Damped Orientational Diffusion Model of Polymer Local Main-Chain Motion. 1. General Theory

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ABSTRACT: An exactly solvable damped diffusion model for the local main-chain polymer orientational motion is presented. This model is based on the cutoff diffusion model of Bendler and Yaris but their long-wavelength cutoff is replaced by a more physically reasonable damping term in the diffusion equation. Exact expressions for the autocorrelation function and spectral density are derived as well as the expressions necessary for applying this model to dielectric loss measurements.

I. Introduction

Several years ago Bendler and Yaris[1,2] (henceforth referred to as BY) presented an exactly solvable model of polymer main-chain dynamics. The BY model started with a Markovian master equation for a single-bond conformational jump probability. The master equation represented three-bond conformational rearrangements, i.e., the "Boyer crankshaft" model.[3] By going over to a continuum limit of the master equation, a diffusion equation was obtained. Using the eigenfunctions (which are plane waves) and eigenvalues of the spatial part of the diffusion equation (which is proportional to $\partial^2/\partial x^2$), the dipole correlation function and the power spectrum for main-chain motion were evaluated. One could not, however, allow solutions for all values of the wavelength to be used. A short-wavelength cutoff was introduced to account for the physical fact that in a polymer molecule there must be a smallest unit that can be displaced. There was also a long-wavelength cutoff, which accounted for the fact that a displacement traveling down the polymer chain will damp out after traveling for some distance (short compared to the length of the chain) due to frictional terms (hence, we will sometimes refer to this model as the cutoff diffusion model). The resulting equation contained two parameters which have to be fit to experiment. The BY model was then used to calculate NMR relaxation rates and compared to the calculated results of the model[4] of Valeur, Jarry, Gény, and Monnerie (VJGM) (this model also contains two parameters which are fit to experiment). The fit obtained in the BY paper showed the BY model and the VJGM model agree with the NMR results equally well and both were within experimental error.

In the present paper we will show that an arbitrary feature of the BY model can be removed, while still retaining the attractive feature of a solvable model. That is, rather than use a long-wavelength cutoff to approximate the effects of the damping, we will include a damping term directly in the diffusion equation. This solvable model (which we will refer to as the SY model and also as the damped diffusion model) will also be a two-parameter model. In a companion paper[5] we will compare and contrast the results obtained in fitting the SY, the BY, and the VJGM models to the proton magnetic resonance relaxation times for poly(vinyl acetate) (PVA) in toluene-d_8 solution at a number of different temperatures.[6] (The fitting algorithm used is a considerable improvement over that used in the BY paper.) We shall also compare and contrast the results obtained by these three models for the dielectric relaxation of PVA in toluene solution.[7] It should be mentioned that the damped diffusion model and the cutoff diffusion model yield the same results when fit to experiment and that everywhere in the experimentally interesting range the autocorrelation functions and power spectra obtained from these two models agree to better than 1%.

In section II we will briefly review the cutoff diffusion model. In section III we will derive the expressions for the autocorrelation function and power spectrum of the damped diffusion model. In section IV we will derive the necessary equations for calculating the dielectric response in both the BY and SY models. We will postpone the discussion of the present damped diffusion model to the conclusion of the accompanying companion paper[5] after the three models have confronted the experimental data.

II. Cutoff Diffusion Model

Valeur and co-workers have shown[4] that for three-bond "Boyer crankshaft" motion[3] the polymer backbone bond configurational probability $\rho(\mathbf{e},t)$ satisfies a master equation

$$\partial\rho/\partial t = -D_0\mathbf{K}\rho \qquad \text{(II-1)}$$

where $\rho_n(\mathbf{e},t)$ is the probability that bond n has direction $\mathbf{e}$ at time t, D_0 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

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

The autocorrelation function Valeur et al.[4] obtained from eq II-1 and II-2 was found to decay too slowly with time, and thus they appended an exponential decay factor to the derived equation (it is this modified function which we will refer to as the VJGM model). Jones and Stockmayer[8] observed that eq II-2 is isomorphic with the Hückel molecular orbital Hamiltonian matrix for a linear chain molecule. Using the well-known eigenvalues and eigenfunction of this Hamiltonian,[9] they were able to solve eq II-1 in a finite matrix representation and so obtain an autocorrelation function.

