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References and Notes

(1) Bueche, F.; Cashin, W. M.; Debye, P. *J. Chem. Phys.* **1952**, *20*, 1956.
(2) Duda, J. L.; Ni, Y. C.; Vrentas, J. S. *Macromolecules* **1979**, *12*, 459.
(3) Boss, B. D.; Stejskal, E. O.; Ferry, J. D. *J. Phys. Chem.* **1967**, *71*, 1501.
(4) Tanner, J. E.; Liu, K.-J.; Anderson, J. E. *Macromolecules* **1971**, *4*, 586.
(5) Bueche, F. "Physical Properties of Polymers"; Interscience: New York, 1962.
(6) Graessley, W. W. *Adv. Polym. Sci.* **1974**, *16*, 1.
(7) Graessley, W. W. *Polymer* **1980**, *21*, 258.
(8) Tulig, T. J.; Tirrell, M. *Macromolecules* **1981**, *14*, 1501.
(9) Vrentas, J. S.; Duda, J. L. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 403.
(10) Vrentas, J. S.; Duda, J. L. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 417.
(11) Vrentas, J. S.; Duda, J. L. *Macromolecules* **1976**, *9*, 785.
(12) Vrentas, J. S.; Duda, J. L. *J. Appl. Polym. Sci.* **1977**, *21*, 1715.
(13) Vrentas, J. S.; Duda, J. L. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1085.
(14) Vrentas, J. S.; Duda, J. L. *AIChE J.* **1979**, *25*, 1.
(15) Ferry, J. D. "Viscoelastic Properties of Polymers"; Wiley-Interscience: New York, 1970.
(16) Haward, R. N. *J. Macromol. Sci., Rev. Macromol. Chem.* **1970**, *C4*, 191.
(17) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971.
(18) Berry, G. C.; Fox, T. G. *Adv. Polym. Sci.* **1968**, *5*, 261.
(19) Ju, S. T.; Liu, H. T.; Duda, J. L.; Vrentas, J. S. *J. Appl. Polym. Sci.* **1981**, *26*, 3735.
(20) Duda, J. L.; Vrentas, J. S.; Ju, S. T.; Liu, H. T. *AIChE J.* **1982**, *28*, 279.
(21) Barlow, A. J.; Lamb, J.; Matheson, A. J. *Proc. R. Soc. (London), Ser. A* **1966**, *A292*, 322.
(22) Callaghan, P. T.; Pinder, D. N. *Macromolecules* **1980**, *13*, 1085.

Damped Orientational Diffusion Model of Polymer Local Main-Chain Motion. 3. Inclusion of Chain–Chain Interactions

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ABSTRACT: The damped orientational model of polymer local main-chain motion is generalized to include chain–chain interactions using multiple scattering theory in the mean field approximation and an optical potential. The resulting dynamical equation, which is in the form of a complex damped diffusion equation, still permits analytic solutions for the bond orientational correlation function and the spectral density. Thus by incorporating chain–chain interactions into an orientational diffusion model, the theory should be capable of describing local motions for concentrations outside the dilute solution regime. The resulting three-parameter analytic expression for the spectral density is fit to the low-temperature-phase ^{1}H NMR relaxation times of poly(vinyl acetate) (PVA) in toluene. In this phase PVA is a compact random coil. Both the real and complex dampled diffusion models are found to fit the data equally well. The real damped diffusion model parameters fit to the low-temperature phase are considerably different in magnitude from those for the high-temperature phase. Therefore the low-temperature parameters presumably are effective parameters and reflect the role of intrachain interactions. The complex and real damped diffusion models also are capable of fitting the high-temperature proton relaxation data equally well. Thus, based on goodness of fit and given the uncertainty of some of the NMR relaxation data, the real and complex damped diffusion models cannot be distinguished at this time.

I. Introduction

In a recent pair of papers (papers 1 and 2 of this series) we developed a damped diffusion model of polymer local main-chain motion and applied this model to calculate both ^{1}H NMR relaxation times and dielectric relaxations of poly(vinyl acetate) (PVA) in toluene solution.[1,2] The damped diffusion model is a natural extension of the cutoff diffusion model of Bendler and Yaris[3,4] in that the long-wavelength cutoff introduced by them to "mock up" the damping has been replaced by an explicit damping term in the diffusion equation. The resulting model is analytically solvable for the dipole correlation function and its Fourier transform, the spectral density function.

When the two-parameter expression for the spectral density function is fit to the measured PVA proton relaxation times,[5] a very good fit is obtained (the results for the cutoff diffusion model and the damped diffusion model are indistinguishable) except at the lowest temperature, −45 °C. At −45 °C, the two parameters required to give a good fit to the PVA proton relaxation times are substantially different from those for the high-temperature phase. A search for parameters of the same order of magnitude as for the high-temperature phase required that the short-wavelength cutoff, representing the smallest motional unit, be larger than the damping length.[2] The reason for this is that there is a phase transition at −20 °C (observed by dielectric relaxation[6]). Above the phase transition temperature, PVA is in a loose random coil configuration with little chain–chain interaction. Below the phase transition temperature, the polymer is in a compact random coil configuration with presumably considerable chain–chain interaction. Thus it is not at all surprising that the two parameters fit to the real damped diffusion model are substantially different in the low-temperature fit from those in the high-temperature fit. The damping parameter in the context of real damped diffusion model is an effective parameter that implicitly incorporates chain–chain interactions.

