Macromolecules 1988, *21*, 1813–1818

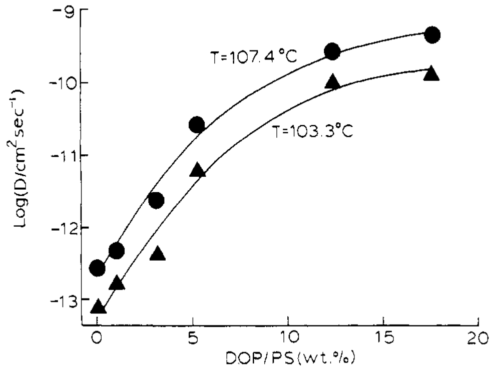

Figure 2. Diffusion coefficients of camphorquinone in the DOP–PS system, as a function of DOP concentration, at two temperatures.

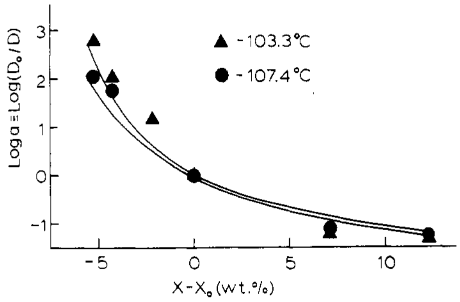

Figure 3. Fit of experimental diffusion coefficients as a function of x_0 (DOP concentration–reference DOP concentration) to the WLF equation (modified for plasticizer induced free volume increase): the reference concentration is 5.3%; ▲, T = 103.3 °C; ●, T = 107.4 °C.

where B is a constant close to unity and f_1 and f_2 are the fractional free volumes at states 1 and 2, respectively. States 1 and 2 can be due to difference in temperature, pressure, or any other quantities as long as it is associated with the change of free volume and no glass transition or any phase change is involved. In the present case, states 1 and 2 differ only in the degree of plasticization.

When the concentration of the plasticizer is not too high, it is reasonable to assume fractional free volume linearly increases with the concentration of the plasticizer or

$$f_2(T,x_2) = f(T,x_1) + \alpha(x_2 - x_1) \qquad (4)$$

where α is a proportional constant that is determined by the plasticizer's effectiveness in increasing the free volume. Inserting eq 4 to eq 3, we obtain for constant temperature

$$\log\,(a_x) = \log\left(\frac{D(x)}{D_0}\right) = \frac{+B}{2.3f_0}\left\{\frac{x - x_0}{f_0/\alpha + (x - x_0)}\right\} \qquad (5)$$

where a_x is the shift factor for the plasticizer concentration equal to x, x_0 is the reference concentration of the plasticizer, and D_0 is the diffusion coefficient of CQP at $x = x_0$. The fractional free volume $f(x_0) = f_0$ at $x = x_0$ is a function of temperature.

Shown in Figure 3 is the fit of the experimental points at T = 103.3 and 107.4 °C to eq 5, with x_0 being 5.26%. The fit is satisfactory and shows that eq 5 can be used to describe the change of D with the plasticizer concentration. The best fit yields values: $B/2.303f(x_0) = 6.35$, $f(x_0)/\alpha = 0.103$ for the T = 103.3 °C curve and $B/2.303f(x_0) = 6.21$, $f(x_0)/\alpha = 0.116$ for the T = 107.4 °C curve. These best fit values are qualitatively correct as B and a are constants and are not expected to change appreciably with T and x. We thus expect a lower value of $B/(2.303f(x_0))$ and a higher value of $f(x_0)/\alpha$ as T increases. This is consistent with the fit results. Due to the uncertainty in the diffusion data, we cannot determine quantitatively the change in $f(x_0)$ over the small temperature difference. However, this change is expected to be only about 10%.

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Effect of an Inhomogeneity on Local Chain Dynamics: Conformational Autocorrelation Function

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ABSTRACT: The influence of an inhomogeneity such as a fluorescence or ESR label on local polymer main chain dynamics is investigated theoretically by using a bistable conformational model including isolated transitions and correlated pair transitions. The conformational autocorrelation function is determined by a perturbative treatment within the limit of a far chain end inhomogeneity. The model suggests two types of behavior according to the dynamic properties of the inhomogeneity. A flexible inhomogeneity yields a decrease of the cooperative relaxation time and an increase of the main-chain mobility while the opposite case is obtained with a rigid one. The results are compared with Hall–Helfand's model, generalized diffusion and loss model, and the recent study of Pant et al. relative to the effect of a probe on polymer chain dynamics.

