A Solvable Model of Polymer Main-Chain Dynamics with Applications to Spin Relaxation

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ABSTRACT: A conformational jump model, of the kind recently put forth by Valeur, Jarry, Gény, and Monnerie, but not restricted to a lattice, is solved in the continuum limit. Large and small cutoffs are introduced into the frequency spectrum and are the two free parameters of the theory. Since the high molecular weight limit is taken, overall rotation of the molecule is neglected. The theory is applied to ^{13}C and ^{1}H spin relaxation data for polymers in solution and in the solid state.

The problem of the dissipative mechanism(s) of polymer dynamics is a ubiquitous one as it appears in studies of viscosity, dielectric dispersion, NMR relaxation, and mechanical properties. While it would undoubtedly be aesthetically pleasing (as well as theoretically useful) to solve for such dissipative mechanisms from first principles the complexity of the polymer dynamical problem makes this impractical. Hence most theoretical studies are studies of dynamical models which greatly simplify the physical situation yet (hopefully) preserve part of the relevant physics. We here present one such simple model and compare it with NMR relaxation data for polymers in solution and in the rubber state in the hope that such a study will shed further light on the complicated physical situation.

A familiar approach to polymer dynamics is the study of the propagation of collective dynamical modes within individual polymer molecules. While physically attractive, such a description is complicated by chain flexibility and the host of internal rotameric states. The Rouse–Zimm[2] treatment of the polymer dynamics of isolated chain molecules (given a firm theoretical basis by Bixon,[3] Zwanzig,[4] and others) restricts attention to the long wavelength, low frequency modes of the polymer chain. Such theories can ignore detailed local chain structure, and a proper description of the dynamical coupling between the Rouse–Zimm modes and local chain motions is expectantly awaited. Moreover, there is limited understanding of the character of the local dynamical chain motions which determine the high-frequency response of the polymer molecule to external stresses.[5]

While fundamental uncertainties remain, practical progress has been made in the ability to match to low frequency dilute solution data, especially for the case of mechanical shear response, by the introduction of an "internal viscosity" of the Rouse–Zimm polymer bead.[6–8] The use of an internal viscosity glosses over basic ignorance of the intermediate frequency regime but provides a mechanism for dissipating the Rouse–Zimm mode energies into the temperature "bath" of the rapidly varying local motions. By positioning a restoring force on a bead dependent on the velocity of the bead, the internal viscosity theories can account for nonlinear visoelastic effects observed experimentally.[9] Though the status of internal viscosity remains controversial, its formal relationship to the "memory kernels" of rigorous projection operator[3,4] theories is known, and recently Adelman and Freed have attempted an explicit calculation assuming anharmonicity in the Rouse–Zimm potential.[10]

Theoretical efforts to describe the short-time behavior (i.e., high frequency or low temperature) involving local conformational processes of polymer chains are not as numerous as those elaborating on the bead-spring models. Partly this may be owing to the variety of pathways imaginable for the dissipation of a local excitation (side-group motion,[11] coupling to overall rotary diffusion,[12] coupling to Rouse–Zimm modes,[13,14] intermolecular relaxation[15,16]), and partly it may be due to experimental problems[16,17] which do not allow clear choices to be made between various relaxation models. Yet the situation is not nearly as discouraging as might be thought since several facts suggest that improved understanding is possible and perhaps not too difficult to achieve:

(1) NMR and dielectric relaxation rates are relatively insensitive to molecular weight (M) at sufficiently high M (for $M \geq 10^4$) so that coupling to the Rouse–Zimm modes can be ignored.[16,17]

(2) Ad-hoc introduction of correlation–time distributions seems able to patch-up the single-relaxation time frequency spectra so that ^{13}C NMR relaxation times for polymer molecules in solution can be adequately fitted.[18,19]

(3) Varying polymer concentrations in solution has little or no effect on magnetic relaxation measurements of T_1 and nuclear Overhauser enhancements (NOE) in the 1–10% range,[20] so that the solvent–polymer pathway for spin relaxation can be neglected to first order.

Recently two theoretical developments have occurred which successfully exploit the (putative) physical simplicity of local dissipation processes implied by the above observations. The first is the presentation and solution of a diamond lattice conformation jump model by Valeur, Jarry, Gény, and Monnerie (VJGM)[21,22] which allows a computation of the backbone bond autocorrelation function needed for a description of spin relaxation. They consider three-bond segmental reorientations of the "Boyer-crankshaft"[23] variety. Such concerted three-bond motions are of a local character and do not necessitate long-range cooperation of segments. Valeur and co-workers derive a Markovian equation of motion (master equation) for the bond configurational probability $\rho(\mathbf{e},t)$

$$\partial\rho/\partial t = -\upsilon_0 \mathbf{K}\rho \qquad (1)$$

where $\rho_n(\mathbf{e},t)$ is the probability that bond n has direction $\mathbf{e}$ at time t, υ_0 (a scalar) is the probability per unit time that any particular three-bond segment undergoes a conformational jump, and $\mathbf{K}$ is the bond–bond interaction matrix