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The purpose of the present paper is to address this deficiency in the damped diffusion model by including chain–chain interactions explicitly. We shall do this while still retaining the attractive features of the damped diffusion model, namely (i) the physical simplicity of a hydrodynamic approach, (ii) the inattention to specialized details (such as potential surfaces etc.) in favor of experimentally fit parameters, and (iii) the ability to analytically solve the resulting expressions for the correlation function and the spectral density function. The present work not only allows us to fit the low-temperature data of PVA, which we shall demonstrate in section V, but also allows us to extend the theory out of the dilute regime to more concentrated solutions and perhaps even into the melt and glass.

In section II we present a very brief review of the major results of paper 1. We do this since we will need the expressions obtained there for the dipole correlation function and the spectral density function. Any reader desiring to see detailed derivations of the expressions is advised to refer to paper 1. In section III we use a multiple scattering approach to derive the equation for the diffusion of probability including the chain–chain interaction as a complex damping term. We then solve for the correlation function and spectral density in section IV. We shall do so using the average value of the complex damping term, deferring a treatment of the fluctuation terms to the Appendix. In section V the model will be fit to the low-temperature NMR relaxation data on PVA on toluene. This is followed by a discussion of the results (section VI).

II. Damped Diffusion Model

An equation for the time evolution (diffusion along the polymer backbone) of the single-bond orientational probability $\rho(x)$ is given by the damped diffusion equation

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

where x is the position along the polymer chain, D is the diffusion constant (jump probability), and β is the damping constant. The origin of such a diffusion equation comes from treating a bond motion, such as a "Boyer crankshaft",[7] by means of a master equation for a first-order Markov process and then going over to the continuum limit. We now prefer to think of the diffusion equation itself as the basic equation of a hydrodynamic approach to the polymer motion and then try to analyze the experimentally fit parameters of the model in order to obtain more specific information about the type(s) of motion involved. Using the eigenfunctions of the spatial part of eq II-1

$$D\frac{\partial^2}{\partial x^2} - \beta$$

we can find a set of plane wave solutions to eq II-1 as

$$\rho(x,t) = \exp[i(k^2 - \beta/D)^{1/2}x]\,\exp(-Dk^2t) \qquad \text{(II-2a)}$$

where

$$k^2 \geq \beta/D \qquad \text{(II-2b)}$$

The solution for $k^2 < \beta/D$ is not continuously twice differentiable; hence it is unacceptable.

Using the solutions eq II-2 in the diffusion equation, eq II-1, we obtain after considerable manipulation (see paper 1 for the details of the procedure) an expression for the normalized dipole correlation function

$$\Phi(t)_{\mathrm{DD}} = \frac{e^{-\beta t}}{2}\left(\frac{\pi}{\delta t}\right)^{1/2} \operatorname{erf}\,[(\delta t)^{1/2}] \qquad \text{(II-3)}$$

$$\delta = D\omega_{\mathrm{c}}^2 \qquad \text{(II-4a)}$$

and

$$\omega_{\mathrm{c}} = (k_{\max}^2 - \beta/D)^{1/2} \qquad \text{(II-4b)}$$

is the short-wavelength cutoff, corresponding to the fact that there is a smallest displacable unit in the polymer backbone. The spectral density is the Fourier transform of the correlation function

$$J(\omega)_{\mathrm{DD}} = \operatorname{Re}\int_{-\infty}^{\infty}\mathrm{d}t\;\Phi(t)_{\mathrm{DD}}e^{i\omega t} \qquad \text{(II-5a)}$$

where the correlation function is given by eq II-3. Interchanging the order of integration, i.e., doing the time integration first, yields

$$J(\omega)_{\mathrm{DD}} = \delta^{-1}\int_0^1 \mathrm{d}z\;\frac{z^2 + \beta/\delta}{(z^2 + \beta/\delta)^2 + (\omega/\delta)^2} \qquad \text{(II-5b)}$$

Performing the spatial integral gives

$$J(\omega)_{\mathrm{DD}} = \delta^{-1}\left[\frac{c(\omega)}{4k(\omega)}\ln\frac{A(\omega)}{B(\omega)} + \frac{s(\omega)}{2k(\omega)}\tan^{-1}\left(\frac{2k(\omega)s(\omega)}{k^2(\omega) - 1}\right)\right] \qquad \text{(II-6a)}$$

where

$$A(\omega) = 1 - 2k(\omega)c(\omega) + k^2(\omega) \qquad \text{(II-6b)}$$

$$B(\omega) = 1 + 2k(\omega)c(\omega) + k^2(\omega) \qquad \text{(II-6c)}$$

$$k(\omega) = \left(\frac{\omega^2 + \beta^2}{\delta^2}\right)^{1/4} \qquad \text{(II-6d)}$$

$$c(\omega) = \{{}^1\!/\!_2[1 - \beta/(\omega^2 + \beta^2)^{1/2}]\}^{1/2} \qquad \text{(II-6e)}$$

and

$$s(\omega) = \{{}^1\!/\!_2[1 + \beta^2/(\omega^2 + \beta^2)^{1/2}]\}^{1/2} \qquad \text{(II-6f)}$$

III. Multiple Scattering Treatment of Chain–Chain Interaction

The damped diffusional model of paper 1 described in the previous section can be thought of as an idealized system in which waves going down the polymer chain interact with the high-frequency modes of the solvent. It is this interaction that leads to the frictional damping term. We shall refer to this model in what follows as the unperturbed system, and the solvent damped wave as an unperturbed wave.

