A closed form solution for the internal dynamics of polymer chains. I. Bonds with independent rotational potentials

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(Received 27 June 1989; accepted 4 December 1989)

An analytical solution to the master equation governing the conformational dynamics of linear polymer chains is formulated. Symmetric chains with N bonds subject to independent rotational potentials are considered. The eigenvalues of the transition rate matrix, which characterize the frequencies of the various relaxation modes, and the corresponding eigenvectors and eigenrows are obtained in closed form. A simple recurrence equation permits one to express the eigenvalues of the N-bond motion in terms of the nonzero eigenvalues associated with the isomeric transitions of single bonds. This leads to a clear understanding of the increase in conformational mobility with N.

INTRODUCTION

The dynamics of a polymer chain result from coordinated motions of its bonds. The types of bond motions investigated in the present work are torsional rotations about the covalent backbone bonds. Within the approximation of the rotational isomeric state model,[1] the rotational motions, or rotameric transitions, of a bond take place from one isomeric state to another. The present work investigates the time evolution of configurational changes of a polymer chain resulting from rotameric transitions of the backbone bonds.

The problem of the dynamics of a chain finds an exact analogy with the time-dependent statistics of the Ising model. The latter was treated first by Glauber[2] where the transition probabilities of a spin depend on the states of the neighboring spins. The three distinct configurations of three adjacent spins are shown in Fig. 1(a). Although the central spin is up in all three cases, three distinct configurations result from the relative orientations of the first neighbors. Similarly the three states (*trans* t, *gauche*$^+$ g^+, and *gauche*$^-$ g^-) of a central bond in a group of three consecutive bonds in a polymer chain are shown in Fig. 1(b). In analogy to the spins of Fig. 1(a), the three states t, g^+, and g^- for the central bond are defined on the basis of the relative orientations of its first neighbors. Thus the transition probabilities of the middle bond depend on the configuration formed by the group of three consecutive bonds. This problem is intrinsically analogous to that of the spins shown in Fig. 1(a).

The dynamics of polymer chains where the sequence of bonds are idealized as the spins of the Glauber model has been treated by several authors.[3-6] These studies treat the one-dimensional spin picture of Glauber at various levels of approximation by solving the relevant master equation and obtaining time correlation functions. None of these treatments however, incorporate the actual structural parameters of the real polymer chain into the formulation.

A mathematical formalism where the structural parameters of the real polymer chain (such as torsional energies, bond angles, loci of energy minima, etc.) can be incorporated into the dynamics of the chain is given by Jernigan.[7] The method, which may be regarded as an improved version of the Glauber treatment is essentially an extension of the equilibrium rotational isomeric state calculations to include time effects. The model rests on the formulation of the master equation and calculating its eigenvalues numerically to obtain the time delayed conditional probabilities for a sequence of N bonds. This model, referred to as the dynamic rotational isomeric state (DRIS) model, was subsequently adopted and improved for the interpretation of various phenomena in polymeric systems resulting from local orientational dynamics.[8-17]

In the present study, we obtain a closed form solution to the master equation of the DRIS model which so far has been

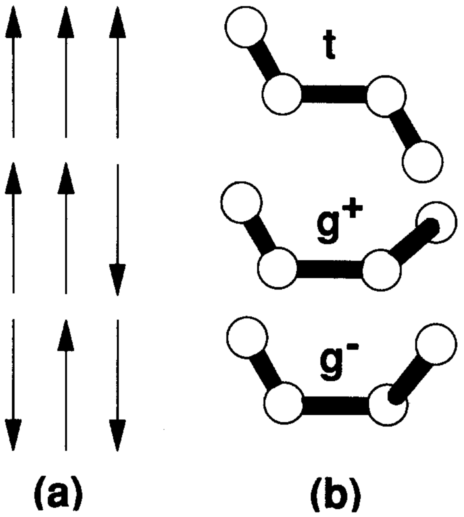

FIG. 1. (a) Three different configurations of three adjacent spins. The central spin is up in all three cases. (b) The three states, t, g^+, and g^- for the central bond in a group of three consecutive bonds.

