Entangled linear polymer chains in melts: n.m.r. and Rouse or reptation models; stress relaxation

J. P. Cohen-Addad
*Laboratoire de Spectrométrie Physique associé au CNRS, Université Scientifique et Médicale de Grenoble, B.P.*68, 38402, *Saint-Martin D'Heres Cedex, France*
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This study deals with detailed descriptions proposed to analyse slow chain diffusional process effects on n.m.r. properties of nuclei linked to long linear polymer molecules in melts or in concentrated solutions. It aims to predict relationships among macroscopic viscoelastic properties and semi-local dynamical properties observed from n.m.r. These relationships are discussed considering two main models of low-frequency chain fluctuations in melts: a multiple relaxation-mode spectrum analogous to a Rouse model or a single relaxation-mode spectrum analogous to a reptation model. The two descriptions are compared with each other. The Rouse model was chosen because n.m.r. properties might be sensitive to the equilibration process of conformational fluctuations within a so-called 'tube' as well as to the reptation in a 'tube'. Also, the Rouse model is more easily handled than the reptation one. Local molecular properties are transferred to the unusual n.m.r. semi-local space scale (<30 Å) through the submolecule concept: every monomeric unit is supposed to have a uniform average orientational order within a given submolecule. Semi-local dynamical properties are analysed from the transition of the spin-system response from a pseudo-solid behaviour to a liquid-like one, induced by shortening polymer molecules or by slightly diluting them. This transition is currently observed from the transverse magnetic relaxation function of nuclei linked to entangled polymer chains. This spin-system response is contrasted to the longitudinal response only sensitive to local high relaxation frequency motions. Also, it is shown how stress-relaxation processes induced on a macroscopic scale can be monitored on a semi-local space scale from n.m.r. Relaxation rates of the transverse magnetization are shown to depend strongly upon both the initial stretching ratio λ of the polymer sample and the structure of its chain relaxation spectrum.

Keywords Polymer; nuclear magnetic resonance; entanglements; dynamics; stress relaxation

INTRODUCTION

It is now well established that the spin-system response of nuclei linked to entangled chains in a melt exhibits a transition from pseudo-solid-like properties to liquid-like ones, by shortening polymer chains or by slightly diluting them[1-3]. Pseudo-solid properties of the relaxation function of the transverse magnetic component reflect the residual energy of interactions of nuclear spins. This non-zero average is observed whenever chain entanglements dissociate in a time interval too long compared with the characteristic time of n.m.r. measurements. In this case low-frequency fluctuations are perceived from n.m.r. as frozen; it is like observing the random rotation of a small molecule, in a time scale considerably shorter than its own correlation time. Liquid-like properties of the spin-system response are observed on nuclei linked to short polymer chains which are still entangled but which undergo a random diffusion process fast enough to be perceived as isotropic from n.m.r. The situation is depicted in *Figure 1*. When the temperature of any glassy polymer sample is raised, the transverse magnetic relaxation rate Δ is usually observed to decrease strongly, right above the glass transition temperature T_g. Then, either of two cases must be considered: On the one hand, the relaxation rate Δ measured on long linear chains slowly decreases around a value δ_M^e corresponding to a residual spin-interaction strength equal to $\sim 10^2$ Hz (*Figure 1a*); the solid-like spin-system response is easily controlled, without any ambiguity from a shortening of δ_M^e induced by sample rotation[4,5]. On the other hand, for short chains, the relaxation rate is found to decrease slowly around a value δ_M^l equal to ~ 1. Hz, as is usually observed on any conventional liquids (*Figure 1a*). Accordingly, at a given temperature $T_i > T_g$, a transition from $\delta_M^e \sim 10^2$ Hz to $\delta_M^l \sim 1$ Hz is induced by shortening polymer chains (*Figure 1b*).

It is worth emphasizing that the motional averaging observed from δ_M^e to δ_M^l is necessarily induced by slow molecular random processes associated with the diffusional motion of polymer chains. Such a transition of n.m.r. properties would also be observed by diluting polymer chains or by raising their temperature.

Most recent studies of relaxation properties of the transverse nuclear magnetization attempted to identify these slow molecular processes with characteristic mechanisms of chain diffusion in melts or in concentrated solutions[1-3,6-8]. N.m.r. is until now, to our knowledge, the only measuring technique which can be used to investigate slow chain diffusion processes ($D \gtrsim 10^{-12}\,\mathrm{s}^{-1}$)

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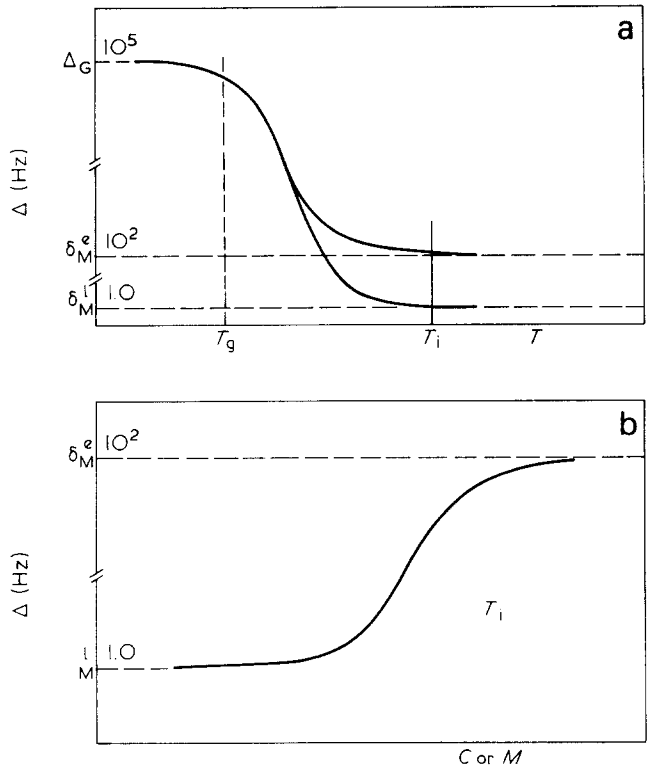

Figure 1 Schematic representation of the transition of n.m.r. properties from a solid-like spin-system response to a liquid-like one. (a) The relaxation rate Δ of the transverse magnetization is plotted as a function of temperature T_g is the glass transition temperature. (b) The relaxation rate Δ is plotted at a given arbitrary temperature $T_i > T_g$ as a function of chain molecular weight or polymer concentration

in melts both on a semi-local space scale and on a time scale of about 0.1 s. Macroscopic dynamical properties are usually obtained either from viscoelastic measurements[9] or from observations of chains labelled with radiotracers[10] or deuterium[11] and diffusing through a whole sample from one end to the other. Neutron scattering[12], forced Rayleigh light scattering[13] or n.m.r. pulsed field gradient[8] techniques are applicable to the observation of diffusion processes of short chains in melts or longer chains in semi-dilute solutions. For example, the self-diffusion coefficient of polystyrene chains in benzene was found to vary in accordance with the predicted chain molecular weight and concentration dependences[14],

$$D_{\text{self}} \propto M^{-2\pm0.1} C^{-1.7\pm0.1}$$

using forced Rayleigh light scattering measurements performed on chains labelled with a photochromic probe[15]. Chain molecular weights were lower than 8×10^5 while polymer concentrations were smaller than 0.2 g/g. Also, the self-diffusion coefficient of deuterated polyethylene chains was found to be in agreement with the predicted M^{-2} dependence ($D_{\text{self}} \propto M^{-2\pm0.1}$) in melts[11]; chain molecular weights were lower than 3×10^4.

Besides viscoelastic properties or local dynamical properties easily characterized from relaxation processes of the longitudinal nuclear magnetization, there is a lack of information about detailed mechanisms associated with slow chain diffusion processes observed on a semi-local space scale.

The present paper aims to describe relaxation properties of the transverse nuclear magnetization specifically induced by any chain diffusion process in a melt or in concentrated solutions. More precisely, the purpose of this paper is to provide detailed characteristic n.m.r. properties which should help in identifying chain relaxation spectra observed on a semi-local space scale. Two main models will be discussed: the Rouse model[16] and the reptation model[17]. According to the Rouse model the spatial memory of a chain is lost at any time at any point of the chain, whereas according to the reptation model the spatial memory is lost at chain ends only. This latter model implicitly describes strong topological constraints which prevent sustained lateral chain motions. The Rouse model will be considered in either of the following two ways: First it will be used to describe the chain diffusion process as a whole although some viscoelastic properties are now known to be described in a more correct way by the reptation model; however, the Rouse model is appropriate to the illustration of general n.m.r. properties induced by a slow chain diffusion process. Alternately, this model will also be considered as possibly describing the equilibrium of conformational fluctuations within a 'tube'[18], its longest relaxation time being proportional to M^2.