When the polymer chain is in close proximity to another chain, one can have a chain–chain interaction. One should note that another chain means in practice either a topologically different chain or the same chain which has doubled back on itself after some distance (long compared to the damping length). These two situations are really the same in the context of this work. Hence when the unperturbed wave comes into the region where there is an intersection with another chain, the wave scatters due to the chain–chain interaction. The unperturbed wave undergoes all of the standard scattering phenomena: reflection, dephasing (or phase shifting), refraction, etc. As the, now, scattered wave moves beyond the intersection region of the two polymer chains, the scattered or perturbed wave continues to propagate and interacts only with the solvent. This scattering can then be repeated. This process is completely analogous to multiple scattering in quantum mechanics and can be treated by the propagator ordered operator calculus first introduced into quantum field theory by Feynman[9] and Dyson.[10]

The unperturbed solution to the damped diffusion equation, eq II-1, at time t, $\rho_0(t)$, can be written in terms of the solution at time t_0 as

$$\rho_0(t) = e^{(t-t_0)\mathcal{D}_0}\rho_0(t_0) = U_0(t|t_0)\rho_0(t_0) \qquad \text{(III-1)}$$

where the operator $\mathcal{D}_0$ is given by

$$\mathcal{D}_0 = \partial^2/\partial x^2 - \beta \qquad \text{(III-2)}$$

and where $U_0(t|t_0)$ is the unperturbed propagator from time t_0 to t. Those waves which scatter once between t_0 and t can be written as

$$\rho_1(t) = \int_{t_0}^{t} \mathrm{d}t'\, U_0(t|t')V(t')U_0(t'|t_0)\rho_0(t_0) \qquad \text{(III-3)}$$

That is, the wave propagates unperturbed from t_0 till a time t' where it interacts with another chain and is scattered by the (as-yet unspecified) potential $V(t')$. The scattered wave is then propagated unperturbed until the time of interest t. The integration over t' just refers to the fact that the interaction could have happened at any time between t_0 and t and we must sum (or rather integrate) over all of the possibilities. Similarly, the waves that scatter twice between t_0 and t can be written as

$$\rho_2(t) = \int_{t_0}^{t} \mathrm{d}t''\, U_0(t|t'')V(t'') \int_{t_0}^{t''} \mathrm{d}t'\, U_0(t''|t')V(t')U_0(t'|t_0)\rho_0(t_0) \qquad \text{(III-4)}$$

Here, the unperturbed wave propagates to the first chain–chain intersection at time t', where it is scattered, and the scattered wave propagates unperturbed to a second intersection at time t'', where it is again scattered, and it finally is propagated to the time of interest t. Again the time integrations just sum over all possible times of interaction. Obviously, we can continue this procedure, and the total scattered wave $\rho(t)$ is just the sum of the waves that have not been scattered plus those that have been scattered once plus those that have been scattered twice etc.; i.e.

$$\rho(t) = \sum_{n=0}^{\infty} \rho_n(t) \qquad \text{(III-5)}$$

In order to perform the sum in eq III-5 we introduce the time-ordering (or chronological) operator T, which is defined by its action on the operators $A(t)B(t)$ as

$$\mathrm{T}\{A(t')B(t'')\} = A(t')B(t'') \qquad t' > t'' \qquad \text{(III-6a)}$$

$$\mathrm{T}\{A(t')B(t'')\} = B(t'')A(t') \qquad t' < t'' \qquad \text{(III-6b)}$$

That is, operators which occur first in time operate first, independent of the order in which they are written. Using the time-ordering operator and invoking the symmetry between $V(t')$ and $V(t'')$, we can rewrite eq III-4 as

$$\rho_2(t) = \mathrm{T}\left\{\int_{t_0}^{t} \mathrm{d}t''\, U_0(t|t'')V(t'') \int_{t_0}^{t''} \mathrm{d}t'\, U_0(t''|t')V(t')U_0(t'|t_0)\right\}\rho_0(t_0) = \tfrac{1}{2}\left[\mathrm{T}\left\{\int_{t_0}^{t} \mathrm{d}t'' \int_{t_0}^{t} \mathrm{d}t'\, U_0(t|t'')V(t'')U_0(t''|t')V(t')U_0(t'|t_0)\right\}\rho_0(t_0)\right] = \tfrac{1}{2}\left[\mathrm{T}\left\{U_0(t|t_0)\left[\int_{t_0}^{t} \mathrm{d}t'\, V(t')\right]^2\right\}\right] \qquad \text{(III-7)}$$

since

$$U_0(t|t'')U_0(t''|t') = U_0(t|t')$$

Repeating this process for all of the terms in eq III-5 yields

$$\rho(t) = \mathrm{T}\left\{U_0(t|t_0)\sum_{n=0}^{\infty}\frac{1}{n!}\left[\int_{t_0}^{t} \mathrm{d}t'\, V(t')\right]^n\right\}\rho_0(t_0) = \mathrm{T}\left\{\exp[(t-t_0)\mathcal{D}_0]\exp\left[\int_{t_0}^{t} \mathrm{d}t'\, V(t')\right]\right\}\rho_0(t_0) = \mathrm{T}\left\{\exp\left[(t-t_0)\mathcal{D}_0 + \int_{t_0}^{t} \mathrm{d}t'\, V(t')\right]\right\}\rho_0(t_0) = \mathrm{T}\left\{\exp\left[\int_{t_0}^{t} \mathrm{d}t'\, \mathcal{D}(t')\right]\right\}\rho_0(t_0) \qquad \text{(III-8)}$$

where

$$\mathcal{D}(t') = \mathcal{D}_0 + V(t') = D\frac{\partial^2}{2x^2} - \beta_0 + V(t') \qquad \text{(III-9)}$$

and we have introduced the subscript zero on β_0 (for reasons that will become apparent shortly).