0021-9606/90/074513-06$03.00

treated only numerically. In addition to introducing a significant amount of economy in computation time, the present analytical treatment provides a way of better understanding and improving the DRIS model.

THEORY

The model and assumptions

An arbitrary configuration of a chain with N bonds is shown in Fig. 2. Bonds are numbered from 1 to N as indicated. A coordinate system xyz is rigidly affixed to the first bond with the x axis coinciding with the bond direction. We assume that each bond may be in any one of three isomeric states t, g^+, and g^-. Extension to a larger number of isomeric states per bond is straightforward. The sequence shown in Fig. 2 represents either a chain of N bonds or a portion of a longer chain with tails on both ends. The sequence of N bonds is referred to as the mobile group.

The present treatment is based on the following three assumptions: (i) Only a single transition at a time is considered; (ii) bonds are subject to independent rotational potentials; (iii) the torsional potential is symmetric.

The first assumption has been the subject of various theoretical and experimental studies over the last two decades. On the theoretical side the problem has been addressed most thoroughly by Helfand who classifies the types of orientational motions into three groups.[18] The first leaves the tails of the mobile group unchanged. Those are coordinated motions and are alternatively referred to as crankshaftlike motions.[19] Such motions require simultaneous rotations of two skeletal bonds and hence are opposed by stronger internal effects. On the other hand, experimental investigations show[20] that the activation energies measured for long chains in dilute solution equate to a single barrier crossing at a time. These observations thus discard crankshaftlike transitions from the list of most probable motions. A second type of motion is characterized by pure translation of the tails. They take place cooperatively such that a single bond rotation is immediately followed by a counterrotation of a second neighbor. A rigorous introduction of such correlated motions into the dynamic scheme requires a more detailed treatment than that undertaken in the present study. The analysis of those correlated motions is carried out in the work of Hall and Helfand[5] through the use of Pauli spin matrices. A similar investigation according to the dynamic rotational isomeric state formalism is currently under study.[24] Brownian dynamics simulations of Helfand and collaborators[21-23] show that about 30% of conformational transitions belong to this group of correlated motions. The most common mechanism of transitions is, however, observed to be isolated single bond *trans–gauche*-type transitions in which the large swinging of the tails are avoided by compensating fluctuations of the various degrees of freedom of the chain. Such distortions among which the bond torsional potentials are the softest minimize the motion of the chain. A recent study by the dynamic rotational isomeric state scheme has also led to similar conclusion.[13] Under the light of the theoretical and experimental evidence cited, single bond transitions may be a reasonable starting point for the local dynamics of chains.

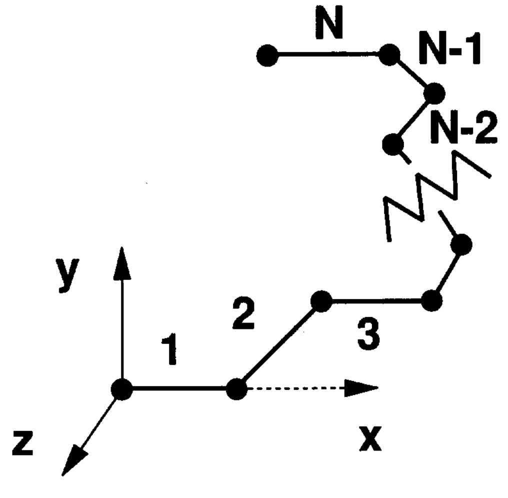

FIG. 2. An arbitrary configuration of a chain with N bonds. A coordinate system xyz is rigidly affixed to the first bond with the x axis coinciding with the bond direction.

