Interpretation of quasi-elastic light scattering data for flexible chains: model dependence

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The autocorrelation functions and corresponding relaxation times obtained from the forward depolarized quasi-elastic light scattering experiment are exhibited for two quite similar models of flexible polymer chains in solution. A very small change in the chain dynamics is found to be sufficient to change the relaxation time from a relatively short time independent of chain length, with an autocorrelation function suggestive of an unweighted sum of contributions from all the relaxation times in the spectrum of chain motion, to a long time with an autocorrelation function identical with that for the end-to-end vector, strongly dependent upon chain length and dominated by the longest relaxation time in the spectrum. These results raise the question whether widely-used models in which information about short-range chain structure and motion is deliberately omitted can be expected to be appropriate for the interpretation of depolarized scattering experiments.

Keywords End-to-end length; light scattering; polarizability; polymer chain dynamics; quasi-elastic light scattering; relaxation times

INTRODUCTION

During the past decade, quasi-elastic light scattering has become an important experimental means for studying the dynamics of macromolecules in solution[1]. It may be used to determine translational and rotational diffusion constants and to provide information about intramolecular motions. In particular, the forward depolarized scattering experiment is sensitive to the entire frequency spectrum of internal motions of high-polymer chains. Since this technique senses fluctuations in molecular polarizability, a model of chain dynamics is needed to relate experimental results to molecular parameters.

The dynamical behaviour of flexible polymer chains has been the subject of many studies for the last few decades. The basis for most of this work has been the familiar Rouse–Zimm model[2,3]. In this model, a polymer chain is represented by a number of statistical segments, each corresponding to a subchain of the polymer composed of perhaps 10–50 monomer units. Each statistical segment of the chain is modelled by a bead and spring, the former a massless sphere interacting with a continuum solvent via Stokes' law, the latter a Hooke's law spring of zero equilibrium length. Thus information about motions of shorter range than one statistical segment is deliberately sacrificed to produce a tractable model for describing slower, longer-range motions. This model, with various modifications, has achieved considerable success in describing the long-range motions of polymers which can be observed in dielectric, neutron scattering, and viscoelastic mechanical measurements[4–10].

To date, most of the theoretical treatments of depolarized scattering from polymer chains have employed a modification of the Rouse–Zimm model proposed by Ono and Okano[11]. In order to use a Rouse–Zimm model for this purpose, it is necessary to postulate a polarizability tensor associated with each statistical segment. For a real molecule, of course, the components of the segment polarizability tensor will depend upon the conformations of the chemical units which are idealized by a 'segment'. Ono and Okano used the representation of a segment polarizability tensor originally proposed by Zimm[3], i.e., a tensor cylindrically symmetric about the direction of the instantaneous segment extension, with an anisotropy proportional to the extension. Their calculations predict that the frequency spectrum obtained from the forward depolarized scattering from a flexible polymer chain should consist of a sum of uniformly weighted Lorentzians. Norisuye and Yu[12] subsequently argued that this result should be true over a wide range of chain models with differing chain dynamics. Experimental data obtained by Han and Yu[13] on isotactic polystyrene in tetrahydrofuran appear to fit an unweighted sum of Lorentzians. However, the depolarized scattering experiments of Bauer, Brauman and Pecora[14] on atactic polystyrene in CCl_4 yield spectra dominated by a single long relaxation time, corresponding to a frequency spectrum consisting of a single, low-frequency Lorentzian. Moro and Pecora[15] then showed that the dynamical wormlike coil model of Harris and Hearst[16],

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which includes local chain stiffness, yields relaxation spectra dominated by the long relaxation times. However, their theoretical results were difficult to compare directly with experiment. Thus it is far from clear what chain dynamics models are appropriate for interpreting depolarized scattering experiments, and to what extent theoretical calculations of the depolarized scattering from flexible polymer chains are model dependent.

