol{\Gamma}^{(b)}\cdot\mathbf{M})^{-1}\cdot\mathbf{R}\right]\right\rangle_{\{\mathbf{R}\}} \qquad (5.3)$$

where

$$\boldsymbol{\Gamma}^{(b)} = \gamma^{(b)} - N_b^{-1}\sum\gamma^{(b)}$$

Set $\mathbf{Q}^{-1} = \mathbf{M}^{-1} - \boldsymbol{\Gamma}^{(b)}$; then (5.3) can be written as

$$g(\Delta,t;\mathbf{b},\mathbf{R}) = \left\langle \frac{(\det\mathbf{Q})^{1/2}}{(\det\mathbf{M})^{1/2}}\exp\left(\frac{1}{2}\mathbf{R}\cdot\frac{\mathbf{Q}}{N^2}\cdot\mathbf{R}\right)\right\rangle_{\{\mathbf{R}\}}$$

and evaluated, using (3.3), to give

$$g(\Delta,t;\mathbf{b},\mathbf{R}) = N[\det[\mathbf{Q}\cdot(1 - N_b^{-2}\gamma^{(R)}\cdot\mathbf{Q})^{-1}]]^{1/2}/(\det\mathbf{M})^{1/2} = N(\det[\mathbf{W}])^{1/2}/(\det\mathbf{M})^{1/2} \qquad (5.4)$$

where

$$N_b^{-2}\mathbf{W}^{-1} = \mathbf{Q}^{-1} - N_b^{-2}\gamma^{(R)}$$

As before the physical problem at hand is given by $\mathbf{M} = 3i\Delta\epsilon/b^2 1$ so that

$$\frac{3i\Delta\epsilon}{N_b^2 b^2}\mathbf{W}^{-1} = \mathbf{1} - \frac{3i\Delta\epsilon}{b^2}\left\{\boldsymbol{\Gamma}^{(b)} + \frac{\gamma^{(R)}}{N_b^2}\right\}$$

and hence

$$g(\Delta,t;\mathbf{b},\mathbf{R}) = \det\left\{1 - \frac{3i\Delta\epsilon}{b^2}\left\{\boldsymbol{\Gamma}^{(b)} + \frac{\gamma^{(R)}}{N_b^2}\right\}\right\}^{-1/2} \qquad (5.5)$$

By use of the same transformation (3.14) for the α representation, the result for the relaxation function $g(\Delta,t;\{b\},\{R\})$ for the hierachical chain $(\{b\},\{R\})$ can be written as

$$g(\Delta,t;\{b,R\}) = \prod_\alpha\left\{1 - 3i\left(\frac{\Delta t}{b^2}\Gamma_\alpha^{(b)} + \frac{\Delta t}{N_b}\frac{\gamma_{\alpha}^{(R)}}{N_b b^2}\right)\right\}^{-1/2} \qquad (5.6)$$

This is a major result of this paper for the investigation of the NMR properties of networks and entangled or otherwise constrained systems. The required input consists of the dynamic correlation functions $\langle b_k(0)b_j(t')\rangle$ and $\langle R_J(0)R_J(t')\rangle$ for the subchains $\{\mathbf{b}\}$ and $\{\mathbf{R}\}$ expressed as Fourier transforms over the finite time interval 0–t; i.e.

$$\Gamma_\alpha^{(b)} = \frac{1}{t^2}\int_0^t \mathrm{d}t'\,(t-t')\cos\left(2\pi t'\frac{\alpha}{t}\right)\{\langle b_j(0)b_j(t')\rangle - N^{-1}\sum_k\langle b_k(0)b_j(t')\rangle\} \qquad (5.7a)$$

and

$$\gamma_\alpha^{(R)} = \frac{1}{t^2}\int_0^t \mathrm{d}t'\,(t-t')\cos\left(2\pi t'\frac{\alpha}{t}\right)\langle R_J(0)R_J(t')\rangle \qquad (5.7b)$$

As a check on this result and especially the structure of the term $\Gamma_\alpha^{(b)}$, it is interesting to consider the case when the dynamics of the $\{\mathbf{R}\}$ chain are the same as those of the $\{\mathbf{b}\}$ subchains. In this case part of the hierarchical structure, shown in Figure 1, should disappear. This is reflected in a partial cancellation between the $\gamma^{(R)}$ and $\Gamma^{(b)}$ correlation functions. To see this recall that since $\mathbf{R} = \sum\mathbf{b}$ and if the dynamics are the same, then

$$\langle R_J(0)R_J(t')\rangle_{\{R\}} = \sum_{kj=1}^{N_b}\langle b_k(0)b_j(t')\rangle_{\{b\}}$$

i.e.

$$\gamma_{jj}^{(R)} = N_b\gamma_{jj}^{(b)}$$

With the definition of Γ_α from (5.7a), the combination $(\Gamma_\alpha^{(b)} + \gamma_\alpha^{(R)}/N_b^2)$ in the denominator of (5.6) becomes

$$\left(\Gamma_\alpha^{(b)} + \frac{\gamma_\alpha^{(R)}}{N_b^2}\right) = \gamma^{(b)} - N^{-1}\sum\left(\gamma^{(b)} + \frac{\gamma_\alpha^{(R)}}{N_b^2}\right) = \gamma^{(b)}$$

i.e.

$$g(\Delta,t;\{b,R\}) = \prod_\alpha\left\{1 - 3i\frac{\Delta t}{b^2}\gamma_\alpha^{(b)}\right\}^{1/2} \qquad (5.8)$$

As expected this is the result for an unconstrained chain of $\{\mathbf{b}\}$ bonds.

It is not the intention in this paper to present a detail account of the application of (5.6) to the experimental NMR properties of entangled or network systems. However, in order to demonstrate the main features and principal experimental consequences of the theoretical results derived in this paper a simplified model based on the

Rouse and reptation models for the chain dynamics is considered in the next section.