In BY it was realized that by going over to a continuum representation, the eigenfunctions of eq II-2 are plane waves and eq II-1 becomes a one-dimensional diffusion equation for the time evolution (diffusion along the polymer backbone) of the single-bond probability

$$\frac{\partial\rho}{\partial t} = D_0\frac{\partial^2\rho}{\partial x^2} \qquad \text{(II-3)}$$

where x is the position along the polymer chain. Our present view of the physical situation is that eq II-3 is the

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basic equation of the BY model, along with the long- and short-wavelength cutoffs. We feel that tying the diffusion equation of bond probabilities to a specific jump model such as the Boyer crankshaft is unnecessary and confining. We prefer to leave the particular bond motion open, as it is unnecessary in this context. The dipole–dipole time correlation function is defined as

$$\phi(t) \equiv \tfrac{1}{2}\langle 3(\mathbf{e}(t)\cdot\mathbf{e}(0))^2 - 1\rangle \qquad \text{(II-4)}$$

where the angular brackets denote a statistical mechanical configurational average. Expanding the probability function $\rho(\mathbf{e},x,t)$ in Legendre polynomials $P_n(\cos\theta)$, where θ is the angle between $\mathbf{e}(t)$ and a molecular fixed axis z

$$\rho(\mathbf{e},x,t) = \sum_{n=0}^{\infty} B_n(x,t)P_n(\cos\theta)$$

one finds on integrating over the angular coordinates

$$\phi_n(t) = \frac{4}{(2n+1)^2}4\pi^2\langle B_n(x,t)B_n^*(x,0)\rangle_x \qquad \text{(II-5)}$$

where the subscript x on the bracket denotes the configurational average over the chain. By (i) using as the initial condition that at $t = 0$ only the bond at the origin $x = 0$ is displaced from equilibrium,[15] i.e.

$$B_n(x,0) = B_n(0)\delta(x) \qquad \text{(II-6)}$$

(ii) using the plane wave eigenfunction expansion, and (iii) introducing cutoffs in wave vector space $k_A < k_B$ corresponding to the long- and short-wavelength cutoffs discussed above, one finds that

$$\langle B_n(x,t)B_n^*(x,0)\rangle_x \propto \frac{[B_n(0)]^2}{2\pi}\int_{-\infty}^{\infty}dx\int_{k_A}^{k_B}dk\int_{k_A}^{k_B}dk'\exp[i(k-k')x - Dk^2t] \qquad \text{(II-7)}$$

which, after the x and k' integrations are performed, yields

$$\phi(t) \propto \int_{k_A}^{k_B}dk\, e^{-Dk^2t} \qquad \text{(II-8)}$$

Performing the k integration led to the normalized autocorrelation function

$$\Phi_{BY} = \frac{\phi_n(t)}{\phi_n(0)} = \frac{1}{2}(\pi/t)^{1/2}(\omega_B^{1/2} - \omega_A^{1/2})^{-1}\{\text{erfc}\,[(\omega_A t)^{1/2}] - \text{erfc}\,[(\omega_B t)^{1/2}]\} \qquad \text{(II-9a)}$$

where

$$\omega_A = k_A^2 D$$
$$\omega_B = k_B^2 D \qquad \text{(II-9b)}$$

and erfc is the complementary error function.[10] Observe that the right-hand side of eq II-9a is independent of n, the rank of the correlation function. Hence the normalized vector and tensor correlation functions are equal.

The spectral density or power spectrum is the Fourier transform of the autocorrelation function given by

$$J(\omega) = \int_{-\infty}^{\infty}dt\,\phi(t)e^{i\omega t} \qquad \text{(II-10)}$$

The Fourier transform was obtained by interchanging the order of integration between eq II-10 and eq II-8

$$J_{BY}(\omega) = (k_B - k_A)^{-1}\int_{k_A}^{k_B}dk\int_{-\infty}^{\infty}dt\, e^{-Dk^2t}e^{i\omega t} = 2(\omega_A^{1/2} - \omega_B^{1/2})^{-1}\int_{\omega_A^{1/2}}^{\omega_B^{1/2}}dk\,\frac{k^2}{k^2+\omega^2} \qquad \text{(II-11)}$$

A closed-form expression for (II-11) was found[11] as

$$J_{BY}(\omega) = 2(\omega_B^{1/2} - \omega_A^{1/2})^{-1}\times\left\{[4(2\omega)^{1/2}]^{-1}\left[\ln\left(\frac{\omega_B - (2\omega\omega_B)^{1/2} + \omega}{\omega_B + (2\omega\omega_B)^{1/2} + \omega}\right) - \ln\left(\frac{\omega_A - (2\omega\omega_A)^{1/2} + \omega}{\omega_A + (2\omega\omega_A)^{1/2} + \omega}\right)\right] + [2(2\omega)^{1/2}]^{-1}\times\left[\tan^{-1}\left(\frac{(2\omega\omega_B)^{1/2}}{\omega - \omega_B}\right) - \tan^{-1}\left(\frac{(2\omega\omega_A)^{1/2}}{\omega - \omega_A}\right)\right]\right\} \qquad \text{(II-12)}$$