I. Introduction

Many studies have dealt with local dynamics in polymers since 1960. With this aim in view, correlation functions which are statistical quantities directly available to experiments have been exploited as a useful intermediary between theory and experiment. Techniques such as NMR, Kerr effect, dielectric relaxation, picosecond holographic grating spectroscopy, and fluorescence anisotropy

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decay are sensitive to orientational autocorrelation functions (OACF). Several dynamic models have been developed to describe the behavior of macromolecular chains on a local scale and the OACF has been given in each case. Some of these models rely on a dimensional diffusion equation as in the model of Valeur et al.[1] To avoid the unrealistic first derivative at time $t = 0$ in the continuum limit related to this model, two kinds of cutoff have been proposed: Jones and Stockmayer[2] arbitrary truncated Rouse's matrix whereas Bendler and Yaris[3] introduced long-wavelength and short-wavelength cutoffs.

More recently, Hall and Helfand[4] proposed a conformational dynamic model. Their theory is supported by the existence of isolated transitions and correlated pair transitions which take place with relaxation times τ_2 and τ_1, respectively. The conformational autocorrelation function may be written as

$$c_0(t) = \exp(-t/\tau_2)\exp(-t/\tau_1)I_0(t/\tau_1) \qquad (1)$$

where I_0 is a modified Bessel function of order 0. Hall and Helfand have suggested that the expression for the conformational autocorrelation function $c_0(t)$ may be a good approximation for the OACF. Viovy et al.[5] extended this result on an empirical basis (generalized diffusion and loss model (GDL)).

Techniques such as NMR or ESR require an a priori choice of a model while fluorescence anisotropy decay and picosecond holographic grating methods provide a quasi-continuous sampling of the autocorrelation function and have proved to be very useful in choosing the OACF.[5,6] Owing to those two techniques, both conformational models (Hall and Helfand's and GDL) and the Bendler–Yaris model seem to be adequate for describing local dynamics in polymers. These methods use a fluorophore attached to the macromolecule chain to probe polymer dynamics whereas the models presented above deal with an ideal chain, i.e., homogeneous and eventually infinitely long.

We may expect that the presence of a label perturbs the local dynamics of the chain which may lead to a modification of the OACF.

Pant et al.[7] have been recently interested in the effect of labeling on polymer dynamics. The probe is treated as a localized structureless molecule which does not affect the intrinsic short-wavelength cutoff. In their paper, the label yields a loss of orientational diffusion and an increase of the rate of decay of the OACF compared with the case of no probe.

In the present work, we propose to consider the label as a partial reflector instead of an absorber. We include the effect of spatial inhomogeneity in the Hall–Helfand model and express the conformational autocorrelation function using the Pauli matrices formalism. We may note that this treatment is not restricted to a label but may be generalized to any inhomogeneity such as a cross-link or structure and microstructure defects.

In section II, we develop a model of chain dynamics perturbed by an inhomogeneity. The calculation of the eigenvalues of the system requires further approximations such as a specification of the location of the inhomogeneity in the main chain. Our study will be then applied to the case of an inhomogeneity placed in the middle of the chain which is the usual configuration in fluorescence depolarization techniques. The spectrum of the hamiltonian is presented in section III. Section IV develops a formal expression for the conformational autocorrelation function.

II. The Model

Using Hall and Helfand's notations and arguments, we consider the macromolecule chain as a N-bond one-dimensional chain containing a heterogeneity (label, ...) between the $n - 1$ and n bonds. Each bond may be in either of two states: short (s) and long (l) states (Figure 1). The state of bond j may be described with a quantum number μ_j which is equal to +1 for long state and −1 for short state. The state of a chain is denoted by $\mu = (\mu_1, ..., \mu_N)$, there are 2^N such states.

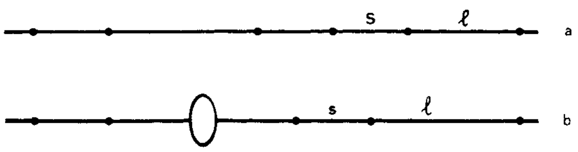

Figure 1. (a) Homogeneous chain; (b) inhomogeneous chain.

