(13) Fawcett, A. H.; Ivin, K. J. *Polymer* **1972**, *13*, 439.
(14) Stockmayer, W. H.; Matsuo, K.; Guest, J. A.; Westphal, W. B. *Makromol. Chem.* **1979**, *180*, 281.
(15) Ivin, K. J.; Navrátil, M. *J. Polym. Sci., Polym. Chem. Ed.* **1970**, *8*, 3373.
(16) Kessler, H.; Gehrke, M.; Griesinger, C. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 490.
(17) Chemical shifts actually are correctly obtained by extrapolating the diagonal intersections on the midaxis (corresponding to $J = 0$) perpendicularly downward to the lower horizontal axis. J values are given by spacings along the vertical axis, not along the diagonals. In practice, slices (not shown) are generated along the diagonals and J values estimated from their spacings, corrected for slant.
(18) If discrimination occurs in both directions, one will resolve 16 pentad sequences. In general, for chains such as these, having a directional sense and with a single chiral center per monomer unit, the number of tactic sequences observable in principle is 2^{n-1}, where n is the number of monomer units in each tactic sequence, dyad, triad, etc. If equal or comparable discrimination does in fact prevail in both directions, only "odd-ads" will have observational significance no matter what group is being observed.
(19) It has been suggested[12] that the generation of helical conformations may require the existence of substantial syndiotactic sequences, embracing as many as four olefin units. But in a random chain, an *RSRS* (or *SRSR*) sequence has a probability of only $(1/2)^4$ or 0.0625.
(20) (a) Karplus, M. *J. Chem. Phys.* **1959**, *30*, 11; (b) *J. Am. Chem. Soc.* **1963**, *85*, 2870; (c) *J. Chem. Phys.* **1960**, *33*, 1842.

NMR Transverse Relaxation Function Calculated for the Rouse Model

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Received November 23, 1988; Revised Manuscript Received February 4, 1989

ABSTRACT: The relaxation of the transverse components of magnetization, due to dipolar interactions between a spin pair on an isolated bond along a polymer chain, has been calculated by using the Rouse model for the chain dynamics. Explicit expressions for the relaxation function are given in terms of a suitably defined NMR time scale Δ, the fastest Rouse relaxation time τ, and the degree of polymerization of the chain N. For times t greater than the longest Rouse mode $\sim\tau N^2$ we show that the relaxation function is given by the real part of an exponential form: $\exp(-\lambda^*(\Delta\tau,N)t)$. The functional dependence of λ^* on $\Delta\tau$ and N shows a variety of different behaviors depending on whether the combinations $\Delta\tau$ and $N\Delta\tau$ are greater or less than 1. For $\Delta\tau \ll 1$, λ^* is real, whereas for $\Delta\tau \gg 1$, λ^* is complex and the relaxation function is modulated by a cosine term. The decay of the relaxation function is determined by the real part of λ^*, which can be identified with the inverse of the spin–spin relaxation time T_2. We show that λ^* increases linearly as τ for $\Delta\tau \ll 1$, reaches a maximum for $\Delta\tau \sim 1$, and decreases as $\tau^{-1/2}$ for $\Delta\tau \gg 1$. The molecular weight dependence of λ^* shows a ln (N) dependence when $\Delta\tau \ll 1$ up to a maximum value $N_{\max} \sim 1/\Delta\tau$ and for $N > N_{\max}$ is independent of molecular weight. The frequently used second moment approximation is shown to be valid only when $\Delta\tau \ll 1$ and $N \ll N_{\max}$. For times $t < \tau N^2$ the relaxation function no longer has a simple exponential form. An algebraic expression is available for $\tau \to \infty$.

1. Relaxation Function

The simplest theoretical model with which to study the NMR phenomena in polymer molecules consists of two spin-$^1/_2$ nuclei a distance d apart, fixed to a single bond in a chain of identical bonds. Dipolar interactions between this spin pair are considered, while those with spins pairs on other bonds are neglected.[1]

For a single spin in a magnetic field B along the z direction, the transverse components of the magnetization m_x and m_y can be considered as precessing with an angular frequency ω_0 (the Larmour frequency):

$$m_x(t) = m_x \cos(\omega_0 t) \qquad m_y(t) = m_y \sin(\omega_0 t)$$

The combination of transverse components of the magnetization given by

$$m(t) = m_x(t) + im_y(t)$$

can be described by the oscillator equation

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

The presence of the other spin contributes a dipolar field at the site of the first spin and leads to an additional interaction energy of $\hbar\Delta\omega(\alpha)$, where

$$\Delta\omega(\alpha) = \frac{3\gamma^2\hbar}{4d^3}(3\cos^2\alpha - 1) \tag{1.2}$$

γ is the gyromagnetic ratio, d is the distance apart of the two spins, and α is the angle that this makes with the magnetic field B.

The system can now be regarded as an oscillator with a natural frequency $\omega_0 + \Delta\omega(\alpha)$. For a mobile bond, the angle α is a function of the time $\alpha = \alpha(t)$ and is determined by the dynamics of the main-chain bond. The oscillator equation (1.1) integrates to give

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

The dephasing of the transverse components of the magnetization due to the dipole interaction is described by the term

$$\exp\int_0^t i\Delta\omega(\alpha(t'))\,\mathrm{d}t'$$

and the transverse relaxation function $G(t)$ is defined to be[2]

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

where the averaging is done over all the dynamic configurations of the bond angle $\alpha(t)$.

In this paper we will present an analytical calculation of $G(t)$ for a chain where the dynamical behavior of the bonds is governed by the Rouse model.[3] Since the use of this model is really only applicable to a scaled invariant version of the original polymer chain, we must consider

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the behavior of dipolar interactions under a rescaling of the chain. This is described in the next section.

2. Scale-Invariant Model for NMR

The spatial configuration and dynamical behavior of the bonds carrying the NMR-active spins will, at a local level, be determined by the atomic details of the particular polymer. This level of detail would preclude any analytic treatment and is in general not necessary, especially for long chains where the concept of scale invariance plays an important role.[4] This idea is already familiar in structural considerations and has already been adapted to the NMR case in a series of papers by Cohen-Addad.[5-7] We start by briefly summarizing the approach of Cohen-Addad. The atomic bond carrying the NMR spin pair is considered along with neighboring bonds $\{\mathbf{a}_i\}$ as part of a larger submolecule. The dipole interaction energy $\epsilon(\alpha) = \hbar\Delta\omega(\alpha)$ given by (1.2) is then averaged over all configurations of this submolecule subject only to the constraint that the end vector $\sum a_i$ has a given value b, i.e., the rescaled dipole interaction ϵ^* to be associated with the submolecule is given as

$$\epsilon^* = \frac{3\gamma^2\hbar^2}{4d^3}\langle(3\cos^2\alpha - 1)\rangle_{|\sum a_i|^2 = b^2} \qquad (2.1)$$

From a dynamic point of view we have assumed at the atomic level the rate of configurational change of the molecular bonds of the submolecule is much faster than the time scale $(3\gamma^2\hbar^2/4d^3)^{-1}$ set by the dipole interaction (1.2). For a sufficiently large number N_s of atomic bonds $\{a_l\}$ eq 2.1 can be evaluated,[7] and the leading term is

$$\epsilon^*(\vartheta) = \frac{3\gamma^2\hbar^2}{4d^3}\,\frac{\{2z^2 - x^2 - y^2\}}{N_s^{\,2}a^2} = \hbar\Delta\omega^* \qquad (2.2)$$

where (x,y,z) are the coordinates of the submolecule end-to-end vector $\mathbf{b}$ ($b^2 = x^2 + y^2 + z^2$). Equation 2.2 can also be written as

$$\epsilon^*(\vartheta) = \frac{3\gamma^2\hbar^2}{4d^3N_s}\left(\frac{b^2}{N_sa^2}\right)\{3\cos^2(\vartheta(t)) - 1\} \qquad (2.3)$$

where ϑ is the angle between b and the magnetic field B. If the process is repeated for all bonds in the chain, then the average value of b will be given by $\langle b^2\rangle = N_sa^2$.