$$K_{ij} = 2\delta_{ij} - \delta_{i,j-1} - \delta_{i,j+1} \qquad (2)$$

The autocorrelation function VJGM obtained from eq 1 and 2 was found to decay too slowly with time, so that an exponential decay factor had to be introduced.[24a] Thus modified, the VJGM theory has been found to give a good account of fluorescence depolarization,[24b] dielectric relaxation,[24c] and nuclear spin relaxation[24d] for polymers in solution. We show in the present article that it also provides a good description of NMR relaxation in rubbery systems. Heatley and coworkers have concluded that the VJGM model is able to account for ^{13}C and ^{1}H relaxation of vinyl polymers in solution.[19,25,26]

More recently Jones and Stockmayer[27] examined the same Markovian conformational jump model but imposed a sharp

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cutoff on the extent of bond directional correlations. Their method is equivalent to solving eq 1 and 2 as a matrix problem for a finite subset of segments rather than for the whole polymer chain. It is found that either the VJGM or the Jones and Stockmayer models give a consistent interpretation to ^{19}F spin relaxation in poly(p-fluorostyrene) and poly(m-fluorostyrene) solutions.[20]

In this article we present an alternative closed form solution to the Markovian conformational jump model and apply the resulting correlation function to treat spin relaxation in polymers. One goal is to derive an expression for the bond correlation function (and its spectral density) which has practical applicability (as do those of VJGM and Jones and Stockmayer) and to do so in a manner which perhaps sheds further light on the physical meaning of the free parameters. Like Jones and Stockmayer, we introduce a finite cutoff to the range of correlation so as to secure proper (i.e., nearly exponential) decay at long times. We discover that some high-frequency motions can be correlated over quite long distances.

We first present our solution to the polymer master equation, eq 1. The autocorrelation function and spectral density for segment reorientation are derived and compared to previous results. Applications are then made to polymer solution and rubber NMR data and the theory is shown to be as successful as the VJGM theory. Finally we discuss the results and mention experimental ambiguities which render inconclusive quantitative determination of the theoretical parameters.

Solution of the Conformational Jump Model

As mentioned in the introduction, the conformational jump model of eq 1 and 2 has been employed previously[21,22,24,27] and its appearance in connection with a variety of physical phenomena other than polymer dynamics is pointed out by Stockmayer and co-workers.[24,28] As a first-order equation in time, it is not immediately tied to a microscopic dynamical model, but presumably the necessary "preaveraging" using appropriate projection operators[3,4] can be accomplished starting from a realistic Hamiltonian for the local chain coordinates and momenta. Such a derivation would entail all of the well-known problems of going from a dynamical equation of motion to a master equation. We avoid this and rather focus on the consequences of the Markovian conformation jump model for dynamic polymer behavior. Our physical ignorance will be embodied in two free parameters which we hope to later rationalize in terms of detailed chain structures.

Jones and Stockmayer[27] noticed that eq 2 looked at as a finite matrix equation is isomorphic to the Hamiltonian matrix for a linear chain molecule in Hückel molecular orbital theory, and its eigenfunctions and eigenvalues are well known. Using these they obtain the solution to eq 1 and thus the probability autocorrelation function. This approach is quite reasonable if the number of cooperating units along the main chain is rather small (they consider ranges of five to nine units). However, if long-range cooperative effects in the decay of main chain motions are important, as is indicated by the magnetic relaxation studies of Schaefer and co-workers,[29] then the finite matrix method of Jones and Stockmayer becomes unwieldy. In the limit of large N the eigenfunctions of eq 2 are plane waves and eq 2 can be solved in the same manner as Jones and Stockmayer except that the finite sum over the eigenstates of k becomes an integral over the wave vector of the plane waves. Essentially one replaces the discrete Markovian lattice model by a continuum lattice model. However, one does not want to allow all possible wavelengths. Since the polymer molecule really does have the smallest unit that can be displaced it would be unphysical to allow for waves which had a smaller wavelength than such a unit. Hence we impose a small wavelength cutoff which is roughly the size of such a displaceable unit. One also cannot allow arbitrarily long wavelengths since for long enough wavelengths one is describing motions of the polymer chain as a whole (the polymer really is of finite size). Actually the long wavelength cutoff will be shorter than the polymer chain. A transient conformational displacement traveling down the main chain will damp out in a fraction of the molecular length (for large M) owing to the sundry dissipative mechanisms. It is therefore physically sensible to impose a long wavelength cutoff as a rough measure of the correlation length (this corresponds to a continuum version of Jones and Stockmayer's finite matrix cutoff).