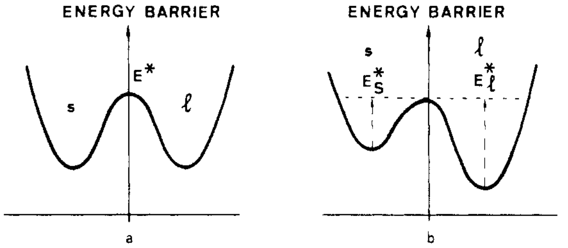

Figure 2. (a) Energy barrier of a homogeneous chain (Hall and Helfand's model); (b) energy barrier near an inhomogeneity.

Let $f(\mu,t)$ be the probability of μ state at time t where $f(\mu,t)$ satisfies the master equation:

$$\mathrm{d}f(\mu,t)/\mathrm{d}t = \sum_{\mu' \neq \mu} \{K(\mu,\mu')f(\mu',t) - K(\mu',\mu)f(\mu,t)\} \qquad (2)$$

where $K(\mu',\mu)$ is the rate of transition from μ' to μ. Let us consider $f(\mu,t)$ as a 2^N component vector. Equation 2 becomes

$$\mathrm{d}f/\mathrm{d}t = -Mf \qquad (3)$$

which leads to the formal equation

$$f(\mu,t) = \exp(-Mt)f(0) \qquad (4)$$

where M is a $2^N \times 2^N$ matrix.

Chain dynamics of bonds far from the label is described by Hall and Helfand's conformational model. This model takes into account isolated transitions: $\mathrm{l} \rightleftarrows \mathrm{s}$ which occur with a rate called λ_0 and correlated pair transitions which are restricted to first-neighbor bond pairs: $(\mathrm{l,s}) \rightleftarrows (\mathrm{s,l})$ the rate of which is λ_1. These assumptions lead to the time autocorrelation function (1) where $\lambda_1 = 1/\tau_1$ and $\lambda_0 = 1/\tau_2$.

s and l states have the same energy in the Hall–Helfand model. This hypothesis is kept in our model for bonds which are far from the label. But we may expect that l and s are not equiprobable for label conformations. Let us consider that the l state is more stable than the s state (Figure 2). Even though those two states are not equiprobable we may consider that

$$M(\mu,\mu) = -\sum_{\mu' \neq \mu} M(\mu',\mu) \qquad (5)$$

The calculation of $M(\mu',\mu)$ will be performed for an infinite chain.

Jump Probabilities. j refers to the index of a bond. Let us consider isolated transitions first: If μ and μ' differ by the state of a single bond j being different from $n - 1$ or n, then

$$M(\mu,\mu') = -\lambda_0$$

It is necessary to specify the probability of single bond state change for bonds $n - 1$ and n to take into account the nature of those particular bonds and the difference of activation energy between l and s conformations. Let λ_0^{l} and λ_0^{s} be the jump probabilities for l → s and s → l motions, respectively. If l is more stable than s, then $\lambda_0^{l} < \lambda_0^{s}$.

Let us now consider cooperative pair transition processes: If the label perturbation is restricted to first-neighbor bonds, the probability of $(n-1,n)$ conformation exchange will be denoted λ'_1 while $M(\mu,\mu) = -\lambda_1$ for j different from $n - 1$ and n.

Expression of M. The hamiltonian of the system, M, may be expressed in terms of Pauli spin operators which act as creation and annihilation operators for bond j and conformation l. Let σ_j^{+} and σ_j^{-} be those operators,

$$\sigma_j^{+}|\mu_1, ..., \mu_j, ..., \mu_N\rangle = \frac{1}{2^{1/2}}(1 - \mu_j)^{1/2}|\mu_1, ..., \mu_j + 2, ..., \mu_N\rangle \quad (6a)$$

$$\sigma_j^{-}|\mu_1, ..., \mu_j, ..., \mu_N\rangle = \frac{1}{2^{1/2}}(1 + \mu_j)^{1/2}|\mu_1, ..., \mu_j - 2, ..., \mu_N\rangle \quad (6b)$$

Using the formalism of Pauli matrices, M may be written as

$$M = M_0 + M_1$$

where M_0 is given by

$$M_0 = -\lambda_0 \sum_{j\in\varphi} (\sigma_j^{+} + \sigma_j^{-} - \sigma_j^{-}\sigma_j^{+} - \sigma_j^{+}\sigma_j^{-}) - \lambda_0^{s} \sum_{j\notin\varphi} (\sigma_j^{+} - \sigma_j^{-}\sigma_j^{+}) - \lambda_0^{l} \sum_{j\notin\varphi} (\sigma_j^{-} - \sigma_j^{+}\sigma_j^{-})$$