The basic assumptions underlying the n.m.r. approach to the observation of chain diffusion processes are as follows:

(i) The broad chain relaxation spectrum consists of two well separated dispersions called Ω_1 and Ω_2; Ω_1 is the transition spectrum while Ω_2 is the terminal spectrum associated with the collective motion of all parts of a long linear polymer chain.

(ii) A n.m.r. submolecule concept may be used, which results from the split of the chain relaxation spectrum into two parts. According to this submolecule concept a small space domain may be defined from its intrinsic physical quantities obtained from an average over all segment diffusional motions associated with the Ω_1 transition spectrum. The split of the relaxation spectrum into two parts is reflected by a cut of chain fluctuations in space: there is no stochastic dependence of segmental fluctuations between different submolecules. On the other hand, because of the Ω_2 spectrum, submolecules cannot be considered as being at full equilibrium. Physical quantities averaged over the Ω_1 spectrum are still slowly varying time functions closely associated with the diffusion process of a whole chain: low-frequency fluctuations of submolecules are not stochastically independent of one another.

It will be shown below that local molecular properties may be transferred to an unusual n.m.r. semi-local space scale ($\lesssim 30$ Å) through the submolecule concept. The magnetic relaxation rate δ_M^e is one of the physical quantities resulting from an average calculated over any given submolecule, in a strongly entangled chain system. It is a residual energy of nuclear spin interactions, and δ_M^e will serve as an internal reference frequency to explore the chain diffusion spectrum modified by shortening polymer molecules or by diluting them. In the transition region of n.m.r. properties, the residual spin energy has a significant time variation and the effect of δ_M^e on magnetic relaxation is progressively blurred from a dynamical average induced by chain diffusion which leads to the relaxation rate value $\delta^{\mathrm{l}}_{\mathrm{M}}$ (*Figure 1*). Therefore, the diffusion process of a whole chain is perceived from n.m.r. in a semi-local space scale defined over a submolecule; but this is, of course, associated with the whole relaxation spectrum describing collective motions of all submolecules.

The main features to be discussed below are related to:

(i) the structure of the spectrum actually perceived from n.m.r.; number of relaxation modes characterized by their corresponding weight factors;

(ii) the chain molecular weight dependence of this spectrum;

(iii) the observation of stress relaxation from n.m.r.

The Rouse model and the reptation model will be used to predict characteristic n.m.r. properties which should permit one generally to distinguish a multiple relaxation-mode spectrum from a single-mode one, by analysing n.m.r. measurements.

Recently, de Gennes analysed diffusion processes observed on a space scale r_i smaller than the coil size of a chain. He defined[19] a partial diffusion coefficient $D_{\mathrm{self}}(r_i)$. It will be shown below that n.m.r. measurements are also associated with a partial rotational diffusion process of a chain. The transfer of local properties to a semi-local space scale through the submolecule concept will now be discussed; detailed relationships among dynamical semi-local properties and viscoelastic properties will be established in later sections; all results will finally be discussed. It is the first time, to our knowledge, that it is shown how stress-relaxation processes induced at a macroscopic scale can be monitored from n.m.r.

SUBMOLECULE CONCEPT

Viscoelastic submolecules

It is currently considered that the whole relaxation spectrum of long linear flexible entangled chains in melts or in concentrated solutions must consist of two well separated dispersions Ω_1 and Ω_2. The Ω_1 transition spectrum is associated with high-frequency relaxation processes of short segments within a so-called submolecule. Any real chain is divided into submolecules of equal contour length $L_e = N_e a$, where a is the mean length of a main chain bond. L_e is given by the usual formula[9,20,21]:

$$N_e = \rho RT/m_0 G_N^0 \qquad (1)$$

with m_0 the average molecular weight of a main chain bond and G_N^0 the shear modulus in the viscoelastic plateau region; ρ is the polymer density. The mean size of any submolecule is assumed to be:

$$\sigma_e = \langle r_e^2 \rangle^{1/2} = N_e^{1/2} a$$

There are no correlations between chain fluctuations occurring within different space domains defined from submolecules. The spatial cut in fluctuations is usually considered as defined by entanglement loci: submolecule properties are independent of chain molecular weight M. The Ω_2 terminal relaxation spectrum describes the low-frequency relaxation process of a whole chain resulting from collective dissipative motions of submolecules; Ω_2 depends strongly upon chain molecular weight.

In the present paper, the submolecule concept will be taken into consideration by considering that averages of most physical quantities can be calculated in two steps. In the first one, low-frequency fluctuations (Ω_2 spectrum) are considered as frozen—it is like assuming that chains are embedded in a temporary network. The partial average of any nuclear magnetic quantity calculated over a given submolecule will be considered as a function of only the end-to-end vector $\boldsymbol{r}_e$ of the submolecule; the Ω_1 spectrum will not be perceived through such an average whereas the symmetry of segment motions may play a crucial role on n.m.r. quantities. In the second step, low-frequency fluctuations are not assumed to be frozen anymore and partial averages are assumed to vary slowly with time according to the Ω_2 spectrum; the end-to-end vector $\boldsymbol{r}_e$ participates in the collective motion occurring within a chain observed as a whole.

N.m.r. model

The n.m.r. model to be used in the present discussion has been extensively described in several references[2,22]: submolecules are pictured as freely jointed chain segments of step length a, the number of bonds in a submolecule is N_e and the number of submolecules in a given chain is N_s, and the chain contour length is $L = N_e N_s a$. Any bond $\boldsymbol{a}$ is supposed to carry a proton pair (*Figure 2*), dipolar interactions between different proton pairs are neglected, and n.m.r. properties are calculated from the dipolar interaction defined within each proton pair only.

The typical quantity governing this dipolar interaction and to be averaged within a submolecule is:

$$\varepsilon_0(\boldsymbol{a}(t)) = 3\gamma^2 \hbar (3\cos^2\theta_a - 1)/4b^3 \qquad (2)$$

$\boldsymbol{a}(t)$ is the bond vector which carries the proton pair in which we are interested, b is the distance between the two nuclei, γ is the gyromagnetic ratio, and θ_a is the angle that $\boldsymbol{a}$ makes with the steady magnetic field $\boldsymbol{B}_0$.

Monomeric unit average orientational order

Any non-zero end-to-end vector $\boldsymbol{r}_e^n$ of the nth submolecule may be considered as describing a topological constraint exerted on this part of the chain. It has already been shown that such a constraint induces a non-isotropic

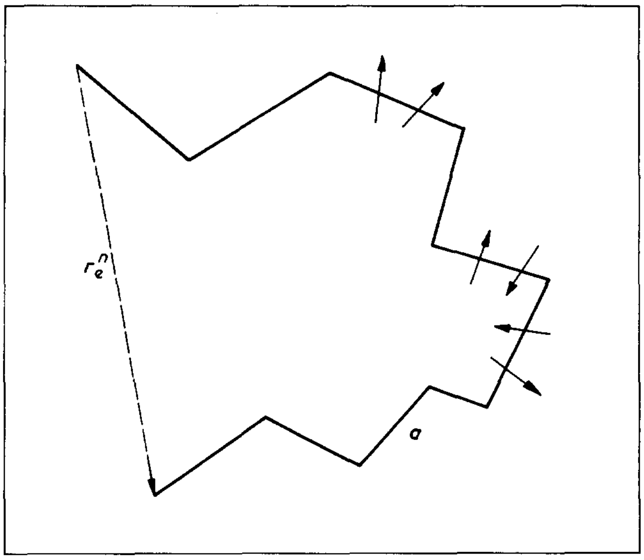

Figure 2 The n.m.r. model of submolecule is a freely jointed segment; every bond $\boldsymbol{a}$ is assumed to carry a proton pair

rotation of bond segments $\boldsymbol{a}$: these are not free to rotate in all directions of space[23]. For a fixed end-to-end vector $\boldsymbol{r}_e^n$, the non-isotropic partial average of $\varepsilon_0(\boldsymbol{a}(t))$, corresponding to the Ω_1 spectrum and resulting from such a constraint, is expressed as[22,23]:

$$\varepsilon_M^r(\boldsymbol{r}_e^n) = \langle \varepsilon_0(\boldsymbol{a}(t)) \rangle \boldsymbol{r}_e^n$$
$$= (3\delta_M/2)(3\cos^2\theta_{r_e}n - 1)(r_e^n)^2/\sigma_e^2 \qquad (3)$$

with $\delta_M = \sqrt{0.2}\,\Delta_G\sigma_e^2/L_e^2$; Δ_G^2 is the second moment of the resonance line which would be observed in the glassy state; θr_e^n is one of the angular coordinates of $\boldsymbol{r}_e^n$. Such a simple formula clearly shows how dynamical local properties associated with $\boldsymbol{a}(t)$ are transferred to a semi-local n.m.r. space scale defined from the average size of a submolecule: $\sigma_e^3 \lesssim (30\ \text{Å})^3$. Collective motions of submolecules in a chain are involved in the transverse nuclear magnetic relaxation process through the slow time dependence of $\boldsymbol{r}_e^n(t)$ end-to-end vectors ($n = 1,2,\ldots$).