The effective interaction energy $\epsilon^*(\vartheta)$ is similar in form to the original expression (1.2) but reduced by the factor N_s^{-1}. The important difference for this calculation is that the coordinates (x,y,z) of the bond vector $\mathbf{b}_i$ of the submolecule can, as we will see, be treated as Gaussian random variables, whereas the original atomic bond vectors $\{\mathbf{a}_i\}$, being of fixed length and restricted angles, cannot. For the NMR-active bond in the submolecule of the rescaled chain the relaxation function is defined as

$$G(t) = \left\langle\cos\int_0^t \Delta\omega^*(\vartheta(t'))\,\mathrm{d}t'\right\rangle \qquad (2.4)$$

The averaging is now to be done over all configurations of the sub-molecule bonds $\{\mathbf{b}_i\}$ forming the rescaled molecule. With use of (2.2), the relaxation function $G(t) \equiv G(\Delta,t)$ can be written in the more convenient form

$$G(\Delta,t) =$$

$$\text{real part: } \left\langle\exp\left[\frac{3i\Delta}{2b^2}\int_0^t\{2z^2(t') - x^2(t') - y^2(t')\}\,\mathrm{d}t'\right]\right\rangle \qquad (2.5)$$

We have set the averaged length b of the scaled submolecule bond vectors as $b^2 = Na^2$, and the time scale is set by Δ^{-1}, where

$$\Delta = \frac{\gamma^2\hbar^2}{2N_sd^3} \qquad (2.6)$$

For a proton pair with the distance apart d measured in angstroms

$$\Delta = 1.59 \times 10^4/(N_sd^3)\ \mathrm{s}^{-1} \qquad (2.7)$$

If we consider the dynamics of the three coordinates to be independent, then the statistical problem is completely contained in the term

$$g(\Delta,t) = \left\langle\exp\left[\frac{3i\Delta}{2b^2}\int_0^t x^2(t')\,\mathrm{d}t'\right]\right\rangle \qquad (2.8)$$

so that

$$G(\Delta,t) = \text{real part: } \{g(2\Delta,t)\ g(-\Delta,t)\ g(-\Delta,t)\} \qquad (2.9)$$

To evaluate (2.8), we need a dynamical model for the chain constructed from the bond vectors $\{\mathbf{b}_i\}$ and a method of doing the averaging over all dynamical configurations of this chain. These are considered in the next section.

3. Calculation of the Relaxation Function

To describe the dynamical behavior of the chain we use the Rouse model, where the equation of motion for each component (x_j,y_j,z_j) of the bond vectors can be written as

$$\nu\frac{\mathrm{d}}{\mathrm{d}t}x_j(t) - \frac{3kT}{b^2}(x_{j+1} - 2x_j + x_{j-1}) = \zeta_j(t) \qquad (3.1)$$

ν is a local friction coefficient, T is the temperature, and ζ_j is an environmental random force acting on the jth bond. $\zeta_j(t)$ and hence $x_j(t)$ are considered as Gaussian random variables. For a chain of $N - 1$ bonds, the following normal mode transformation[8]

$$x_j = \sum_{p=0}^{N} X_p \sin\frac{\pi pj}{N} \qquad j = 0, 1, ..., N \qquad (3.2)$$

diagonalizes the equation of motion (3.1) to give

$$\frac{\mathrm{d}}{\mathrm{d}t}X_p + \frac{1}{\tau_p}X_p = \zeta_p \qquad (3.3)$$

where the spectrum of relaxation times τ_p is given by

$$\tau_p = \frac{\tau}{\sin^2 \pi p/2N} \qquad \text{with } \tau = b^2\nu/12kT \qquad (3.4)$$

The principal feature of the equation of motion (3.3) that we will need to evaluate $g(\Delta,t)$ given by (2.8) is the dynamic correlation function:

$$\langle X_p(t)\ X_q(t')\rangle = \frac{2b^2}{3N}\delta_{pq}\exp(-|t - t'|/\tau_p) \qquad (3.5)$$

To see how this can be used to evaluate

$$g_j(\Delta,t) = \left\langle\exp\left[\frac{3i\Delta}{2b^2}\int_0 x_j^{\,2}(t')\,\mathrm{d}t'\right]\right\rangle \qquad (3.6)$$

we note that $x_j(t)$ is a dynamic Gaussian random variable, i.e., its statistical properties are completely specified by the mean and variance:

$$\langle x_j(t)\rangle = 0$$

$$\langle x_j(t)\ x_j(t')\rangle = \frac{2b^2}{3N}\sum_{p=0}\sin^2\frac{\pi pj}{N}\exp\left[\frac{-|t - t'|}{\tau_p}\right] \qquad (3.7)$$

(The last result is obtained by using (3.5) and (3.2).)

It is a property of Gaussian variables that the average of the exponential of a Gaussian random variable is given by the exponential of the average according to

$$\langle \exp x \rangle = \exp(\tfrac{1}{2}\langle x^2 \rangle) \qquad (3.8)$$

Unfortunately the statistical problem posed by (3.6) involves the average of the exponential of $x_j^2(t)$ and not $x_j(t)$. However, we can use an auxillary variable φ to linearize the term x_j^2 by means of the mathematical identity

$$(2\pi)^{1/2} \exp(x_j^2/2) = \int_{-\infty}^{\infty} \mathrm{d}\varphi \exp\{-(\varphi^2/2) + x_j\varphi\}$$

The statistical averaging over the bond vectors can now be carried out by using (3.8). The extra technicalities needed to deal with the time integral in (3.6) are described in the Appendix. The remainder of the calculation is also completed in the Appendix, where we show that a systematic calculation of the function $g_j(\Delta,t)$ can be performed. The leading term can be written as a product of integer expressions:

$$g(\Delta,t) = \prod_{\alpha=-\infty}^{\alpha=+\infty} \left[1 - \frac{3i\Delta}{b^2} t\Gamma_{j\alpha}(t) \right]^{-1/2} \qquad (3.9)$$

where

$$\Gamma_{j\alpha}(t) = \frac{2b^2}{3N}\sum_p \sin^2 (\pi pj/N)/\Gamma_p(\alpha,t) \qquad (3.10)$$

$$\Gamma_p(\alpha,t) = \frac{2}{(\omega_\alpha\tau_p)^2 + 1}\,\frac{1}{t/\tau_p}\left[1 + \frac{(\omega_\alpha\tau_\mathrm{p})^2 - 1}{(\omega_\alpha\tau_p)^2 + 1}\left\{\frac{1 - \exp(-|t|/\tau_p)}{t/\tau_\mathrm{p}}\right\}\right] \qquad (3.11)$$

with $\omega_\alpha = 2\pi\alpha/t$.