φ denotes 1, ..., $n - 2$, $n + 1$, ..., N bonds. Then

$$M_0 = \lambda_0 \sum_{j\in\varphi} (1 - \sigma_j^{x}) + \lambda_0^{s} \sum_{j\notin\varphi} (1 - \sigma_j^{x}) + \lambda \sum_{j\notin\varphi} (\sigma_j^{-} - \sigma_j^{+}\sigma_j^{-}) \quad (7)$$

where $\lambda = \lambda_0^{s} - \lambda_0^{1}$ and 1 indicates the identity operator. σ_j^{x} and σ_j^{y} are defined by

$$\sigma_j^{x} = \sigma_j^{+} + \sigma_j^{-} \quad (8a)$$

$$\sigma_j^{y} = i(\sigma_j^{-} - \sigma_j^{+}) \quad (8b)$$

M_1 may be written as

$$M_1 = \tfrac{1}{2}\lambda_1 \sum_{\substack{j\in\varphi \\ \text{or } j=n}} (1 - \sigma_j\sigma_{j+1}) + \tfrac{1}{2}\lambda'_1(1 - \sigma_{n-1}\sigma_n) \quad (9)$$

M_0 and M_1 commute, let $|1_j\rangle$ be a common base of eigenvectors

$$|1_j\rangle = \sigma_j^{z}|0\rangle \quad (10)$$

$|1_j\rangle$ represents an excitation on site j and $|0\rangle$ is an eigenvector of M with eigenvalue 0. Let us consider the spin waves set of eigenvectors

$$|\tilde{1}_p\rangle = \sum_{j=1}^{N} e^{ipj}|1_j\rangle \quad (11)$$

where $p = 2\pi n_p/N$, n_p is an integer which varies within the range $(-N/2,N/2)$. In fact, there is a phase difference between bonds $n - 1,n$ and the other bonds. This one is not taken into account because it does not appear in the autocorrelation function calculation.

III. Spectrum of M_0 and M_1

Noticing the analogy between hamiltonian M and a $^1/_2$ spin chain in the Heisenberg model, it is easy to find M_0 eigenvalues for the label

$$\hbar\omega_s^{(0)} = (\lambda_0^{s}\lambda_0^{l})^{1/2} \quad (12)$$

where $\omega_s^{(0)}$ is the jump frequency of the inhomogeneity due to M_0.

We will now focus attention on the calculation of M_1 eigenvalues which is more complex because of coupling terms. The solution of the system may be found by setting the determinant **D** equal to zero (Chart I) where $\beta = \lambda_1/\lambda'_1$, in the limit $N \to \infty$. This determinant is symmetrical with regards to the label position. In the case of bonds far from the label, $\omega_j^{(1)}$ is described by the limiting value obtained by Hall and Helfand:

$$\lim \omega_j^{(1)} = \frac{\lambda_1}{\hbar}(1 - \cos(p))$$

To extend the calculation, new hypotheses are required. First, we suppose the label–chain system to be symmetric, thus

$$\hbar\omega_{n-(j+1)} = \hbar\omega_{n-j} \quad (13)$$

We may note that this is not a restricting condition insofar as the inhomogeneity is very far from the ends of the polymer chain. Second, we suppose the label to create reflected and transmitted waves. Then σ_j^{x} and σ_j^{y} operators may be expressed as a sum of incident, reflected, and transmitted waves. From the formalism of spin waves,

$$\begin{cases} \sigma_{n-1}^{x} = ue^{-i\omega_{n-1}t}[e^{ip(n-1)} + \rho e^{-ip(n-1)}] \\ \sigma_{n-1}^{y} = ve^{-i\omega_{n-1}t}[e^{ip(n-1)} + \rho e^{-ip(n-1)}] \end{cases} \quad (14a)$$

$$\begin{cases} \sigma_{n}^{x} = u\tau e^{-i\omega_n t} \\ \sigma_{n}^{y} = v\tau e^{-i\omega_n t} \end{cases} \quad (14b)$$