In this paper we report a study of the effects of details of chain dynamics upon the results of the forward depolarized scattering experiment. We exhibit the relaxation behaviour of two simple dynamic models of flexible chains in solution, with very similar local move rules. The relaxation of the end-to-end vector, taken as reflecting the longest-range, slowest motions of the chains, in both these models is similar to that of the Rouse–Zimm model in the appropriate (free-draining) limit. However, the relaxation of the component of the chain polarizability tensor sampled by the depolarized scattering experiment is drastically different in the two models, the relaxation time being proportional to the square of chain contour length in one case and independent of chain contour length in the other. Thus the question is raised whether models which deliberately sacrifice information about short-range chain structure and motion in order to gain tractability for long-range behaviour can be expected to be appropriate for the interpretation of depolarized scattering experiments.

MODEL

We model a flexible polymer chain in solution by a linearly connected set of $N-1$ segments, each of unit length, which join the centres of N beads. The angle between two adjacent segments along the chain is arbitrary and may assume any value resulting from application of the move rules. Further, in this study the 'beads' are taken to be of zero diameter and serve only as a convenience for describing the point of connection of two adjacent segments along the chain. Brownian motion of the chain resulting from random collisions with the solvent is simulated by choosing a bead at random and then moving just this bead to a new position, leaving the other beads unmoved. This process, which we shall call a bead cycle, is taken to represent $1/N$ units of time (since the rate at which a real polymer chain collides with solvent is presumably proportional to the length of the chain). Let the beads be numbered along the chain from 1 to N and the segments from 1 to $N-1$. Then if bead i is selected and i is not 1 or N, bead i is rotated through an angle ξ about the line joining beads $i-1$ and $i+1$. When an end bead ($i=1$ or N) is chosen, a 'phantom' bead 0 or $N+1$ is created a unit distance from the chosen end bead in a randomly chosen direction, the algorithm for moving a non-end bead is carried out, and the 'phantom' bead is discarded. For one of the two models of chain motion which we have employed here, which we shall call the Random Rotation (RR) model, at the start of each bead cycle a value of ξ is chosen at random in the range $\{-\pi,\pi\}$; for the other, which we shall call the Fixed Rotation (FR) model, ξ is always π. Neither of these models is new. Orwoll and Stockmayer[17] have shown analytically that the long-time relaxation behaviour of the FR model is identical with that of the free-draining Rouse–Zimm model, and Stockmayer, Gobush and Norvich[18] have shown the same thing for a class of bead-stick models which includes both the RR and the FR models as special cases. Thus the relaxation of the end-to-end vector is expected to be the same in both models. Our concern in the present paper is with the relaxation of the chain polarizability tensor.

We associate with each segment a segment polarizability tensor $\boldsymbol{\alpha}_i$ which is cylindrically symmetric about the segment and is the same for each segment. Let $\alpha_{i,\mathrm{pa}}$ be the component of $\boldsymbol{\alpha}_i$ parallel to the segment and $\alpha_{i,\mathrm{pe}}$ the component perpendicular to the segment, and let the coordinates of the i-th bead in a laboratory-fixed coordinate system by $\{X_i,Y_i,Z_i\}$. Then the yz-term α_{yz} of α_i is given[1,15] by:

$$\begin{aligned}\alpha_{i,yz} &= (\alpha_{i,\mathrm{pa}}-\alpha_{i,\mathrm{pe}})(Y_{i+1}-Y_i)(Z_{i+1}-Z_i)\\ &= (\alpha_{i,\mathrm{pa}}-\alpha_{i,\mathrm{pe}})\sin\theta_i\cos\theta_i\sin\varphi_i,\end{aligned} \tag{1}$$

where θ_i and φ_i are the usual laboratory-fixed polar coordinates for the orientation of segment i. The chain polarizability tensor $\boldsymbol{\alpha}$ is taken[19] to be the sum of the individual segment polarizability tensors $\boldsymbol{\alpha}_i$. Then the yz-term α_{yz} of the chain polarizability tensor is given by:

$$\alpha_{yz} = \sum_{i=1}^{N-1} \alpha_{i,yz} \tag{2}$$

In the forward depolarized scattering experiment, let us suppose that the incident light propagates along the x-axis, linearly polarized with its E-vector along the y-axis, and that we observe forward-scattered light with E-vector along the z-axis. Then the fluctuations in the intensity of the observed scattered light are proportional to the fluctuations in α_{yz}, and we can obtain the relaxation behaviour of α_{yz} from the autocorrelation function $\rho(\alpha_{yz},\alpha_{yz},t)=\langle\alpha_{yz}(0)\alpha_{yz}(t)\rangle/\langle\alpha_{yz}{}^2\rangle$, where the angle brackets denote equilibrium ensemble averages. The power spectrum of the scattered light is proportional to the Fourier transform of the autocorrelation function.

RESULTS

Random rotation model

Relaxation of the RR model was studied by computer simulation. Random starting configurations of chains of 9, 15, 33 and 63 beads were generated, then moved as described in the preceding section for large numbers of bead cycles corresponding to several hundred times the relaxation time for the end-to-end vector $\mathbf{l}$. At intervals the values of α_{yz} and $\mathbf{l}$ were sampled and products $\alpha_{yz}(0)\alpha_{yz}(t)$ and $\mathbf{l}(0)\cdot\mathbf{l}(t)$ formed and added into running sums, from which estimates of the equilibrium ensemble averages $\langle\alpha_{yz}(0)\alpha_{yz}(t)\rangle$ and $\langle\mathbf{l}(0)\cdot\mathbf{l}(t)\rangle$ were formed. Finally, the autocorrelation functions $\rho(\alpha_{yz},\alpha_{yz}t)=\langle\alpha_{yz}(0)\alpha_{yz}(t)\rangle/\langle\alpha_{yz}{}^2\rangle$ and $\rho(\mathbf{l},\mathbf{l},t)=\langle\mathbf{l}(0)\cdot\mathbf{l}(t)\rangle/\langle l^2\rangle$ were calculated.

Semilogarithmic plots of the autocorrelation functions obtained for $\mathbf{l}$ vs. t are shown in *Figure 1*. It will be seen that after an initial rapid decay, they each appear to approach linear behaviour suggestive of a unique longest relaxation time. We have therefore extracted two measures of relaxation time from each function: A relaxation time τ_l for $\mathbf{l}$ itself, defined by $\rho(\mathbf{l},\mathbf{l},\tau_l)=e^{-1}$, and a 'longest' relaxation time τ_1 obtained by fitting the autocorrelation function to the form $\rho=a\exp(-t/\tau_1)$ in the region $\rho<0.6$, beyond the initial rapid decay. The resulting values of τ_l and τ_1 are given in *Table 1*, in units of N^3 bead cycles.

In order to compare the relaxation behaviour of the RR model with that of the free-draining Rouse–Zimm model, we can make use of the dimensionless ratio $D\tau_1/\langle l^2\rangle$, where D is the translational diffusion constant of the centre of mass of the chain. For the RR model $\langle l^2\rangle$ is just $N-1$ and D can easily be shown from the move rules to be $(1/6)N^{-2}$ (bead cycles)$^{-1}$, or $N/6$ (N^3 bead cycles)$^{-1}$. Thus the ratio $D\tau_1/\langle l^2\rangle$ has the value $\tau_1 N/[6(N-1)]$. For the free draining Rouse–Zimm model of N beads and $N-1$ springs, the ratio has the value $csc^2[\pi/(2N)]/[12N(N-1)]$. Values of this expression and of $\tau_1 N/[6(N-1)]$ are shown in *Table 1*; they may be seen to be in reasonable agreement.

Semilogarithmic plots of autocorrelation functions for α_{yz} in the RR model are shown in *Figure 2*. It will be seen that they decay in a time approximately proportional to N bead cycles, and therefore independent of chain contour length. Relaxation times τ_α, defined by $\rho(\alpha_{yz},\alpha_{yz},\tau_\alpha)=e^{-1}$, are given in *Table 1*.