We now invoke the adiabatic theorem,[11] which says that if we start with a solution of the unperturbed systems and turn on the interaction very slowly, we end up with a solution of the fully perturbed system. We shall also replace the time-dependent interaction $V(t)$ by an ensemble-averaged time-independent interaction $\bar{V}$. Thus we are averaging over all possible types of interactions that can occur between the two polymer chains. In the Appendix we will treat the first fluctuation term about the average interactions. Hence $\rho(t)$ satisfies the propagator equation

$$\rho(t) = \exp\left\{(t-t_0)\left[D\frac{\partial^2}{\partial x^2} - \beta_0 + \bar{V}\right]\right\}\rho(t_0) \qquad \text{(III-10a)}$$

or taking the infinitesimal generator of the time translation, $\rho(t)$ satisfies the perturbed damped diffusion equation

$$\frac{\partial\rho}{\partial t} = D\frac{\partial^2\rho}{\partial x^2} - \beta_0\rho + \bar{V}\rho \qquad \text{(III-10b)}$$

To proceed further we must model the average chain–chain interaction potential $\bar{V}$. We shall use an optical potential.[12] Optical potentials have been widely used in scattering theory and can be formulated exactly in terms of the irreducible self-energy for the one-particle Green's function. We shall, however, think of the optical potential in terms of the original optical analogue—an optical wave propagating through a system with a refractive index (a scalar quantity). In general, such a refractive index is complex to allow for sinks (absorptions) and sources (emissions). Going through a medium where the refractive index changes gives all of the scattering phenomena we desire. Of course, using a phenomenological (macroscopic) refractive index eliminates from the description the underlying microscopic mechanism. Hence for our diffusion equation we have the same effect by using a complex damping; that is we set

$$\bar{V} = -\beta_1 - i\gamma \qquad \text{(III-11)}$$

where the real term β_1 allows for increased damping caused by the chain–chain interactions and the complex part γ allows the exchange of waves (that is, an exchange of energy and therefore an exchange of orientational correlation) between the chains. Hence

$$\frac{\partial\rho}{\partial t} = D\frac{\partial^2\rho}{\partial x^2} - (\beta + i\gamma)\rho \qquad \text{(III-12a)}$$

where

$$\beta = \beta_0 + \beta_1 \qquad \text{(III-12b)}$$

Hence our diffusion equation has become a complex damped diffusion equation. Using only the average values of β and γ as we shall do in the next section, i.e., leaving out the spatial dependence of the damping, is equivalent to treating the scattering of the waves in a mean field approximation. To derive the mean field values of β and γ would require a microscopic treatment of the optical potential, which would take us far beyond the scope of this paper. In the Appendix we shall give (but not use) the first-order corrections to this mean field treatment.

IV. Solution of the Complex Damped Diffusion Model

In order to solve for the dipole correlation function and spectral density using the damped diffusion equation with an average complex damping, eq III-12a, we again use the eigenfunctions of the spatial part of the equation

$$\left(\frac{\partial^2}{\partial x^2} - \frac{\beta}{D} - \frac{i\gamma}{D} + u\right) f(x) = 0 \qquad \text{(IV-1)}$$

The solutions are again plane waves

$$f(x) = \exp[ix(k^2 - \beta/D)^{1/2}] \qquad \text{(IV-2a)}$$

with

$$k^2 > \beta/D \qquad \text{(IV-2b)}$$

required so that $f(x)$ is continuously twice differentiable. The eigenvalues are

$$u = Dk^2 + i\gamma \qquad \text{(IV-2c)}$$

hence the time-dependent solutions to eq III-12a are

$$\rho(x,t) = \exp[i(k^2 - \beta/D)^{1/2}x] \exp[-(Dk^2 + i\gamma)t]$$

$$k^2 > \beta/D \qquad \text{(IV-3)}$$

Following exactly the same procedure as was done in paper 1, we arrive at the integral expression for the normalized dipole correlation function

$$\Phi(t)_{\mathrm{CD}} = \phi(t)_{\mathrm{CD}}/\phi(0)_{\mathrm{CD}} \qquad \text{(IV-4a)}$$

where

$$\phi(t)_{\mathrm{CD}} = e^{-i\gamma t}e^{-\beta t}\int_0^{\omega_c} \mathrm{d}y\, e^{-Dy^2t} = e^{-i\gamma t}\phi(t)_{\mathrm{DD}} \qquad \text{(IV-4b)}$$

Hence

$$\Phi(t)_{\mathrm{CD}} = e^{-i\gamma t}\Phi(t)_{\mathrm{DD}} \qquad \text{(IV-4c)}$$

where the subscript CD denotes complex damping. In the Appendix we will look at the first corrections to the mean field scattering theory by replacing

$$\beta \rightarrow \bar{\beta} + \Delta\beta$$

and

$$\gamma \rightarrow \bar{\gamma} + \Delta\gamma$$

in eq IV-4b and evaluating the fluctuation terms.

Since the spectral density is the Fourier transform of the correlation function

$$J(\omega)_{\mathrm{CD}} = \mathrm{Re}\int_{-\infty}^{\infty} \mathrm{d}t\ \Phi(t)_{\mathrm{CD}}e^{i\omega t} = \mathrm{Re}\int_{-\infty}^{\infty} \mathrm{d}t\ \Phi(t)_{\mathrm{DD}}e^{i(\omega-\gamma)t} = J(\omega-\gamma)_{\mathrm{DD}} \qquad \text{(IV-5)}$$

Hence the spectral density is just the damped diffusion result of paper 1, eq II-10, except that the frequency is shifted by γ.