$$\begin{cases} \sigma_{n-2}^{x} = ue^{-i\omega_{n-2}t}[e^{ip(n-2)} + \rho e^{-ip(n-2)}] \\ \sigma_{n-2}^{y} = ve^{-i\omega_{n-2}t}[e^{ip(n-2)} + \rho e^{-ip(n-2)}] \end{cases} \quad (14c)$$

$$\begin{cases} \sigma_{n+1}^{x} = u\tau e^{-i\omega_{n+1}t} e^{ip(n+1)} \\ \sigma_{n+1}^{y} = v\tau e^{-i\omega_{n+1}t} e^{ip(n+1)} \end{cases} \quad (14d)$$

where ρ and τ are the coefficients of reflection and transmission for the waves and are linked by the relation $\rho + \tau = 1$. Assuming that $\omega_{n-1} = \omega_n = \omega_s^{(1)}$ has a real value where $\omega_s^{(1)}$ is the jump frequency of the label due to M_1 and in the limit

$$\frac{\lambda_1 - \lambda'_1}{\lambda_1} \ll 1$$

This relation assumes that the effect of the inhomogeneity on the chain dynamics may be considered as a perturbation. The eigenvalue of M_1, $\omega_s^{(1)}$, may be written as

$$\hbar\omega_s^{(1)} = \tfrac{1}{2}\{(\lambda_1 + \lambda'_1)(1 - \cos(p)) - (\lambda_1 - \lambda'_1)\sin(p)\tan(p)\} \quad (15)$$

The global expression of the label jump frequency is then

$$\hbar\omega_s = (\lambda_0^{s}\lambda_0^{l})^{1/2} + \tfrac{1}{2}\{(\lambda_1 + \lambda'_1)(1 - \cos(p)) - (\lambda_1 - \lambda'_1)\sin(p)\tan(p)\} \quad (16)$$

which depends on isolated transitions of the label $(\lambda_0^{s},\lambda_0^{l})$ and cooperative motion of the chain and of bonds close to the label.

IV. Expression for the Autocorrelation Function

We may note that the conformational autocorrelation function must describe the motion of the probe since its

Chart I

$$\mathbf{D} = 0 = \begin{array}{cccccccccccccc|c}
1\ldots & n-6 & n-5 & n-4 & n-3 & n-2 & n-1 & n & n+1 & n+2 & n+3 & n+4 & n+5 & n+6\ldots & \\
 & 1 & -4 & -A\omega^1_{n-4}+6 & -4 & 1 & & & & & & & & & n-6 \\
 & & 1 & -4 & -A\omega^2_{n-3}+6 & -4 & 1 & & & & & & & & n-5 \\
 & & & 1 & -4 & -A\omega^2_{n-2}+6 & -(3+\beta) & \beta & & & & & & & n-4 \\
 & & & & 1 & -(3+\beta) & -A\omega^2_{n-1}+2(1+\beta+\beta^2) & -2\beta(1+\beta) & \beta & & & & & & n-3 \\
 & & & & & \beta & -2\beta(1+\beta) & -A\omega^2_n+2(1+\beta+\beta^2) & -(3+\beta) & 1 & & & & & n-2 \\
 & & & & & & \beta & -(3+\beta) & -A\omega^2_{n+1}+6 & -4 & 1 & & & & n-1 \\
 & & & & & & & 1 & -4 & -A\omega^2_{n+2}+6 & -4 & 1 & & & n \\
 & & & & & & & & 1 & -4 & -A\omega^2_{n+3}+6 & -4 & 1 & & n+1 \\
 & & & & & & & & & 1 & -4 & -A\omega^2_{n+4}+6 & -4 & 1 & n+2 \\
 & & & & & & & & & & & & & & n+3 \\
 & & & & & & & & & & & & & & n+4 \\
 & & & & & & & & & & & & & & n+5 \\
 & & & & & & & & & & & & & & n+6
\end{array}$$

behavior is the only one available to experiment. The time-autocorrelation function is defined by

$$c_0(t) = \frac{1}{(2\pi)^2}\int_{-\pi}^{+\pi}\int_{-\pi}^{+\pi} \mathrm{d}p\,\mathrm{d}q\,\exp(-i(p-q)j)\langle\tilde{1}_q|\exp(-Mt)|\tilde{1}_p\rangle \tag{17}$$

$$c_0(t) = \frac{1}{2\pi}\int_{-\pi}^{+\pi}\mathrm{d}p\,\exp\left\{\left(-(\lambda_0^{\mathrm{s}}\lambda_0^{\mathrm{l}})^{1/2} + \frac{\lambda_1+\lambda'_1}{2}(1-\cos(p)) - \frac{\lambda_1-\lambda'_1}{2}\sin(p)\tan(p)\right)t\right\} \tag{18a}$$