The result (3.9) and (3.10) and (3.11) are the major results of this paper. They permit a full evaluation of the NMR relaxation function $G(\Delta,t)$ given by (2.9), of a bond located at the jth position on a chain molecule of $N - 1$ bonds in terms of the NMR relaxation rate Δ, given by (2.6) and the relaxation time τ of the fastest Rouse mode. The results are in a form suitable for numerical computation; however, various analytic results can be obtained and compared to known results or other approximations.

4. Frozen Chain Limit ($\tau \rightarrow \infty$)

In the limit that all the relaxation times become very long ($\tau_p \rightarrow \infty$), the chain becomes frozen and the relaxation function $g(\Delta,t)$ can be evaluated directly from (2.9) by using a Gaussian distribution of bond vectors. The result can be written as

$$g(\Omega,t) = \left(\frac{3}{2\pi b^2}\right)^{1/2} \int \mathrm{d}x \exp\frac{(-3x^2)}{2b^2}\left\{\exp\left[\frac{3i\Delta t x^2}{2b^2}\right]\right\} = (1 - i\Delta t)^{-1/2} \qquad (4.1)$$

From the full dynamic expressions (3.9)–(3.11) we can obtain this result by observing that the contribution of all the $\alpha \neq 0$ terms in (3.9) tend to zero, i.e.

$$\Gamma_p(\alpha,t) \rightarrow 0 \quad \text{as} \quad \tau_p \rightarrow \infty \qquad \alpha \neq 0$$

Only $\alpha = 0$ gives a nonzero contribution in the frozen limit, since from (3.11)

$$\Gamma_\mathrm{p}(0,t) \rightarrow 1 \quad \text{as} \quad t/\tau_p \rightarrow 0_p$$

$$g(\Delta,t) = 1 - \frac{3i\Delta t}{b^2}\Gamma_{j0}(t) \qquad (4.2)$$

Then from (3.10)

$$\Gamma_{j0}(t) = \frac{2b^2}{3N}\sum_p \sin^2\left[\frac{\pi pj}{N}\right]\Gamma_p(0,t) = \frac{b^2}{3N} \qquad (4.3)$$

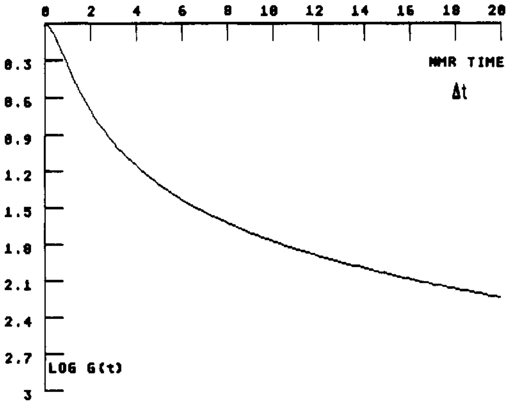


Figure 1. Behavior of the transverse relaxation function for a chain of frozen bonds.

and the known result (4.1) follows from substituting (4.3) in (3.9). The full NMR relaxation function is given by

$$G(\Delta,t) = \text{real part: } \{g(2\Delta,t)\, g(-\Delta,t)\, g(-\Delta,t)\}$$

This can be manipulated into an algebraic form[5] with the following limiting behavior:

$$G(\Delta,t) \approx (\Delta t)^{-3/2} \qquad \text{as } t \rightarrow \infty$$

$$\approx 3(\Delta t)^2/2 \qquad \text{as } t \rightarrow 0 \qquad (4.4)$$

The full dependence of $G(\Delta,t)$ in this frozen limit is shown in Figure 1.

5. General Long-Time Behavior

The time dependence of the relaxation function is completely contained in the term $\Gamma_p(\alpha,t)$ given by (3.11). For times longer than the maximum Rouse relaxation time, i.e., $t > \max(\tau_p) \sim \tau N^2$, $\Gamma_p(\alpha,t)$ is given from (3.11) by

$$t\Gamma_p(\alpha,t) = \frac{2\tau_p}{(\omega_\alpha\tau_p)^2 + 1} \qquad (5.1)$$

recall $\tau_p = \tau/\sin^2 (\pi p/2N)$, hence $\Gamma_{j\alpha}(t)$ given by (4.3) can be written in the scaled form

$$t\Gamma_{j\alpha} = (2b^2/3)\tau F(\omega_\alpha\tau,N) \qquad (5.2)$$

where

$$F(\omega_\alpha\tau,N) = \frac{2}{N}\sum_{p=0}^{N} \sin^2 (\pi pj/N)\left\{\frac{\sin^2 (\pi p/2N)}{(\omega_\alpha\tau)^2 + \sin^4 (\pi p/2N)}\right\} \qquad (5.3)$$

Then $g(\Delta,t)$ from (2.8) can be written in the form

$$g(\Delta,t) = \exp[-\tfrac{1}{2} \sum_{\alpha=-\infty}^{+\infty} \ln \{1 - 2i\Delta\tau F(\omega_\alpha\tau,N)\}] \qquad (5.4)$$

Recall that $\omega_\alpha\tau = 2\pi\alpha\tau/t$, and since we are considering $t \gg \tau$, then we can treat ω_α as a continuous variable and replace

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

Then (5.4) can be written as

$$g(\Delta,t) = \exp(-\lambda^*(\Delta\tau,N)t) \qquad (5.5)$$

where $\lambda^*(\Delta\tau,N)$ is given by ($x = \omega_\alpha\tau$)

$$\lambda^*(\Delta\tau,N) = \tau^{-1}\int_0^{\infty} (\mathrm{d}x/2\pi) \ln \{1 - 2i\Delta\tau F(x,N)\} \qquad (5.6)$$

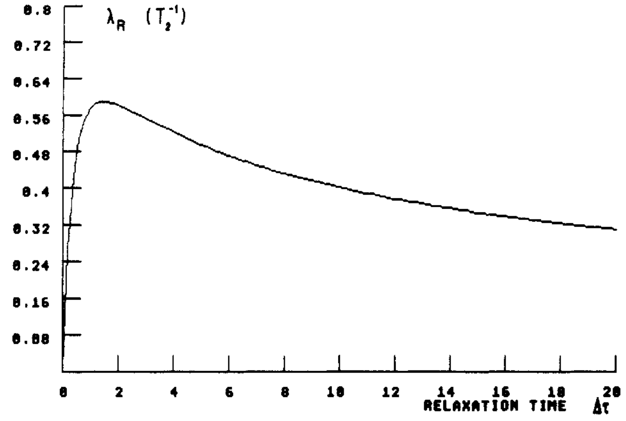


Figure 2. Spin–spin relaxation time as a function of the single bond relaxation time τ.