We would like to briefly comment on the concentration dependence of the damping constants. Since γ comes only from the chain–chain interactions, it must depend on the square of the local density of polymer segments. Hence

$$\gamma = \gamma_{\mathrm{int}}c^2 \qquad \text{(IV-6)}$$

where c^2 is the local mole fraction of damping lengths. Notice that this is not the same as the mole fraction of polymer in solution times the number of damping lengths per polymer chain, i.e., the global mole fraction of damping lengths. This can easily be seen by considering the example of a tightly coiled polymer molecule in the limit that the concentration of polymer molecules is going to zero. The global concentration of damping lengths is clearly going to zero but within the tightly coiled polymer unit, the local concentration of damping lengths is not changing and it is precisely this local concentration of segments which is leading to all of the chain–chain intersections, and hence all of the interaction. Thus, in general, the local concentration will be a function of both the polymer concentration and the nature of the polymer configuration (tightness of coiling etc., which would depend, of course, on the temperature and the nature of the solvent). Further consideration of this would be far beyond the scope of this study.

The constant β has two terms, eq III-12b, the β_0 term, which is just damping due to the solvent and hence has as its concentration dependence

$$\beta_0 = \beta_{\mathrm{solv}}(1 - c) \qquad \text{(IV-7a)}$$

and the β_1 term, which comes from the chain–chain interactions and has as its concentration dependence

$$\beta_1 = \beta_{\mathrm{polym}}c^2 \qquad \text{(IV-7b)}$$

In the Appendix when we discuss the fluctuations in β and γ, we shall have to treat the fluctuations in c.

V. Fit to Experiment

In this section we will fit the complex damped diffusion model developed in the previous two sections to the low-temperature ^{1}H NMR relaxation data of Heatley and Cox on PVA in toluene-d_8.[5] In paper 2, the higher temperature relaxation data were successfully fit using the two-parameter damped diffusion model (which, however, appeared to fail at −45 °C). In the two-parameter model, the parameters were fit to the experimental values of T_{AA} and T_{XX} (X is a methylene proton and A is a methine proton) and the values of the Overhauser enhancement factors N_{A} and N_{X} were predicted. In actuality, these four experimental numbers are not really independent since there is a relation between them.

$$T_{\mathrm{AX}} = 2T_{\mathrm{AA}}/N_{\mathrm{A}} = T_{\mathrm{XX}}/N_{\mathrm{X}} \qquad \text{(V-1)}$$

The equations relating T_{AA}, T_{XX}, and T_{AX} to the spectral density are given by Heatley and Cox.[3,5]

In the present work since we must fit a three-parameter model to experiment we must use all three experimental relaxation times T_{AA}, T_{XX}, and T_{AX}, leaving no predictions. We used the data at both measured concentrations, 17 and 134 mg/mL, and fit the model to the data using the same nonlinear least-squares algorithm used in paper 2 (adapted to a three-parameter fit). There were three problems encountered in using this set of experimental data: (1) The low-temperature data except for −45 °C data and the 10 °C data at the lower concentration (17 mg/mL) were not in tabulated form and we had to read the experimental numbers off the graphs. Hence the accuracy is somewhat less than with the tabulated numbers, which we were able to do in paper 2. (2) The values of T_{AX} can be obtained in two different ways from the values of T_{AA}, T_{XX}, N_{A}, and N_{X}; see eq V-1. The resulting "experimental" values of T_{AX} obtained in each of the two ways differed from each other considerably, with the largest difference being a factor of 2.6 at 10 °C and a concentration of 134 mg/mL. (3) The magnitudes of T_{AX} were considerably larger than either

Table I
Experimental ^{1}H Relaxation Parameters for PVA in Toluene[a]

T, °C	concn, mg/mL	T_{AA}, ms	T_{XX}, ms	T_{AX}, ms	W_T[b]
−45	17	180	330	−475	0.79
	134	71	168	−193	0.65
−34	17	200	340	−680	0.22
	134	105	210	−301	0.20
−22	17	280	320	−883	0.25
	134	167	250	−503	0.33
+2	17	430	280	−2560	0.06
	134	330	265	−1040	0.13
+10	17	470	270	−4800	0.067
	134	420	270	−2400	0.048

[a] Reference 5. [b] This is the weighting function used to multiply the T_{AX} term in the fitting algorithm; see text.

T_{AA} or T_{XX}, being in some cases almost 10 times as large. This causes a problem in that in fitting the sum of the squares of the difference between the calculated and experimental T's, we would clearly weight largest the relaxation time T_{AX}, the quantity that is least accurately known from experiment.

The procedure we used to minimize the effects of problems 2 and 3 was as follows: (i) We used the average of the two "experimental" values of T_{AX}. (ii) We then weighted the value of T_{AX}(exptl) − T_{AX}(calcd) in the fitting algorithm by a factor to get the order of magnitude of T_{AX} in the same range as T_{AA} and T_{XX}, typically to a value in between the two. (iii) We further weighted the T_{AX} term in the fitting algorithm to take account of the difference in the error between the direct relaxation terms (T_{AA} and T_{XX}) and the cross-relaxation term (T_{AX}). We assumed that the error in the direct relaxation terms was the 10% experimental error claimed by Heatley and Cox.[5] For the error in T_{AX} we used half of the difference between the two different "experimental" values. The weighting factor for the error was then the square root of the ratio of the error in the direct relaxation times (10%) divided by the error in the cross-relaxation time. (iv) The total weighting factor used for the T_{AX} term in the fitting algorithm was the product of the factors obtained in (i)–(iii). This weighting factor is listed in Table I along with the experimental values of the relaxation times.