Put

$$\frac{1}{\tau_1} = \frac{\lambda_1+\lambda'_1}{2} \tag{18b}$$

and

$$\frac{1}{\tau_2} = (\lambda_0^{\mathrm{s}}\lambda_0^{\mathrm{l}})^{1/2} \tag{18c}$$

The expansion of the term $\exp\{(0.5(\lambda_1-\lambda'_1)\sin(p)\tan(p))t\}$ leads to

$$c_0(t) = \exp(-t/\tau_2)\exp(-t/\tau_1)\left\{I_0(t/\tau_1) + \sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{\lambda_1-\lambda'_1}{2}\right)^n t^n\,\frac{1}{2\pi}\int_{-\pi}^{+\pi}(\sin(p)\tan(p))^n \times \exp((t/\tau_1)\cos(p))\,\mathrm{d}p\right\} \tag{19}$$

The term of order one is obtained after an integration in the complex plane:

$$c_0(t) = \exp(-t/\tau_2)\exp(-t/\tau_1)\{I_0(t/\tau_1) + \alpha(t/\tau_1) \times (-I_1(t/\tau_1) + 2\sum_m(-1)^m I_{2m+1}(t/\tau_1))\} \tag{20a}$$

where

$$\alpha = \frac{\lambda_1-\lambda'_1}{\lambda_1+\lambda'_1} \tag{20b}$$

This result may be generalized to terms of higher order,

$$c_0(t) = \exp(-t/\tau_2)\exp(-t/\tau_1) \times \left\{I_0(t/\tau_1) + \sum_{n=1}^{\infty}\frac{1}{n!}\alpha^n\left(\frac{t}{\tau_1}\right)^n\left[\sum_{\substack{l=0\\2l<n}}^{n}(-1)^l C_n{}^l 2^{n-2l} \times \sum_{m,k}\frac{(-1)^m}{k!(2m+k+n-2l)!}S_{n-2l}^{(m)}\left(\frac{t}{2\tau_1}\right)^{2m+2k+n-2l} + \sum_{\substack{l=0\\2l\geq n}}^{n}(-1)^l C_n{}^l 2^{n-2l}\sum_{k=0}^{2p-n}C_{2l-n}{}^k I_{2k+n-2l}\left(\frac{t}{\tau_1}\right)\right]\right\} \tag{21}$$

where I_p is a modified Bessel function of order p and $S_p(m)$ is the following series:

$$S_1(m) = 1$$

$$S_p(m) = \frac{(m+1)\ldots(m+p+1)}{1\ldots(p-1)} \quad \text{for} \quad p > 1$$

Expression 20 is analogous to the Hall–Helfand OACF for $\lambda_1 = \lambda'_1$, i.e., when there is no probe. For large times, $c_0(t)$

tends toward zero and exhibits a time dependence on $t^{-1/2} \exp(-t/\theta)$.

V. Discussion

Considering the approximations involved in the analytical treatment on one hand and the available experimental accuracy on the other hand, the details contained in relation 21 are probably not worth considering, and we restrict our discussion to the first-order perturbation result (relation 20) which reveals several interesting and nontrivial differences with the unperturbed Hall and Helfand expression (relation 1).

Generally speaking, the inhomogeneity modifies both the values of correction times and the analytical shape of the OACF. As in the model previously proposed by Pant et al.[7] we predict a modification of the diffusive correlation time τ_2. However, in our conformational model τ_2 can be smaller or longer than the unlabeled chain damping time, depending on conformations available near the probe, whereas the model of Pant et al. always predicts a decrease in τ_2.

Moreover, we also predict a modification of the correlated jumps conformational time τ_1, according to the weighted balance expressed by relation 18a which was not predicted in ref 7. When the inhomogeneity is more flexible than the polymer main chain, the present model predicts a decrease of the correlated pair-transition relaxation time relative to the case of no probe. The mobility of the chain increases since the rate of OACF decay grows up. But when the inhomogeneity induces a hindrance, i.e., $\lambda_1 < \lambda'_1$, the chain mobility decreases and the cooperative relaxation time increases. Hence, if the representation of the label used in our model is correct, we expect the most easily available labels (such as anthracene) to increase significantly the local rigidity of the chain and to increase τ_1, at least for flexible chains. This is consistent with the common observation that fluorescence labeling correlation times are significantly higher than NMR correlation times obtained with similar chains.