Fixed rotation model

In the FR model, the angle through which a selected bead is rotated about the line between its neighbouring beads along the chain is always π, rather than being randomly chosen each move. When bead i is selected, this 'rotation' merely exchanges the vector from bead $i-1$ to bead i with the vector from bead i to bead $i+1$. This model has been treated previously[17,20]; the relaxation of the end-to-end vector is very similar to that of the free-draining Rouse–Zimm model of N beads and $N-1$ springs. In both the FR model and the free-draining Rouse–Zimm model, the autocorrelation function $\rho(\mathbf{l},\mathbf{l},t)$ is given[20,21] by:

$$\rho(\mathbf{l},\mathbf{l},t)=\frac{2}{N(N-1)}\sum_{k=1}^{N-1}{}' \cot^2\left(\frac{k\pi}{2N}\right)\exp(-t/\tau_k) \qquad (3)$$

where the prime on the summation means that it is taken over odd values of k. It is clear from equation (3) that the relaxation of $\mathbf{l}$ is dominated by the longest relaxation time τ_1. The relaxation times τ_k are given in terms of D by $\tau_k(\mathrm{FR})=(-3N^2D\ln\{1-(4/N)\sin^2[k\pi/(2N)]\})^{-1}$ for the FR model, and by $\tau_k(\text{Rouse–Zimm})=\{12ND\ \sin^2[k\pi/(2N)]\}^{-1}$ for the free-draining Rouse–Zimm model. It will be seen that the two expressions give very similar values of τ_k when k/N is small or when N is large.

By an extension of the method employed in ref. 20, we can also obtain the autocorrelation function for α_{yz} in the FR model. In particular, we can show that for this model, the relaxation of α_{yz} is *identical* with that of $\mathbf{l}$. Let the chain configuration be represented by a set of vectors $\boldsymbol{\sigma}_1,\boldsymbol{\sigma}_2,\ldots,\boldsymbol{\sigma}_{N-1}$, where $\boldsymbol{\sigma}_i$ is the vector from bead i to bead $i+1$, and let us look at the effect of the FR move rules upon a particular $\boldsymbol{\sigma}_i$. Most bead cycles will not affect it, since they will call for an exchange elsewhere along the chain, but selection of bead i or bead $i+1$ will cause $\boldsymbol{\sigma}_i$ to exchange positions with $\boldsymbol{\sigma}_{i-1}$ or $\boldsymbol{\sigma}_{i+1}$, respectively, thus

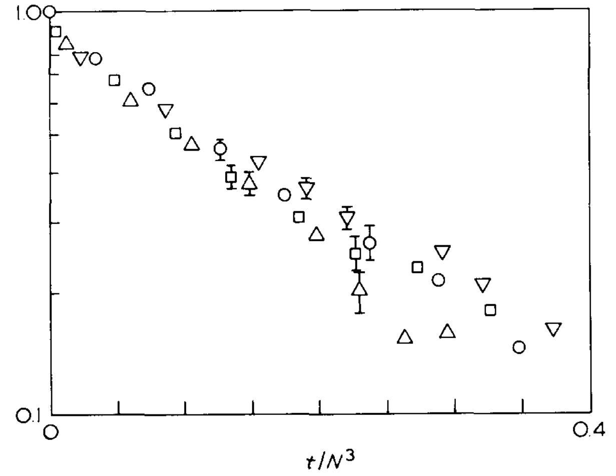

Figure 1 Semilogarithmic plot of autocorrelation functions $\rho(\mathbf{l},\mathbf{l},t)$ of the end-to-end vector $\mathbf{l}$ vs. time in units of N^3 bead cycles, for Random Rotation chains of N beads. The vertical bars extend upward and downward one sample deviation. (○) N = 9; (□) N = 15; (△) N = 33; (▽) N = 63