In order to mathematically carry out the above procedure we note that in the limit of infinitely large N,[27,30] eq 1 becomes a one-dimensional diffusion equation for the time evolution of the single bond probability

$$\partial\rho/\partial t = \upsilon_0(\partial^2\rho/\partial^2 x) \tag{3}$$

where x is the position along the polymer chain. Since our object is to calculate the time correlation function $\Phi(t)$ which governs relaxation caused by magnetic dipole–dipole coupling between two nuclei[31]

$$\Phi(t) \equiv {}^1\!/\!_2 \langle 3(\mathbf{e}(t)\cdot\mathbf{e}(0))^2 - 1 \rangle \tag{4}$$

(the fences $\langle\,\rangle$ signify a statistical mechanical configurational average) we restrict attention to this quantity and expand $\rho(\mathbf{e},x,t)$ in Legendre polynomials P_n of $\cos\theta_1$, where θ_1 is the angle between $\mathbf{e}(t)$ and a molecule-fixed reference axis $\mathbf{z}$

$$\begin{aligned}\rho(\mathbf{e},x,t) = B_0(x,t)P_0(\cos\theta_1) + B_1(x,t)P_1(\cos\theta_1)\\ + B_2(x,t)P_2(\cos\theta_1) + \ldots\end{aligned} \tag{5}$$

Equation 5 is an approximation and assumes that the probability ρ depends only on the polar component of $\mathbf{e}$. Substituting eq 5 into eq 3, multiplying both sides by $P_n(\cos\theta_1)$, and integrating over $\cos\theta_1$ yields the equation of motion of the nth coefficient:

$$\frac{\partial}{\partial t}B_n(x,t) = \left(\frac{2}{2n+1}\right)\upsilon_0\frac{\partial^2 B_n(x,t)}{\partial x^2} \tag{6}$$

That eq 6 is relevant for the present needs follows from an explicit calculation of $\Phi(t)$ in eq 4. By definition

$$\begin{aligned}\Phi(t) \equiv \langle P_2(\cos\theta_{01})\rangle = \Big\langle P_2(\cos\theta_0)P_2(\cos\theta_1)\\ + {}^1\!/\!_3 P_2^1(\cos\theta_1)\cos(\phi_1 - \phi_0)\\ + \frac{1}{12}P_2^2(\cos\theta_0)P_2^2(\cos\theta_1)\cos(2\{\phi_1 - \phi_0\})\Big\rangle\end{aligned} \tag{7}$$

where the P_n^m are the associated Legendre polynomials and ϕ_0 and ϕ_1 are the azimuthal angles locating $\mathbf{e}(0)$ and $\mathbf{e}(t)$ with respect to the fixed frame. Using the probabilities $\rho(\mathbf{e},x,t)$ and $\rho(\mathbf{e}_0,x,0)$ given in eq 5 one finds

$$\Phi(t) = \frac{4}{25}\langle B_2(x,t)B_2(x,0)\rangle_x \tag{8}$$

the fences $\langle\,\rangle_x$ signify that the configurational average over the chain has yet to be performed.

The solution to eq 6 is found in standard texts;[32]

$$B_n(x,t) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}x'\int_{-\infty}^{\infty}\mathrm{d}k\,e^{ik(x'-x)-\upsilon_n k^2 t}B_n(x',0) \tag{9}$$

where

$$\upsilon_n = \left(\frac{2}{2n+1}\right)\upsilon_0$$

We suppose that at $t = 0$, only the bond at the origin $x' = 0$ is displaced from equilibrium

$$B_n(x',0) = B_n^0\delta(x') \tag{10}$$

Next, we recognize that all wave vectors k in eq 9 are not physically available for the relaxation of the bond fluctuation, but that

$$|k_{\mathrm{A}}| \leq |k| \leq |k_{\mathrm{B}}| \tag{11}$$

corresponding to the long and short wavelength cutoffs discussed above. Then eq 9 becomes

$$B_n(x,t) = \frac{B_n^0}{2\pi}\int_{k_{\mathrm{A}}}^{k_{\mathrm{B}}} \mathrm{d}k e^{ikx - \upsilon_n k^2 t} \tag{12}$$

and we have

$$\langle B_n(x,t)B_n(x,o)\rangle_x = C\left[\frac{(B_n^0)^2}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}x\int_{k_{\mathrm{A}}}^{k_{\mathrm{B}}}\mathrm{d}k \times \int_{k_{\mathrm{A}}}^{k_{\mathrm{B}}}\mathrm{d}k' e^{i(k+k')x-\upsilon_n k^2 t}\right] \tag{13}$$

where C is a normalization constant. Performing the x integration

$$\Phi(t) = C'\int_{k_{\mathrm{A}}}^{k_{\mathrm{B}}}\mathrm{d}k e^{-(2/5)\upsilon_0 k^2 t} \tag{14}$$

with C' a new constant. The integration in eq 14 leads to the normalized autocorrelation function