III. Damped Diffusion Model

As indicated in the Introduction the principal motivation behind the present work is to replace the long-wavelength cutoff introduced in the BY model to account for long-wavelength damping by an explicit inclusion of a damping term in the diffusion equation. Thus the diffusion equation (II-3), describing the diffusion of the single-bond probability along the polymer backbone (i.e., the time evolution of the single-bond probability), becomes

$$\frac{\partial\rho}{\partial t} = D\frac{\partial^2\rho}{\partial x^2} - \beta\rho \qquad \text{(III-1)}$$

where D is the diffusion constant (jump probability) and β is the damping constant. The solutions to the spatial eigenvalue equation

$$\frac{\partial^2\rho}{\partial x^2} + \left(-\frac{\beta}{D} + k^2\right)\rho = 0 \qquad \text{(III-2)}$$

are

$$\rho = e^{\alpha x} \qquad \text{(III-3a)}$$

where

$$\alpha^2 = \beta/D - k^2 \qquad \text{(III-3b)}$$

and

$$k^2 \geq \beta/D \qquad \text{(III-3c)}$$

The solutions for $k^2 < \beta/D$ are not continuously twice differentiable; hence they are not acceptable solutions. We will still have to introduce a finite wave vector cutoff k_{max} corresponding to the short-wavelength cutoff; i.e., there is still a "smallest" motional unit.

Using eq III-3 and eq II-6

$$B_n(x,t) = \frac{B_n(0)}{2\pi}\left\{\int_{(\beta/D)^{1/2}}^{\infty}dk\,\exp(-Dk^2t)\,\exp[i(k^2 - \beta/D)^{1/2}x] + \int_{-\infty}^{-(\beta/D)^{1/2}}dk\,\exp(-Dk^2t)\,\exp[i(k^2 - \beta/D)^{1/2}x]\right\} \qquad \text{(III-4)}$$

Introducing the finite wave vector cutoff, k_{max}, defining

$$\omega_c = +(k_{max}^2 - \beta/D)^{1/2} \simeq k_{max} \qquad \text{(III-5a)}$$

utilizing the fact that the integrals in eq III-4 are even functions of k, and changing variables to

$$y^2 = k^2 - \beta/D \qquad \text{(III-5b)}$$

eq III-4 simplifies to

$$B_n(x,t) = \frac{B_n(0)}{\pi}\int_0^{\omega_c}dy\, y(y^2 + \beta/D)^{-1/2}\,e^{iyx}e^{-\beta t}e^{-Dy^2t} \qquad \text{(III-6)}$$

Hence

$$\langle B_n(x,t)B_n^*(x,0)\rangle_x = \frac{B_n(0)^2}{\pi}\int_{-\infty}^{\infty}dx\int_0^{\omega_c}dy\int_0^{\omega_c}dy' \; yy'(y^2+\beta/D)^{-1/2}(y'^2+\beta/D)^{-1/2}e^{-\beta t}e^{-Dy^2t}e^{i(y-y')x} \quad \text{(III-7)}$$

Integrating eq III-7 over x [which gives a factor $2\pi\delta(y-y')$] and y' yields

$$\langle B_n(x,t)B_n^*(x,0)\rangle_x = \frac{2B_n(0)}{\pi}e^{-\beta t}\int_0^{\omega_c}dy\,\frac{y^2}{y^2+\beta/D}e^{-Dy^2t} \quad \text{(III-8)}$$

Now, we are interested in a dipole correlation function and it follows from eq II-5 that

$$\phi_{SY}(t) = \frac{2B_n(0)^2}{\pi}e^{-\beta t}\int_0^{\omega_c}dy\,\frac{y^2}{y^2+\beta/D}e^{-Dy^2t} \quad \text{(III-9a)}$$

and

$$\phi_{SY}(0) = \frac{2B_n(0)^2}{\pi}\int_0^{\omega_c}dy\,\frac{y^2}{y^2+\beta/D} \quad \text{(III-9b)}$$

Equation III-9b can be integrated[12] to yield

$$\phi_{SY}(0) = \frac{2B_n(0)^2}{\pi}\omega_c\left[1-\frac{\beta}{D\omega_c^2}\tan^{-1}(\beta/D\omega_c^2)^{-1/2}\right] \quad \text{(III-10)}$$

We have been unable to integrate eq III-9a exactly; however, we can find a very good analytic approximation to it. We rewrite eq III-9a as

$$\phi(t) = \frac{2B_n(0)^2}{\pi}e^{-\beta t}(I_1 - I_2) \quad \text{(III-11a)}$$

where

$$I_1 = \int_0^{\infty}dy\,\frac{y^2}{y^2+\beta/D}e^{-Dy^2t} = \frac{1}{2}\left(\frac{\pi}{Dt}\right)^{1/2} - \frac{\pi}{2}\frac{\beta}{D}e^{\beta t}\,\mathrm{erfc}\,(\beta t)^{1/2} \quad \text{(III-11b)}$$

and

$$I_2 = \int_{\omega_c}^{\infty}dy\,\frac{y^2}{y^2+\beta/D}e^{-Dy^2t} \quad \text{(III-12)}$$