It will be assumed throughout the present paper that the above formula (3) can be extended to real chains. More generally, any submolecule will be considered as a space domain roughly determined by entanglement loci. All magnetic interactions of nuclei linked to a chain will be assumed not to be averaged to zero within a submolecule, in a time interval smaller than all relaxation times of the Ω_2 spectrum. The corresponding residual spin energy will be considered as a single parameter function entirely determined by L_e. Nuclear spin interactions consist of two contributions: one comes from dipole–dipole interactions established between nuclei located on different chain segments, while the other comes from dipolar couplings existing within chemical species like methyl or methylene proton groups. However, the first contribution can be considered as negligible on average because of the strong internuclear distance dependence of dipolar interactions (r^{-3}). In the second contribution, distances between protons are fixed, and the residual spin energy results from an orientational average only. Such an analysis is easily satisfied by observing ^{13}C nuclei in natural abundance, for example; but it also applies to protons on rotating methyl groups, or to methylene protons linked to highly flexible chains. Therefore, it can be considered that single chain magnetic properties are observed although all chains are in dynamical interactions with one another.

Transverse magnetic relaxation function

The transverse magnetic relaxation function associated with the residual energy ε_M^r of spin interactions can be expressed according to two main formulae. The first of these may be written as:

$$M_M^e(t) = [\cos(\varepsilon_M^r(\boldsymbol{r}_e^n)t]_{\text{orient.}} \qquad (4)$$

for all proton pairs linked to strongly entangled chains when low-frequency fluctuations are supposed to be frozen; $[\quad]_{\text{orient.}}$ means an average calculated over end-to-end vectors of all submolecules. Note that the second moment of the resonance line determined from $M_M^e(t)$ is defined by

$$[(-\mathrm{d}^2M_M^e/\mathrm{d}t^2)_{t=0}]_{\text{orient.}} = [(\varepsilon_M^r)^2]_{\text{orient.}} = 3\delta_M^2$$

$M_M^e(t)$ reflects characteristic properties of n.m.r. submolecules. The submolecule concept has already been applied in two ways to n.m.r. studies of two polymer systems. Considering long linear polyisobutylene chains in concentrated solutions the magnetic relaxation function of protons linked to these chains has been shown to obey a superposition property in the concentration range $c = 0.98$ to $0.47\ \mathrm{g\,cm^{-3}}$; this was observed whatever the complex shape of the relaxation function[3]. In that case, the concentration acts as a simple parameter governing all magnetic properties within any submolecule, through the contour length L_e (formula (1)). Also, considering a pure *cis*-1,4-polybutadiene sample which is known to have a high density of entanglement loci, the resonance line spectrum calculated from formula (4) has been shown to be in reasonable agreement with experimental results[24].

The magnetic relaxation function can also be written as:

$$M_M^d(t) = N_s^{-1}\sum_n \overline{\cos\left(\int_0^t \mathrm{d}t'\,\varepsilon_M^r(\boldsymbol{r}_e^n(t'))\right)} \qquad (5)$$

for chain entanglements which dissociate quickly enough to be perceived from n.m.r. Characteristic properties resulting from formula (5) and relationships among viscoelastic properties and n.m.r. will be analysed in the next sections from two different models describing the collective motions of all submolecules: the Rouse and reptation models. Time-dependent probability distribution functions associated with the Rouse model are Gaussian functions while those characterizing the reptation model are not easily handled and all time averages are directly calculated instead of using distribution functions[25,26]. Consequently, the spin-system response will be conveniently expressed within a second-order cumulant expansion[27]:

$$M_M^d(t) \simeq \exp\left(-\int_0^t (t-\tau)N_s^{-1}\sum_n \mathscr{C}_n(\tau)\,\mathrm{d}\tau\right) \qquad (6)$$

with

$$\mathscr{C}_n(t) = \overline{\varepsilon_M^r(\boldsymbol{r}_e^n(0))\varepsilon_M^r(\boldsymbol{r}_e^n(t))} \qquad (7)$$

$\mathscr{C}_n(t)$ is the correlation function describing the loss of memory of $\boldsymbol{r}_e^n(t)$; it will be calculated in the next two sections.

N.M.R. AND THE REPTATION MODEL

The tube concept was first introduced by Edwards to describe time-independent properties of chains at equilibrium in melts[28]. Then, de Gennes built the reptation model based on a two-step process[17,29]. The first step is an equilibration of conformational fluctuations within a tube; this was described as a migration of defects along the chain. An equilibrium is reached when the concentration of defects is uniform. Such a process has been shown to be characterized by a spectrum of relaxation times, the longest of which, T_d, has a chain molecular weight dependence: $T_d \propto M^2$. Possible effects of this equilibration process on n.m.r. properties will be analysed in the next section. Properties of the second step of the reptation mechanism have been extensively developed by Doi and Edwards and are in reasonable agreement with viscoelastic measurements[26]. According to this model, any chain moves randomly forwards and backwards only, along itself, or more precisely along the so-called primitive path of the chain (*Figure 3*). Any initial conformation of a portion of the primitive path is destroyed whenever either of the two chain ends diffuses through it. One of the main advantages of the tube model is to eliminate the many-chain problem; this is replaced with the study of a single-chain system, confined in the tube. The end-to-end vector of the nth submolecule is described by a vector $\boldsymbol{R}_{n+1}-\boldsymbol{R}_n=\boldsymbol{d}$ of constant length $d=N_e^{1/2}a$; therefore, according to formula (3):

$$\varepsilon_M^r(\boldsymbol{d})=\langle\varepsilon_0(\boldsymbol{a}(t))\rangle_{\boldsymbol{d}}=1.2\sqrt{\pi}\,\Delta_G/N_e Y_2^0(\Omega_d) \qquad (8)$$

The sperical harmonic $Y_2^0(\Omega_d)$ is a function of the angular coordinates Ω_d of $\boldsymbol{d}$. Considering now that $\boldsymbol{d}$ can vary slowly with time, two cases will be analysed.

Infinite tube

Consider first the case that a polymer chain is trapped in an infinitely long tube of random conformation. The displacement of the nth vector $\boldsymbol{R}_{n+1}-\boldsymbol{R}_n=\boldsymbol{d}_n$ along the tube at rest induces an angular diffusion of this vector which depends upon the static stiffness of the tube. The probability distribution function of angular coordinates of any given vector $\boldsymbol{d}$ is written as:

$$\mathscr{P}(\Omega_d^0,t;\Omega_d,t)=k(\Omega_d^0,s_0;\Omega_d,s) \quad \Pi(s_0,t;s,t) \qquad (9)$$

with

$$\Pi(s_0,t_0;s,t) = (4\pi D_{cv}|t-t_0|)^{-1/2}\exp\left(-\frac{(s-s_0)^2}{4D_{cv}|t-t_0|}\right) \qquad (10)$$