$$Q(t) \equiv \frac{\Phi(t)}{\Phi(0)} = \tfrac{1}{2}\left(\frac{\pi}{t}\right)^{1/2}(\omega_{\mathrm{B}}{}^{1/2} - \omega_{\mathrm{A}}{}^{1/2})^{-1} \times \{\mathrm{erfc}\,[(\omega_{\mathrm{A}}t)^{1/2}] - \mathrm{erfc}\,[(\omega_{\mathrm{B}}t)^{1/2}]\} \tag{15}$$

where

$$\omega_{\mathrm{A}} = \tfrac{2}{5}k_{\mathrm{A}}^2\upsilon_0$$
$$\omega_{\mathrm{B}} = \tfrac{2}{5}k_{\mathrm{B}}^2\upsilon_0 \tag{16}$$

The autocorrelation function is frequently expressed as a distribution over exponential decay times, i.e.,[18]

$$\phi(t) = \int_{-\infty}^{\infty}\mathrm{d}s\, G(s)e^{-st} \tag{17}$$

where $s = 1/\tau$. Hence, $G(s)$ is the inverse Laplace transform of $\phi(t)$ and is given for the present model (eq 15) by

$$G(s) = \begin{cases}[2(k_{\mathrm{A}}^{1/2} - k_{\mathrm{B}}^{1/2})\, s^{1/2}]^{-1} & k_{\mathrm{A}} < s < k_{\mathrm{B}} \\ 0 & s < k_{\mathrm{A}} \text{ or } s > k_{\mathrm{B}}\end{cases} \tag{18}$$

At short times the autocorrelation function of eq 15 is given by

$$\lim_{t\to 0}\phi(t) \sim 1 - \tfrac{1}{3}(\omega_{\mathrm{A}} + (\omega_{\mathrm{A}}\omega_{\mathrm{B}})^{1/2} + \omega_{\mathrm{B}})|t| + \ldots \tag{19}$$

and since at long times erfc $(Z) \sim (\pi Z)^{-1/2}e^{-Z^2}$

$$\lim_{t\to\infty}\phi(t) \sim \mathrm{e}^{-\omega A|t|}[2|t|(\omega_{\mathrm{B}}{}^{1/2} - \omega_{\mathrm{A}}{}^{1/2})\omega_{\mathrm{A}}{}^{1/2}]^{-1} + \ldots \tag{20}$$

Typically, $\omega_{\mathrm{B}} \simeq 10^{10}\ \mathrm{s}^{-1}$ and $\omega_{\mathrm{A}} \simeq 10^8\ \mathrm{s}^{-1}$, so that $\omega_{\mathrm{B}} - \omega_{\mathrm{A}} \simeq \omega_{\mathrm{B}}$. The autocorrelation function of eq 15 is similar to the VJGM[24] result

$$\phi_{\mathrm{VJGM}}{}^{(t)} = e^{-|\mathrm{t}|T_0{}^{-1}}e^{|t|T_{\mathrm{d}}{}^{-1}}\,\mathrm{erfc}\,[(|t|T_{\mathrm{d}}{}^{-1})^{1/2}] \tag{21}$$

where the exponential decay term with T_0 was introduced to achieve the proper long-time behavior. In the VJGM theory, there is no obvious relation between T_0 and T_{d}. In our theory the long-time behavior is determined by the small k cutoff in the spectrum of relaxation times. If we let $k_{\mathrm{A}} \to 0$ (corresponding to infinite wavelength), we would have a too-slow decay of correlations, as in the original VJGM theory.[21,22] In Figure 1 the autocorrelation function corresponding to our theory, eq 15, and the VJGM theory, eq 21, are plotted together for comparison.

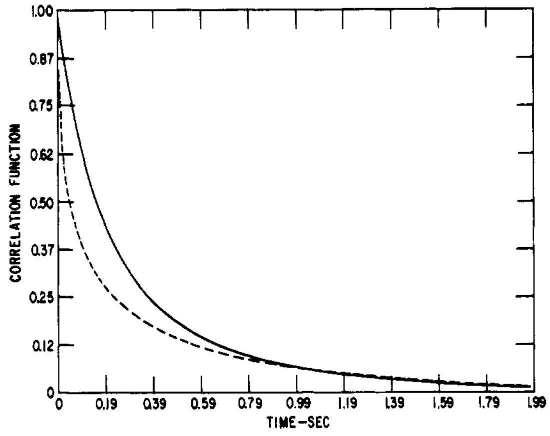

Figure 1. Time dependence of the correlation functions of the present theory, eq 15 (solid), and the VJGM theory, eq 21 (broken). The parameters of the two theories are chosen so that identical asymptotic behavior results. For the present theory, $\omega_{\mathrm{A}} = 1$ and $\omega_{\mathrm{B}} = 10$, and for the VJGM result, $T_0 = 1$ and $T_{\mathrm{d}} = 0.1$.