This result demonstrates that for times greater than the longest relaxation time, the relaxation function has a simple exponential form. It should be noticed that λ^* can be complex-, so that the complete relaxation function (2.10) will have the form

$$G(t) = \exp(-\lambda_R t) \cos(\lambda_I t) \qquad t \gg \tau N^2 \tag{5.7}$$

where

$$\lambda_R + i\lambda_I = \lambda^*(2\Delta\tau,N) + 2\lambda^*(-\Delta\tau,N) \tag{5.8}$$

λ_R^{-1} can be identified with the spin–spin relaxation time T_2 and depends directly on the Rouse relaxation times $\{\tau_p\}$, and through them it depends indirectly on the temperature and molecular weight. It is relatively straightforward to give an accurate treatment of the single relaxation time model. This is a single-bond model that is obtained by setting $N = 2$ and is treated in the next section.

6. Results for a Single Relaxation Time Model

If we set $N = 2$, then there is only one normal mode $p = 1$, the dynamics of which are governed by a single relaxation time $\tau_1 = 2\tau$. from (5.6), $\lambda^*(\Delta\tau,N)$ can be written as

$$\lambda^*(\Delta\tau,N) = \tau_1^{-1} = \int_0^\infty (\mathrm{d}x/2\pi) \ln\left\{\frac{x^2 + 1 - i2\Delta\tau}{x^2 + 1}\right\} \tag{6.1}$$

The integral can be evaluated as

$$\lambda^*(\Delta\tau,N) = (1/2\tau_1)((1 - 2i\Delta\tau_1)^{1/2} - 1) \tag{6.2}$$

hence the relaxation function

$$g(\Delta,t) = \exp(-t/2\tau_1)((1 - 2i\Delta\tau_1)^{1/2} - 1) \tag{6.3}$$

and the full relaxation function is given as

$$G(\Delta,t) = \text{real part: } (-g(2\Delta,t)\, g(-\Delta,t)\, g(-\Delta,t)) = \exp(-\lambda_R t) \cos(\lambda_I t)$$

where

$$\lambda^* = \lambda_R + i\lambda_I = (1/2\tau_1)((1 - 4i\Delta\tau_1)^{1/2} + 2(1 + 2i\Delta\tau_1)^{1/2} - 3) \tag{6.4}$$

The overall decay rate of the relaxation function T_2^{-1} is determined by λ_R, which is gotten from the real part of (6.4). The dependence on the relaxation time τ is interesting since this shows a maximum when $\Delta\tau \approx 1$. The full dependence obtained from (6.4) is shown in Figure 2.

Since τ depends on the temperature in a single-valued manner, this result implies a corresponding temperature dependence for the relaxation rate. Two limits are of particular interest (we set $\tau_1 = 2\tau$): For $\Delta\tau \ll 1$

$$G(\Omega,t) = \exp(-3\Delta t\tau) \tag{6.5}$$

and λ_R increases as τ, whereas for $\Delta\tau \gg 1$

$$G(\Omega,t) = \exp\left(-\frac{\Delta t}{(\Delta\tau)^{1/2}}\frac{(1 + 2^{1/2})}{2}\right) \cos\left(\frac{\Delta t}{(\Delta\tau)^{1/2}}\frac{(1 - 2^{1/2})}{2}\right) \tag{6.6}$$

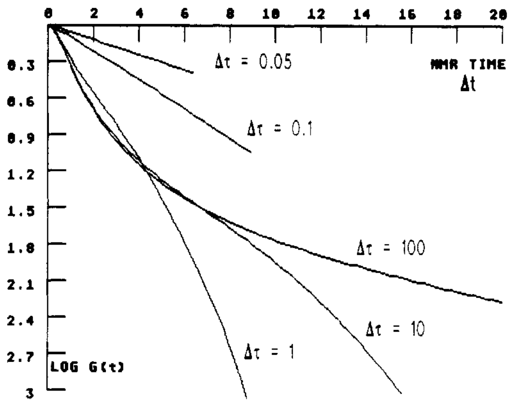


Figure 3. Numerical calculation of the relaxation function given by eq 3.9–3.11, for a dynamical model governed by one relaxation time τ.

which contains an additional cosine modulation and where λ_R decreases as $\tau^{-1/2}$. In fact this linear increase for small τ and $\tau^{-1/2}$ decrease for large τ are quite general and hold equally well for large N. This is shown in section 7 as a consequence of the molecular weight dependence of $\lambda^*(\Delta\tau,N)$. Returning to the single-bond case, the full relaxation function valid over the entire t range has been numerically computed from (3.9)–(3.11) and is shown in Figure 3 for various values of the dimensionless quantity $\Delta\tau$. Over the range shown the analytic formulas (6.5) and (6.6) give excellent fits to these curves, which also confirm the previous result that the decay rate is a maximum when $\Delta\tau \approx 1$. The sharp downturn of the $\Delta\tau = 1$, 10 curves is due to the cosine factor of (6.6).

The present result, especially in the region $\Delta\tau \gg 1$, represents a considerable improvement on taking the second-order term of a cumulant expansion (second moment approximation), an approximation frequently used in NMR work. For completeness we mention here that the second moment approximation for the exponential of a random variable $\psi(t)$ can be stated as

$$\langle \exp(\psi(t)) \rangle \sim \exp\left(\frac{1}{2}\langle \psi(t)^2 \rangle\right) \tag{6.7}$$

It is exact only when $\psi(t)$ is a Gaussian random variable. The problem we are considering has

$$\psi(t) = \frac{3i\Delta}{2b^2}\int_0^t x^2(t')\, \mathrm{d}t'$$

which is not a Gaussian random variable. For the Rouse model

$$\langle \psi(t)^2 \rangle = -\left(\frac{3\Delta}{2b^2}\right)^2 \int_0^t \int_0^t \langle x_j^2(t')\, x_j^2(t'') \rangle\, \mathrm{d}t'\, \mathrm{d}t''$$

and can be evaluated for a chain of only one active mode ($\tau_1 = 2\tau$). The result can be written as[9]

$$G(t) = \exp[-3\Delta^2\tau_1(t/\tau_1 - (1 - \exp(-t/\tau_1)))] \tag{6.8}$$

For $t > \tau$

$$G(t) \approx \exp(-3\Delta^2\tau t) \tag{6.9}$$

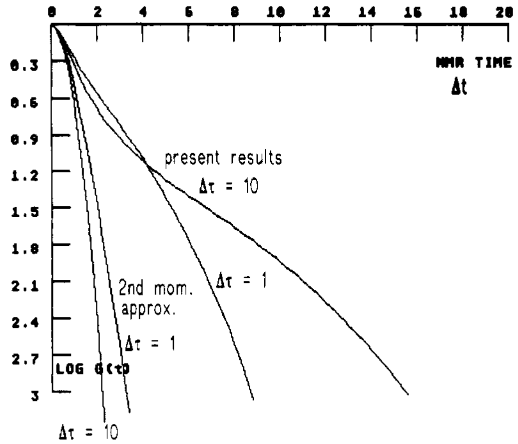


Figure 4. Comparison of the present results with the second moment approximation.

This second moment approximation result agrees with our full result only in the $\Delta\tau \ll 1$ limit. The functional form given by (6.8) is plotted in Figure 4 together with a comparison of the numerical results shown in Figure 3.