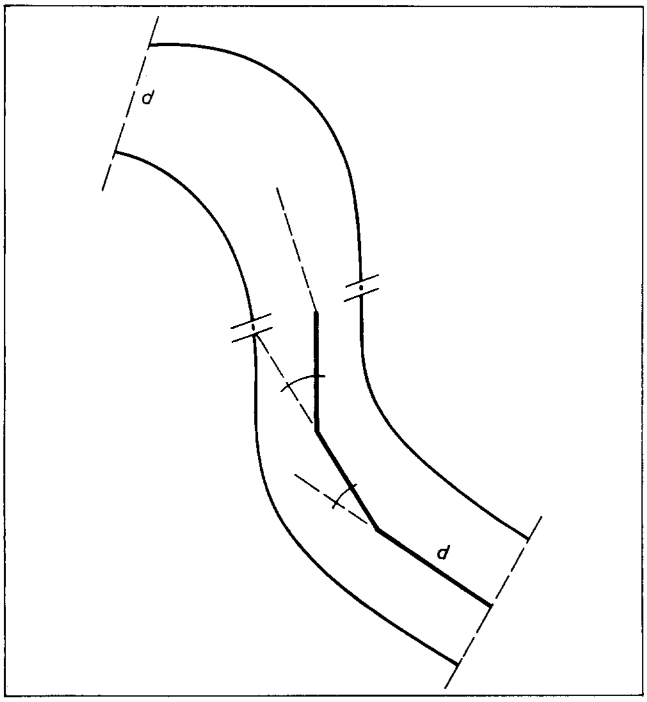

Figure 3 ***d*** vectors of submolecule are assumed to move backwards or forwards along the primitive path, in a tube which prevents sustained lateral motions

For convenience, the subscript n is replaced by an arc length coordinate s, and D_{cv} is the curvilinear diffusion coefficient of the chain along the tube. Also:

$$k(\Omega_d^0,s_0;\Omega_d,s) = (4\pi)^{-1}\sum_{l,m} Y_l^{m*}(\Omega_d^0)Y_l^m(\Omega_d)\exp(-|s-s_0|/fl) \qquad (11)$$

with

$$1/fl=l(l+1)D_f/d^2 \qquad (12)$$

The $k(\Omega_d^0,s_0;\Omega_d,s)$ function was assumed to obey a conventional rotational diffusion equation with an angular diffusion coefficient D_f which reflects the static flexibility of the tube. The correlation function we are interested in is expressed as:

$$\mathscr{C}_s(0,t)=1.8\delta_M^2\exp(D_{cv}t/f_2^2)|1-\theta(D_{cv}t/f_2^2)^{1/2}| \qquad (13)$$

where $\theta(x)$ is the error function.
When t is long enough $(D_{cv}t/f_2^2>>1)$:

$$\mathscr{C}_s(0,t)_{t\to\infty}\simeq 0.06d^2\Delta_G^2/N_e^2[D_f(\pi D_{cv}t)^{1/2}]^{-1} \qquad (14)$$

Also, at short times $(D_{cv}t/f_2^2<1)$:

$$\mathscr{C}_s(0,t)_{t\to 0}\simeq 1.8\delta_M^2(1-12(D_f[D_{cv}t/\pi]^{1/2})/d^2) \qquad (15)$$

$\mathscr{C}_s(0,t)$ is of course very different from the usual exponential time function observed on small molecules in ordinary liquids. Correspondingly, the mean square translational displacement of any point $\boldsymbol{R}_n$ has been calculated by de Gennes[17]:

$$\overline{[\boldsymbol{R}_n(t)-\boldsymbol{R}_n(0)]^2}=2d(D_{cv}t/\pi)^{1/2} \qquad (16)$$

This result is also very different from a Fick law description. The correlation function (15) reported in formula (6) would be observed at short times, when a real tube may be roughly considered as infinite.

The magnetic relaxation function calculated for short times should be expressed for formulae (6) and (7) as:

$$M_M^d(t)\simeq\exp\left\{-\frac{1.8\delta_M^2}{2}t^2\left[1-\left(\frac{t}{\theta}\right)^{1/2}\right]\right\} \qquad (17)$$

with $\theta=\pi d^4/(40D_f^2D_{cv})$. A significant deviation from a Gaussian function may be observed if the time constant $(\theta/\delta_M^2)^{2/5}$ has the same order of magnitude as δ_M^{-1}, i.e. if $\theta\simeq\delta_M^{-1/2}$; such a condition mainly depends upon the curvilinear diffusion constant D_{cv}.

Tube of finite size

We consider the case where chain ends can move randomly in all directions in space, at any time. It will be shown now that such a property leads to a correlation function very different from that expressed by formula (12). The quantity we are concerned with has already been calculated by Doi and Edwards[26] to analyse viscoelastic properties; this quantity was called:

$$S_{\alpha\beta}(s,t)=\overline{[d_\alpha(s,t)d_\beta(s,t)-d^2\delta_{\alpha\beta}/3]}/d^2 \qquad (18)$$

α and β subscripts represent x, y and z components of $\boldsymbol{d}(s)$. Once again an arc length coordinate s is used. Because of random properties of chain ends, the boundary condition for $S_{\alpha\beta}(s,t)$ is $S_{\alpha\beta}(s,t)=0$ at $s=0$ and $s=L$; therefore

$S_{zz}(s,t)$ is conveniently expressed as a series expansion of orthogonal functions $\sin(\pi ps/L)$, $p=1,2,\ldots$:

$$S_{zz}(s,t)=\sum_{p=1}^{\infty} h_p(t)\sin(\pi ps/L) \qquad (19)$$

with

$$h_p(t)=h_p(0)\exp[-(\pi^2p^2D_{\mathrm{cv}}t/L^2)] \qquad (20)$$

Note that the chain molecular weight dependence of the characteristic time $T_{\mathrm{R}}=L^2/\pi^2D_{\mathrm{cv}}$ associated with this model is necessarily proportional to M^3, if the diffusion constant D_{cv} is assumed to vary as M^{-1}. The initial condition of $S_{zz}(s,t)$ depends upon the experiment considered on a given sample.

Chain fluctuations at equilibrium. When chain fluctuations are observed at equilibrium, initial orientations of different $d(s)$ vectors are uncorrelated; therefore, the function $S_{zz}(s',0)S_{zz}(s,t)$ averaged over all initial orientations:

$$\Gamma_z(s,s';t)=[S_{zz}(s',0)S_{zz}(s,t)]_{\mathrm{orient.}} \qquad (21)$$

must obey the initial condition:

$$\Gamma_z(s,s';0)=(4/45)\delta(s-s')$$

$$(8d/45L)\sum_{p=1}\sin(\pi ps/L)\sin(\pi ps'/L) \qquad (22)$$

The average correlation of the submolecule s with all submolecules s' of a given chain is:

$$d^{-1}\int_0^L \Gamma_z(s,s';0)\,\mathrm{d}s'=4/45 \qquad (23)$$

Therefore:

$$\mathscr{C}(s,t)=1.8\delta_{\mathrm{M}}^2\sum_{p,\mathrm{odd}}(4/\pi p)\sin(\pi ps/L)\exp(-p^2t/T_{\mathrm{R}}) \qquad (24)$$

Two types of labelled chains may now be considered.

(i) *Fully labelled chains.* When polymer chains observed from n.m.r. are fully labelled with protons or ^{13}C nuclei, for example, the average of the above $\mathscr{C}(s,t)$ function over all submolecules of a given chain is:

$$L^{-1}\int_0^L \mathscr{C}(s,t)\,\mathrm{d}s=1.8\delta_{\mathrm{M}}^2\sum_{p,\mathrm{odd}}(8/\pi^2p^2)\exp(-p^2t/T_{\mathrm{R}}) \qquad (25)$$

The above time function is analogous to the correlation function of the end-to-end vector of a chain, already calculated by de Gennes[17]. It is also analogous to the shear relaxation modulus calculated in ref. 26:

$$G_{\mathrm{R}_p}(t)=G_{\mathrm{N}}^0\sum_{p,\mathrm{odd}}(8/\pi^2p^2)\exp(-p^2t/T_{\mathrm{R}})$$

From formulae (25) and (6) the magnetic relaxation function is written as:

$$M_{\mathrm{R}_p}(t)=\exp\Bigl(-1.8\delta_{\mathrm{M}}^2\sum_{p,\mathrm{odd}}(T_{\mathrm{R}}/p^2)^2(8/\pi^2p^2)$$
$$\times[\exp(-p^2t/T_{\mathrm{R}})+p^2t/T_{\mathrm{R}}-1]\Bigr) \qquad (26)$$

The relaxation function $M_{\mathrm{R}_p}(t)$ behaves like a single relaxation-mode function because of the strong weight factor $8/\pi^2p^2$ $(p=1,3,\ldots)$. Also, it does not apply to very short times; more precisely, it applies at times longer than T_{d}, where T_{d} characterizes the wriggling motion in a 'tube', T_{d} being equal[17] to $\sim N_{\mathrm{s}}T_{\mathrm{R}}$. Limit expressions of formula (26) are analysed in the following way. When the terminal relaxation T_{R} is much longer than δ_{M}^{-1}, the kinetics of disentanglement are too slow to be perceived from n.m.r. Then the magnetic relaxation function $M_{\mathrm{R}_p}^{\mathrm{e}}$ has a solid-like behaviour easily observed from a sample rotation effect; from formula (26), $M_{\mathrm{R}_p}^{\mathrm{e}}$ is expressed as:

$$M_{\mathrm{R}_p}^{\mathrm{e}}(t)\simeq\exp[-(\delta_{\mathrm{M}}^{\mathrm{e}})^2t^2/2] \qquad (27)$$

with $\delta_{\mathrm{M}}^{\mathrm{e}}=\sqrt{1.8}\delta_{\mathrm{M}}$.