By hypothesis, the minimum-wavelength cutoff is much smaller than the damping length; hence, in wave vector space

$$\omega_c \gg \beta/D$$

Therefore, since in I_2 y is bounded from below by ω_c, $y^2 \gg \beta/D$ over the whole domain of integration, and we can expand the denominator of I_2

$$I_2 \simeq \int_{\omega_c}^{\infty}dy\,e^{-Dy^2t} - \int_{\omega_c}^{\infty}dy\,\frac{\beta}{Dy^2}e^{-Dy^2t} \quad \text{(III-13)}$$

The first integral in eq III-13 can be put into standard form by the substitution

$$x = y(Dt)^{1/2}$$

yielding

$$\int_{\omega_c}^{\infty}dy\,e^{-Dy^2t} = \frac{1}{2}\left(\frac{\pi}{Dt}\right)\mathrm{erfc}\,[(Dt)^{1/2}\omega_c] \quad \text{(III-14a)}$$

The second integral in (III-13) can be put into standard form by the substitution

$$u = Dy^2t$$

yielding

$$\beta\int_{\omega_c}^{\infty}dy\,(Dy^2)^{-1}e^{-Dy^2t} = \frac{\beta}{2}\left(\frac{t}{D}\right)^{1/2}\Gamma\left(-\frac{1}{2}, Dt\omega_c^2\right) \quad \text{(III-14b)}$$

where $\Gamma(a,x)$ is an incomplete gamma function.[13] Combining eq III-11a to III-14b yields

$$\phi_{SY}(t) \simeq \frac{2B_n(0)^2}{\pi}\left\{\frac{e^{-\beta t}}{2}\left(\frac{\pi}{Dt}\right)^{1/2}\mathrm{erf}\,[(Dt)^{1/2}\omega_c]\right\} - \frac{\pi}{2}\left(\frac{\beta}{D}\right)^{1/2}\mathrm{erfc}\,(\beta t)^{1/2} + \frac{\beta e^{-\beta t}}{2}\left(\frac{t}{D}\right)^{1/2}\Gamma\left(-\frac{1}{2}, Dt\omega_c^2\right) \quad \text{(III-15)}$$

It should be mentioned that eq III-15 agrees with the results obtained by numerically integrating eq III-9a over the range of experimentally reasonable parameters ω_c and β/D (in fact over a considerably wider range) to within 1% over the whole range of t. Hence eq III-15 can be considered an analytic solution for the time correlation function of the damped diffusion model.

As in the BY model, the SY model gives normalized correlation functions that are independent of the rank of the correlation function.

The spectral density is the Fourier transform of the normalized correlation function; hence

$$J(\omega) = \phi_1(0)^{-1}\,\mathrm{Re}\int_{-\infty}^{\infty}dt\;\phi_1(t)e^{i\omega t} \quad \text{(III-16)}$$

where $\phi_1(t)$ is given by eq III-9a without the factor $2B_n(0)^2/\pi$ and $\phi_1(0)$ is given by eq III-10, again without the factor of $2B_n(0)^2/\pi$. Interchanging the order of integration, i.e., integrating eq III-16 first over time, yields after a little manipulation

$$J_{SY}(\omega) = [D\phi_1(0)]^{-1}\int_0^{\omega_c}dy\,\frac{y^2}{(y^2+\beta/D)^2+(\omega/D)^2} \quad \text{(III-17)}$$

While it appears that $J(\omega)$ is a three-parameter expression of (ω_c, β, and D), in fact a change of variables

$$z = y/\omega_c$$

and a little manipulation reduce eq III-17 to

$$J_{SY}(\omega) = [D\omega_c\phi_1(0)]\int_0^1 dz\,\frac{z^2}{(z^2+\beta/D\omega_c^2)^2+\omega^2/(D\omega_c^2)^2} \quad \text{(III-18)}$$

Replacing $\phi_1(0)$ in eq III-18 by eq III-10 yields

$$J_{SY}(\omega) = \{\delta[1-(\beta/\delta)^{1/2}\tan^{-1}(\beta/\delta)^{-1/2}]\}^{-1}\times\int_0^1 dz\,\frac{z}{(z^2+\beta/\delta)^2+(\omega/\delta)^2} \quad \text{(III-18a)}$$

Thus as is the case with the BY treatment we have a two-parameter theory: β and

$$\delta = D\omega_c^2 \quad \text{(III-18b)}$$

The integral in eq III-18a can be done analytically[12] to yield

$$J_{SY}(\omega) = \{\delta[1-(\beta/\delta)^{1/2}\tan^{-1}(\beta/\delta)^{-1/2}]\}^{-1}[8k(\omega)c(\omega)]^{-1}\times\ln\left[\frac{A(\omega)}{B(\omega)}\right] + [4k(\omega)s(\omega)]^{-1}\tan^{-1}\left[\frac{2k(\omega)s(\omega)}{k^2(\omega)-1}\right] \quad \text{(III-19a)}$$

where

$$A(\omega) = 1 - 2k(\omega)c(\omega) + k^2(\omega) \quad \text{(III-19b)}$$

$$B(\omega) = 1 + 2k(\omega)c(\omega) + k^2(\omega) \quad \text{(III-19c)}$$

$$k(\omega) = \left(\frac{\omega^2 + \beta^2}{\delta^2}\right)^{1/4} \quad \text{(III-19d)}$$

$$c(\omega) = \{\tfrac{1}{2}[1 - \beta/(\omega^2 + \beta^2)^{1/2}]\}^{1/2} \quad \text{(III-19e)}$$

and

$$s(\omega) = \{\tfrac{1}{2}[1 + \beta/(\omega^2 + \beta^2)^{1/2}]\}^{1/2} \quad \text{(III-19f)}$$