Nuclear spin relaxation parameters are usually expressed in terms of the spectral density

$$J(\omega) \equiv \int_{-\infty}^{\infty}\phi(t)e^{i\omega t}\,\mathrm{d}t \tag{22}$$

In order to perform this Fourier transform we interchange the order of integrations in eq 14 and 22

$$J(\omega) = \int_{-\infty}^{\infty}e^{i\omega t}\left\{(k_{\mathrm{B}} - k_{\mathrm{A}})^{-1}\int_{k_{\mathrm{A}}}^{k_{\mathrm{B}}}e^{-\upsilon_2 k^2|t|}\,\mathrm{d}k\right\}\mathrm{d}t = (k_{\mathrm{B}} - k_{\mathrm{A}})^{-1}\int_{k_{\mathrm{A}}}^{k_{\mathrm{B}}}\left[\frac{2\upsilon_2 k^2}{(\upsilon_2 k^4 + \omega^2)}\right]\mathrm{d}k \tag{23}$$

or changing variables to $x = k(\omega_2/\omega)^{1/2}$

$$J(\omega) = \frac{2}{\omega^{1/2}(\omega_{\mathrm{B}}{}^{1/2} - \omega_{\mathrm{A}}{}^{1/2})}\int_{(\omega_{\mathrm{A}}/\omega)^{1/2}}^{(\omega_{\mathrm{B}}/\omega)^{1/2}}\frac{x^2}{1 + x^4}\,\mathrm{d}x \tag{24}$$

One can find a closed form expression for eq 24 (this is done in Appendix A); however the integral representation of $J(\omega)$ as given in eq 24 is easier to work with and more suitable for machine calculations.

To account for the tumbling motion of the polymer chain as a whole which occurs in solution, both our autocorrelation function eq 15 and VJGM's eq 21 are multiplied by a rotational diffusion contribution $e^{-tT_{\mathrm{r}}{}^{-1}}$ where the rotational diffusion relaxation time can be obtained from

$$T_{\mathrm{r}} = 2M[\eta]\eta_0/3RT$$

where $[\eta]$ is the intrinsic viscosity of the polymer of molecular weight M in a solvent of viscosity η_0.[26,27] For polymers where $M > 10^4$ the rotational diffusion contribution is negligible, and we will neglect this effect though the analysis can be extended to include rotational diffusion with only slightly more effort. From eq 24 it is not hard to ascertain the limiting behavior of $J(\omega)$:

$$\lim_{\omega\to 0}J(\omega) \sim J(0) - A\omega^2 + \ldots$$

where

$$A = \frac{1}{5}\left[\frac{\omega_{\mathrm{B}}{}^{5/2} - \omega_{\mathrm{A}}{}^{5/2}}{\omega_{\mathrm{B}}{}^{1/2} - \omega_{\mathrm{A}}{}^{1/2}}\right](\omega_{\mathrm{A}}\omega_{\mathrm{B}})^{-5/2} \tag{25}$$

and $J(0) = (\omega_{\mathrm{A}}\omega_{\mathrm{B}})^{-1/2}$

$$\lim_{\omega\to\infty}J(\omega) \sim D/\omega^2 + \ldots$$

where

Table I
Experimental and Theoretical ^{13}C relaxation Parameters for the Methine Carbon of Three Polymers at 22.6 MHz and 35 °C

		Exptl. results[a]			Present theory[b]					VJGM theory[c]				
								Best parameters					"Best" parameters	
Polymer	State	T_1, ms	T_2, ms	NOEF	T_1	T_2	NOEF	ω_A, Hz	ω_B, Hz	T_1	T_2	NOEF	T_0, s	T_d, s
Isotatic polystyrene	*o*-Dichlorobenzene solution	65	26	0.8	65	26	1.1	6.3×10^6	4×10^9	66	25	0.8	3.5×10^{-8}	1.9×10^{-9}
cis-Polyisoprene	Solid	95	29	1.2	93	28	1.20	2.5×10^6	1×10^{10}	91	30	1.0	8×10^{-8}	5×10^{-10}
cis-Polybutadiene	Solid	600	48	1.4	600	51	1.32	1×10^5	5.6×10^{11}	582	48	1.3	4×10^{-6}	5×10^{-12}

[a] From ref 18. [b] Using eq 24 in text. [c] Using eq 27 in text.