6. A Model System with Applications to Networks and Entanglements

It has been shown in some generality that in order to calculate the transverse spin–spin relaxation function with a hierarchical scale-invariant model the only inputs needed are the unconstrained bond vector correlation functions of the chains involved at each level of the hierarchy. In the present case, represented by eq 5.6, only two levels of chain dynamics were considered as represented by the {**b**} and {**R**} subchains. The {**R**} subchains were introduced to describe more global phenomena such as entanglements or networks. The {**b**} subchain represents the smaller (and faster) level of description and is most appropriately described by the Rouse model.[35] In this model the bond vector correlation function is given as a spectrum of relaxation times:

$$\langle \mathbf{b}_j(0)\cdot\mathbf{b}_j(t)\rangle = 2b^2\sum_{p=0}^{N_b}\sin^2\left(\frac{\pi p j}{N_b}\right)\exp(-t/\tau_p) \tag{6.1a}$$

p is an integer variable representing the normal modes associated with a linear chain and τ_p is the relaxation time of the pth mode.

$$\tau_p = \tau/\sin^2(\pi p/2N_b) \sim 4\tau N_b^2/p^2$$

τ is the fastest relaxation time (i.e., the $p = N$ mode) and is essentially a parameter of the model, while the slowest relaxation time depends on the degree of polymerization N as N^2. In this paper the {**b**} subchains have been considered to form a new level of structure of either entanglements or networks, which are described by the {**R**} chains. These two cases are now considered.

6.1. A Model for Entangled Chains. If the {**R**} chains are considered to represent entangled molecules then the reptation model of de Gennes[32] or the tube model of Edwards[36] can be used. These give for the {**R**} chain bond vector correlation function a result similar to (6.1a) except that a new relaxation spectrum τ_p^{rep} is involved, with

$$\langle \mathbf{R}_j(0)\cdot\mathbf{R}_j(t)\rangle = 2R^2\sum_{p=0}^{N_R}\sin^2\left(\frac{\pi p j}{N_R}\right)\exp(-t/\tau_p^{\text{rep}}) \tag{6.1b}$$

and

$$\tau_p^{\text{rep}} \sim \tau N^3/p^2$$

The proportionality to N^3 rather than N^2 is the crucial feature of this result. Use of the Rouse description (6.1a) of chain dynamics on a relatively local level and the reptation description (6.1b) of entanglements on a larger scale completes the input to the general result for the NMR relaxation function (5.6). Unfortunately the used of a spectrum of relaxation times makes explicit analytic progress very difficult and algebraically complex. To demonstrate the content of the present theoretical results a single relaxation time (τ_b,τ_R) will be used in each case with

$$\tau_b \sim N_b^2 \quad \text{(Rouse)}$$

$$\tau_R \sim N_R^3 \quad \text{(reptation)}$$

so that

$$\langle \mathbf{R}_j(0)\cdot\mathbf{R}_j(t)\rangle = 2R^2\exp(-t/\tau_p^{\text{rep}}) \tag{6.1c}$$

and for the constrained {**b**} subchain the following result will be used

$$\langle \mathbf{b}_j(0)\mathbf{b}_j(t')\rangle - N^{-1}\sum_k\langle \mathbf{b}_k(0)\mathbf{b}_j(t')\rangle = b^2\exp(-t'/\tau_b) \tag{6.1d}$$

6.2. The Model for Networks. If {$\mathbf{R}_J$} vectors represent chain elements between network cross-link points then the dynamics of these points will be quite different.[37] The easiest model to use would be to simply fix the cross-link points so that the {**R**} chain has no dynamics. We will use a single relaxation time τ_{R} result similar to (6.1c), but without the molecular weight dependence so that the particular static limit $\tau_{\text{R}} \rightarrow \infty$ can be studied in a more general dynamic context.

The magnitude R of the {**R**} chain vectors will depend on the deformation of the network and is written as $R^2 \equiv R^2(\lambda)$, where λ is the deformation tensor. The problem of how a macroscopic deformation actually effects the cross-link points has a large literature. Work by Flory[38] and Edwards[39] contains useful summaries of the present situation. For illustration the simplest model employing an affine deformation will be used where **R** can be written as

$$R^2 \equiv R^2(\lambda) = \lambda_x^2X^2 + \lambda_y^2Y^2 + \lambda_z^2Z^2 = N_bb^2(\lambda_x^2 + \lambda_y^2 + \lambda_z^2)/3 \tag{6.2}$$

6.3. Analytical Results for the NMR Transverse Spin Relaxation Function. The relaxation of the transverse components of the spin magnetization is given as

$$G(\Delta,t) = \langle\cos\left[\int_0^t\Delta\omega(\alpha(t'))\,dt'\right]\rangle = \text{real part: } \{g(2\Delta,t)g(-\Delta,t)g(-\Delta,t)\}$$

The theory presented in this paper gives the function $g(\Delta,t)$ by (5.6), which requires the two correlation functions as input. The two correlation functions $\gamma_\alpha^{(R)}$ and $\Gamma_\alpha^{(b)}$ describing the chain dynamics in the mode (α) representation are given by using (6.1c) or (6.1d) in (3.14). However, in order to substantiate the remarks made in section 3 about the dominance of the diagonal terms, the complete form, using (3.13), will first be given. By use of the expressions (6.1a,b) the integrals can be solved to give, e.g.

$$\frac{\gamma_{\alpha\beta}^{(R)}}{Nb^2} = \frac{\tau_R}{t}\frac{2}{1+(\omega_\alpha\tau_R)^2}\left[\delta_{\alpha,-\beta} - \frac{\tau_{\text{R}}}{t}(1 - \exp(-t/\tau_R))\frac{\{1+(\omega_\alpha\omega_\beta\tau_R^2)\}}{\{1+(\omega_\beta\tau_R)^2\}}\right] \tag{6.3}$$

with $\omega_\alpha = 2\pi\alpha/t$. The dominance of the diagonal terms $\alpha = -\beta$ can be seen by inspection and are given by

$$\frac{\gamma_\alpha^{(R)}}{Nb^2} = \frac{2\tau_R}{t}\left[\frac{1}{1+(\omega_\alpha\tau_R)^2} - \frac{\tau_R}{t}\frac{[1-(\omega_\alpha\tau_R)^2]}{[1+(\omega_\alpha\tau_R)^2]^2}(1 - \exp(-t/\tau_R))\right] \tag{6.4}$$

A similar expression holds for $\Gamma_\alpha^{(b)}/b^2$ but with $\tau_R \rightarrow \tau_b$. With (6.4) and the corresponding expression for $\Gamma_\alpha^{(b)}/b^2$, the relaxation function $g(\Delta,t;b,R)$, given by (5.6), can be readily evaluated numerically to show the dependence of the NMR relaxation function on the two relaxation times τ_b and τ_R and the state of deformation of the network. These results will be presented shortly, however, since for entanglements $\tau_b \sim N^2$ while $\tau_R \sim N^3$ and therefore the time ranges for the configurational relaxation of the $\{b\}$ and $\{R\}$ chains vary greatly. This is also a reasonable assumption for the network case. Under these conditions further useful analytic progress can be made that gives some insight into the nature of the transverse spin relaxation function.