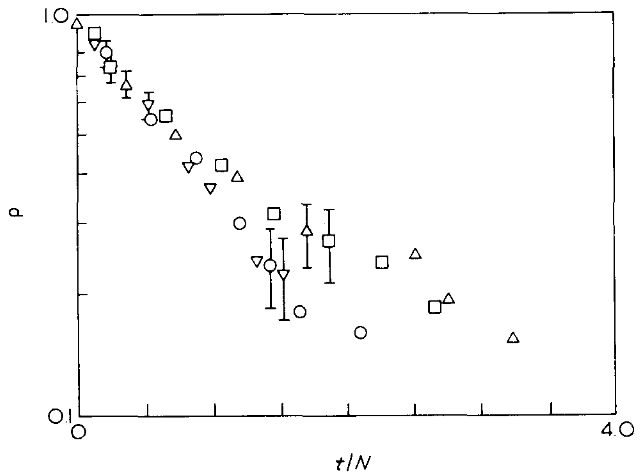

Figure 2 Semilogarithmic plot of autocorrelation functions $\rho(\alpha_{yz},\alpha_{yz},t)$ of the yz- component of the chain polarizability tensor α vs. time in units of N bead cycles, for Random Rotation chains of N beads. The vertical bars extend upward and downward one sample standard deviation. Symbols as *Figure 1*

Table 1 Values of τ_l/N^3, τ_1/N^3, $D\tau_1/\langle l^2\rangle$, $[csc^2(\frac{1}{2}\pi/N)]/[12N(N-1)]$, and τ_α/N, where τ_l, τ_1, and τ_α are the relaxation time for the end-to-end vector $\mathbf{l}$, the limiting long-time relaxation time, and the relaxation time for the yz-component of the chain polarizability tensor $\boldsymbol{\alpha}$, respectively, for Free Rotation model chains of N beads, in units of bead cycles. D is the translational diffusion constant of the centre of mass of the chain. The values of τ_l and τ_α were estimated by eye from the autocorrelation functions $\rho(\mathbf{l},\mathbf{l},t)$ and $\rho(\alpha_{yz},\alpha_{yz},t)$ in *Figure 1* to satisfy $\rho(\mathbf{l},\mathbf{l},\tau_l)=\rho(\alpha_{yz},\alpha_{yz},\tau_\alpha)=e^{-1}$. The values of τ_1 were obtained by least-squares fits of $\rho(\mathbf{l},\mathbf{l},t)$ to a $\exp(-t/\tau_1)$ in the region $\rho<0.6$. The values in parentheses are sample standard deviations in the τ's inferred from the sample standard deviations in the ρ's

N	τ_l/N^3	τ_1/N^3	$D\tau_1/\langle l^2\rangle$	$csc^2(½\pi/N)/[12N(N-1)]$	τ_α/N
9	0.16 (0.01)	0.1882 (0.0048)	0.035	0.038	1.1 (0.1)
15	0.15 (0.01)	0.2062 (0.0056)	0.037	0.036	1.3 (0.2)
33	0.15 (0.01)	0.1502 (0.0029)	0.026	0.035	1.2 (0.2)
63	0.18 (0.01)	0.2233 (0.0057)	0.038	0.034	1.0 (0.2)

moving one position along the chain in one direction or the other. Eventually it will migrate to one end of the chain, where the subsequent selection of the corresponding end bead may cause it to be exchanged with a new, randomly chosen $\boldsymbol{\sigma}$. In the meantime, it executes a well-defined random walk on a one-dimensional lattice of $N-1$ sites, with absorbing boundaries at both ends. The walk is characterized by the probability $p_{ij}(t)$ that a vector which starts at position i at time 0 will be in position j after exactly t bead cycles.