A more quantitative discussion of this problem would be possible by using labels of variable size or rigidity, but the synthesis of well-defined ad hoc labeled chains is not an easy chemical task and to our knowledge, such experiments have not been attempted yet.

The last remarkable point in relation 20 is the presence of higher order Bessel functions which disappear in the limit $\lambda_1 = \lambda'_1$. According to expression 20a an absolute measure of the perturbation due to the label on correlated jumps should be given by a fit of the shape of the conformational correlation function to experimental data. Then, the knowledge of τ_1 and α should provide an absolute measure of the pure chain jump frequency λ_1, together with the local jump frequency λ'_1.

The expected difference in conformational correlation functions is illustrated in Figure 3, where $c_0(t)$ is plotted for an arbitrary (and typical) ratio $\tau_2/\tau_1 = 30$ and values of α ranging from 0 to 0.5. The empirical GDL expression

$$c_0(t) = \exp(-t/\tau_2) \exp(-t/\tau_1)\{I_0(t/\tau_1) + aI_1(t/\tau_1)\} \quad (22)$$

is also plotted for comparison, using the particular value $a = 1$ which seems to provide a significative improvement over Hall and Helfand's expression in several fluorescence labeling experiments. Indeed, both expression 20a and 22 seem to modify the conformational correlation function in a qualitatively similar manner. This deviation would support the early suggestion that the label could be the origin of the deviations from Hall and Helfand's expression observed in labeling experiments. However, numerous complications have been ignored and a lot of caution is required here:

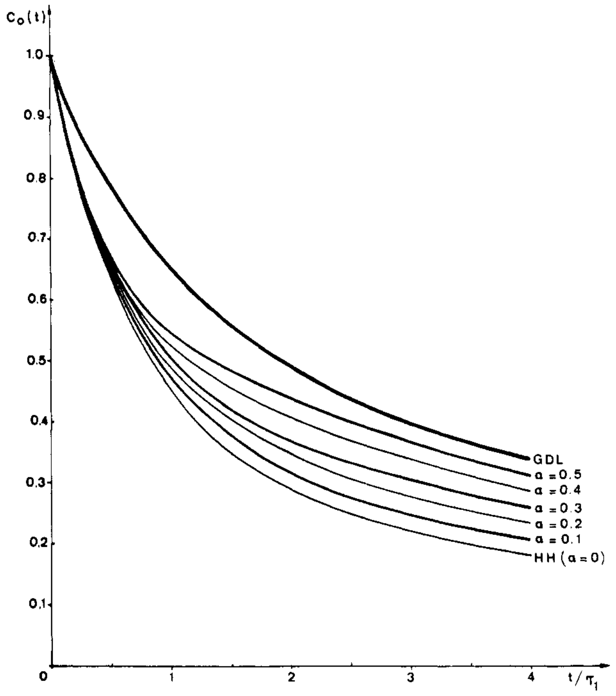

Figure 3. Comparison of chain behavior for Hall and Helfand (HH), generalized diffusion and loss (GDL) models, and label effect for α equal to 0, 0.1, 0.2, 0.3, 0.4, and 0.5 and $\tau_2/\tau_1 = 30$.

First, $c_0(t)$ is a prediction for the conformation correlation function. Using computer simulation, Weber and Helfand[8] have shown that the OACF of model chains was rather reasonably described by a conformational correlation function of the Hall-Helfand type, but it is hard to assess how quantitatively this result can be generalized.

Second, our treatment is based on a variational approach. It is not uncommon that such approaches remain surprisingly accurate even far from their expected domain of validity, but this optimistic view cannot be taken as a general rule, and relation 20a should not be considered as quantitative when λ'_1 becomes very different from λ_1 (which is indeed the case if $(\lambda_1 - \lambda'_1)/(\lambda_1 + \lambda'_1) \simeq 0.5$).

Third, as previously indicated by Hall and Helfand,[4] the "two-state elements" chain which leads to a relative simple and analytical treatment is certainly a crude and oversimplified representation of real chains which generally present three conformational potential wells or more.