Although both correlation functions are described by the same form, the α dependence is radically different, depending on the criterion $\tau_b \ll t \ll \tau_R$. For the $\{\mathbf{b}\}$ subchains, which are percieved as being very fast, i.e., $t/\tau_b \gg 1$, expression 6.4, when applied to $\Gamma_\alpha^{(b)}$, reduces to the form

$$\frac{\Gamma_\alpha^{(b)}}{b^2} = \frac{2\tau_b}{t}\frac{1}{1 + (\omega_\alpha\tau_b)^2} \tag{6.5}$$

and $\omega_\alpha\tau_b = 2\pi\alpha\tau_b/t$ can be treated as a continuous variable.

In contrast to this behavior the correlation function $\gamma_\alpha^{(R)}$ for the $\{\mathbf{R}\}$ chain, which will be considered as dynamically slow, i.e., $t/\tau_R \ll 1$, is dominated by the small α modes. In particular the $\alpha = 0$ mode must be treated separately from the rest to give

$$\gamma_\alpha^{(R)}/R^2 = 1 \qquad \text{for} \quad \alpha = 0, t/\tau_R \ll 1$$

and

$$\gamma_\alpha^{(R)}/R^2 = \frac{1}{\tau_R}\frac{1}{\pi^2\alpha^2} \qquad \text{for} \quad \alpha \neq 0, t/\tau_R \ll 1 \tag{6.6}$$

In other words the $\alpha = 0$ mode completely dominates the dynamics in the near static limit $\tau_R \gg t$.

By separating out the $\alpha = 0$ mode, the relaxation function $g(\Delta,t;\{b\},\{R\})$ given by (5.6) can be written as a product of fast and slow contributions. From (6.5) and (6.6)

$$g(\Delta,t;\{x,X\}) = \left\{1 - \frac{3i\Delta t}{N_b}\frac{X^2}{Nb}\right\}^{-1/2}\prod_{\alpha=1}^{\infty}\left\{1 - \frac{2i\Delta\tau_b}{1 + (\omega_\alpha\tau_b)^2}\right\}^{-1} \tag{6.7}$$

where the first term is the slow and the second the fast contribution. Since $\omega_\alpha\tau_b = 2\pi\alpha\tau_b/t$ can be treated as a continuous variable, the infinite product of factors can be treated in the manner set out in section 4.2 and expressed as an exponential function

$$\prod_{\alpha=1}^{\infty}\left\{1 - \frac{2i\Delta\tau_b}{1 + (\omega_\alpha\tau_b)^2}\right\}^{-1} = \exp[-\beta(\Delta,\tau_b)t] \tag{6.8}$$

where

$$\beta(\Delta,\tau_b) = \tau_b^{-1}\int_0^\infty \frac{\mathrm{d}y}{2\pi}\ln\left\{\frac{y^2 + (1 - 2i\Delta\tau_b)}{y^2 + 1}\right\}$$

This can be evaluated to give

$$\beta(\Delta,\tau_b) = \frac{1}{2\tau_b}[(1 - 2i\Delta\tau_b)^{1/2} - 1] \tag{6.9}$$

So that

$$g(\Delta,t;\{x,X\}) = \left\{1 - \frac{i\Delta t}{N_b}\lambda_x^2\right\}^{-1/2}\exp\left[-((1 - 2i\Delta\tau_b)^{1/2} - 1)\frac{t}{2\tau_b}\right] \tag{6.10}$$

where (6.2) has been used for R^2. Finally the complete NMR relaxation function is given by

$$G(\Delta,t;\{\mathbf{b},\mathbf{R}\}) = \text{real part: } g(2\Delta,t;\{z,Z\})g(-\Delta,t;\{x,X\})g(-\Delta,t;\{y,Y\}) \tag{6.11}$$

Although the real part can be explicitly found, it is algebraically complicated and will not be written down here. Instead the main features of the result (6.11), with $g(\Delta,t;\{x,X\})$ given by (6.10), will be considered: (a) The term $(1 - i\Delta t\lambda_x^2/N_b)^{-1/2}$, which originated from the $\alpha = 0$ mode of the $\{\mathbf{R}\}$ dynamics, is exactly the result for a Gaussian distribution of frozen $\{\mathbf{R}\}$ vectors carrying a dipole–dipole interaction of strength $\Delta^* = \Delta/N_b$.[34] This can readily be seen; the component $g(\Delta,t{:}X)$ of the relaxation function associated with the $\{\mathbf{R}\}$ chain is given by

$$g(\Delta,t;X) = \left\langle\exp\left[\frac{3i\Delta^*}{2R_0^2}\int_0^t X^2(t')\,\mathrm{d}t'\right]\right\rangle \tag{6.12}$$

For frozen bonds the $X(t')$ have no dynamics, i.e., $X(t') = X$, and if the X are Gaussianly distributed then (6.12) is evaluated as

$$g(\Delta,t;X) = \left(\frac{6\pi}{R^2}\right)^{1/2}\int_\infty^\infty \mathrm{d}X\exp\left(\frac{-X^2}{2\langle X^2\rangle}\right)\left\{\exp\left(\frac{3i\Delta^*t}{2R_0^2}X^2\right)\right\} = (1 - i\Delta^*t\lambda^2)^{-1/2} \tag{6.13}$$

where

$$\lambda_x^2 = 3\langle X^2\rangle/R_0^2$$

(b) The exponential term $\exp[-\beta(\Delta,\tau_b)t]$ is appropriate for an (almost) unrestricted $\{\mathbf{b}\}$ chain with a dipolar interaction strength of Δ. (For an unrestricted chain the correlation function γ_{jj} rather than $\Gamma_{jj} = \gamma_{jj} - \sum\gamma_{ij}$ would be used.)