$$D = \tfrac{1}{3}[\omega_A + (\omega_B\omega_A)^{1/2} + \omega_B] \tag{26}$$

In the next section the spectral function of eq 24 is employed to quantitatively account for ^{13}C and ^{1}H magnetic relaxation measurements on polymers in bulk (rubber) and in solution. We compare our calculations with results obtained using the VJGM expression[24] (eq 21) which to date is the most successful model of polymer main-chain dynamics. The spectral density corresponding to eq 21 is[21,22]

$$J_{\mathrm{VJGM}}(\omega) = \left\{\frac{T_0T_d(T_0 - T_d)}{(T_0 - T_d)^2 + \omega^2T_0^2T_d^2}\right\} \times \left[\left(\frac{T_0}{2T_d}\right)^{1/2}\left\{\frac{(1 + \omega^2T_0^2)^{1/2} + 1}{1 + \omega^2T_0^2}\right\}^{1/2} + \left(\frac{T_0}{2T_d}\right)^{1/2}\frac{\omega T_0T_d}{T_0 - T_d} \times \left\{\frac{(1 + \omega^2T_0^2)^{1/2} - 1}{1 + \omega^2T_0^2}\right\}^{1/2} - 1\right] \tag{27}$$

Experimental Section

We first consider ^{13}C data, which Schaefer[18] found could not be explained in terms of a *single* relaxation time. The measurements of ref 18 were made at 22.6 MHz, and therein are found the spectral function expressions for the methine carbon spin–lattice relaxation times T_1, line widths T_2, and nuclear Overhauser enhancements NOEF, assuming the mechanism of spin relaxation is pure dipolar coupling of the ^{13}C nucleus to its directly bonded protons. The method of fitting the present theory to the data of ref 18 consists of picking (on a digital computer) a set of values (ω_A, ω_B), calculating the resulting T_1, T_2, and NOEF, and computing the relative deviation of the theoretical and experimental values. The selection of pairs of cutoff frequencies is iterated so as to find the "best" set of (ω_A, ω_B) as measured by the squared relative deviations in T_1, T_2. The NOEF is *not* included in this minimization process and so is "predicted" by theory. For comparison, the same procedure is adopted to test the ability of the VJGM theory eq 21 and 27 to fit the data of ref 18. Both results are presented in Table I. It is clear from Table I that both the present and the VJGM theories provide good fits to the ^{13}C data of Schaefer.

Next we fit the ^{1}H poly(vinyl acetate) solution data of Heatley and Cox,[27] which is probably a more stringent test than the ^{13}C case since both the high and low frequency portions of the spectral density are probed.

Heatley and Cox give expressions for the methine (A) and backbone methylene (B) proton–proton cross-relaxation times T_{AA}, T_{XX}, T_{AX}, and T_{XA} associated with the dipolar proton–proton interactions.[27] Their measurements were performed at 300.25 MHz. They report enhancement factors N_A and N_X for each kind of proton, where

$$\begin{aligned} N_A &= 2T_{AA}/T_{AX} \\ N_X &= T_{XX}/2T_{XA} \end{aligned} \tag{28}$$

and $T_{AX} = 2T_{XA}$. From eq 28 it is apparent that T_{AX} can be determined in two ways: from the experimental enhancement factors N_A and N_X and from the relaxation parameters T_{AA} and T_{AX}. These two sets of T_{AX}'s found using Heatley and Cox's data are given in Table II. Table II is a consistency check on the data since in calculating the NOE enhancement factor from a spectral density function, we calculate only one T_{AX}. One should keep the results of Table II in mind (and the relatively large discrepancies) when comparing calculated and experimental NOE enhancement factors. In Table III are the results of fitting the present theory and the VJGM theory to the Heatley and Cox relaxation data. This is done in the same manner as for Schaefer's data but now we fit T_{AA} and T_{AX} and predict the NOE enhancement factors N_A and N_X.

Discussion

It is apparent from the fit to the experimental results that the present theory and the VJGM theory fit the NMR relaxation data equally well for both bulk polymers (rubbers) and polymers in solution. In Figure 2 we give a sample plot of the spectral density functions for both theories using parameters fit to experimental data on isotactic polystyrene dissolved in dichlorobenzene at 35 °C. (See Table I for the appropriate numerical values of ω_A, ω_B and T_0, T_d.) It is apparent from Figure 2 that a much wider range of frequencies must be used to distinguish between these two theoretical descriptions of main chain polymer relaxation. We can only leave this as a future problem for experimentalists.

Since our theory has built into it the idea of a correlation length we would like to get this out of the theory as this can give us an insight into the physics of the relaxation processes. From eq 16 it is clear that the fit parameters ω_A and ω_B reflect the cutoff wavelengths as they depend on the reciprocal of the square of the cutoff wavelengths. However, ω_A and ω_B also depend on the intrinsic polymer jump probability, which we do not know. Thus, we cannot deduce the correlation lengths directly, but by defining a correlation range R

$$R \equiv (\omega_A/\omega_B)^{1/2} \tag{29}$$

we can obtain a relative measure. R is roughly the number of smallest displaceable units the correlation goes over. The correlation range is given in Table IV for Schaefer's data and Heatley and Cox's data. We should emphasize that the correlation range given here is clearly model dependent and factors of 2 or 3 should not be taken too seriously. However, the basic physics should be reflected in the range parameters.