7. Molecular Weight Dependence

If we consider times greater than the longest Rouse mode ($t > \tau N^2$), then we can use the analytic result (5.5) for the relaxation function. In particular the molecular weight (N) dependence is completely contained in the function $F(x,N)$ given by (5.3). For sufficiently large N we can replace the sum over normal modes by an integral, according to

$$(1/N)\sum_p \rightarrow \int \mathrm{d}p/N$$

and replace $\sin^2 (\pi p/2N) \rightarrow (\pi p/2N)^2$. Then from (5.3)

$$F(x,N) = \frac{4}{\pi}\int_{\pi/2N}^{\pi/2} \mathrm{d}q \sin^2\left(2qj\left\{\frac{q^2}{x^2+q^4}\right\}\right) \qquad (7.1)$$

where $q = \pi p/2N$.

The complete evaluation of $\lambda^*(\Delta\tau,N)$, given by (5.6), presents some technical difficulties due to the intractable nature of the integrals involved. We can, however, deal with the limit $\Delta\tau \ll 1$ by expanding

$$\lambda^*(\Delta\tau,N) = \tau^{-1}\int_0^\infty (\mathrm{d}x/2\pi) \ln \{1 - 2i\Delta\tau F(x,N)\} = (\tau^{-1}/2\pi)\int_0^\infty \mathrm{d}x\, \{-2i\Delta\tau F(x,N) + 2(\Delta\tau)^2F^2(x,N) + 2i(\Delta\tau)^3(F(x,N))^3 + ...\} \qquad (7.2)$$

The first term does not contribute to the final result because we eventually need the combination of $2\Delta,-\Delta,-\Delta$, and so the linear terms cancel. The quadratic term involves standard integrals and gives

$$\lambda^*(\Delta\tau,N) = (\Delta\tau)^2 \frac{\ln N}{\pi\tau} \qquad (7.3)$$

The complete result for the relaxation function can be written as

$$g(\Delta,t) = \exp[-\Delta\tau \ln (N)t/\pi]$$

$$G(\Delta,t) = \exp[-6\Delta^2\tau \ln (N)t/\pi] \qquad (7.4)$$

The ln (N) dependence of $\lambda^*(\Delta\tau,N)$, or equivalently the NMR relaxation time T_2, was originally found by Ullman,[11] who assumed from the outset a Rouse–Zimm model for the bonds carrying the spin pairs. In the free-draining limit the ln (N) dependence was obtained, whereas for a strong hydrodynamic interaction no dependence on N was found. In Ullman's work the second moment or cumulant approximation was used to perform the statistical averaging. However, the validity of this approximation is further limited for long chains as can be seen by evaluating the next term, $\sim(\Delta\tau)^3$, in the expansion (7.2). The result is the imaginary term $3i(\Delta\tau)^3N/2\pi$, which consequently contributes an oscillating term to the relaxation function, i.e.

$$G(\Delta,t) = \exp\left[-\frac{6}{\pi}(\Delta\tau)^2 \ln (N)\frac{t}{\tau}\right] \cos\left[\frac{9}{\pi}(\Delta\tau)^3N\frac{t}{\tau}\right] \qquad (7.5)$$

Furthermore, the cosine term has the unexpected molecular weight dependence N, which limits the validity of the expansion from $\Delta\tau \ll 1$ to $(\Delta\tau)^3N \ll 1$. To explore the $N \rightarrow \infty$ limit, we have to try and evaluate the term $F(x,N)$. The qualitative behavior of the relaxation function in this limit can be obtained as follows: the exact expression (7.1) for the term $F(x,N)$ which carries all the molecular weight dependence can be evaluated: For $j = N/2$ and $\sin^2 qN = {}^1/_2$, the integral in (7.1) can be done exactly to give

$$F(x,N) = \frac{1}{4\pi(2x)^{1/2}}\left\{\ln \frac{q^2 - (2x)^{1/2}q + x^2}{q^2 + (2x)^{1/2}q + x^2} + 2 \tan^{-1} \frac{(2x)^{1/2}q}{x^2 - q^2}\right\}\Bigg|_{\pi/2N}^{\pi/2} \qquad (7.6)$$

This form is intractable for the x integration in (7.2) needed to evaluate λ^*; however, if we let $N \rightarrow \infty$, then for $x < \pi/2$

$$F(x,N) = a/x^{1/2} \quad (a = 1/2^{3/2})$$

and for $x > \pi/2$

$$F(x,N) = b/x^2 \quad (b = (\pi/2)^3/3) \qquad (7.7)$$

Without trying to match these functions up, we can attempt to evaluate

$$\lambda^*(\Delta\tau,N) = \tau^{-1}\int_0^\infty \frac{\mathrm{d}x}{2\pi} \ln \{1 - 2i\Delta\tau F(x,N)\}$$

as

$$\lambda^*(\Delta\tau,N) = \tau^{-1}\int_0^{\pi/2} \frac{\mathrm{d}x}{2\pi} \ln \{1 - 2i\Delta\tau a/x^{1/2}\} + \tau^{-1}\int_{\pi/2}^\infty \frac{\mathrm{d}x}{2\pi} \ln \{1 - 2i\Delta\tau b/x^2\} \qquad (7.8)$$

Both of these integrals can be done, and for purely cosmetic results we will use 1 instead of $\pi/2$ as the crossover point. In which case

$$\lambda^*(\Delta\tau,N) = (1/2\pi\tau)\{(1 - (2i\Delta\tau a)^2) \ln (1 - 2i\Delta\tau a) + (2i\Delta\tau a)^2 \ln (-2i\Delta\tau a)\} + (1/2\pi\tau)\{\pi(-2i\Delta\tau b)^{1/2} - 2(-2i\Delta\tau b)^{1/2} \tan^{-1} (1/-2i\Delta\tau b)^{1/2} - \ln (1 - 2i\Delta\tau b)\} \qquad (7.9)$$

(Terms linear in Δ have been omitted as they ultimately do not contribute.) For $\Delta\tau \ll 1$, the dominant term comes from the first term and is

$$\lambda^*(\Delta\tau,N) \sim (1/2\pi\tau)(2i\Delta\tau a)^2 \ln (-2i\Delta\tau a) = -(1/2\pi\tau)(2\Delta\tau a)^2\{\ln (2\Delta\tau a) + \sin (\Delta)i\pi(3/2)\} \qquad (7.10)$$

hence as $N \rightarrow \infty$

$$G(\Delta,t) = \exp[-(4/\pi)(\Delta\tau a)^2\{2 \ln (4\Delta\tau a)^{-1} + \ln (2\Delta\tau a)^{-1}\}(t/\tau)] \cos \{6\tau^{-1}(\Delta\tau a)^2(t/\tau)\} \qquad (7.11)$$

The result indicates that when the molecular weight exceeds the value $N_{\max}$, given by $N_{\max} \sim 1/(\Delta\tau)$, then the effect of the molecular weight saturates. In other words the dynamics of a single bond, as perceived by NMR, is sensitive only to the other bonds up to a maximum number given by $N_{\max}$. It can also be seen from (7.11) that the real part of λ^* depends linearly on the relaxation time τ. Similarly for $\Delta\tau \gg 1$ the second terms of (7.9) dominate and the real part of $\lambda^* \sim \tau^{-1/2}$. Thus the behavior of λ^* found analytically for the single-bond case also holds in the general case.