6.4. Computed Results. In the full relaxation function $G(\Delta,t;b,R)$ (6.11) there is an intermixing of the real and imaginary parts of both of the g functions given by (6.10), which in general complicates the interpretation of the final result. Two limiting cases, which can be relatively easily discussed, are $\Delta\tau_b \ll 1$ and $\Delta\tau_b \gg 1$.

6.4.1. Fast {b} Subchain Dynamics ($\Delta\tau_b \ll 1$). The $\{\mathbf{b}\}$ chain relaxation is fast compared to the NMR time Δ^{-1}, and in this case the exponential term is entirely real. This can be seen by expanding $\beta(\Delta,\tau_b)$, given by (6.9), as

$$\beta(\Delta,\tau_b) \approx -i\Delta/2 + \Delta^2\tau_b/4 \tag{6.14}$$

The required combination $\beta(2\Delta,\tau_b) + 2\beta(-\Delta,\tau_b)$ is real and from (6.11)

$$G(\Delta,t;\{b,R\}) = \exp(-3\Delta^2\tau_b t/2) \times \text{real part: } \left\{\left(1 - 2i\frac{\Delta t}{N_b}\lambda_z^2\right)\left(1 + i\frac{\Delta t}{N_b}\lambda_x^2\right)\left(1 + i\frac{\Delta t}{N_b}\lambda_y\right)\right\}^{-1/2} \tag{6.15}$$

In which case the full NMR relaxation function is a product of two terms: one, coming from the fast $\{b\}$ chain, is exponential in time and the other, coming from the static $\{\mathbf{R}\}$ chain, is an algebraic function of t. In the limit that the $\{\mathbf{b}\}$ subchains relax very fast ($\tau_b \rightarrow 0$) the NMR relaxation function is given entirely by the algebraic part:

$$G(\Delta,t;\{b,R\}) = \text{real part: } \left\{\left(1 - 2i\frac{\Delta t}{N_b}\lambda_z^2\right)\left(1 + i\frac{\Delta t}{N_b}\lambda_x^2\right)\left(1 + i\frac{\Delta t}{N_b}\lambda_y\right)\right\}^{-1/2} \tag{6.16}$$

This is shown in Figure 2 for an $\{\mathbf{R}\}$ chain, where each bond vector is spanned by a $\{\mathbf{b}\}$ subchain made up of $N_b = 50$ units and subjected to a range of uniaxial extensions: $\lambda = 1, 2, 4$, up to $\lambda_{\max} \sim N_b^{1/2} \sim 7$, with $\lambda_z = \lambda$ and $\lambda_x = \lambda_y = 1/\lambda^{1/2}$. The behavior, as expected, is nonexponential and the time scale is set by the reduced scale $\Delta t/N_b$. The convergence of the curves at long times, for

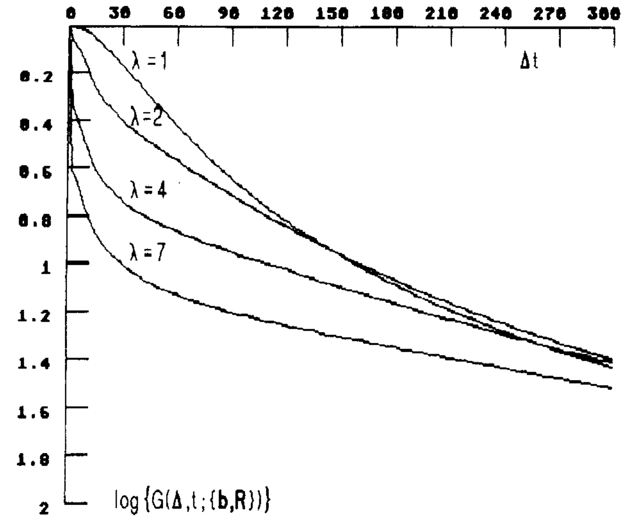

Figure 2. NMR relaxation function for a static network of {**R**} chain vectors ($\tau_R \rightarrow \infty$) deformed with an end-to-end distance R given by $R^2 = (\lambda^2 + 2/\lambda)N_b b^2/3$. Each **R** vector is spanned by a {**b**} subchain of $N_b = 50$ units, which is considered dynamically fast ($\tau_b \rightarrow 0$).

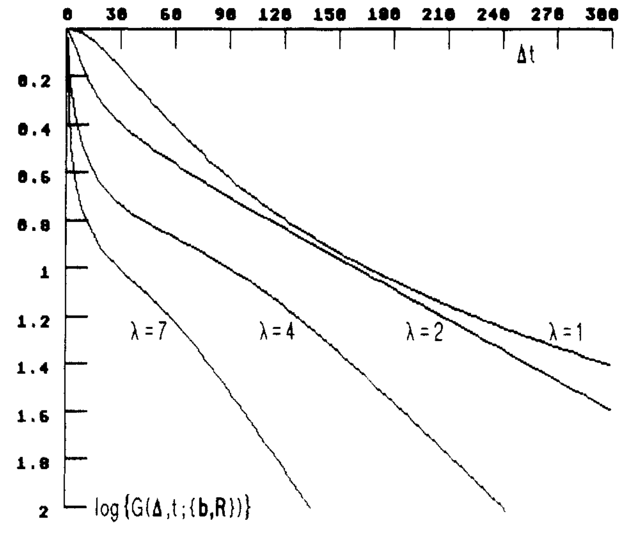

Figure 3. Effect on the NMR relaxation function of a slow relaxation time $\Delta\tau_R = 10^3$ for the {**R**} network vectors. As in Figure 2, $N_b = 50$ and $\Delta\tau_b = 0$.

different deformations, is readily seen by using (6.15). At long times $G(\Delta,t) \approx (\Delta t\lambda_x{}^2\lambda_y{}^2\lambda_z{}^2)^{-3/2}$, and since for incompressible systems $\lambda_x\lambda_y\lambda_z = 1$, $G(\Delta,t)$ is independent of the deformation.