The second assumption of independent bond potentials forms the basis of the present model. The effect of neighbor dependent potentials may approximately be introduced into the present formulation through equilibrium probabilities. This has been done previously by Jernigan[7] and by two of the present authors.[8]

General formulation

The transitions over a single bond are represented by the following master equation:

$$d\mathbf{P}^{(1)}(t)/dt = \mathbf{A}^{(1)}\mathbf{P}^{(1)}(t). \quad (1)$$

Here, $\mathbf{P}^{(1)}(t)$ represents the vector of probabilities for the single bond

$$\mathbf{P}^{(1)}(t) = \mathrm{col}(p_t, p_g, p_{g^-}), \quad (2)$$

where p_t, p_g, and p_{g^-} represent the probabilities of the three states *trans*, *gauche*$^+$, and *gauche*$^-$, respectively. The superscript in parenthesis in Eqs. (1) and (2) signifies that a single bond is being considered. The transition rate matrix $\mathbf{A}^{(1)}$ is of the following general form:

$$\mathbf{A}^{(1)} = \begin{bmatrix} -2r_{tg} & r_{gt} & r_{gt} \\ r_{tg} & -(r_{gt}+r_{gg^-}) & r_{gg^-} \\ r_{tg} & r_{gg^-} & -(r_{gt}+r_{gg^-}) \end{bmatrix}, \quad (3)$$

where r_{ij} represents the rate constant for the transition from state i to state j. Here r_{ij} is related to the energy barrier E_{ij} between states i and j in a high-friction medium by the Kramers expression[8,25]

$$r_{ij} = (\gamma\gamma^*)^{1/2}(2\pi\zeta)^{-1}\exp(-E_{ij}/\mathrm{RT}), \quad (4)$$

where γ and γ^* are, respectively, the curvature of the torsional energy minimum at the ith state and that of the energy barrier between the ith and jth states. Because of the symmetry of the potential, $r_{tg} = r_{tg^-}$, $r_{gt} = r_{g^-t}$, and $r_{gg^-} = r_{g^-g}$.

The probability vector $\mathbf{P}^{(N)}(t)$ for a sequence of N bonds is written as

$$\mathbf{P}^{(N)}(t) = \mathbf{P}_1^{(1)}(t) \otimes \mathbf{P}_2^{(1)}(t) \otimes \cdots \otimes \mathbf{P}_{N-1}^{(1)}(t) \otimes \mathbf{P}_N^{(1)}(t), \tag{5}$$

where $\otimes$ denotes the direct product. The subscripts in Eq. (5) as well as in the subsequent equations identify the location of the bond along the sequence. Differentiating both sides of Eq. (5) with respect to time leads to the master equation for the sequence

$$\frac{d\mathbf{P}^{(N)}(t)}{dt} = \sum_{j=1}^{N} [(\mathbf{I}_3)^{\otimes(j-1)} \otimes \mathbf{A}_j^{(1)} \otimes (\mathbf{I}_3)^{\otimes(N-j)}]\mathbf{P}^{(N)}(t) \equiv \mathbf{A}^{(N)}\mathbf{P}^{(N)}(t). \tag{6}$$

Here, $\mathbf{I}_3$ is the third-order identity matrix and $(\mathbf{I}_3)^{\otimes(i)}$ signifies the direct product of $\mathbf{I}_3$ with itself i times. The rate matrix $\mathbf{A}^{(N)}$ for the sequence of N bonds is defined by Eq. (6) as

$$\mathbf{A}^{(N)} = \sum_{j=1}^{N} (\mathbf{I}_3)^{\otimes(j-1)} \otimes \mathbf{A}_j^{(1)} \otimes (\mathbf{I}_3)^{\otimes(N-j)}. \tag{7}$$

Expansion of the sum in Eq. (7) for $N = 2, 3, \ldots$ leads to the following recurrence expression:

$$\begin{aligned} \mathbf{A}^{(2)} &= \mathbf{A}^{(1)} \otimes \mathbf{I}_3 + \mathbf{I}_3 \otimes \mathbf{A}^{(1)}, \\ \mathbf{A}^{(3)} &= \mathbf{A}^{(1)} \otimes \mathbf{I}_3 \otimes \mathbf{I}_3 + \mathbf{I}_3 \otimes \mathbf{A}^{(1)} \otimes \mathbf{I}_3 \\ &\quad + \mathbf{I}_3 \otimes \mathbf{I}_3 \otimes \mathbf{A}^{(1)} \\ &= \mathbf{A}^{(1)} \otimes \mathbf{I}_9 + \mathbf{I}_3 \otimes \mathbf{A}^{(2)}, \end{aligned} \tag{8}$$