Now consider a function F of chain coordinates of the form:

$$F=\sum_i f_i, \tag{4}$$

where $f_i=f(\boldsymbol{\sigma}_i)$. The function f may be a vector or a scalar, and must have $\langle f\rangle=0$; $\langle f_i f_j\rangle=\delta_{ij}\langle f^2\rangle$. We seek the autocorrelation function for F: $\rho(F,F,t)=(\langle F(0)\cdot F(t)\rangle-\langle F\rangle^2)/(\langle F^2\rangle-\langle F\rangle^2)$. First we note the obvious: $\langle F\rangle=0$; $\langle F^2\rangle=(N-1)\langle f^2\rangle$. Now we need:

$$\langle F(0)\cdot F(t)\rangle=\sum_{ij}\langle f_i(0)\cdot f_j(t)\rangle \tag{5}$$

Consider the right-hand side of equation (5). Since by hypothesis the $\boldsymbol{\sigma}$'s, and therefore the f's are uncorrelated, each term $\langle f_i(0)\cdot f_j(t)\rangle$ will just be equal to $\langle f_i(0)\rangle\cdot\langle f_j(t)\rangle=0$ *except* when the vector which was at position i at time 0 migrates to position j in time t; in this case the value of the term is $\langle f^2\rangle$. We therefore have:

$$\begin{aligned}\langle F(0)\cdot F(t)\rangle&=\langle f^2\rangle\sum_{ij}p_{ij}(t);\\ \rho(F,F,t)&=(N-1)^{-1}\sum_{ij}p_{ij}(t).\end{aligned} \tag{6}$$

Thus *any* function that can be written in the form of equation (4) with its associated constraints has the autocorrelation function given by equation (6). The form of the autocorrelation function depends upon the nature of $p_{ij}(t)$, which is determined by the move rules, but does not depend upon what the function F is.

Finally, we note that both $\mathbf{l}$ and α_{yz} can be so written; for the end-to-end vector we have $f_i=\boldsymbol{\sigma}_i$ and for α_{yz} we have $f_i=(\boldsymbol{\sigma}_i\cdot\mathbf{e}_y)(\boldsymbol{\sigma}_i\cdot\mathbf{e}_z)$, where $\mathbf{e}_y$ and $\mathbf{e}_z$ are unit vectors in the positive y- and z-directions, respectively. It follows that the autocorrelation functions, and therefore the relaxation times, of $\mathbf{l}$ and α_{yz} are identical. Thus the relaxation of α_{yz} in the FR model, in contrast to the RR model, is dominated by the longest relaxation time.

CONCLUSION

In summary, we have exhibited the relaxation behaviour of two freely jointed bead-stick models of flexible polymer chains. The two models are very similar, differing only in the details of their local moves. The relaxation of the end-to-end vector in both models is very similar to that shown by the freely draining Rouse–Zimm model. However, the two models give drastically different predictions for the relaxation of the chain polarizability tensor component sampled by the forward depolarized quasi-elastic light scattering experiment. For the version we have called the Random Rotation model, relaxation of this component is relatively fast and independent of chain length, a result qualitatively similar to the predictions of the Ono–Okano result and the experimental data of Han and Yu. For the Fixed Rotation model, relaxation is identical with that of the end-to-end vector, and is therefore dominated by the longest relaxation time, in qualitative agreement with the experimental data of Bauer, Brauman and Pecora. It was pointed out long ago[18] that differences in short-range relaxation behaviour are to be expected for different bead-stick models with similar long-time relaxation behaviour. Our results offer a rather striking demonstration of these differences in the case of the chain polarizability tensor.

In view of these results, it appears that the predictions of models in which short-range detail is deliberately suppressed, such as both these bead-stick models and, equally, the Rouse–Zimm bead-spring model, are not to be trusted for the relaxation of the chain polarizability tensor. Considerable insight into the details of its relaxation on a monomer-scale level appears to be needed for the construction of a model appropriate for the interpretation of the forward depolarized scattering experiment. This suggests that the experimental results may be non-trivially dependent upon the chemical structure of the chain monomer units.

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