At shorter times the dominant term is $(\lambda_x{}^2 + \lambda_y{}^2 - 2\lambda_z{}^2)(\Delta t)^{1/2}$, which is absent in the undeformed state but is increasingly important for $\lambda \neq 1$. The effect of allowing a slow relaxation of the originally static {**R**} chain is shown in Figure 3, where the relaxation time τ_R is decreased from the static value ∞ to $10^3\ \Delta^{-1}$. The full result (5.6) together with (6.1) was used to numerically calculate the relaxation function $G(\Delta,t;\{\mathbf{b},\mathbf{R}\})$. The effect on the deformation dependence is relatively dramatic, especially at longer times. The other possibility of keeping the network {**R**} chain static and increasing the relaxation time of the {**b**} subchains from very fast ($\Delta\tau_b = 0$) to very slow ($\Delta\tau_b = 1000$) for the same range of deformations is shown in Figures 4–6. It is useful to distinguish between "fast" {**b**} chain dynamics, i.e., $\Delta\tau_b < 1$, as shown in Figures 4 and 5, and "slow" dynamics $\Delta\tau_b > 1$, as shown in Figure 6.

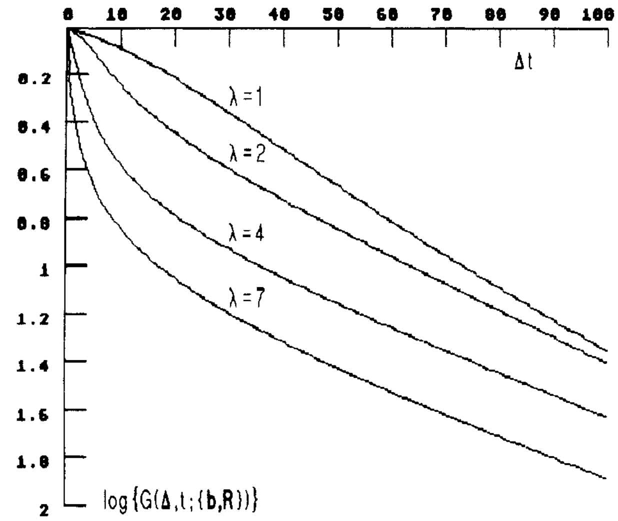

Figure 4. Relaxation time $\Delta\tau_b = 0.01$ for the {**b**} subchains was used. The network {**R**} chains are kept static and $N_b = 50$.

For $\Delta\tau_b < 1$ exponential behavior is seen in Figures 4 and 5, imposed on the algebraic behavior due to the static network chain shown in Figure 2. The time scale is set, from (6.15), by the combination $(\Delta^2\tau_b)^{-1}$. When the dynamics of the {**b**} subchains become slow on the NMR time scale set by Δ^{-1}, i.e., $\Delta\tau_b \gg 1$, this case has to be considered separately.

6.4.2. Slow {b} Subchain Dynamics ($\Delta\tau_b > 1$). While the expansion (6.14) in powers of $\Delta\tau_b$ is consistent with the second moment approximation, for $\Delta\tau_b \gg 1$ the full expression (6.9) for $\beta(\Delta,\tau_b)$ must be used, as the imaginary part now becomes increasingly important. The simple exponential behavior is now modified by a cosine factor according to (4.7), resulting once again in nonexponential behavior and an ambiguous interpretation of T_2. For $\Delta\tau_b \gg 1$ the relaxation rate $\beta(\Delta,\tau_b)$, given by (6.9), can be expanded to give the complex quantity

$$\beta(\Delta,\tau_b) \approx \left(\frac{\Delta}{\tau_b}\right)^{1/2}\left\{\frac{(1 + 2^{1/2}) + i(1 - 2^{1/2})}{2^{1/2}}\right\} \qquad (6.17)$$

So that the exponential term in (6.10) has both a decaying and an oscillating part. The result is shown in Figure 6 for $\Delta\tau_b = 10$ and 1000, $N_b = 50$, $\tau_R = \infty$, and $\lambda = 1, 7$. The sharp downturn of the curve for $\Delta\tau_b = 10$ is due to the influence of the cosine factor (4.7) coming from the imaginary part of $\beta(\Delta,\tau_b)$. The curve for $\Delta\tau_b = 1000$ shows that the chain is already beginning to act like a frozen chain (notice that the time scale is an order of magnitude smaller than that displayed in Figure 2).

7. Conclusions

7.1. The Shape of the Relaxation Curves. Even in the absence of any deformation ($\lambda = 1$) the relaxation curves shown in Figures 2–6 are, to varying degrees, nonexponential. This makes the analysis in terms of an enforced T_2 parameter artificial. It was shown in section 4.2 that only when the dynamical relaxation times satisfy $\Delta\tau < 1$ is the NMR relaxation a simple exponential decay. Under these circumstances the second moment approximation is valid and the spin relaxation time T_2 is given by (1.7). Departures from exponential behavior are seen when the polymer chain relaxation times satisfy $\Delta\tau > 1$. The initial departure ($\Delta\tau \geq 1$) from simple exponential behavior is primarily due to an oscillatory contribution arising from the complex decay rate $\beta(\Delta,N)$ given by (4.6a). The $\lambda = 1$ and $\tau_b = 10$ of Figure 6 show this effect. As $\tau \rightarrow \infty$ a purely algrebraic result (6.13) is obtained, where the NMR relaxation function decays as

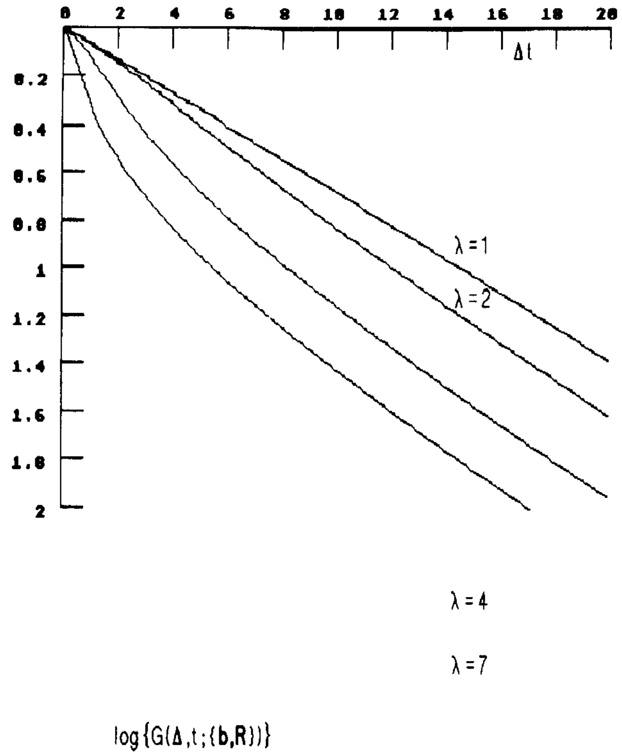

Figure 5. Relaxation time $\Delta\tau_b = 0.1$ for the {**b**} subchains was used. The network {**R**} chains are kept static and $N_b = 50$. At small times the effect of the deformation becomes less as the chain begins to "freeze" within the NMR time scale.