For the solution data it is seen that except for the −45 °C PVA results the ranges are all within a factor of 2 of 25 units. The −45 °C result perhaps reflects the fact that those relaxation measurements can be adequately described by a single relaxation time. This is easily seen from eq 17 and 18 since if $\omega_A \simeq \omega_B$

$$\phi(t) \simeq e^{-t/\tau}$$

The correlation ranges for the rubbers (especially polybutadiene) are considerably different. Their magnitude suggests the possibility that R represents a volume effect rather than a linear effect. To understand this we might imagine that rotational jumps in the rubber are transmitted *between* chains

Table II
Values of T_{AX} Calculated Using Experimental Data of Heatley and Cox[a]

Temp, °C	T_{AA}[b]	T_{XX}	N_A	N_X	T_{AX}	
					$2T_{AA}/N_A$	$T_{XX}/2N_X$
−45	180	330	−0.9	−0.6	−400	−500
10	470	270	−0.25	−0.08	−3760	−3375
30	550	250	0	0	∞	∞
110	970	400	0.23	0.07	8435	5714

[a] Reference 26. The last two columns are computed using eq 33 in the text. [b] The T's are given in ms.

Table III
^{1}H Relaxation Parameters[b] For PVA in Toluene-d_8 at 300 MHz

Temp,	Experiment (ref 27)				Present theory						VJGM theory					
°C	T_{AA}[a]	T_{XX}	N_A	N_X	T_{AA}	T_{XX}	N_A	N_X	ω_A, Hz	ω_B, Hz	T_{AA}	T_{XX}	N_A	N_X	T_0, s	T_d, s
−45	180	330	−0.9	−0.6	199	278	−0.44	−0.31	2.5×10^8	2.53×10^8	154	242	−0.46	−0.36	5.6×10^{-9}	1.8×10^{-6}
10	470	270	−0.25	−0.08	460	266	−0.16	0.05	2×10^7	5×10^7	485	243	−0.9	−0.02	2.5×10^{-9}	3.8×10^{-10}
30	550	250	0	0	554	259	−0.05	−0.01	7.9×10^7	4×10^{10}	523	239	−0.03	−0.01	1.8×10^{-9}	3.2×10^{-10}
110	970	400	0.23	0.07	970	400	0.03	0.01	1.8×10^8	1.1×10^{11}	972	405	0.023	0.005	2×10^{-9}	3.2×10^{-11}

[a] The T_{AA} and T_{XX} are given in ms. [b] Methylene ≡ X; methine ≡ A.

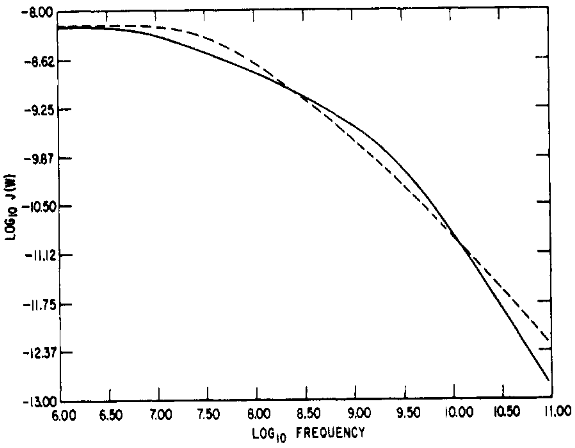

Figure 2. Frequency dependence of the spectral functions of the present theory, eq 24 (solid), and the VJGM theory, eq 27 (broken). The parameter pairs employed for each function are those which are found to give a good representation of the ^{13}C relaxation behavior of isotatic polystyrene in dichlorobenzene solution at 35 °C (see Table I and ref 18): $(\omega_A, \omega_B) = 6.3 \times 10^6, 4 \times 10^9$ Hz; $(T_0, T_d) = 3.5 \times 10^{-8}, 1.9 \times 10^{-9}$ s^{-1}.

with something like the facility that they are transmitted *along* a chain. This is not unreasonable because the chains are somewhat cross-linked and the floppy motions of the rubber allow for good communication between the chains. This idea is also in accord with the notion that a rubber is a "liquid like" phase. The possibility that we are dealing with a correlation volume in the rubbers implies that $R^{1/3}$ is the quantity which can be identified as the correlation range (these are also listed in Table IV for the rubbers). These considerations of the interchain communication allow us to predict that if a rubber is solvated causing it to swell then R should go down dramatically.

Lastly we would like to emphasize that although the present treatment of the correlation range of polymer main-chain dynamic motion is rather crude, it may prove to be a useful way to think about and treat such dynamical problems.

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Table IV
Effective Range of Coherence

	Range[a]	$V(R^{1/3})$
Isotactic polystyrene–*o*-chlorobenzene solution	16.4	
cis-Polyisoprene rubber	63.2	4.0
cis-Polybutadiene rubber	2370	13.3
PVA in toluene		
−45 °C	1	
10 °C	50	
30 °C	22.5	
110 °C	24.7	

[a] Calculated as $(\omega_B/\omega_A)^{1/2}$, where ω_B and ω_A are found in Tables I and III.