Equations III-19 can readily be evaluated by using the Fortran ATAN2 function.

The asymptotic limiting behaviors of both the spectral density and the autocorrelation functions are not particularly useful. We have evaluated them and compared them with the exact answer and the only conclusion we can come to is that "asymptotia" is *very* far out. Hence, we shall not bother the reader with them.

IV. Dielectric Relaxation

In this section we derive the expressions necessary for evaluating dielectric relaxation in the BY and SY models. The necessary expressions for the VJGM model are given by Gêny and Monnerie.[14]

Neglecting local field effects, the complex dielectric constant

$$\epsilon^* = \epsilon' - i\epsilon'' \quad \text{(IV-1)}$$

is determined by the time derivative of the normalized first-rank dipole autocorrelation function $\Phi(t)$

$$\frac{\epsilon^* - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = -\int_0^\infty dt\, \frac{d\Phi(t)}{dt} e^{-i\omega t} \quad \text{(IV-2)}$$

where ϵ_0 and ϵ_∞ are the dielectric constants at zero and infinite frequency. We remind the reader that in the context of the model, normalized first- and second-rank correlation functions are equal. The unnormalized vector and tensor correlation functions differ by a constant term; see eq II-5b.

While it would certainly be possible to take the analytic forms of $\Phi(t)$ for the BY and SY models, eq II-9 and III-15, respectively, differentiate them, insert them in eq IV-1, and thus obtain the real and imaginary parts of the dielectric constant, the complexity of the analytic expressions argue against that approach. We shall instead differentiate the integral forms of the autocorrelation functions and then perform the necessary integrations in order to obtain analytic expressions for the dielectric constant.

Cutoff Diffusion Model. Differentiating eq II-8 with respect to time yields

$$-\frac{d\Phi_{BY}(t)}{dt} = (\omega_B^{1/2} - \omega_A^{1/2})^{-1} \int_{\omega_A^{1/2}}^{\omega_B^{1/2}} dy\, y^2 e^{-y^2 t} \quad \text{(IV-3)}$$

where $y^2 = Dk^2$ and eq II-9b has been used. Hence from (IV-1)

$$\frac{\epsilon^* - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = (\omega_B^{1/2} - \omega_A^{1/2})^{-1} \int_{\omega_A^{1/2}}^{\omega_B^{1/2}} dy\, y^2 \int_0^\infty dt\, e^{-(y^2 + i\omega)t} =$$

$$(\omega_B^{1/2} - \omega_A^{1/2})^{-1} \int_{\omega_A^{1/2}}^{\omega_B^{1/2}} dy\, \frac{y^2}{y^2 + i\omega} =$$

$$(\omega_B^{1/2} - \omega_A^{1/2})^{-1} \int_{\omega_A^{1/2}}^{\omega_B^{1/2}} dy\, \frac{y^4 - i\omega y^2}{y^4 + \omega^2} \quad \text{(IV-4)}$$

Therefore

$$\frac{\epsilon' - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = (\omega_B^{1/2} - \omega_A^{1/2})^{-1} \int_{\omega_A^{1/2}}^{\omega_B^{1/2}} dy\, \frac{y^4}{y^4 + \omega^2} \quad \text{(IV-5a)}$$

and

$$\frac{\epsilon''}{\epsilon_0 - \epsilon_\infty} = (\omega_B^{1/2} - \omega_A^{1/2})^{-1} \omega \int_{\omega_A^{1/2}}^{\omega_B^{1/2}} dy\, \frac{y^2}{y^4 + \omega^2} \quad \text{(IV-5b)}$$