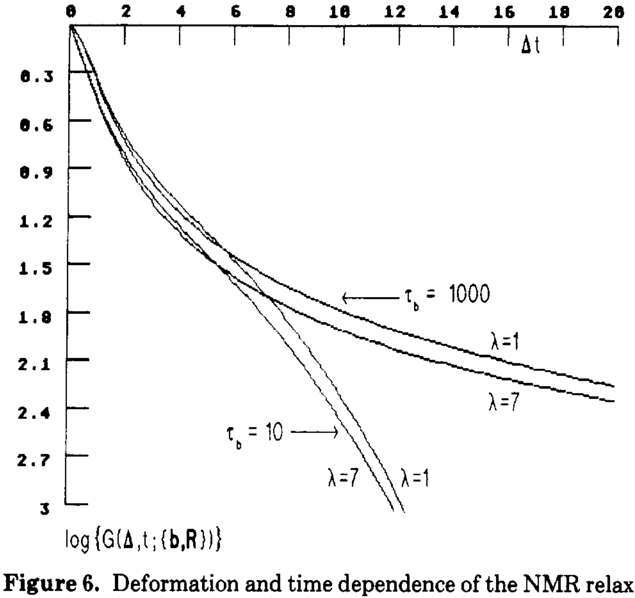

Figure 6. Deformation and time dependence of the NMR relaxation function for relatively slow $\Delta\tau_b \gg 1$ subchains.

$t^{-3/2}$, for example, the $\lambda = 1$ curve shown in Figure 2. Exponential behavior in the spin relaxation function is related to the ability of the spin to reorient in the NMR time period set by Δ^{-1}. Deformations of a network structure or molecular weights in the entangled regime prevent this from occurring and the experimental curves are inevitably nonexponential.[3-5,7] Under these circumstances the commonly used second moment approximation (1.9) is also unreliable.

The approach adopted toward this problem is one of expediency. Charlseby et al.[12] have tried fitting the curve to a form reminisent of the Williams–Watt form, i.e.

$$G(t) \sim \exp[-(t/T_2)^x]$$

where x is a parameter ~ 1.5.

In the work of Kimmich[7] a practical point of view is taken of defining a T_2 as the time for the decay to reach $1/e$ of its original value. Schmit and Cohen-Addad[40] have used parameterized fitting functions that conform to some of the mathematical requirements imposed by NMR theory. In general the shape of the relaxation curves obtained from NMR experiments are without any particular distinguishing features and what is really required is the variation in shape as an experimental parameter such the temperature, deformation, or molecular weight is varied. A detailed comparison of the present theory with experiments conducted on stretched networks and entangled systems is planned in anticiation of the results shown in Figures 2 and 3.

7.2. Deformation Effects. If the {**R**} chain is considered as part of a deformable network, then from Figures 4–6 it is clear that the effect of the deformation progressively decreases as the relaxation time τ_b of the {**b**} subchain connecting the cross-link points increases. In other words the subchains, as perceived by NMR on a time scale Δ^{-1} set by the dipolar interaction, lose their elasticity as their dynamics becomes slower, i.e., as τ_b increases. For $\Delta\tau_b > 1$ the chain does not have enough time to explore all possible configurations or degrees of freedom of the chain and consequently does not fully perceive the elasticity inherent to these degrees of freedom or the imposed constraints.

Roughly speaking these curves are governed by two dimensionless functions of time, i.e., $(\Delta^2 t\tau_b)$ and $\Delta t\lambda^2/N_b$. The influence of the deformed network is perceived in an NMR experiment for times t and deformation ratios λ that satisfy $t\lambda^2/N_b > \tau_b$. For $\Delta\tau_b \ll 1$ this criterion is relatively easy to satisfy despite the factor N_b^{-1}, e.g., the values used to produce Figure 4 give $\Delta t\lambda^2/N_b = 0.02\Delta t$ for $\lambda = 1$ and $\Delta\tau_b = 0.01$. Hence for all deformations and all times $\Delta t > 1$, the NMR relaxation is dominated by the deformed network. However, for the marginal case $\Delta\tau_b \leq 1$ the criterion $\Delta t\lambda^2/N_b > \Delta\tau_b$ may not be satisfied at small times and small deformations, e.g., in Figure 5 the parameters used give $\Delta t\lambda^2/N_b = 0.08\Delta t$ for $\lambda = 2$ and $\Delta\tau_b = 0.1$. In this figure it can be seen that the effect of the $\lambda = 2$ deformation is not seen until $\Delta t > 2$.

For $\Delta\tau_b > 1$ the dominant time scale is always governed by $\Delta\tau_b$ since $\lambda^2 < N$ and the influence of the {**R**} chain on the NMR properties of the {**b**} subchains is relatively ineffective, e.g., Figure 6.

7.3. Entanglement and Molecular Weight Effects. For entanglement process the two relaxation times have different molecular weight dependences, i.e., $\tau_b \sim M_c^2$ and $\tau_R \sim (M/M_c)^{3.4}$, where M_c is the critical molecular weight between entanglements. The experimental curves are inevitably nonexponential,[3-5,7] which once again makes the analysis in terms of an enforced T_2 parameter problematic. Furthermore, since the entanglement relaxation time τ_R relative to the NMR time Δ^{-1} satisfies $\Delta\tau_R > 1$, the commonly used second moment approximation is unreliable. It is hoped to apply the methods developed in this paper to these problems in more detail at a later date.