When T_{R} is much shorter than δ_{M}^{-1}, then a motional averaging of the residual energy of spin interactions is expected to occur and the magnetic relaxation function is written as:

$$M_{\mathrm{R}_p}^{\mathrm{l}}(t)\simeq\exp(-\delta_{\mathrm{M}}^{\mathrm{l}}t) \qquad (28)$$

with

$$\delta_{\mathrm{M}}^{\mathrm{l}}=1.8\delta_{\mathrm{M}}^2\sum_{p,\mathrm{odd}}(T_{\mathrm{R}}/p^2)(8/\pi^2p^2) \qquad (29)$$

The transition of n.m.r. properties (*Figure 1*) from a pseudo-solid response of the spin system (characterized by a relaxation rate $\delta_{\mathrm{M}}^{\mathrm{e}}$) to a liquid-like response (characterized by a relaxation rate δ_{M}) is described by formula (26) at intermediate values of T_{R} : $T_{\mathrm{R}}\sim\delta_{\mathrm{M}}^{-1}$. Such a transition was calculated and reported on *Figure 4*. The order of magnitude of δ_{M} is usually 10^2 Hz, and therefore T_{R} should be equal to $\simeq 2\times10^{-3}$ s to be observed from n.m.r.,

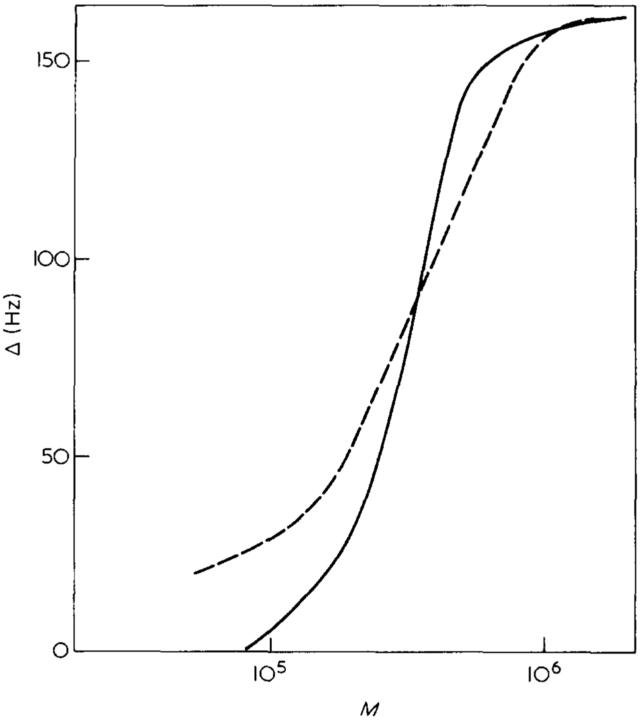

Figure 4 Transition curve of n.m.r. properties described according to a reptation model from formula (26); with $1.8\delta_{\mathrm{M}}$ = 130 rad s^{-1}, and T_{R} = 5 x 10^{-3} s for M = 4.1 x 10^5. The chain molecular weight dependence of T_{R} is proportional to M^3. The broken line is a typical experimental transition curve

considering the reptation model. It will be shown below that a very different estimate of chain relaxation times will be obtained according to the Rouse model while the magnetic relaxation function will be shown to behave like a multiple relaxation-mode function.

(ii) *Partly labelled chains.* Let us consider now proton chains labelled with deuterium nuclei on their middle part only; the length of the deuterated segment is supposed to be that of a submolecule. Then the relaxation function involved in n.m.r. is:

$$\mathscr{C}(L/2,t)=1.8\delta_{\mathrm{M}}^{2}\sum_{p,\mathrm{odd}}(4/\pi p)\exp(-p^{2}t/T_{\mathrm{R}}) \tag{30}$$

the weight factor associated with the pth relaxation mode is now p^{-1}. The difference from p^{-2} would be significant enough to consider that, according to formulae (30) and (5), a multiple relaxation-mode process governs the magnetic relaxation mechanism.

Stress-relaxation process. The question that arises from the above description is to know whether or not the magnetic relaxation function could be sensitive to the so-called second relaxation process associated with the disengagement of a chain from a deformed 'tube' resulting from a sudden application of deformation[26]. Then, for the sake of simplicity, the initial condition of $S_{zz}(s,t)$ is supposed to be a constant number P_0, independent of s (all submolecules have the same small orientational polarization at $t=0$). Therefore:

$$S_{zz}(s,t)=P_{0}\sum_{p,\mathrm{odd}}(4/\pi p)\sin(\pi ps/L)\exp(-p^{2}t/T_{\mathrm{R}}) \tag{31}$$

and

$$S(s,t)=9|P_{0}^{2}|_{\mathrm{orient.}}\delta_{\mathrm{M}}^{2}\Big/4\sum_{p,\mathrm{odd}}(4/\pi p)\times\sin(\pi ps/L)\exp(-p^{2}t/T_{\mathrm{R}}) \tag{32}$$

To describe the stretching process of the sample we make the assumption of a finite deformation. Now λ is the stretching ratio along the steady magnetic field direction, and the average of P_0^2 over all orientations of submolecules is:

$$[P_{0}^{2}]_{\mathrm{orient.}}=(2\lambda^{2}+\lambda^{-1})^{2}/5+\lambda^{-2}-2(2\lambda^{2}+\lambda^{-1})/3\lambda \tag{33}$$

as it is calculated from:

$$P_{0}=[(2\lambda^{2}+\lambda^{-1})\cos^{2}\theta_{\mathrm{d}}-(1/\lambda)]d^{2}$$

Once again, the average over all submolecules leads to a relaxation spectrum with a weight factor per relaxation mode equal to $8/\pi^2p^2$.

The stress-relaxation process should be monitored from the magnetic relaxation function $M_{\mathrm{R}_p}^{\mathrm{S}}(t)$ obtained from formula (6) and from the correlation function $\mathscr{C}^{\mathrm{S}}(s,t)$ describing chain dynamical properties:

$$M_{\mathrm{R}_p}^{\mathrm{S}}(t)\simeq\exp\left(-\int_{0}^{t}(t-\tau)\mathscr{C}^{\mathrm{S}}(s,\tau)\,\mathrm{d}\tau\right) \tag{34}$$

However, two cases must be discussed depending upon the value of the chain relaxation time T_{R} compared with δ_{M}^{-1}.

(i) *Fast stress relaxation,* $T_{\mathrm{R}}\delta_{\mathrm{M}}<1$. Properties of the relaxation function $M_{\mathrm{R}_p}(t)$ (formula (26)) showed that the motional averaging process described by the correlation function $\mathscr{C}^{\mathrm{S}}(s,t)$ is observed in the only case where the relaxation time T_{R} is about equal to or shorter than δ_{M}^{-1}. This general n.m.r. property also applies to the above $\mathscr{C}^{\mathrm{S}}(s,t)$ correlation function. Then, the decay of the $M_{\mathrm{R}_p}^{\mathrm{S}}(t)$ function is expected to last over a time interval $(\delta_{\mathrm{M}}^{2}T_{\mathrm{R}})^{-1}>\delta_{\mathrm{M}}^{-1}>T_{\mathrm{R}}$. Therefore, during the time interval ($\sim 10T_{\mathrm{R}}$) which would be necessary to measure a significant decay of $M_{\mathrm{R}_p}^{\mathrm{S}}(t)$, the stress-relaxation process is achieved (in a time interval $\gtrsim T_{\mathrm{R}}$). In other words, the stress-relaxation phenomenon could only be perceived from the initial time-dependent behaviour of the $M_{\mathrm{R}_p}^{\mathrm{S}}(t)$ relaxation function. It is probably difficult to perform such a single-shot measurement. N.m.r. may be applied to monitor stress-relaxation processes in an easier way when the condition $T_{\mathrm{R}}>\delta_{\mathrm{M}}^{-1}$ is fulfilled.