Using[12]

$$\frac{y^4}{y^4 + \omega^2} = 1 - \frac{\omega^2}{y^4 + \omega^2}$$

$$\frac{\epsilon'}{\epsilon_0 - \epsilon_\infty} = 1 - \frac{\omega^2}{\omega_B^{1/2} - \omega_A^{1/2}} \int_{\omega_A^{1/2}}^{\omega_B^{1/2}} dy\, (y^4 - \omega^2)^{-1} =$$

$$1 - \frac{\omega^{1/2}}{\omega_B^{1/2} - \omega_A^{1/2}} \left\{ \frac{1}{4(2^{1/2})} \ln \left[\frac{\omega_B + (2\omega\omega_B)^{1/2} + \omega}{\omega_B - (2\omega\omega_B)^{1/2} + \omega} \right] - \right.$$

$$\frac{1}{4(2^{1/2})} \ln \left[\frac{\omega_A + (2\omega\omega_A)^{1/2} + \omega}{\omega_A - (2\omega\omega_A)^{1/2} + \omega} \right] + \frac{1}{2(2^{1/2})} \times$$

$$\left. \tan^{-1} \left[\frac{(2\omega\omega_B)^{1/2}}{\omega - \omega_B} \right] - \frac{1}{2(2^{1/2})} \tan^{-1} \left[\frac{(2\omega\omega_A)^{1/2}}{\omega - \omega_A} \right] \right\} \quad \text{(IV-6a)}$$

Similarly, integrating (IV-5b) yields

$$\frac{\epsilon''}{\epsilon_0 - \epsilon_\infty} = \frac{\omega^{1/2}}{\omega_B^{1/2} - \omega_A^{1/2}} \{\ \} \quad \text{(IV-6b)}$$

where the term inside the braces is the same as for (IV-6a) except that the numerator and denominator are interchanged for each of the arguments of the logarithm.

The frequency of maximum loss is found from

$$f(\omega) = \frac{\partial}{\partial\omega} \frac{\epsilon''}{\epsilon_0 - \epsilon_\infty} = 0 \quad \text{(IV-7)}$$

Differentiating eq IV-5b and eliminating the constants give

$$f(\omega) = \int_{\omega_A^{1/2}}^{\omega_B^{1/2}} dy\, \frac{y^2}{y^4 + \omega^2} - 2\omega^2 \int_{\omega_A^{1/2}}^{\omega_B^{1/2}} dy\, \frac{y^2}{(y^4 + \omega^2)^2} \quad \text{(IV-8)}$$

Since

$$\int dy\, \frac{y^2}{(y^4 + \omega^2)^2} = \frac{y^3}{4\omega^2(y^4 + \omega^2)} + \frac{1}{4\omega^2} \int dy\, \frac{y^2}{y^4 + \omega^2}$$

and the remaining intergral is the same as that already evaluated in going from (IV-5b) to (IV-6b), we obtain

$$f_{BY}(\omega) = [4(2\omega)^{1/2}]^{-1} \left\{ \ln \left[\frac{\omega_B - (2\omega\omega_B)^{1/2} + \omega}{\omega_B + (2\omega\omega_B)^{1/2} + \omega} \right] - \right.$$

$$\left. \ln \left[\frac{\omega_A - (2\omega\omega_B)^{1/2} + \omega}{\omega_A + (2\omega\omega_A)^{1/2} + \omega} \right] \right\} +$$

$$\frac{1}{2(2^{1/2})} \left\{ \tan^{-1} \left[\frac{(2\omega\omega_B)^{1/2}}{\omega - \omega_B} \right] - \tan^{-1} \left[\frac{(2\omega\omega_A)^{1/2}}{\omega - \omega_A} \right] \right\} +$$

$$\frac{\omega_A^{3/2}}{\omega_A^2 + \omega^2} - \frac{\omega_B^{3/2}}{\omega_B^2 + \omega^2} \quad \text{(IV-9)}$$

and the frequency of maximum loss in the BY model is found by setting eq IV-9 equal to zero. We will solve the resulting transcendental equation numerically.[5]

Damped Diffusion Model. Differentiating eq III-9a with respect to time gives

$$-\frac{\partial \Phi_{SY}(t)}{\partial t} = \frac{D}{\phi_1(0)} \int_0^{\omega_c} dy\, y^2 \exp[-(\beta + Dy^2)t] \qquad \text{(IV-10)}$$

Hence from (IV-1)

$$\frac{\epsilon^* - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{D}{\phi_1(0)} \int_0^{\omega_c} dy\, y^2 \int_0^{\infty} dt \exp[-(\beta + Dy^2 + i\omega)t]$$

$$= \frac{D}{\phi_1(0)} \int_0^{\omega_c} dy \frac{y^2}{\beta + Dy^2 + i\omega} \qquad \text{(IV-11)}$$

$$= \frac{D}{\phi_1(0)} \int_0^{\omega_c} dy \frac{y^2(\beta + Dy^2 - i\omega)}{(\beta + Dy^2)^2 + \omega^2}$$

Therefore

$$\frac{\epsilon' - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = [D\phi_1(0)]^{-1} \int_0^{\omega_c} dy \frac{y^2(y^2 + \beta/D)}{(y^2 + \beta/D)^2 + (\omega/D)^2} \qquad \text{(IV-12a)}$$

and

$$\frac{\epsilon''}{\epsilon_0 - \epsilon_\infty} = \frac{\omega}{D\phi_1(0)} \int_0^{\omega_c} dy \frac{y^2}{(y^2 + \beta/D)^2 + (\omega/D)^2} \qquad \text{(IV-12b)}$$

The integral in eq IV-12b is the same as in eq III-17; hence

$$\frac{\epsilon''}{\epsilon_0 - \epsilon_\infty} = \omega J(\omega) \qquad \text{(IV-13)}$$

where $J(\omega)$ is given by eq III-17.