Appendix

Evaluation of the Matrix Form

$$[\det(\mathbf{M})]^{1/2}\langle\exp[(1/2)\mathbf{b}_j\cdot\mathbf{M}\cdot\mathbf{b}_j]\rangle_{\Sigma\mathbf{b}_j=\mathbf{R}} \quad \text{(A1)}$$

where $\mathbf{M}$ is a $T \times T$ matrix $M(m,n)$ and $\mathbf{b}_j$ are column matrices of T elements, each one representing a Gaussian random variable with

$$\langle \mathbf{b}_i \cdot \mathbf{b}_j \rangle \equiv \{\langle b_i(n) b_j(m) \rangle\} = \{\gamma_{ij}(n,m)\} \equiv \gamma_{ij}$$

The elements $\{b_j(n)\}$ are subjected to the constraint at each moment of time $t' = n\epsilon$

$$\sum_{k=1}^{N} b_k(n) = R(n) \qquad \text{for each} \quad n = 1\text{–}T \tag{A2}$$

The constraint is expressed as a product of δ functions for each moment of time in the interval 0–t

$$\prod_{n=1}^{T} \delta\{\sum_{i}^{N} \mathbf{b}_i(n) - \mathbf{R}(n)\} \tag{A3}$$

and parameterized as

$$\int \prod_{n} \frac{\mathrm{d}g(n)}{2\pi} \exp[\mathrm{i} \sum_{n} \mathbf{g}(n) \{\sum_{i}^{N} \mathbf{b}_i(n) - \mathbf{R}(n)\}]$$

or in matrix form as

$$\int \mathrm{D}g \exp[i\mathbf{g} \cdot (\sum \mathbf{b} - \mathbf{R})] \tag{A4}$$

In the evaluation of (A1) extensive use will be made of the following result (ref 36, Appendix 2.1), again stated in the matrix form

$$[\det(\mathbf{A})]^{1/2} \int \mathrm{D}\varphi \exp[(-1/2)\varphi \cdot \mathbf{A} \cdot \varphi + \mathbf{c} \cdot \varphi] = \exp(\mathbf{c} \cdot \mathbf{A}^{-1} \cdot \mathbf{c}) \tag{A5}$$

A if a nonsingular matrix and φ and **c** are column matrices. For example, this result can be used to linearize the argument of the exponential in (A1), which is quadratic in the terms $\mathbf{b}_j$, i.e.

$$\exp[(1/2)\mathbf{b}_j \cdot \mathbf{M} \cdot \mathbf{b}_j] = [\det(\mathbf{M}^{-1})]^{1/2} \int \mathrm{D}\varphi \exp[(-1/2)\varphi \cdot \mathbf{M}^{-1} \cdot \varphi + \mathbf{b}_j \cdot \varphi] \tag{A6}$$

The product of constraint-conserving δ functions parameterized by (A4) can now be easily included in (A6) to give

$$\prod \delta(\sum \mathbf{b} - \mathbf{R}) \exp[(1/2)\mathbf{b}_j \cdot \mathbf{M} \cdot \mathbf{b}_j] = [\det(\mathbf{M}^{-1})]^{1/2} \int \mathrm{d}\mathbf{g} \exp(-i\mathbf{g} \cdot \mathbf{R}) \int \mathrm{d}\varphi \exp[(-1/2)\varphi \cdot \mathbf{M}^{-1} \cdot \varphi + \sum_{k} \mathbf{b}_k \cdot (\varphi \delta_{kj} + \mathbf{g})] \tag{A7}$$

The average over the Gaussian random variables $\{\mathbf{b}\}$ is found by using

$$\langle \exp[\sum \mathbf{b}_k \cdot \mathbf{h}_k] \rangle = \exp[(1/2) \sum \mathbf{h}_k \cdot \gamma_{kl} \cdot \mathbf{h}_l] \tag{A8}$$

for an arbitary matrix function $\mathbf{h}_k$. Define

$$\mathbf{Z}(\mathbf{M}) = \langle \prod \delta(\sum \mathbf{b} - \mathbf{R}) \exp[(1/2)\mathbf{b}_j \cdot \mathbf{M} \cdot \mathbf{b}] \rangle \tag{A9}$$

then using (A7)

$$\mathbf{Z}(\mathbf{M}) = [\det(\mathbf{M}^{-1})]^{1/2} \times \int \mathrm{d}\mathbf{g} \exp(-i\mathbf{g} \cdot \mathbf{R}) \int \mathrm{d}\varphi \exp\left[(-1/2)\varphi \cdot \mathbf{M}^{-1} \cdot \varphi + \sum_{kl} (\varphi \delta_{kj} + i\mathbf{g}) \cdot \frac{\gamma_{kl}}{2} \cdot (\varphi \delta_{ij} + i\mathbf{g}) \right] \tag{A10}$$

The $\{\varphi\}$ integrals have the form of (A5) and give

$$\mathbf{Z}(\mathbf{M}) = \frac{[\det(\mathbf{M}^{-1})]^{1/2}}{[\det(\mathbf{M}^{-1} - \gamma_{jj})]^{1/2}} \int \mathrm{d}\mathbf{g} \exp[-i\mathbf{g} \cdot \mathbf{R} - (1/2)\mathbf{g} \cdot \{N \sum \gamma + \sum \gamma \cdot (\mathbf{M}^{-1} - \gamma_{jj})^{-1} \cdot \sum \gamma\} \cdot \mathbf{g}] \tag{A11}$$

The $\{\mathbf{g}\}$ integrals are calculated in a similar manner, by using (A5), to give

$$\mathbf{Z}(\mathbf{M}) = \{[[\det(\mathbf{M}^{-1})]^{1/2} \exp[-(1/2)\mathbf{R} \cdot \{N \sum \gamma + \sum \gamma \cdot (M^{-1} - \gamma_{jj})^{-1} \cdot \sum \gamma\}^{-1}]] / \mathbf{R}[[\det(\mathbf{M}^{-1} - \gamma_{jj})]^{1/2} \times [\det\{N \sum \gamma + \sum \gamma \cdot (\mathbf{M}^{-1} - \gamma_{jj})^{-1} \cdot \sum \gamma\}]]^{1/2}\} \tag{A12}$$

The complete statistical problem is given by

$$\langle \exp[(1/2)\mathbf{b}_j \times \mathbf{M} \times \mathbf{b}_j] \rangle_{\sum \mathbf{b}_j = \mathbf{R}} = \mathbf{Z}(\mathbf{M})\mathbf{Z}(0) \tag{A13}$$