where $\mathbf{I}_k$ is the kth order identity matrix. Continuing to write Eq. (8) for longer sequences leads to

$$\mathbf{A}^{(N)} = \mathbf{A}^{(1)} \otimes \mathbf{I}_{3^{N-1}} + \mathbf{I}_3 \otimes \mathbf{A}^{(N-1)}, \tag{9}$$

which may be written in terms of Eq. (3) in block form as

$$\mathbf{A}^{(N)} = \begin{bmatrix} \mathbf{A}^{(N-1)} - 2r_{tg}\mathbf{I}_{3^{N-1}} & r_{gt}\mathbf{I}_{3^{N-1}} & r_{gt}\mathbf{I}_{3^{N-1}} \\ r_{tg}\mathbf{I}_{3^{N-1}} & \mathbf{A}^{(N-1)} - (r_{gt} + r_{gg^-})\mathbf{I}_{3^{N-1}} & r_{gg^-}\mathbf{I}_{3^{N-1}} \\ r_{tg}\mathbf{I}_{3^{N-1}} & r_{gg^-}\mathbf{I}_{3^{N-1}} & \mathbf{A}^{(N-1)} - (r_{gt} + r_{gg^-})\mathbf{I}_{3^{N-1}} \end{bmatrix}. \tag{10}$$

Solution of the eigenvalue problem

The secular equation for $\mathbf{A}^{(N)}$ is

$$\det(\mathbf{A}^{(N)} - \Lambda^{(N)}\mathbf{I}_{3^N}) = \begin{vmatrix} \mathbf{A}^{(N-1)} - (\Lambda^{(N)} + 2r_{tg})\mathbf{I}_{3^{N-1}} & r_{gt}\mathbf{I}_{3^{N-1}} & r_{gt}\mathbf{I}_{3^{N-1}} \\ r_{tg}\mathbf{I}_{3^{N-1}} & \mathbf{A}^{(N-1)} - (\Lambda^{(N)} + r_{gt} + r_{gg^-})\mathbf{I}_{3^{N-1}} & r_{gg^-}\mathbf{I}_{3^{N-1}} \\ r_{tg}\mathbf{I}_{3^{N-1}} & r_{gg^-}\mathbf{I}_{3^{N-1}} & \mathbf{A}^{(N-1)} - (\Lambda^{(N)} + r_{gt} + r_{gg^-})\mathbf{I}_{3^{N-1}} \end{vmatrix} = 0, \tag{11}$$

where $\Lambda^{(N)}$ denotes the eigenvalues of $\mathbf{A}^{(N)}$. Inasmuch as the columns sum up to zero in transition rate matrices associated with stationary processes, Eq. (11) may be simplified as

$$\det(\mathbf{A}^{(N-1)} - \Lambda^{(N)}\mathbf{I}_{3^{N-1}}) \begin{vmatrix} (r_{tg} - r_{gg^-})\mathbf{I}_{3^{N-1}} & \mathbf{A}^{(N-1)} - (\Lambda^{(N)} + r_{gt} + 2r_{gg^-})\mathbf{I}_{3^{N-1}} \\ -\mathbf{A}^{(N-1)} + (\Lambda^{(N)} + r_{gt} + r_{tg} + r_{gg^-})\mathbf{I}_{3^{N-1}} & -\mathbf{A}^{(N-1)} + (\Lambda^{(N)} + r_{gt} + 2r_{gg^-})\mathbf{I}_{3^{N-1}} \end{vmatrix} = 0. \tag{12}$$