Appendix A. Exact Solution to Equation 24

A closed expression can be found for the spectral function defined by eq 24. Most tables of integrals contain the general form[34,35]

$$\int \frac{k^2}{Ak^4 + B}\,\mathrm{d}k \tag{A1}$$

though misprints are annoying.[35] A resolution of the integrand of eq 24 into partial fractions yields

$$\begin{aligned} J(\omega) &= 2(k_B - k_A)^{-1} \int_{k_A}^{k_B} \left[\frac{\upsilon_2 k^2}{(\upsilon_2 k^2)^2 + \omega^2}\right] \mathrm{d}k \\ &= (2\sqrt{2}(k_B - k_A)\upsilon_2 a)^{-1} \\ &\times \left\{\log\left[\frac{k_B^2 - \sqrt{2}ak_B + a^2}{k_B^2 + \sqrt{2}ak_B + a^2}\,\frac{k_A^2 + \sqrt{2}ak_A + a^2}{k_A^2 - \sqrt{2}ak_A + a^2}\right]\right. \\ &+ 2\tan^{-1}\left(\frac{2k_B + \sqrt{2}a}{\sqrt{2}a}\right) - 2\tan^{-1}\left(\frac{2k_B + \sqrt{2}a}{\sqrt{2}a}\right) \\ &\left. + 2\tan^{-1}\left(\frac{2k_A - \sqrt{2}a}{\sqrt{2}a}\right) - 2\tan^{-1}\left(\frac{2k_A + \sqrt{2}a}{\sqrt{2}a}\right)\right\} \end{aligned} \tag{A2}$$

where $a \equiv w^2/\upsilon_2^2$.

This expression has branch points which arise from the log and $\tan^{-1}$ terms, and it is not easy to use, either for finding limiting behavior or for numerical computation. We prefer the integral representation of eq 24 for both purposes. Numerical integrations were performed to evaluate the relaxation parameters in Tables I and III. The trapezoidal rule was employed with 100 points for each integral. Increasing the number of points to 200 resulted in less than 0.01% relative change in T_1, T_2, and NOEF for one test calculation.

Appendix B. Limiting Behavior of the Autocorrelation Function

Here we derive the long and short time behavior of our correlation function $\phi(t)$ given by eq 15 and the VJGM autocorrelation function given by eq 21. For small values of the argument, we have

$$\underset{Z\to 0}{\operatorname{erfc}}\,(Z) \approx 1 - \frac{2}{\pi^{1/2}}\,(Z) - \frac{Z^3}{3} + \ldots)$$

so

$$\operatorname{erfc}\,[(\omega_{\mathrm{A}}t)^{1/2}] - \operatorname{erfc}\,[(\omega_{\mathrm{B}}t)^{1/2}] \approx \frac{2}{\pi^{1/2}}\left\{t^{1/2}\left[(\omega_{\mathrm{B}}{}^{1/2} - \omega_{\mathrm{A}}{}^{1/2}) + \frac{t}{3}\,(\omega_{\mathrm{A}}{}^{3/2} - \omega_{\mathrm{B}}{}^{3/2})\right] + \ldots\right\}$$

or

$$\lim_{t\to 0} \phi(t) \approx 1 - {}^{1}\!/_{3}(\omega_{\mathrm{A}} + (\omega_{\mathrm{A}}\omega_{\mathrm{B}})^{1/2} + \omega_{\mathrm{B}})t + \ldots \qquad \text{(B1)}$$

And for large t

$$\operatorname{erfc}\,(Z) \approx \frac{\mathrm{e}^{-Z^2}}{\pi^{1/2}Z} + \ldots$$

so

$$\lim_{t\to\infty} \phi(t) \approx \left[\frac{e^{-\omega_{\mathrm{A}}t}\omega_{\mathrm{A}}{}^{-1/2} - e^{-\omega_{\mathrm{B}}t}\omega_{\mathrm{B}}{}^{-1/2}}{2t\,(\omega_{\mathrm{B}}{}^{1/2} - \omega_{\mathrm{A}}{}^{1/2})}\right] + \ldots \qquad \text{(B2)}$$

Using the same limiting expressions as above, we find for the autocorrelation function of the VJGM theory, eq 21:

$$\lim_{t\to 0} \phi_{\mathrm{VJGM}}(t) \approx 1 - \frac{2}{\pi^{1/2}}(t/T_{\mathrm{d}})^{1/2} + \ldots \qquad \text{(B3)}$$

and

$$\lim_{t\to\infty} \phi_{\mathrm{VJGM}}(t) \approx \pi^{-1/2}\left(\frac{T_{\mathrm{d}}}{t}\right)^{1/2} e^{-tT_0{}^{-1}} + \ldots \qquad \text{(B4)}$$

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