(ii) *Slow stress relaxation,* $T_{\mathrm{R}}>\delta_{\mathrm{M}}^{-1}$. We now consider the case that the terminal relaxation time T_{R} is much longer than δ_{M}^{-1}:

$$T_{\mathrm{R}}>>\delta_{\mathrm{M}}^{-1} \tag{35}$$

The time dependence of the correlation function $\mathscr{C}^{\mathrm{S}}(s,t)$ is no longer expected to govern the magnetic relaxation process. The spin-system response has a pure solid–liquid behaviour. Right after a sudden deformation of the sample, the characteristic time T_{m}^{0} of the magnetic relaxation process is determined by $S_{zz}(s,0)$ as it is defined by formula (31):

$$T_{\mathrm{m}}^{0}\simeq(1.8\delta_{\mathrm{M}}^{2}[P_{0}^{2}]_{\mathrm{orient.}})^{-1/2} \tag{36}$$

The relaxation of S_{zz} may be considered as frozen during the time interval T_{m}^{0}, because of the inequality (35). To analyse the n.m.r. study of the slow stress-relaxation process which lasts over about $3T_{\mathrm{R}}$, T_{R} is divided into equal time intervals ΔT_i such that:

$$T_{\mathrm{m}}^{0}<\Delta T_{i}<<T_{\mathrm{R}}$$

The residual energy of spin interactions is expressed at any time $t_j=j\Delta t_i$ ($j=1,2,\ldots$) after the sudden deformation, by $S_{zz}(t_j)$ according to formula (27). The magnetic decay must then occur over a time interval roughly defined by

$$T_{\mathrm{m}}^{j}\simeq(1.8\delta_{\mathrm{M}}^{2}|S_{zz}(t_{j})|)^{-1}$$

with $T_{\mathrm{m}}^{0}<T_{\mathrm{m}}^{j}<<T_{\mathrm{R}}$. The same reasoning may be applied at any time t_j. Finally, when $T_j\gtrsim 3T_{\mathrm{R}}$, the stress-relaxation process is achieved and the magnetic relaxation function is governed by the time constant $(\delta_{\mathrm{M}}^{\mathrm{e}})^{-1}$, corresponding to an isotropic sample. Consequently, the stress-relaxation process should be observed from n.m.r. as a lengthening effect of the time constant of the transverse magnetic relaxation function. A more detailed description of such an effect will be given in the next section by considering a Rouse model to calculate exactly the spin-system response at any time T_j. The stress-relaxation process can be monitored by investigating magnetization decay properties at times $j\Delta T_i$ ($j=0,1,2,\ldots$). The magnetic signal should be recorded as a whole over its decay time interval T_{m}^{j}, using a so-called Carr–Purcell spin–echo procedure[15], to avoid all effects of diamagnetic susceptibility inhomo-

geneities, necessarily induced by any sample deformation. It may be of interest to know how a stress-relaxation phenomenon induced at a macroscopic scale from a sudden sample deformation is perceived on a semi-local scale.

N.M.R. AND THE ROUSE MODEL

The Rouse model is well known[16]; it will be considered in either of the two following ways. On the one hand, it will be assumed to describe slow chain diffusion processes although it is now known that some viscoelastic properties are analysed in a better manner by the reptation model. However, all time-dependent or time-independent probability distribution functions associated with the Rouse model are Gaussian functions which are easily handled. Accordingly, correlation functions involved in n.m.r. can be calculated exactly. Therefore, the Rouse model is appropriate to the illustration of n.m.r. properties induced by chain motions, albeit a qualitative illustration.

On the other hand, the Rouse model will be assumed to describe the equilibration process of conformational fluctuations within a tube[18]. Any chain in a tube can laterally explore the available space but sustained lateral motions are forbidden because of uncrossable spatial constraints.

According to current descriptions, the equilibration time for conformational fluctuations within a tube, T_d, is assumed to be expressed as:

$$T_d = N_s^2 W_0^{-1} \tag{37}$$

where W_0 is an elementary jump frequency. According to the model proposed by de Gennes, the curvilinear diffusion coefficient D_{cv} is defined as [17,29]:

$$D_{cv} = D_0/N_s \tag{38}$$

with

$$D_0 = \lambda^* d^2 W_0 \tag{39}$$

D_0 may be considered as a diffusion coefficient per submolecule; λ^* is a number smaller than one; d and N_s were already defined in an earlier section. During the time interval T_d, the net displacement of a chain as a whole along its own contour is:

$$\langle \Delta s^2 \rangle^{1/2} = (D_{cv} T_d)^{1/2} = (\lambda^* N_s d^2)^{1/2} \tag{40}$$

It is a small function of the root-mean-square end-to-end distance of the whole chain; it is also the space size which is laterally explored. The reptation motion is supposed to occur in a time scale much longer than T_d from elementary steps about equal to $\langle \Delta s^2 \rangle^{1/2}$.

The main difference between the Rouse model and the reptation model considered in the foregoing section may be analysed in the following way. Accordint to the Rouse model space memory of the chain is lost at any point of this chain; whereas according to the reptation model an initial step of the so-called primitive path may survive for a while, preserving its part of the initial conformation and imparting its orientation on whatever portion of the chain that is currently occupying it. Such a constraint must of course have an effect on the magnetic relaxation function which mainly reflects angular averages of tensorial spin interactions.

The spin-system response calculated in this section will be expressed within a second-order approximation for easy comparison with the reptation model developed in the foregoing section. However, it is worth emphasizing that exact calculations can be done by using a Rouse model[2], even though some of them necessitate a numerical analysis.

Fluctuations at equilibrium

The probability distribution function describing time-dependent fluctuation properties of any submolecule of a Rouse chain has already been expressed in ref. 2. For one of the three Cartesian components of the end-to-end vector $\boldsymbol{r}_e^n$ of the nth submolecule:

$$k(x_e^n, t; x_{e'}^{n'}, t') = [2\pi\sigma_e^2(1 - E^2(t,t')/3]^{-1/2}$$
$$\times \exp\{-3[x_e^{n'} - E(t,t')x_e^n]^2/2\sigma_e^2[1 - E^2(t,t')]\} \tag{41}$$

with

$$E(t,t') = N_s^{-1} \sum_p \exp(-|t-t'|/\tau_p) \tag{42}$$

and

$$\tau_p^{-1} = \sigma_1^{-1} \sin^2[\pi_p/(2N_s+1)]/16 \tag{43}$$

The correlation function in which we are interested has already been calculated[2,22]:

$$\mathscr{C}_n(t) = 3\delta_M^2 \sum_{p,q} N_s^{-2} \exp(-t/\tau_{p,q}) \tag{44}$$

with

$$\tau_{p,q}^{-1} = \tau_p^{-1} + \tau_q^{-1}$$

Formula (41) above clearly shows how chain diffusion properties of a whole chain may be perceived from n.m.r. on a semi-local space scale determined from a submolecule size.

Correspondingly, the correlation function of end-to-end vectors of submolecules n and m is:

$$(\boldsymbol{r}_n(t)\boldsymbol{r}_{n+m}(0))^2 = (\sigma_e^2/N_s)\sum_p$$
$$\times \exp(-t/\tau_p)\cos(2\pi pm/N_s) \tag{45}$$

while the relaxation function of the end-to-end vector of the whole chain is:

$$\phi(t) = (\sigma_e^2/N_s)\sum_p \exp(-t/\tau_p)\sin^2(\pi p/2)/\sin^2(\pi p/N_s) \tag{46}$$

or

$$\phi(t) \simeq N_s\sigma_e^2 \sum_{p,\mathrm{odd}} (1/\pi^2 p^2)\exp(-t/\tau_p) \tag{47}$$

$\phi(t)$ has the mathematical structure of the end-to-end vector correlation function calculated from the reptation model[21,25]. Also, from the Rouse model, the relaxation modulus is known to be written as:

$$G_R(t) = (\rho RT/M) \sum_{p=1}^{N_s} \exp(-t/\tau_p) \tag{48}$$

with M the chain molecular weight and ρ the polymer density. Finally, the magnetic relaxation function governed by $\mathscr{C}_n(t)$ is expressed as:

$$M_{\mathrm{R}}(t)=\exp\Big(-3\delta_{\mathrm{M}}^2 N_{\mathrm{s}}^2 \sum_{p,q} \tau_{p,q}^2 \quad [\exp(-r/\tau_{p,q})+t/\tau_{p,q}+1]\Big) \qquad (49)$$

All chain relaxation modes have an equal weight factor N_{s}^{-2}. A residual energy of spin interaction per relaxation mode is defined by $\delta_{\mathrm{M}}^{\mathrm{R}}=\delta_{\mathrm{M}}/N_{\mathrm{s}}$. Contrary to the reptation model the transition of n.m.r. properties from a pseudo-solid spin-system response to a liquid-like one is now described as a progressive motional averaging effect applied on each relaxation mode separately (*Figure 5*). Motional averaging conditions are given by:

$$\tau_{p,q}<(\delta_{\mathrm{M}}^{\mathrm{R}})^{-1} \qquad p,q=1,2,... \qquad (50)$$

instead of the single condition $T_{\mathrm{R}}<\delta_{\mathrm{M}}^{-1}$ obtained from the reptation model.