Table II gives the results of fitting the complex damped diffusion model to experiment along with the model parameters obtained. The residual R is also given so that one can assess the goodness of the fit, where

$$R = [T_{AA}(\text{exptl}) - T_{AA}(\text{calcd})]^2 + [T_{XX}(\text{exptl}) - T_{XX}(\text{calcd})]^2 + W[T_{AX}(\text{exptl}) - T_{AX}(\text{calcd})]^2 \quad \text{(V-2)}$$

with W being the weight parameter. For comparison, in Table III we give the results of fitting the two-parameter damped diffusion model of papers 1 and 2 to all three experimental parameters T_{AA}, T_{AX}, and T_{XX}, since in paper 2 we only used a fit to two experimental parameters, T_{AA} and T_{XX}. We used the same weighting procedure described above. It should be mentioned that two of the measurements in Table II are the same as used in paper 2.

We found that there are multiple solutions for β and δ that give essentially the same value of R, i.e., the same goodness of fit. One set of parameters is nonphysical; i.e., β is greater than δ. This corresponds to the long-wavelength cutoff being less than the short-wavelength cutoff, a clearly nonphysical result. There is another set of parameters, however, as shown in Table III, that gives reasonable results; i.e., δ is greater than β. Using the best-fit parameters for the −45 °C temperature and 17 mg/mL concentration in Table III as the starting guess for β and δ in the two-parameter fit to T_{AA} and T_{XX} and proceeding as in paper 2, we find $\delta = 8.7 \times 10^{12}$ and $\beta = 1.01 \times 10^4$ with $N_A = -0.97$, $N_X = -0.89$, and $R = 3.0 \times 10^{-26}$. Comparison of the 10 °C results of Table III and Table II of

Table II
^{1}H Relaxation Parameters for PVA in Toluene Using the Present Complex Damped Diffusion Model[a]

temp, °C	concn, mg/mL	T_{AA}, ms	T_{XX}, ms	T_{AX}, ms	δ, rad/s	β, rad/s	γ, rad/s	R
−45	17	212	313	−469	7.43 +11	2.26 +5	5.90 +3	1.3 −3
	134	88	166	−178	5.34 +12	1.80 +3	2.73 +3	3.8 −4
−34	17	227	335	−503	8.35 +11	2.22 +5	5.83 +4	2.3 −3
	134	118	205	−246	1.31 +12	3.66 +4	5.86 +3	3.1 −4
−22	17	301	311	−810	1.87 +11	1.72 +6	1.25 +6	8.4 −4
	134	189	244	−446	2.17 +11	5.59 +5	2.99 +5	8.8 −4
+2	17	441	268	−2400	5.23 +10	2.63 +7	2.17 +7	3.6 −4
	134	326	268	−1080	8.03 +10	5.20 +6	4.81 +6	5.0 −5
+10	17	483	249	−4750	3.63 +10	3.52 +7	6.77 +7	6.4 −4
	134	427	263	−2240	5.06 +10	2.66 +7	1.90 +7	1.5 −4

[a] The notation 5.9 +11 ≡ 5.9 × 10^{11}.

Table III
^{1}H Relaxation Parameters for PVA in Toluene Using the Damped Diffusion Model of Paper 1[a] Best Fit to All Three Experimental Relaxation Times[b]

temp, °C	concn, mg/mL	T_{AA}, ms	T_{XX}, ms	T_{AX}, ms	δ, rad/s	β, rad/s	R
−45	17	210	324	−459	1.03 +12	1.56 +5	1.1 −3
	134	88	164	−181	2.92 +12	3.37 +3	3.8 −4
−34	17	226	335	−503	8.34 +11	2.31 +5	2.3 −3
	134	113	209	−230	4.70 +12	3.89 +3	2.6 −4
−22	17	300	312	−810	1.86 +11	2.34 +6	8.4 −4
	134	189	244	−446	2.17 +11	6.70 +5	8.8 −4
+2	17	441	267	−2404	5.20 +10	3.87 +7	3.6 −4
	134	325	268	−1077	8.03 +10	8.18 +6	5.0 −5
+10	17	483	249	−4753	3.62 +10	1.05 +8	6.4 −4
	134	426	263	−2243	5.03 +10	3.62 +7	1.5 −4

[a] Reference 1. [b] The notation 5.9 +11 ≡ 5.9 × 10^{11}.

Table IV
Activation Energies for the Low-Temperature Phase of PVA in Toluene[a]

model	concn, mg/mL	parameter	E_a, kcal/mol
real damped	17	δ	−8.4
	134	δ	−12.8
complex damped	17	δ	−6.8
	134	δ	−15.9
real damped	17	β	13.3
	134	β	26.1
complex damped	17	β	10.0
	134	β	28.3
complex damped	17	γ	26.7
	134	γ	23.2

[a] These were fit to the data at the three low temperatures (−45, −34, and −22 °C).

paper 2 reveals fairly good agreement for the high-temperature phase fits.

We point out that the values of δ and β in the real damped diffusion model for the low-temperature phase of PVA are substantially larger than the high-temperature-phase values. The low-temperature values of β, in particular, presumably are effective values that reflect the role of intrachain interactions. These interactions are explicitly accounted for in the complex damped diffusion model. Given the uncertainty implicit in the use of T_{AX} in the fitting algorithm (as discussed above), and based solely on the goodness of fit, it is apparent from Tables II and III that we cannot differentiate between the real and complex damped diffusion models. However, the fact that β and δ are the same order of magnitude leads one to conclude that intrachain interactions are quite important.

As for the observed concentration dependence of β and γ, we again remind the reader that both quantities depend on the *local* rather than the *global* concentration. At this time we have no theory for relating these two concentrations. Thus the decreasing values of β and γ shown in Table II with increasing macroscopic concentration could reflect the difference in local environments. A detailed exploration of this observation is, in any case, beyond the scope of the present treatment. δ for all practical purposes is essentially concentration independent.