From eq IV-12a

$$D\phi_1(0)\left[\frac{\epsilon' - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty}\right] = \int_0^{\omega_c} dy \frac{y^4}{(y^2 + \beta/D)^2 + (\omega/D)^2} + \frac{\beta}{D} \int_0^{\omega_c} dy \frac{y^2}{(y^2 + \beta/D)^2 + (\omega/D)^2} \qquad \text{(IV-14)}$$

The second integral in eq IV-14 is again the same as in eq III-17. Using[12]

$$\int_0^{\omega_c} dy \frac{y^4}{(y^2 + \beta/D)^2 + (\omega/D)^2} = \omega_c - \left(\frac{\beta^2 + \omega^2}{D^2}\right) \int_0^{\omega_c} dy\, [(y^2 + \beta/D)^2 + (\omega/D)^2]^{-1} - \frac{2\beta}{D} \int_0^{\omega_c} dy \frac{y^2}{(y^2 + \beta/D)^2 + (\omega/D)^2}$$

in eq IV-14, we obtain

$$\frac{\epsilon' - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \{[1 - (\beta/\delta)^{1/2} \tan^{-1}(\beta/\delta)^{-1/2}]\}^{-1} \times \left\{1 - \frac{(\beta^2/\delta^2 + \omega^2/\delta^2)^{1/2}}{4k(\omega)}\left[\frac{1}{2c(\omega)} \ln\left[\frac{B(\omega)}{A(\omega)}\right] + \frac{1}{s(\omega)} \tan^{-1}\left(\frac{2k(\omega)s(\omega)}{k^2(\omega) - 1}\right)\right] - \frac{\beta/\delta}{4k(\omega)}\left[\frac{1}{2c(\omega)} \ln\left[\frac{A(\omega)}{B(\omega)}\right] + \frac{1}{s(\omega)} \tan^{-1}\left(\frac{2k(\omega)s(\omega)}{k^2(\omega) - 1}\right)\right]\right\} \qquad \text{(IV-15)}$$

where δ is given by eq III-18b and $A(\omega)$, $B(\omega)$, $k(\omega)$, $c(\omega)$, and $s(\omega)$ are given by eq III-19b–f.

In order to obtain the frequency of maximum loss, we must differentiate eq IV-12b with respect to ω and set the result equal to zero. Thus after deleting constant terms

$$f_{SY}(\omega) = \int_0^{\omega_c} dy \frac{y^2}{(y^2 + \beta/D)^2 + (\omega/D)^2} - 2\omega^2 \int_0^{\omega_c} dy \frac{y^2}{[y^4 + (2\beta/D)y^2 + (\beta/D)^2 + (\omega/D)^2]^2} \qquad \text{(IV-16)}$$

With some difficulty it can be shown that

$$\int dy \frac{y^2}{(y^4 + 2By^2 + C)^2} = (1 - B^2/C)^{-1}\left\{\frac{y^3 + By}{4C(y^4 + 2By^2 + C)} - \frac{B}{4C} \int \frac{dy}{y^4 + 2By^2 + C} + \frac{1}{4C} \int dy \frac{y^2}{y^4 + 2By^2 + C}\right\} \qquad \text{(IV-17)}$$

(See ref 12 for this integral with $B = 0$.) Doing the integrals results in

$$f(\omega) = [8c(\omega)k(\omega)]^{-1} \times \ln\left[\frac{A(\omega)}{B(\omega)}\right] + [4s(\omega)k(\omega)]^{-1} \tan^{-1}\left[\frac{2k(\omega)s(\omega)}{k^2(\omega) - 1}\right] + (\beta/\delta)[4k^3(\omega)]^{-1}\left\{[2c(\omega)]^{-1} \ln\left[\frac{B(\omega)}{A(\omega)}\right] + \frac{1}{s(\omega)} \times \tan^{-1}\left[\frac{2k(\omega)s(\omega)}{k^2(\omega) - 1}\right] - \frac{1 + \beta/\delta}{(1 + \beta/\delta)^2 + (\omega/\delta)^2}\right\} \qquad \text{(IV-18)}$$

which is set equal to zero and solved for the frequency of maximum loss.

An application of the BY and SY models to the dielectric relaxation spectrum of poly(vinyl acetate) may be found in the companion paper.[5] We defer all discussion of the predictions of our treatment to that work.