Adding the second row of Eq. (12) to the first leads to

$$\det(\mathbf{A}^{(N-1)} - \Lambda^{(N)}\mathbf{I}_{3^{N-1}}) \begin{vmatrix} -\mathbf{A}^{(N-1)} + (\Lambda^{(N)} + 2r_{tg} + r_{gt})\mathbf{I}_{3^{N-1}} & \mathbf{0} \\ -\mathbf{A}^{(N-1)} + (\Lambda^{(N)} + r_{gt} + r_{tg} + r_{gg^-})\mathbf{I}_{3^{N-1}} & -\mathbf{A}^{(N-1)} + (\Lambda^{(N)} + r_{gt} + 2r_{gg^-})\mathbf{I}_{3^{N-1}} \end{vmatrix} = 0, \tag{13}$$

which finally yields

$$\begin{aligned} &\det(\mathbf{A}^{(N)} - \Lambda^{(N)}\mathbf{I}_{3^N}) \\ &= \det[\mathbf{A}^{(N-1)} - (\Lambda^{(N)} - \lambda_1)\mathbf{I}_{3^{N-1}}] \\ &\times \det[\mathbf{A}^{(N-1)} - (\Lambda^{(N)} - \lambda_2)\mathbf{I}_{3^{N-1}}] \\ &\times \det[\mathbf{A}^{(N-1)} - (\Lambda^{(N)} - \lambda_3)\mathbf{I}_{3^{N-1}}] = 0, \end{aligned} \tag{14}$$

where

$$\begin{aligned} \lambda_1 &= 0, \\ \lambda_2 &= -(2r_{tg} + r_{gt}), \\ \lambda_3 &= -(r_{gt} + 2r_{gg^-}), \end{aligned} \tag{15}$$

are the eigenvalues of the single bond transition rate matrix $\mathbf{A}^{(1)}$. Equation (14) shows that the 3^N eigenvalues $\Lambda^{(N)}$ of $\mathbf{A}^{(N)}$ include the 3^{N-1} eigenvalues $\Lambda^{(N-1)}$ of $\mathbf{A}^{(N-1)}$, 3^{N-1} eigenvalues $\Lambda^{(N-1)}$ increased by λ_2 and 3^{N-1} eigenvalues $\Lambda^{(N-1)}$ increased by λ_3. Equation (14) may be written as a set of secular equations

$$
\begin{aligned}
&\det\left[\mathbf{A}^{(N-1)} - (\Lambda^{(N)} - \lambda_1)\mathbf{I}_{3^{N-1}}\right] = 0,\\
&\det\left[\mathbf{A}^{(N-1)} - (\Lambda^{(N)} - \lambda_2)\mathbf{I}_{3^{N-1}}\right] = 0,\\
&\det\left[\mathbf{A}^{(N-1)} - (\Lambda^{(N)} - \lambda_3)\mathbf{I}_{3^{N-1}}\right] = 0.
\end{aligned}
\tag{16}
$$

Consideration of Eq. (16) leads to the following recurrence equation for the 3^N eigenvalues $\Lambda^{(N)}$

$$\Lambda_i^{(1)} = \lambda_i \quad i = 1,2,3$$

and

$$
\Lambda_i^{(N)} = \begin{cases} \Lambda_j^{(N-1)} + \lambda_1, & i = 1,\ldots 3^{N-1}, \\ \Lambda_j^{(N-1)} + \lambda_2, & i = 3^{N-1} + 1,\ldots 2\cdot 3^{N-1}, \\ \Lambda_j^{(N-1)} + \lambda_3, & i = 2\cdot 3^{N-1} + 1,\ldots 3^N, \end{cases}
\tag{17}
$$

with

$$j = 1,2\ldots 3^{N-1}.$$

For a given N, the above recurrence equation shows that there are only three nondegenerate eigenvalues, the remaining ones being degenerate of various orders. Although Eq. (17) uniquely determines all of the eigenvalues, it does not specify the degeneracy of each explicitly. Below, we present an alternate recurrence equation that is suitable for calculations. For this purpose we observe that the eigenvalues given by Eq. (17) may be obtained from the expansion of a trinomial expression