Considering now the problem from an experimental point of view, it must be realized that the independent access to τ_1, τ_2, and α implies fitting experiment curves with four independent parameters. As discussed in recent experimental reports, obtaining these four parameters with good accuracy is still a difficult challenge to experimentalists.

VI. Conclusion

In this paper, we have shown that the Hall and Helfand conformational model of polymer dynamics can be generalized in order to account for a local inhomogeneity (label) which modifies the conformational jump probabilities. The dynamic equations corresponding to the new hamiltonian can be solved analytically at a perturbation level, leading to an approximate expression for the conformational autocorrelation function of the label bond. The expression contains an exponential and a Bessel function term similar to those in the Hall–Helfand model and renormalized correlation times which can be associated with suitably weighted averages of conformational jump times in the vicinity of the label, plus extra terms, which provide a theoretical way to unravel the contributions from the label and from the ideal chain and to extract the intrinsic chain jump frequency. Besides the experimental difficulties involved in this quantitative approach, the model provides a comprehensive qualitative frame for interpreting presently available experiments. Finally, it is worth noticing that this perturbation approach is not restricted to labeling problems but can be extended to any situation involving inhomogeneities in a polymer chain.

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Lattice Models of Branched Polymers: Dynamics of Uniform Stars

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ABSTRACT: We report exact enumeration and Monte Carlo results on the dynamics of uniform star polymers. The treatment is at the level of the Zimm rigid body approximation and we use a lattice model incorporating the effects of excluded volume. We have calculated the sedimentation velocity and intrinsic viscosity, and hence the hydrodynamic radius, as a function of the number of branches in the star and the number of monomers in each branch. We have varied the bare friction by changing the effective bead radius (a) and we discuss the sensitivity of the results to the value of a. We compare our results, for appropriate ratios of quantities for branched and linear polymers, with those of other theoretical treatments and with experimental results.

1. Introduction

In 1980, Zimm[1] introduced a method for calculating dynamical properties of dilute polymer solutions by treating each conformation of the polymer as a rigid body, solving the hydrodynamic equations for each such rigid conformation, and averaging over a Monte Carlo sample of the conformations. This approach avoids solving the Kirkwood diffusion equation. It does not use the preaveraging approximation involved in the Kirkwood–Riseman treatment[2] but is, in itself, an approximation.[3] However, Wilemski and Tanaka[4] and Fixman have shown that Zimm's method yields bounds on the intrinsic viscosity and on the sedimentation coefficient.

Zimm's original calculations[1] were for Gaussian chains but the method has also been applied to "wormlike"[5] and Gaussian[5,6] models of uniform star polymers without excluded volume. Zimm[7] has also compared dynamic properties of uniform stars, with and without excluded volume.

All of the above calculations have been carried out for continuum models. In this paper we apply similar methods to *lattice* models of chains (i.e., to self-avoiding walks) and uniform stars, *with* excluded volume. The advantages of a lattice model are that, for a given amount of computer time, improved statistics can be obtained and, for small systems, enumeration methods can be used so that the *averaging* over conformations is exact. We have established elsewhere[8] that the lattice dependence of certain quantities can be removed by taking appropriate ratios and that these ratios can be successfully compared with experiment.[8,9]

We study the sedimentation velocity (u), and hence the corresponding hydrodynamic radius (R_s), and the intrinsic viscosity ($[\eta]$) for chains and for stars with f branches ($f = 3$–6) on the simple cubic lattice. If each branch has n monomers, the total number (N) of monomers is $N = 1 + nf$. For small N, we have calculated u and $[\eta]$ exactly, within the Zimm algorithm, by enumerating all conformations, and we have extended these results to larger N (less than about 60) by an inversely restricted Monte Carlo method.[10,11] Sample sizes used were typically 5000 configurations. We have investigated the asymptotic behavior (large N) of these quantities as a function of f and of the "bead" radius (a). We compare our results for the viscosity ratio (g') and the ratio (h) of the sedimentation rates with the Kirkwood[2] approximation and with previous theoretical and experimental results.

2. Sedimentation Velocity and Hydrodynamic Radius

The basic idea behind Zimm's approach[1] is to neglect coupling between small scale and center of mass motions. Consequently, each conformation is treated as a rigid body, the hydrodynamic equations are solved for the motion of this rigid body, and quantities such as the sedimentation velocity are calculated for each conformation. Finally, these quantities are averaged over all, or a sample of, the conformations of the molecule.

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