With some simplification of the determinant factors, this can be written as

$$\langle \exp[(1/2)\mathbf{b}_j \cdot \mathbf{M} \cdot \mathbf{b}_j] \rangle_{\sum \mathbf{b}_j = \mathbf{R}} = \frac{[\det(\mathbf{M}^{-1})]^{1/2}}{[\det(\mathbf{M}^{-1} - \gamma_{jj} + N^{-1} \sum \gamma)]^{1/2}} \exp\left(-\mathbf{R} \cdot \frac{\mathbf{Q}}{2N^2} \cdot \mathbf{R}\right) \tag{A14}$$

where $\mathbf{Q} = N^2[\{N \sum \gamma + \sum \gamma \cdot (\mathbf{M}^{-1} - \gamma_{jj})^{-1} \cdot \sum \gamma\}^{-1} - \{N \sum \gamma\}^{-1}]$. The matrix **Q** can be rearranged by the following series of matrix manipulations

$$\begin{aligned}
\mathbf{Q} &= N^2[(N \sum \gamma + \sum \gamma \cdot (\mathbf{M}^{-1} - \gamma_{jj})^{-1} \cdot \sum \gamma)]^{-1} \times [\sum \gamma \cdot (\mathbf{M}^{-1} - \gamma_{jj}) N^{-1}] = \\
&N^2[\{N \sum \gamma \cdot (\mathbf{M}^{-1} - \gamma_{jj})^{-1}\}\{(\mathbf{M}^{-1} - \gamma_{jj}) + N^{-1} \sum \gamma\}]^{-1} [\sum \gamma \cdot (\mathbf{M}^{-1} - \gamma_{jj}) N^{-1}] = \\
&N^2[\{(\mathbf{M}^{-1} - \gamma_{jj}) + N^{-1} \sum \gamma\}]^{-1} (\mathbf{M}^{-1} - \gamma_{jj}) \{N \sum \gamma\}^{-1} [\sum \gamma \cdot (\mathbf{M}^{-1} - \gamma_{jj}) N^{-1}] = \\
&[\{(\mathbf{M}^{-1} - \gamma_{jj}) + N^{-1} \sum \gamma\}]^{-1}
\end{aligned} \tag{A15}$$

set

$$\Gamma = \gamma_{jj} - N^{-1} \sum \gamma$$

then

$$\mathbf{Q}^{-1} = \mathbf{M}^{-1} - \Gamma \tag{A16}$$

and (A14) can be written in the form used in section 3, i.e.

$$[\det(\mathbf{M})]^{1/2} \langle \exp[(1/2)\mathbf{b}_j \cdot \mathbf{M} \cdot \mathbf{b}_j] \rangle_{\sum \mathbf{b}_j = \mathbf{R}} = [\det(\mathbf{Q})]^{1/2} \exp\left[(1/2)\mathbf{R} \cdot \frac{\mathbf{Q}}{N^2} \cdot \mathbf{R} \right]$$

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Static and Dynamic Properties of Poly(ethylene oxide) in Methanol

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ABSTRACT: The properties of poly(ethylene oxide) PEO chains in dilute and semidilute solutions in methanol have been examined using pulsed-field-gradient NMR and static and quasielastic light scattering (QELS). From the temperature dependence of the second virial coefficient the Θ temperature was determined to be close to 16.7 °C. Values of the inverse osmotic compressibility ($\partial\pi/\partial C$), determined independently from static LS and the ratio of the respective diffusion coefficients ($D_{\mathrm{QELS}}/D_{\mathrm{NMR}}$) in dilute solution, were identical within experimental uncertainty and are precisely described by renormalization group theory. The latter also provides a good fit for the concentration dependence of the diffusion coefficient. The self-diffusion coefficients are represented by a universal curve: log (D/D_0) versus log (C/C^*). The dynamic light-scattering measurements showed the presence of molecular clusters (or ordered domains), which appear to constitute a general feature of PEO solutions in both good and poor solvent quality. These clusters diminish in size as the temperature is raised and/or the concentration is lowered. Data for hard spheres (stearic acid coated SiO_2) diffusing in the PEO solutions formed a universal curve, log (D/D_0) versus log (C/C^*), independent of sphere size and gave a dependence on matrix MW of $M^{-0.58}$. Clusters of size similar to the hard spheres have an apparent diffusion rate that is 1 order of magnitude slower at the same matrix polymer concentration.

Introduction

Poly(ethylene oxide) (PEO) has attracted considerable interest for its unusual properties; it is soluble not only in water but also, for example, in dioxane, chloroform, methanol, and benzene. There is also a pronounced tendency for PEO to associate in solution: this has been demonstrated by light-scattering measurements, even in very dilute aqueous solutions,[1-7] and short chains may form spherulites.[3] It would appear, however, that these aggregates, reflected in a slow mode in dynamic light scattering in water solution, represent only a small weight fraction of the material in the solution. Thus, classical gradient diffusion on the high molecular weight polymer gives D values that agree almost precisely with the fast mode deriving from the molecularly dispersed polymer.[6]

In light of the ambiguities, which may have resulted from aggregation in aqueous solutions and which place in question some of the conclusions drawn in earlier studies, it seemed worthwhile to reexamine the behavior of this important polymer in a more congenial solvent. Methanol appears to be such a solvent. Moreover, the Θ state is accessible in methanol in the vicinity of 17 °C, which allows one to examine the influence of solvent quality by varying the temperature. In addition, PEO has a unique proton signal making it possible to perform pulsed-field-gradient NMR (PFG-NMR) measurements of self-diffusion on PEO in the solutions. For this reason, deuteriated methanol (CD_3OD) has been employed as the solvent. This is convenient since, through combination of dynamic light-scattering (QELS) and NMR diffusion coefficients, one may evaluate the thermodynamic contribution to the former quantity in dilute solution and in turn test various theoretical predictions.

Experimental Section

Poly(ethylene oxide) samples were narrow distribution fractions obtained from Toya Soda Ltd., Tokyo. The molecular weights, polydispersities, etc., are provided by the manufacturer.

designation	$M \times 10^{-3}$	M_w/M_n
SE-5	40	1.03
SE-8	74	1.02
SE-15	145	1.04
SE-70	594	1.10
SE-150	1200	1.12