$$
\begin{aligned}
(e^{\lambda_1} + e^{\lambda_2} + e^{\lambda_3})^N &= \sum_{k=0}^{N} \binom{N}{k} (e^{\lambda_2} + e^{\lambda_3})^k e^{\lambda_1 (N-k)} \\
&= \sum_{k=0}^{N} \sum_{l=0}^{k} \binom{N}{k}\binom{k}{l} e^{\Lambda^{(N)}(k,l)},
\end{aligned}
\tag{18}
$$

where $\Lambda^{(N)}(k,l)$ is the eigenvalue given by

$$\Lambda^{(N)}(k,l) = l\lambda_3 + (k-l)\lambda_2 + (N-k)\lambda_1, \quad 0 \leqslant l \leqslant k \leqslant N. \tag{19}$$

Each $\Lambda^{(N)}(k,l)$ is $N(k,l)$-fold degenerate with

$$N(k,l) = \binom{N}{k}\binom{k}{l} = N!/l!(k-l)!(N-k)! \tag{20}$$

It may be shown that there is one-to-one correspondence between $\Lambda_i^{(N)}$ of Eq. (17) and $\Lambda^{(N)}(k,l)$ of Eq. (19).

Equation (6) may be solved formally to yield

$$
\begin{aligned}
\mathbf{P}^{(N)}(t) &= \mathbf{B}^{(N)} \exp(\Lambda^{(N)}t)\,[\mathbf{B}^{(N)}]^{-1}\mathbf{P}^{(N)}(t=0) \\
&= \mathbf{C}^{(N)}\mathbf{P}^{(N)}(t=0),
\end{aligned}
\tag{21}
$$

where $\Lambda^{(N)}$ is the diagonal matrix of eigenvalues $\Lambda_i^{(N)}$, $i = 1$ to $3N$ of $\mathbf{A}^{(N)}$, $\mathbf{B}^{(N)}$ is the eigenvector matrix, $[\mathbf{B}^{(N)}]^{-1}$ is the inverse of $\mathbf{B}^{(N)}$ or the eigenrow matrix, and

$$\mathbf{C}^{(N)} \equiv \mathbf{B}^{(N)} \exp(\Lambda^{(N)}t)\,[\mathbf{B}^{(N)}]^{-1} \tag{22}$$

is the conditional probabilities matrix.

The three eigenvectors of $\mathbf{A}^{(1)}$ corresponding to eigenvalues $\lambda_1,\lambda_2,\lambda_3$ are $\mathbf{u}_1^{(1)}$, $\mathbf{u}_2^{(1)}$, and $\mathbf{u}_3^{(1)}$, respectively,

$$\mathbf{u}_1^{(1)} = \frac{1}{\sqrt{2r_{tg}^2 + r_{gt}^2}} \begin{bmatrix} r_{gt} \\ r_{tg} \\ r_{tg} \end{bmatrix}, \tag{23a}$$

$$\mathbf{u}_2^{(1)} = \sqrt{\frac{2}{3}} \begin{bmatrix} 1 \\ -1/2 \\ -1/2 \end{bmatrix}, \tag{23b}$$

$$\mathbf{u}_3^{(1)} = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 \\ 1 \\ -1 \end{bmatrix}. \tag{23c}$$

The eigenvectors $\mathbf{u}_1^{(1)}$, $\mathbf{u}_2^{(1)}$, and $\mathbf{u}_3^{(1)}$ are normalized to unity for convenience. The eigenvectors of $\mathbf{A}^{(N)}$, i.e., the columns of $\mathbf{B}^{(N)}$, may be written in terms of $\mathbf{u}_1^{(1)}$, $\mathbf{u}_2^{(1)}$, and $\mathbf{u}_3^{(1)}$ according to the following symbolic expression:

$$
\begin{aligned}
\mathbf{u}^{(N)}(k,l) &= {\mathbf{u}_1^{(1)}}^{\otimes(N-k)} \otimes {\mathbf{u}_2^{(1)}}^{\otimes(k-l)} \otimes {\mathbf{u}_3^{(1)}}^{\otimes(l)} \quad 0 \leqslant l \leqslant k \leqslant N \\
&\equiv \underbrace{\mathbf{u}_1^{(1)} \otimes \mathbf{u}_1^{(1)} \otimes \cdots \otimes \mathbf{u}_1^{(1)}}_{(N-k)\text{times}} \otimes \underbrace{\mathbf{u}_2^{(1)} \otimes \mathbf{u}_2^{(1)} \otimes \cdots \otimes \mathbf{u}_2^{(1)}}_{(k-l)\text{times}} \otimes \underbrace{\mathbf{u}_3^{(1)} \otimes \mathbf{u}_3^{(1)} \otimes \cdots \otimes \mathbf{u}_3^{(1)}}_{(l)\text{times}},
\end{aligned}
\tag{24}
$$

where the second line explains the symbolic notation given in the first line. For given N, k, and l, Eq. (24) yields $N(k,l)$ eigenvectors obtained from all possible permutations of $(N-k)\mathbf{u}_1^{(1)}$'s, $(k-l)\mathbf{u}_2^{(1)}$'s, and $l\mathbf{u}_3^{(1)}$'s. All of the $N(k,l)$ eigenvectors $\mathbf{u}^{(N)}(k,l)$ obtained in this manner correspond to the same eigenvalue $\Lambda^{(N)}(k,l)$, which is $N(k,l)$-fold degenerate. There is an ambiguity in the calculation of eigenvectors corresponding to a given degenerate eigenvalue since any linear combination of these $N(k,l)$ eigenvectors is also an eigenvector.

The eigenrows of $\mathbf{A}^{(1)}$ corresponding to eigenvalues $\lambda_1,\lambda_2,\lambda_3$ are $\mathbf{v}_1^{(1)}$, $\mathbf{v}_2^{(1)}$, and $\mathbf{v}_3^{(1)}$, respectively,

$$\mathbf{v}_1^{(1)} = \frac{\sqrt{2r_{tg}^2 + r_{gt}^2}}{2r_{tg} + r_{gt}}\,(1,1,1), \tag{25a}$$

$$\mathbf{v}_2^{(1)} = \frac{\sqrt{3}}{\sqrt{2}(2r_{tg} + r_{gt})}\,(2r_{tg}, -r_{gt}, -r_{gt}), \tag{25b}$$

$$\mathbf{v}_3^{(1)} = \frac{1}{\sqrt{2}}\,(0,1,-1). \tag{25c}$$

The eigenrows of $\mathbf{A}^{(N)}$, i.e., the rows of $[\mathbf{B}^{(N)}]^{-1}$, may be written in terms of $\mathbf{v}_1^{(1)}$, $\mathbf{v}_2^{(1)}$, and $\mathbf{v}_3^{(1)}$ by an expression analogous to Eq. (24) as

$$
\begin{aligned}
&\mathbf{v}^{(N)}(k,l) = {\mathbf{v}_1^{(1)}}^{\otimes(N-k)} \otimes {\mathbf{v}_2^{(1)}}^{\otimes(k-l)} \otimes {\mathbf{v}_3^{(1)}}^{\otimes(l)} \\
&0 \leqslant l \leqslant k \leqslant N.
\end{aligned}
\tag{26}
$$

In writing Eqs. (24) and (26), it is assumed that $\mathbf{u}_i^{(1)}$ and $\mathbf{v}_i^{(1)}$ are normalized according to

$$\mathbf{v}_i^{(1)} \cdot \mathbf{u}_j^{(1)} = \delta_{ij}, \tag{27}$$

where the product on the left-hand side of Eq. (25) is the scalar product and δ_{ij} is the Kronecker symbol.

Equations (22), (24), and (26) represent the complete formulation of the N-chain dynamics in terms of the eigenvalues, eigenvectors, and eigenrows of the transition rate matrix $\mathbf{A}^{(1)}$ of a single bond. If only stationary events are considered, the vector $\mathbf{P}^{(N)}(t=0)$ in Eq. (21) may be equated to the equilibrium probability vector $\mathbf{P}^{(N)}(t=\infty)$. Neighbor dependence may be incorporated into $\mathbf{P}^{(N)}(t=\infty)$ as is commonly done[1] in the equilibrium statistics of polymer chains.