8. Summary

The relaxation of the transverse components of magnetization, due to dipolar interactions between a spin pair on an isolated bond along a polymer chain, has been calculated by first scaling the chain and then using the Rouse model for the chain dynamics. Explicit expressions for the relaxation function are given in terms of an NMR time scale Δ, the fastest Rouse relaxation time τ, the degree of polymerization of the chain N, and the position j of the bond along the chain. The mathematical technique employed allows for a systematic development of the relaxation function in terms of frequency components ω_α labeled by integer values α.

For times t greater than the longest Rouse mode τN^2 we showed that the relaxation function is given by the real part of an exponential form: $\exp(-\lambda^*(\Delta\tau,N)t)$. A variety of different behaviors was found depending on whether the combinations $\Delta\tau$ and $N\Delta\tau$ are greater or less than 1. For $\Delta\tau \ll 1$ $\lambda^*(\Delta\tau,N)$ is real and a pure exponential decay is seen, whereas for $\Delta\tau \gg 1$ $\lambda^*(\Delta\tau,N)$ is complex and the relaxation function is modulated by a cosine term. The decay of the relaxation function, determined by the real part of λ^* and identified with the usual transverse relaxation time T_2^{-1}, is a maximum for $\Delta\tau \sim 1$. It increases linearly as τ for $\Delta\tau \ll 1$ and decreases as $\tau^{-1/2}$ for $\Delta\tau \gg 1$. As $\tau \to \infty$ the frozen limit, which can be obtained independently of the present approach, is correctly obtained. Since τ increase monotonically as the temperature T decreases, then this maximum is also expected in the temperature dependence of the relaxation rate T_2^{-1}.

A maximum in T_2^{-1} has been reported in the work of Geschke and Poschel[12] on polystyrene, Muller et al.[13] on semiflexible liquid-crystal polyesters, and Sillescu et al.[14] on a polystyrene–toluene system. However most investigators, for example, see a recent review by Kimmich,[15] find only T_2^{-1} increasing with $1/T$ and then becoming constant at low temperatures. The work of Sillescu[14] in fact shows both kinds of behavior.

The experimental situation may be confused by the necessity to adopt a working definition for T_2 when the NMR relaxation is not strictly exponential. This occurs quite noticeably as the temperature is lowered and T_2 is taken as the time for the relaxation to fall to $1/e$ of the initial value. The theoretical curves drawn in Figure 3 give a good indication of the difficulties of interpretation that this can lead to. The nonexponential behavior of the curves when $\tau > \Delta^{-1}$ (i.e., lower temperatures) was shown to originate from a cosine term modulating the original exponential behavior, e.g., eq 6.6. Strictly speaking, the analytic work shows that it is the rate of the underlying exponential, i.e., the real part of $\lambda^*(\Delta\tau,N)$, that shows the maximum in the temperature dependence. If the working definition of T_2 were applied to the curves shown in Figure 3, then it is clear by inspection that the value of T_2 obtained would increase continuously through $\Delta\tau = 1$ and become asymptotically constant as $\Delta\tau \to \infty$. This emphasizes the need to fit the relaxation function and not to simply force an exponential fit. It is hoped to return these matters on another occasion.

The molecular weight dependence of $\lambda^*(\Delta\tau,N)$ shows a ln (N) dependence when $\Delta\tau \ll 1$ up to a maximum value $N_{\mathrm{ma}} \sim 1/\Delta\tau$ and for $N > N_{\max}$ is independent of molecular weight. Experimentally the situation is complicated by the fact that when the molecular weight is increased, the validity of the Rouse model is limited up to a critical molecular weight M_c. At higher molecular weights entanglement effects play an increasing important role and the dynamics of the chain are fundamentally changed. The effect of the relaxation time T_2 is well documented in the papers of Cohen-Addad and Kimmich cited in the references. For low molecular weight polyethylene McCall et al.[16] and Kimmich[17] consider a power law relationship $T_2 \sim M^a$ and find a $\sim$-0.5 to -0.6. While it is possible to fit the data to this form, Wright[18] has found that the fit is not as good as the fit to the predicted ln (M) behavior especially at the lowest molecular weights.

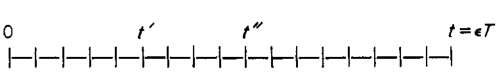
Finally in this paper a new method of computing the NMR relaxation function has been presented. The method does not depend on the use of the Rouse model for the chain dynamics, and other models could have been used. The underlying assumption was only that the dynamics be treated as a Gaussian random process. The Rouse model was used to illustrate various features of the formalism. It was shown that the frequently used second moment or cumulant approximation is valid only when $\Delta\tau \ll 1$ and $N \ll N_{\max}$. For $t < \tau N^2$ the relaxation function does not have a simple exponential form and must in general be computed from (3.9)–(3.11). For the limit $\tau \to \infty$ an algebraic result is obtained.

Appendix

The evaluation of

$$g(\Delta,t) = \left\langle \exp\left[\frac{3i\Delta}{2b^2}\int_0^t x^2(t')\,\mathrm{d}t'\right]\right\rangle \tag{A1}$$

where $x_j(t)$ is a stochastic dynamical variable representing the x component of the jth bond vector $b_j(t)$, is discussed. The dynamics of the $N - 1$ bonds $\{b_j(t)\}$ will be described by the Rouse dynamical equation (3.1). It is convenient to treat time as a discrete variable and to divide the interval from 0 to t into T intervals of duration ϵ, i.e., $t = \epsilon T$



The integral in (A1) is replaced by

$$\int_0^t x_j^2(t')\,\mathrm{d}t' \to \epsilon\sum_{t'=0}^{T} x_j^2(t')$$

$$g(\Delta,t) = \left\langle \exp\left[\frac{3i\Delta}{2b^2}\epsilon\sum_{t'=0}^{T} x_j^2(t')\right]\right\rangle \tag{A2}$$

The quadratic term in the exponential is linearized by using an auxiliary variable $\varphi(t)$ for each time "point" and the mathematical identity

$$\exp\left[\frac{3i\Delta\epsilon}{2b^2}\sum_{t'}^{T} x_j^2(t')\right] = \mathcal{N}\int\cdots\int \prod \mathrm{d}\varphi(t')\,\exp\sum_{t'}^{T}\left\{-\frac{\varphi^2(t')}{6i\Delta\epsilon} + x_j(t')\,\varphi(t')\right\} \tag{A3}$$

where $\mathcal{N}$ is the normalization factor $(6\pi i\Delta\epsilon)^{T/2}$.