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(2) Errata: Heatley, F.; Bendler, J. T. *Polymer* **1979**, *20*, 1578.
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(10) Abramowitz, M.; Stegun, I. A. "Handbook of Mathematical Functions"; Dover: New York, 1965; Chapter 7.
(11) It was pointed out in BY that it was very difficult to evaluate the explicit form of $J(\omega)$ given in eq II-12 due to the branches arising from the $\tan^{-1}$ terms and that it was easier to numerically evaluate the integral in eq II-11. This is no longer the case due to the introduction into Fortran of the ATAN2 function, which is specifically set up to handle such situations.

Using ATAN2 it is quite easy to evaluate eq II-12—of course, the same results are obtained either way.

(12) Petitbois, G. "Tables of Indefinite Integrals"; Dover: New York, 1961.
(13) Reference 10, Chapter 6.
(14) Gény, F.; Monnerie, L. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 1.

(15) In employing the initial condition of eq II-6, we are assuming in the case of "crankshaft-like" motions that all initial conditions have the same Boltzmann factor, i.e., that they are weighted equally. This is an assumption that could yield an unknown error in the resulting correlation function. However, in passing to the continuum limit embodied in eq II-3, we are assuming the polymer chain is, in some average sense, spatially uniform in the distance scale of motions characteristic of orientational diffusion. It is the spatial uniformity of the chain which provides eq II-6 as the appropriate initial condition. If, in fact, the chain were spatially nonuniform, eq II-6 would be incorrect and an average over the various initial conditions (of unknown weight) would be required. The resulting continuum limit would then be a diffusion equation over a spatially varying (i.e., nonuniform) medium. This would add considerable complexity to the model and would require us to specify much more information about the system than we know.

Damped Orientational Diffusion Model of Polymer Local Main-Chain Motion. 2. Application to Poly(vinyl acetate)

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ABSTRACT: The damped diffusion model presented in the previous paper is applied to the ^{1}H NMR relaxation rates and dielectric loss data of poly(vinyl acetate) in toluene. The results are compared to those obtained from the cutoff diffusion model of Bendler and Yaris and the model of Valeur, Jarry, Gény, and Monerie applied to the same system. The damped and cutoff diffusion models give identical fits to experiment. The model of Valeur et al. also fits the experimental results but only at the expense of nonphysical values for the parameters. A tentative interpretation of the physical origin of the molecular motion is presented.

I. Introduction

In paper 1 a new solvable model for main-chain polymer dynamics was presented.[1] Our model was based upon the Bendler–Yaris model[2,3] (BY). However, rather than introduce a long-wavelength cutoff to approximate the effects of damping, we incorporated the damping into the motional diffusion equation. The resulting model contains two parameters, β, a damping term, and δ, a term characteristic of the shortest allowable wavelength motions.

In this paper we will fit both the damped diffusion (SY) and the cutoff diffusion (BY) model to Heatley and Cox's measured NMR relaxation rates[4] for poly(vinyl acetate) (PVA) in toluene-d_8 as a function of temperature and also to Mashimo and Shinohara's dielectric relaxation data,[5] also for PVA in toluene. We shall compare these results to those obtained by fitting Valeur, Jarry, Gény, and Monnerie's (VJGM) model for main-chain dynamics.[6,7] Previously, the BY model has been fit to NMR data[1,8] and the VJGM model has been fit to NMR,[1,8-12] dielectric,[13] and fluorescence anisotropy[14] data; but, to the best of our knowledge, this is the first time either model has been fit to both NMR and dielectric data on the same polymeric system. It has previously been stated[1,8] that both the VJGM model and the BY model fit the data equally well. We shall show that this is not quite the case.

The necessary expressions for the BY and the SY models are in paper 1. For completeness the dipole correlation function in the VJGM model[6,7] is

$$\phi(t)_{\mathrm{VJGM}} = e^{-t/T_0}e^{-t/T_d}\ \mathrm{erfc}\ [(t/T_d)^{1/2}] \qquad (1)$$

In this model T_d is supposed to represent the time associated with three-bond "Boyer-crankshaft" motions on a diamond lattice. The additional exponential decay term with T_0 was introduced[7] to obtain the proper long-time behavior and T_0 is supposed to represent the time associated with four- (or more) bond motion and diffusive motions.

We remind the reader (see paper 1) that dielectric relaxation measures a vector correlation function, while NMR measures a second-rank tensor correlation function, and that the VJGM, SY, and BY models all predict the equivalence of the normalized first- and second-rank autocorrelation functions. The spectral density is obtained by Fourier transforming eq 1 and is

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

A comparison of the autocorrelation functions for the three models is given in Figure 1. Note that $\phi(t)$ for the VJGM model dies off quickest at long times.

In section II we shall fit these models to the NMR data on PVA.[4] The fit algorithm is improved[15] over that used in BY (also several misprints have been corrected and the correct expression[3] has been used for the relaxation rate T_{AX}, which was in error by a factor of 2). Hence the results presented here for the BY and VJGM models should replace those given in the BY paper. In section III the three models will be applied to the dielectric data on PVA.[5] Section IV will consist of a discussion summarizing the comparison of the three models' predictions of the NMR

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