The average $\langle f(t)\rangle$ over all possible configurational transitions at time t, for a function f_{ij} associated with the transition from the jth to the ith state, is expressed in the form[11]

$$\langle f(t)\rangle = \sum_{n=1}^{3^N}\left[\sum_{j=1}^{3^N}\sum_{i=1}^{3^N} B_{in}^{(N)} \times \exp\{\Lambda_n^{(N)}t\}[B_{nj}^{(N)}]^{-1}P_j^{(N)}(0)f_{ij}\right], \qquad (28)$$

where $\Lambda_n^{(N)}$ is the nth eigenvalue of $\mathbf{A}^{(N)}$, $P_j^{(N)}(0)$ is the equilibrium probability of the jth configuration, $B_{in}^{(N)}$ is the ith element of the nth eigenvector, $[B_{nj}^{(N)}]^{-1}$ is the jth element of the corresponding eigenrow. It should be recalled that $\Lambda_n^{(N)}$ is obtainable either from repetitive use of Eq. (17) or from Eq. (19). Each (k,l) pair in the latter is representative of $N(k,l)$ degenerate eigenvalues whose distinct eigenvectors and eigenrows are found, respectively, from the various permutations of Eqs. (24) and (26). For a given n in Eq. (28), the summation in the square brackets require the storage of only the nth column of $\mathbf{B}^{(N)}$ and the nth row of $[\mathbf{B}^{(N)}]^{-1}$, which may conveniently be generated by using Eqs. (24) and (26).

It should be noted that, under the assumption of independent bonds, the whole dynamics is governed by that of single bond probabilities, and all properties can be derived from that. Same behavior is predicted by Hall–Helfand in the absence of correlated transitions. As an alternative to the direct product language adopted in the present work, Hall and Helfand used Pauli matrices and commutativity properties in their treatment of isolated transitions.

CONCLUSION

A mathematical formulation is developed in the present study to obtain a closed form solution to the master equation governing the conformational dynamics of polymer chains with bonds subject to independent rotational potentials. The recurrence equation (17) or equivalently Eq. (19) provides a simple, concise, and useful method for evaluating the eigenvalues $\Lambda_i^{(N)}$, $i=1$ to ν^N, in N-bond chains, with ν states available to each bond. Inasmuch as $-\Lambda_i^{(N)}$ physically represents the frequency of the ith relaxational mode contributing to conformational transitions, its dependence on chain length is essential in understanding the change in orientational mobility with the size of the moving segment. The following two important conclusions are drawn from the above analysis. (i) The $\nu - 1$ nonzero eigenvalues governing single bond transitions persist for all N, as the slowest orientational modes contributing to relaxation. They are N-fold degenerate for N-bond sequences. (ii) However, as the chain length increases they are supplemented by new, faster modes. The fastest $\nu - 1$ modes are nondegenerate and have frequencies proportional to N. The increase in conformational mobility with N, or equivalently, the decrease in the so-called "internal viscosity" of intramolecular origin,[26] was first called to attention by Kuhn,[27] as pointed by de Gennes.[28] This analysis clearly confirms the creation of new, faster relaxational modes with increasing N. However, as N increases, this effect is more than counterbalanced by the intermolecular viscous resistance opposing the motion. With the present better understanding of internal conformational dynamics, the relative strength of the two factors, intramolecular and intermolecular, may be more exactly assessed.

Another practical advantage of the present formulation is the easy determination of the eigenvectors and eigenrows for the N-bond sequence, simply by the direct product of those for single bond, as expressed by Eqs. (24) and (26). The possibility of evaluating eigenvectors and/or eigenrows of order ν^N without inversion or similarity transformation of large transition rate matrices is particularly useful in the computation of average transient properties, $\langle f(t)\rangle$, according to Eq. (28).

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the financial support provided J. E. M. by the National Science Foundation through Grant No. DMR 84-15082 (Polymers Program, Division of Materials Research). We would like to thank Dr. E. Helfand for useful comments.

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