The statistical problem is completely solved since $x_j(t)$ is a Gaussian random variable for which we have the result

$$\langle \exp[\sum_{t'} Q(t')\, x_j(t')] \rangle = \exp[\tfrac{1}{2}\sum_{t'}\sum_{t''} Q(t')\, Q(t'')\langle x_j(t')\, x_j(t'')\rangle] \quad \text{(A4)}$$

Hence (A3) becomes

$$\left\langle \exp\frac{3i\Delta}{2b^2}\epsilon\sum_{t'}^{T} x_j^2(t') \right\rangle = \mathcal{N}\int\cdots\int \prod \mathrm{d}\varphi(t')\, \exp\frac{-1}{6i\Delta\epsilon} \times \sum_{t'_1 t_2}\left[\varphi(t_1)\left\{\delta t_1 t_2 - \frac{3i\Delta}{2b^2}\epsilon\langle x_j(t_1)\, x_j(t_2)\rangle\right\}\varphi(t_2)\right] \quad \text{(A5)}$$

Set

$$H(t_1-t_2) = \delta_{t_1t_2} - \frac{3i\Delta}{2b^2}\epsilon\langle x_j(t_1)\, x_j(t_2)\rangle \quad \text{(A6)}$$

Then

$$g(\Delta,t) = \mathcal{N}\int\cdots\int \prod \mathrm{d}\varphi(t')\, \exp\frac{-1}{6i\Delta\epsilon}\sum_{t_1t_2}[\varphi(t_1)\, H(t_1-t_2)\, \varphi(t_2)] \quad \text{(A7)}$$

To do the multiple integrals over the auxillary variables $\{\varphi(t)\}$ it is useful, on the time interval 0–t, to express the auxillary function $\varphi(t)$ in terms of discrete Fourier components $\varphi\alpha$:

$$\varphi(t) = T^{-1}\sum_{\alpha=-T/2}^{+T/2} \varphi_\alpha \exp\frac{2\pi i\alpha t}{T} \quad \text{(A8)}$$

The number of components φ_α (α an integer in the range $-T/2$ to $T/2$) is the same as the number of discrete components $\varphi(t)$, and $\varphi_{-\alpha} = \varphi^*_\alpha$. Then the exponent in (A7) becomes

$$\sum_{t'_1 t}^{TT}\varphi(t_1)\, H(t_1-t_2)\, \varphi(t) = \sum_{\alpha\beta}^{TT}\varphi_\alpha\varphi_\beta H_{\alpha\beta} \quad \text{(A9)}$$

here

$$H_{\alpha\beta} = T^{-2}\sum_{t_1t_2}^{TT} H(t_1-t_2)\, \exp\left[\frac{2\pi i}{T}(\alpha t_1 + \beta t_2)\right]$$

The advantage of this transformation is, as we will shortly show, that in the long time limit $t \to \infty$ the matrix $H_{\alpha\beta}$ becomes diagonal, i.e.

$$T \to \infty \qquad H_{\alpha\beta} \to H_\alpha \qquad \alpha = \beta$$
$$\to 0 \qquad \alpha \neq \beta$$

Using (A9) and separating the diagonal and off-diagonal terms, (A7) can be written as

$$g(\Delta,t) = \int D\{\varphi\}\, \exp\left(\frac{-1}{2K}\sum_\alpha|\varphi_\alpha|^2 H_{\alpha\alpha}\right)\exp\left(\frac{-1}{2K}\sum_{\alpha\neq\beta}\varphi_\alpha\varphi_\beta H_{\alpha\beta}\right) \quad \text{(A10)}$$

where $K = 3\Delta i\epsilon$.

The exponential containing the off-diagonal terms is expanded

$$g(\Delta,t) = \int D\{\varphi\}\, \exp\frac{-1}{2K}\sum_\alpha|\varphi_\alpha|^2 H_{\alpha\alpha}\left\{1 - \frac{1}{2K\epsilon}\sum_{\alpha\neq\beta}\varphi_\alpha\varphi_\beta H_{\alpha\beta} + \frac{1}{2}\left(\frac{1}{2K\epsilon}\right)^2\sum_{\alpha\neq\beta}\sum_{\gamma\neq\delta}\varphi_\alpha\varphi_\beta H_{\alpha\beta}\varphi_\delta\varphi_\gamma H_{\gamma\delta} - \ldots\right\} \quad \text{(A11)}$$

and then integrated term by term to give

$$g(\Delta,t) = \left(\prod_{\alpha=-\infty}^{\alpha=+\infty} H_{\alpha\alpha}^{-1/2}\right)\left\{1 + \sum_{\alpha\neq\beta}\frac{H_{\alpha\beta}^2}{H_{\alpha\alpha}H_{\beta\beta}} + \ldots\right\} \quad \text{(A12)}$$

For the Rouse model the matrix $H_{\alpha\beta}$ (given by (A6)) can be calculated explicity. The important term in (A6) involves the bond vector correlation $\langle x_j(t_1)\, x_j(t_2)\rangle$ and is given from (3.7) as

$$\langle x_j(t_1)\, x_j(t_2)\rangle = \Gamma_j(t_1 - t_2) = \frac{2b^2}{3N}\sum_p \sin^2\frac{\pi pj}{N}\, \exp\frac{-|t_1 - t_2|}{\tau_p} \quad \text{(A13)}$$

The sums in (A9) over the discrete time points can be converted back into integrals, for example, the term defined by

$$\Gamma_{p\alpha\beta} = \frac{1}{t^2}\int_0^t\int_0^t \mathrm{d}t'\, \mathrm{d}t''\, \exp\frac{-|t' - t''|}{\tau_p}\, \exp\frac{2\pi i\alpha t'}{t} \times \exp\frac{2\pi i\beta t''}{t} = \delta_{\alpha,-\beta}\frac{2}{(\omega_\alpha\tau_p)^2 + 1}\, \frac{1}{t/\tau_p} - \left[\frac{\{(\omega_\beta\omega_\alpha\tau_p^2) + 1\}\{1 - \exp(-|t|/\tau_p)\}}{\{(\omega_\beta\tau_p)^2 + 1\}\{(\omega_\alpha\tau_p)^2 + 1\}(t/\tau_p)^2}\right] \quad \text{(A14)}$$

where $\omega_\alpha = 2\pi\alpha/t$.

The relative contribution of the diagonal term $\Gamma_{p\alpha\alpha}$ and the off-diagonal term $\Gamma_{p\alpha\beta}$ can be judged in the two limits $t \to 0$ and $t > \max(\tau_p)$. As

$$t > \max(\tau_p) \qquad \Gamma_{p\alpha\alpha} \sim 2\tau_p/t$$

$$\text{whereas} \quad \Gamma_{p\alpha\beta} \sim 2/(\tau_p/t)^2$$

and

$$t \to 0 \qquad \Gamma_{p\alpha\alpha} \sim 4t/\tau\alpha_p^2 \qquad \alpha \neq 0$$
$$\sim 1 \qquad \alpha = 0$$

whereas

$$\Gamma'_{p\alpha\beta} \sim t/\tau_p\alpha\beta \qquad \alpha \neq \beta \neq 0$$

In both limits the diagonal term is the dominant one. However, the expansion (A12) allows for a systematic inclusion of the off-diagonal terms. For various test values of the parameter $\Delta\tau$ the off-diagonal terms in (A12) did not appear to significantly alter the result obtained by using only the diagonal terms.