When chain relaxation times of the terminal spectrum are very long, $\tau_{p,q}>(\delta_{\mathrm{M}}^{\mathrm{R}})^{-1}$ for $p=q=N_{\mathrm{s}}$, the kinetics of disentanglement are too slow to be perceived from n.m.r. Then the magnetic relaxation function $M_{\mathrm{R}}^{\mathrm{e}}$ has a solid-like behaviour easily controlled from a sample rotation effect:

$$M_{\mathrm{R}}^{\mathrm{e}}(\delta_{\mathrm{M}}^{\mathrm{e}}t)\simeq\exp(-3\delta_{\mathrm{M}}^2 t^2/2) \qquad (51)$$

with $\delta_{\mathrm{M}}^{\mathrm{e}}=\sqrt{3}\delta_{\mathrm{M}}$. The physical measuring of $\delta_{\mathrm{M}}^{\mathrm{e}}$ was illustrated in *Figure 1*. When chain relaxation times of the terminal spectrum are very short, $\tau_{1,1}<(\delta_{\mathrm{M}}^{\mathrm{R}})^{-1}$, entanglements dissociate quickly enough to give rise to a liquid-like spin-system response; the magnetic relaxation function is:

$$M_{\mathrm{M}}^{\mathrm{l}}(\delta_{\mathrm{M}}^{\mathrm{l}}t)\simeq\exp[-(\delta_{\mathrm{M}}^{\mathrm{l}}t)] \qquad (52)$$

with

$$\delta_{\mathrm{M}}^{\mathrm{l}}=(\delta_{\mathrm{M}}^{\mathrm{R}})^2\sum_{p,q}\tau_{p,q} \qquad (53)$$

The physical meaning of $\delta_{\mathrm{M}}^{\mathrm{l}}$ was also illustrated in *Figure 1*. It is worth emphasizing that formula (49) describes a transition from the Gaussian function (51) to the exponential time function (52). These correspond to resonance lines which are a Gaussian function and a Lorentzian curve, respectively. It is well known that resonance lines actually observed on polymer melts look more like super-Lorentzian curves than like Gaussian functions. The transition of the spin-system response from a super-Lorentzian curve to a Lorentzian one has been given an exact treatment from a proton pair model in ref. 2. However, it is not easily handled to describe stress-relaxation effects on n.m.r., for example.

The relaxation times, $\tau_{1,1}$ and T_{R}, determined from n.m.r., clearly appear as the time intervals required to perceive any chain rotational diffusion process as an isotropic motion. At intermediate conditions:

$$\tau_{p,q}>(\delta_{\mathrm{M}}^{\mathrm{R}})^{-1} \qquad \text{for} \quad p,q=1,2,...,p_0$$

and

$$\tau_{p,q}<(\delta_{\mathrm{M}}^{\mathrm{R}})^{-1} \qquad \text{for} \quad p,q>p_0,$$

formula (49) may be considered as picturing an averaging mechanism induced by a partial rotational diffusion of the chain. Therefore, it is perceived as a non-isotropic process from n.m.r. This is analogous with the semi-local translational diffusion coefficient defined in ref. 19 to describe chain diffusion processes on a space scale smaller than the coil size.

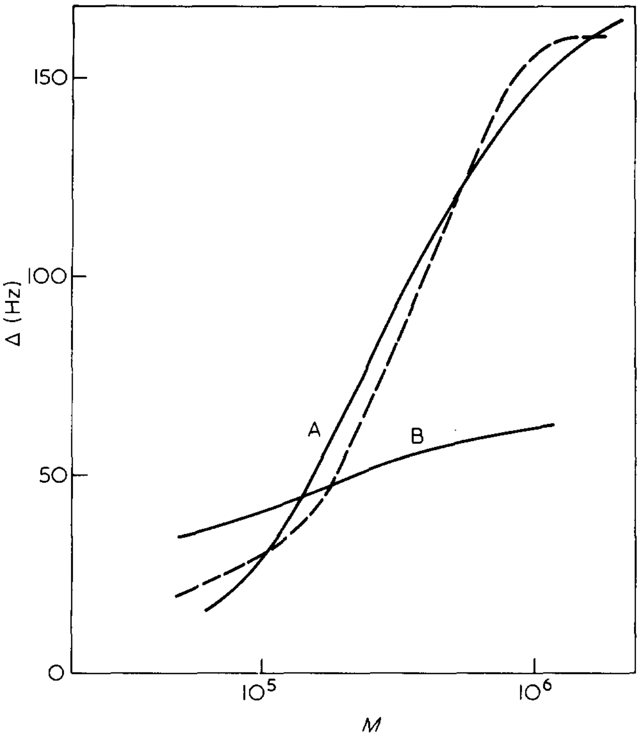

Figure 5 Transition curve of n.m.r. properties described according to a Rouse model from formula (49); with $\delta_{\mathrm{M}}^{\mathrm{e}}$ = 150 rad s^{-1} and $\tau_{1.1}$ = 0.5 s for M = 4.1 x 10^5. The chain molecular weight dependence is: curve A, $\tau_{1.1}\propto M^3$; curve B, $\tau_{1.1}\propto M^2$. The broken line is a typical experimental transition curve

Slow stress relaxation

Assuming now that the condition $\tau_{p,q}>>(\delta_{\mathrm{M}}^{\mathrm{R}})^{-1}$ is fulfilled for all p,q values, the spin-system response has a pure solid-like behaviour. A slow stress-relaxation n.m.r. study may be analysed in the way already described in the last section. However, more details will now be given using a Rouse model. Considering a sample stretched in the steady magnetic field direction, the residual energy of spin coupling resulting from the sudden sample deformation is expressed at any time t as:

$$\varepsilon_{\mathrm{R}}(\lambda,t)=(3\delta_{\mathrm{M}}/2\sigma_{\mathrm{e}}^2)[2z_n^2(\lambda,t)-x_n^2(\lambda,t)-y_n^2(\lambda,t)] \quad (54)$$

with x_n, y_n and z_n the three Cartesian components of a given end-to-end vector $\boldsymbol{r}_n(\lambda,t)$ at time t. The average over all submolecules having the same initial orientation $\boldsymbol{r}_n^0(\lambda,0)$ gives:

$$\varepsilon_{\mathrm{R}}(\lambda,t)=3\delta_{\mathrm{M}}/2\sigma_{\mathrm{e}}^2E^2(t) \quad \times\{2\lambda^2(z_n^0)^2-(1/\lambda)[(x_n^0)^2+(y_n^0)^2]\} \qquad (55)$$

with λ the initial stretching ratio and with

$$E(t)=N_{\mathrm{s}}^{-1}\sum_p\exp(-t/\tau_p)$$

The above formula is derived from well known mathematical properties of the Rouse model; for example:

$$x_n^2(t)=(x_n^0)^2E^2+\sigma_e^2(1-E^2)/3 \qquad (56)$$

and

$$x_n^2(\lambda,t)=(x_n^0)^2E^2/\lambda+\sigma_e^2(1-E^2)/3 \qquad (57)$$

making the assumption of a finite deformation.