In Table IV we give the activation energies for the parameters of the complex damped diffusion model using the three low-temperature sets of data. It should be noted that the activation energy for δ is negative in both the real and complex damped diffusion models. This is to be contrasted with the high-temperature results obtained in paper 2, where the activation energy was +2 kcal/mol, a typical bond conformational transition energy. We do not have a good explanation for this behavior but one should recall (see eq II-5b) that δ is composed of the product of two terms, the diffusion constant (or jump probability) and the short-wavelength cutoff. It could be that the diffusion constant is behaving in the expected way, i.e., a positive E_a of the order of a bond conformational transition energy, but that the smallest diffusing unit is increasing in size in the low-temperature phase as temperature increases so that the observed results are obtained.

The activation energies for β extracted at a given concentration from both the real and complex damped diffusion models are essentially the same and increase with increasing concentration. Within the uncertainty of the experiment, the activation energies of γ at the two concentrations are the same. The energies for β and γ are all reasonable values for a system where chain–chain interactions contribute substantially to the dynamics of local main-chain motions.

VI. Summary

In this paper we extended our damped diffusion model of local main-chain orientational motion in polymers to include the effects of chain–chain interactions. We included these effects by treating these interactions via a multiple scattering approach. We approximated the scattering by use of an optical potential and a mean field treatment. This leads to a diffusion equation with a complex damping term, thus leading to a three-parameter model. Analytic expressions for the time correlation function and spectral density for this model were obtained.

The model was then fit to the low-temperature ^{1}H NMR relaxation data on PVA. The complex damped diffusion model can be fit to the NMR data for the low-temperature phase, with a physically reasonable parameterization, as can the diffusion model with a real damping constant. The damping term in the real damped diffusion model is seen to differ substantially in magnitude and activation energy in the low-temperature phase of PVA from that in the high-temperature phase. Coupled with the relative magnitudes of β and γ in the complex damped diffusion model, this leads us to conclude that intrachain interactions are important in the low-temperature phase of PVA. For the high-temperature phase the complex and real damped models yield the same spectral density function. Thus the ability to fit the low-temperature-phase experiments, where chain–chain interactions are important (since the low-temperature phase is a tightly coiled random coil), indicates that the present model is treating chain–chain interactions in a reasonable approximation. This is encouraging since this is probably as far as this simple analytic hydrodynamic approach can be profitably pushed.

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Appendix

In this Appendix we treat the terms due to fluctuations in the complex damping parameters β and γ necessary to go beyond the mean field treatment given in the body of the paper. Although it is possible (and we have, in fact, done it) to explicitly include these corrections in the correlation function as well as the spectral density function, in the interest of brevity we shall just consider $J(\omega)$. After explicitly obtaining the form for $J(\omega)$ we shall decompose the fluctuations into density fluctuations and those due to the averaging over the environment.

Spectral Density Function. Writing

$$\beta = \bar{\beta} + \Delta\beta \qquad \text{(A-1a)}$$

and

$$\gamma = \bar{\gamma} + \Delta\gamma \qquad \text{(A-1b)}$$

in eq II-9b which has had the frequency shifted by γ, yields

$$J(\omega) = \delta^{-1}\int_0^1 \mathrm{d}y \, \frac{y^2 + (\bar{\beta} + \Delta\beta)/\delta}{(y^2 + \bar{\beta}/\delta + \Delta\beta/\delta)^2 + (\omega - \bar{\gamma} - \Delta\gamma)^2/\delta^2} \qquad \text{(A-2)}$$

Expanding the denominator in the expression for $J(\omega)$ and keeping linear terms in the fluctuations yields

$$J(\omega) = J_0(\omega - \gamma) + \frac{\Delta\beta'}{\delta}\int_0^1 \frac{\mathrm{d}z}{\Phi_0} - \frac{2\Delta\beta'}{\delta} \times \int_0^1 \frac{\mathrm{d}z(z^2 + \beta')^2}{{\Phi_0}^2} + \frac{2\Delta\gamma'(\omega' - \gamma')}{\delta}\int_0^1 \frac{\mathrm{d}z(z^2 + \beta')}{{\Phi_0}^2} \quad \text{(A-3)}$$

with $\Delta\beta' = \Delta\beta/\delta$, $\beta' = \bar{\beta}/\delta$, $\Delta\gamma' = \Delta\gamma/\delta$, and $\gamma' = \bar{\gamma}/\delta$ and

$$\Phi_0 = \Phi(z) = (z^2 + \beta')^2 + \omega'^2 \quad \text{(A-4)}$$

where $\omega' = \omega/\delta$.

$J_o(\omega - \gamma)$ is given by eq II-6. Performing the integrals gives

$$J(\omega) = J_0(\omega - \gamma) + \{2\Phi(1)[\beta'^2 + (\omega' - \gamma')^2]\delta\}^{-1}\{(1 + 2\beta') \times (\omega' - \gamma')\Delta\gamma' + \Delta\beta'[-\beta' + (\omega' - \gamma')^2 - \beta'^2]\} + \frac{\alpha(\omega) - q(\omega)}{8k(\omega)c(\omega)} \ln \frac{A(\omega)}{B(\omega)} + \frac{\alpha(\omega) + q(\omega)}{4k(\omega)s(\omega)} \tan^{-1}\left[\frac{2k(\omega)s(\omega)}{k^2(\omega) - 1}\right] \quad \text{(A-5)}$$

with $A(\omega)$, $B(\omega)$, $k(\omega)$, $c(\omega)$, and $s(\omega)$ defined in eq II-6b–f, respectively, and

$$\alpha(\omega) = \frac{(\omega' - \gamma')\Delta\gamma' - \beta'\Delta\beta'}{2\delta[\beta'^2 + (\omega' - \gamma')^2]} \quad \text{(A-6a)}$$

$$q(\omega) = k^{-2}(\omega)\left\{\left(-\frac{\Delta\beta'}{\delta}\right) + \frac{\Delta\beta'[\beta'^2 + 3(\omega' - \gamma')^2] + 2\beta'(\omega' - \gamma')\Delta\gamma'}{2[\beta'^2 + (\omega' + \gamma')^2]}\right\} \quad \text{(A-6b)}$$

Nature of the Fluctuations. As was discussed in the text, the complex damping has a term that depends on the averaging over configuration and a term that depends on the concentration dependence of the damping length (eq IV-6 and IV-7). The fluctuation term contains the deviation of each of these terms from their average value.