Retaining only the diagonal contributions, the relaxation function given by (A12) can be written as

$$g(\Delta,t) = \prod_{\alpha=-\infty}^{\alpha=+\infty} H_{\alpha\alpha}^{-1/2} = \prod_{\alpha=-\infty}^{\alpha=+\infty}[1 - 3i\Delta t\Gamma_{j\alpha}(t)]^{-1/2} \quad \text{(A15)}$$

where

$$\Gamma_{j\alpha}(t) = \frac{2b^2}{3N}\sum_p \sin^2\frac{\pi pj}{N}\, \Gamma_{p\alpha}(t)$$

and $\Gamma_{p\alpha}(t)$ is given by the diagonal part of (A14):

$$\Gamma_{p\alpha}(t) = \frac{2}{(\omega_\alpha\tau_p)^2 + 1}\, \frac{1}{t/\tau_p}\left[1 + \frac{\{(\omega_\alpha\tau_p)^2 - 1\}}{\{(\omega_\alpha\tau_p)^2 + 1\}}\, \frac{\{1 - \exp(-|t|/\tau_p)\}}{t/\tau_p}\right] \quad \text{(A16)}$$

Acknowledgment. I thank Prof. I. Ward for bringing this problem to my attention and providing the impetus to find a full solution for the relaxation function. I have also greatly benefited from conversations with Drs. N. Boden and P. Klein on the experimental results obtainable from NMR.

References and Notes

(1) Slichter, C. P. *Principles of Magnetic Resonance*; Springer-Verlag: Berlin, 1978.
(2) Kubo, R. In *Fluctuation, Relaxation and Resonance in Magnetic Systems*; ter Haar, D., Ed.; Oliver & Boyd: Edinburgh, 1962.

3674 *Macromolecules* **1989**, *22*, 3674-3681

(3) Rouse, P. *J. Chem. Phys.* **1953**, *21*, 1272.
(4) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*: Cornell University Press: Ithaca, NY, 1979.
(5) Cohen-Addad, J. P.; Dupeyre, R. *Polymer* **1983**, *24*, 400.
(6) Cohen-Addad, J. P.; Guillermo, J. *J. Polym. Sci.* **1984**, *22*, 931.
(7) Cohen-Addad, J. P. *J. Phys. (Les Ulis, Fr.)* **1982**, *43*, 1509.
(8) Cohen-Addad, J. P.; Domard, M. *J. Chem. Phys.* **1982**, *76*, 2744.
(9) Cohen-Addad, J. P.; Boileau, S. *J. Chem. Phys.* **1981**, *75*, 4107.
(10) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, 1986.
(11) Ullman, R. *J. Chem. Phys.* **1965**, *43*, 3161.
(12) Geschke, D.; Poschel, K. *Colloid Polym. Sci.* **1986**, *264*, 482.
(13) Muller, K.; Schleicher, A.; Ohmes, E.; Ferrarini, A.; Kothe, G. *Macromolecules* **1987**, *20*, 2761.
(14) Rossler, E.; Sillescu, H.; Spiess, H. W. *Polymer* **1985**, *26*, 203.
(15) Kimmich, R.; *Prog. Nucl. Magn. Reson. Spectros. 20*, **1988**, 385.
(16) McCall, D.; Douglass, D.; Anderson, E. *J. Polym. Sci.* **1962**, *59*, 301.
(17) Kimmich, R.; Bachus, R. *Colloid Polym. Sci.* **1982**, *260*, 911.
(18) Wright, P. Thesis, University of Leeds, 1988.

Correlation of Phase-Separation Behavior in Polymer Blends with Thermodynamic Measurements in the One-Phase Region

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ABSTRACT: When a polymer blend is heated to within the unstable region of the temperature composition diagram, spinodal decomposition may be observed using small-angle neutron scattering. In the one-phase region, scattering has been used to obtain the temperature and composition dependence of the second derivative with respect to composition of the Gibbs free energy of mixing. Correlation of these two types of measurements not only tests the current theories of spinodal decomposition but also provides insight into the molecular parameters controlling domain morphology in phase-separating blends.

Introduction

If the temperature of a partially miscible polymer blend is raised from the one-phase region to the two-phase region, then concentration fluctuations become unstable, and phase separation results via spinodal decomposition.[1,2] The driving force for this process is provided by the gradient of the chemical potential.[3] There has been a recent surge of interest in the theory[4-7] and the experimental observation[8-10] of phase separation in polymer blends both because of the technological interest in polymeric materials and because the high viscosities of these systems slow down the process and allow the kinetics in the early stages to be observed and thus test the theoretical predictions.

For the most commonly studied system—polystyrene with poly(vinyl methyl ether)—the wavelength of the unstable concentration fluctuations lies dominantly around 10^4 Å, and therefore light-scattering techniques have been employed. Recently, Meier and Strobl[11] employed SAXS to study a blend of polystyrene with poly(styrene-*co*-bromostyrene) well away from the dominant distance scale. However, for a number of systems, we have noted length scales of less than 10^3 Å in the scattering from two-phase blends. An example of such a system is poly(methyl methacrylate) with solution chlorinated polyethylene,[12] and in this case SANS and SAXS techniques were the obvious choices of scattering techniques.

In several recent papers[13-19] it has been shown that small-angle neutron-scattering measurements from the concentration fluctuations in a single-phase two-component polymer blend may be used to determine the Flory interaction parameter of the blend. The concentration fluctuations in such a system were originally shown by Einstein[20] to depend on the concentration gradient of the chemical potential, which Debye and Bueche[21] subsequently related to interactions in the system using the Flory–Huggins equation.[22]

If the temperature and concentration dependences of the chemical potential gradient are determined, then, by extrapolation, it is possible to obtain values inside the phase boundary and thus to predict the dominant length scale for phase separation. In this paper we test, for the first time, this correlation between neutron scattering from the stable and unstable regimes of the phase diagram for a blend of poly(methyl methacrylate) (PMMA) with poly(α-methylstyrene-*co*-acrylonitrile) (PAMSAN).

The linearized theory of spinodal decomposition was originally developed for small-molecule systems by Cahn and Hilliard,[1,2] subsequently adapted to polymeric systems by van Aartsen,[3] and reformulated on the basis of mean-field theory to predict the behavior of the intensity of scattered radiation as function of time by Pincus,[4] de Gennes,[5] and most extensively by Binder.[6]

The influence of thermal fluctuations was first introduced to the theoretical development by Cook,[23] and the significance was further explored by Binder.[24] Okada and Han[10] showed that the contribution to the observed scattering from thermal fluctuations was negligible except when experiments were carried out very close to the spinodal temperature (in this case, "very close" meant within 1°). The small-angle neutron-scattering data from blends of PMMA/PAMSAN presented in this paper are used to test the theoretical predictions; for spinodal decomposition, in particular, the influence of thermal fluctuations near the spinodal temperature is examined in some detail.

Thermodynamics of Polymer Blends

The free energy of mixing, ΔG_m for a polymer blend may be calculated from the Flory–Huggins lattice model.[22] ΔG_m is here expressed per lattice segment and

$$\Delta G_m/RT = n_1 \ln \Phi_1 + n_2 \ln \Phi_2 + \Phi_1\Phi_2\chi_{12} \qquad (1)$$

n_1 and n_2 are the molar numbers of polymers 1 and 2, respectively. Φ_1 and Φ_2 are the volume fractions of the components. χ_{12} is the interaction parameter. In the original Flory–Huggins theory[22] χ_{12} was independent of concentration and inversely dependent on temperature. However, with such a simple description of χ_{12} eq 1 is

0024-9297/89/2222-3674$01.50/0