The average over initial orientations of all submolecules leads to:

$$[\varepsilon_R(\lambda,t)]_{\text{orient.}}=\delta_M E^2(t)(\lambda^2-1/\lambda) \qquad (58)$$

It is equal to zero in the absence of any stretching ($\lambda=1$) as is expected. Also, it goes to zero when the stress-relaxation process of the sample is achieved; the sample is then isotropic. On the other hand, the mean square average: $[\varepsilon_R^2(\lambda,t)]_{\text{orient.}}=(\delta_M^2/4)\{12(1-E^2)+8E^2(1-E^2)$

$$\times(\lambda^{-1}+2\lambda^2)+2E^4(\lambda^{-2}+6\lambda^4-4\lambda+3\lambda^{-1})\} \qquad (59)$$

is never equal to zero; it goes to $3\delta_M^2$ at infinite time values or when $\lambda=1$ (isotropic sample). We now consider that the time interval $\tau_{1,1}$ is divided into equal small time intervals Δt_i such that:

$$(\delta_M^e)^{-1}<\Delta t_i<<\tau_{1,1} \qquad (60)$$

Then, for any submolecules n at any time $t>t_j=j\Delta t_i$, the magnetic relaxation function reads:

$$m_R^R(n,t_j;t-t_j)=\cos\{\varepsilon_R(\lambda,t)|t-t_j|\} \qquad (61)$$

and for all submolecules:

$$M_R^R(t_j;t-t_j)=[\cos\{\varepsilon_R(\lambda,t_j)|t-t_j|\}]_{\text{orient.}} \qquad (62)$$

or

$$M_R^R(t_j;t-t_j)=\phi(t-t_j)\times\exp\{i[\varepsilon_R(\lambda,t_j)]_{\text{orient.}}|t-t_j|\} \qquad (63)$$

with

$$\phi(t-t_j)=\exp[-\chi^2(\lambda,t_j)|t-t_j|^2/2] \qquad (64)$$

A second-order cumulant expansion was used to derive $M_R^R(t_j;t-t_j)$:

$$\chi^2(\lambda,t_j)=[(\varepsilon_R(\lambda,t_j)-[\varepsilon_R(\lambda,t_j)]^2_{\text{orient.}})^2]_{\text{orient.}}$$

$$=(\delta_M E^4/2)[2\lambda^4+8\lambda^2+4\lambda-7\lambda^{-1}+3\lambda^{-2}+4E^2(2\lambda^2+\lambda^{-1})+6(1-E^2)^2] \qquad (65)$$

$\chi^2(\lambda,t_j)$ goes to $3\delta_M^2$ at infinite time values ($E\rightarrow 0$) or when $\lambda=1$ (isotropic sample) while $[\varepsilon_R(\lambda,t_j)]_{\text{orient.}}$ goes to zero, as expected. Formulae (63), (64) and (65) clearly show that the initial stretching of any sample may induce both a high-frequency modulation and a high relaxation rate of the transverse nuclear magnetization. They are both proportional to $\lambda^2E^2(t_j)\delta_M$, when λ is large enough. An approach to the characterization of the terminal chain relaxation spectrum $E(t)$ may be obtained from n.m.r. by varying the initial stretching ratio λ and by monitoring the magnetic relaxation process as a whole from a Carr–Purcell spin–echo procedure performed at equal time intervals. Such a chain relaxation spectrum characterized from n.m.r., i.e. from a semi-local observation, may then be compared with the relaxation spectrum obtained from viscoelastic properties.

To conclude this section, it may therefore be noticed that n.m.r. may be used in either of the following two ways:

(i) to observe chain fluctuations at equilibrium, on a semi-local space scale when entanglements dissociate quickly enough; or

(ii) to monitor the slow stress-relaxation process of a sample induced on a macroscopic scale while it is observed on a semi-local space scale; such an experimental procedure can be used when entanglements dissociate very slowly.

DISCUSSION: A NON-ISOTROPIC ROUSE MODEL?

The n.m.r. approach to the characterization of polymer chain diffusion processes in melts or in concentrated solutions attempts to determine:

(i) the exact nature of the chain relaxation spectrum associated with properties observed on a semi-local space scale because these reflect collective motions of submolecules within a whole chain;

(ii) relationships between the spectrum observed from n.m.r. and that characterized from viscoelastic measurements; the structure of the observed spectrum (number of relaxation modes, weight factors) and its chain molecular weight dependence should help to identify it as a possible Rouse spectrum or a reptation one.

The reptation model considered showed that a single chain relaxation-mode process is expected to govern the magnetic relaxation mechanism. The transition of n.m.r. properties from a pseudo-solid response of the spin system to a liquid one induced by shortening polymer chains or by diluting them should be sharp. At the middle point of the transition, the chain relaxation time T_R should be roughly equal to $\delta_M^{-1}\simeq 2\times10^{-3}$ s.

On the other hand, the transition of n.m.r. properties described from a Rouse model results from a multiple-mode motional averaging process. It should be smooth. At the middle point of the transition, the terminal relaxation time $\tau_{1,1}$ should be roughly equal to $(\delta_M/N_s)^{-1}\simeq 2\times10^{-1}$ s (N_s is the number of chain relaxation modes).

Recent experimental n.m.r. studies of polyisobutylene–carbon disulphide[3] or pure molten poly(dimethyl siloxane) systems[1] have been analysed by using either a multiple relaxation-mode spectrum or a single relaxation-mode and a molecular weight dependence of $\tau_{1,1}$ or T_R proportional to M^2 or M^3 (M is the chain molecular weight). Surprisingly enough, the multiple relaxation-mode spectrum, associated with an M^3 dependence of $\tau_{1,1}$, was found to fit the experimental results better than the single relaxation-mode spectrum. More precisely, considering a reptation model T_R was found to be about 100 times shorter than the fundamental time scale of viscoelastic properties η_0/G_N^0 (G_N^0 is the shear modulus in the viscoelastic plateau region)[20] and its molecular weight dependence would have been proportional to M^2 instead of M^3. While using a Rouse model, $\tau_{1,1}$ was found to be about 10 times longer than η_0/G_N^0 and its molecular weight dependence was proportional to M^3 (instead of M^2).

Considering experimental n.m.r. results obtained from a few polymer systems so far in this chain motion frequency range it is suggested that one assumes that the Rouse model is a heuristic description because it takes into consideration both a diffusional process of the chain mainly characterized by a $\tau_{1,1}$, $\tau_{1,2}$, $\tau_{2,1}$ and an M^3 molecular weight dependence, and additional nuclear relaxation mechanisms roughly characterized by other relaxation times and probably corresponding to internal motions of chain segments in submolecules.

The result $\tau_{1,1} \sim 10\eta_0/G_N^0$ may be understood by considering that n.m.r. measurements are based on a criterion of chain motion isotropy; $\tau_{1,1}$ is the time interval required to perceive the chain diffusion as an isotropic motion. The reference parameter of isotropy is δ_M/N_s. This criterion may attenuate the reptation picture. We could equally well consider that the chain motion perceived as a whole from n.m.r. is a transient non-isotropic Rouse process characterized by two terminal relaxation spectra: one of them, Ω_2^Z, describes a longitudinal chain diffusion along a given axis, say a Z-axis for example; while the other one, Ω_2^T, describes the transverse diffusion of the given chain. Ω_2^T is assumed to consist of relaxation times much longer than those defined from the Ω_2^Z spectrum. Any chain may therefore be pictured as losing its space memory more rapidly in one direction than in the transverse one. Such a model leads of course to an isotropic space distribution of the chain at infinite times, at equilibrium. The corresponding magnetic relaxation function reads:

$$M_R^A(t) = M_{R,Z}^A(t) M_{R,T}^A(t) \tag{66}$$

$$M_{R,Z}^A = \exp\left(-2\delta_M^2/N_s^2 \sum_{p,q} (\tau_{p,q}^Z)^2 \times \left[\exp(-t/\tau_{p,q}^Z) + t/\tau_{p,q}^Z - 1\right]\right) \tag{67}$$

and

$$M_{R,T}^A = \exp\left(-\delta_M^2/N_s \sum_{p,q} (\tau_{p,q}^T)^2 \times \left[\exp(-t/\tau_{p,q}^T) + t/\tau_{p,q}^T - 1\right]\right) \tag{68}$$

$M_R^A(t)$ also describes the transition of the spin-system response from a pseudo-solid response to a liquid-like one. The longest relaxation times measured from n.m.r. should correspond to about $10\eta_0/G_N^0$. Experimental n.m.r. results obtained until now are closer to a non-isotropic Rouse model than to a reptation one.

To conclude this paper it is worth emphasizing that n.m.r. is a powerful technique of chain fluctuation investigations because both the transition spectrum and the terminal relaxation spectrum may be explored using different specific pulse sequences to obtain spin-system responses which characterize either high-frequency local motions ($\sim 10^9$ Hz, longitudinal magnetic relaxation) or low-frequency chain motions like disentanglement mechanisms ($\simeq 10$ Hz, transverse magnetic relaxation). N.m.r. should also be used to investigate cross-relaxation properties to monitor relaxations of sudden sample deformations induced at a macroscopic scale, while observations are made in a semi-local space scale. Further experimental n.m.r. investigations of polymer properties observed on partly labelled monomeric units are necessary to identify clearly the relaxation spectrum observed on a semi-local space scale.

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