Thus from eq IV-6

$$\bar{\gamma} + \Delta\gamma = (\bar{\gamma}_{\text{int}} + \Delta\gamma_{\text{int}})(\bar{c} + \overline{\Delta c})^2 \quad \text{(A-7a)}$$

and since $\langle \Delta c \rangle = 0$

$$\Delta\gamma = \Delta\gamma_{\text{int}}\bar{c}^2 + \gamma_{\text{int}}\overline{\Delta c^2} \quad \text{(A-7b)}$$

If we assume for concreteness that the configurations are randomly distributed, we can obtain the average value of $\Delta\gamma_{\text{int}}$ from the width of the Gaussian distribution

$$\langle \Delta\gamma_{\text{int}} \rangle = \frac{\int_{\bar{\gamma}}^{\infty} \mathrm{d}\gamma(\gamma - \bar{\gamma})e^{-\sigma_\gamma(\gamma - \bar{\gamma})^2}}{\int_{\bar{\gamma}}^{\infty} \mathrm{d}\gamma\, e^{-\sigma_\gamma(\gamma - \bar{\gamma})^2}} = (\sigma_\gamma\pi)^{1/2} \quad \text{(A-8)}$$

One can obtain a thermodynamic expression for $\overline{\Delta c^2}$ since at constant temperature and pressure[13]

$$\overline{\Delta c^2} = (kT/N_s)(\partial\mu_p/\partial c) \quad \text{(A-9a)}$$

where N_s is the number of solvent molecules and μ_p is the chemical potential of the polymer. One can use thermodynamics to rewrite eq A-9a in various ways. One way that might be useful for polymers that eq A-9a can be approximated in the limit of long polymer chains is

$$\overline{\Delta c^2} \simeq \frac{X_p dkT}{V(\partial\Pi/\partial X_p)} \quad \text{(A-9b)}$$

where X_p is the mole fraction of polymer chains, d is the number of damping lengths per chain, and Π is the osmotic pressure—hence $\overline{\Delta c^2}$ is related to the osmotic pressure virial coefficient.[14] Thus combining eq A-7b, A-8, and A-9b

$$\Delta\gamma = \frac{\bar{\gamma}X_p d^2kT}{V(\partial\Pi/\partial X_p)} + \frac{\overline{c^2}}{(\pi\sigma_\gamma)^{1/2}} \quad \text{(A-10)}$$

Starting from eq IV-7, we can perform the same analysis for the $\Delta\beta$ term. Here, we shall assume that the intrinsic fluctuations in the β_{solv} term are negligible (clearly this assumption can be removed). The resulting expression for $\Delta\beta$ is

$$\Delta\beta = \bar{\beta}_{\text{polym}}\frac{X_p d^2kT}{(\partial\Pi/\partial X_p)} + \frac{\overline{c^2}}{(\pi\sigma_\beta)^{1/2}} \quad \text{(A-11)}$$

where σ_β is the half-width of the Gaussian distribution of β.

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References and Notes

(1) Skolnick, J.; Yaris, R. *Macromolecules* **1982**, *15*, 1041. See also: Yamakawa, H. *Macromolecules* **1983**, *16*; and correction to paper 1: Skolnick, J.; Yaris, R. *Ibid.*, **1983**, *16*. Section 2 also contains the corrected equations for paper 1.

(2) Skolnick, J.; Yaris, R. *Macromolecules* **1982**, *15*, 1046. See also correction to paper 2: Skolnick, J.; Yaris, R. *Macromolecules* **1983**, *16*.

(3) Bendler, J. T.; Yaris, R. *Macromolecules* **1978**, *11*, 650.

(4) Erratum: Heatley, F.; Bendler, J. T. *Polymer* **1979**, *20*, 1578.

(5) Heatley, F.; Cox, M. *Polymer* **1977**, *18*, 225.

(6) Mashimo, S.; Shinohara, K. *J. Phys. Soc. Jpn.* **1973**, *34*, 1141.

(7) Boyer, R. F. *Rubber Chem. Technol.* **1963**, *34*, 1303.

(8) Abromowitz, M.; Stegun, I. A. "Handbook of Mathematical Functions"; Dover Publications, Inc.: New York, 1965.

(9) Feynman, R. P. *Phys. Rev.* **1951**, *84*, 108.

(10) Dyson, F. J. *Phys. Rev.* **1949**, *75*, 486, 1736.

(11) Gell-Mann, M.; Low, F. E. *Phys. Rev.* **1951**, *84*, 350.

(12) Csanak, Gy.; Taylor, H. S.; Yaris, R. *Adv. Atomic Mol. Phys.* **1971**, *7*, 287.

(13) Landau, L. D.; Lifshitz, E. M. "Statistical Physics"; Addison-Wesley: Reading, MA, 1958.

(14) McMillan, W. G.; Mayer, J. E. *J. Chem. Phys.* **1945**, *13*, 276.