Stochastics of rotational isomeric transitions in polymer chains

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(Received 25 April 1989; accepted 8 August 1989)

The stochastic process of conformational transitions between isomeric states in polymer chains is considered. In analogy with the conventional treatments of chain statistics where equilibrium configurations are assigned statistical weights based on near neighbor intramolecular potential, stochastic weights are defined for the configurational transitions undergone by chains of pairwise interdependent bonds. The stochastic weights are expressed by $\nu^N \times \nu^N$ matrices for $N$ mobile bonds with $\nu$ isomeric states accessible to each bond. For a given time, serial multiplication of stochastic weight matrices yields the configurational transition partition function corresponding to the space of time-delayed probabilities of occurrence of two distinct configurations for a mobile segment. A matrix multiplication scheme is devised to determine the fraction of bonds and/or segments that undergo specific isomeric transitions in a given time interval.

I. INTRODUCTION

It is evident from several theoretical and experimental studies that the rotational isomeric states (RIS) model$^{1-3}$ is a powerful tool to investigate the configurational statistics of polymer chains. Its fundamental assumption of discrete values for the rotational angles for each skeletal bond leads to a discrete set of configurations which may conveniently be analyzed to estimate and/or understand the configuration-dependent properties of the chain. That the conformational statistics of polymer bonds has a Markov nature, in the sense that first neighbor dependence governs the probabilistic occurrence of different isomeric states, is confirmed by several accumulating studies. Early studies of the equilibrium statistics of polymers using realistic structural and conformational characteristics along those lines were performed by Lifson,$^4$ Nagai,$^5$ Birshtein and Pitsyn.$^6$ The basic approach is to formulate a configurational partition function in conformity with the short-range intramolecular potential prescribing the interdependent rotations of consecutive bonds. A convenient scheme for the construction of the partition function is the matrix method of statistical mechanics originally devised by Kramers and Wannier$^7$ on the basis of the one-dimensional Ising model.$^8$ The matrix multiplication scheme with statistical weights and generator matrices has been extensively used in subsequent analytical treatments of polymer statistics.$^{1,9}$

Recently, a description of local chain dynamics in terms of conformational transitions between isomeric states was developed.$^{10}$ The approach, referred to as the dynamic rotational isomeric states (DRIS) model, relies on the fundamental postulates underlying the conventional RIS model of equilibrium statistics, such as the adoption of bond torsional angles as the major variables identifying a given configuration, the pairwise-dependent character of bond conformational behavior, the validity of short-range intramolecular potentials impeding bond rotations, etc. Comparison with previous experimental and theoretical work lends support to the use of the DRIS model as a tool to investigate local chain dynamics.$^{11-14}$ A critical examination of the model in relation to constraints opposing the motion such as the environmental viscous resistance and the chain connectivity validates its application to high frequency motions of short polymeric segments in dilute solution.$^{15}$

The principal assumption in the DRIS model is that only single bond rotations take place at a time. The same assumption is also present in Glauber's time-dependent Ising model where no more than a single spin can change sign during an infinitesimal time interval $(\tau, \tau + dt)$. Brownian dynamics simulations also show that the majority of local motions in polymers originates from isolated single bond isomeric transitions.$^{17}$

The location and heights of the isomeric minima in two-dimensional energy maps specify the type and statistical weights of the various isomeric states available to a given pair of bonds. Alternatively, on the premise of pairwise interdependent dynamics, the heights of the saddles between minima fix the corresponding transition rates provided that the influence of the detailed shape of the energy path to be crossed is neglected. Thus, in contrast to the depth of the isomeric minima in the treatments of equilibrium statistics, the heights of the maxima are the quantities of interest to determine chain stochastics. It should be noted, however, that the knowledge of activation energies in the forward and reverse directions for a given transition automatically fixes the relative heights of the energy minima and hence equilibrium probabilities are inherently obtainable from chain stochastics.

The purpose of the present paper is to develop a convenient mathematical scheme to analyze the configurational stochastics of polymeric segments. All possible types of isomeric transitions are considered and assigned stochastic weights in analogy to the conventional treatment of equilibrium statistics. The space of the time-delayed joint probabilities of pairs of configurations now replaces that of the single configurations considered in equilibrium treatments. A con-
figurational transition partition function will be defined for a
given time $\tau$, from the combination of the stochastic weights
corresponding to various isomeric transitions accessible
within the time interval $\tau$. The matrix multiplication scheme
which has proved to be a tractable means to evaluate equilib-
rium properties will be employed to deduce dynamic proper-
ties such as average orientational correlations, the time-de-
dendent probability of occurrence of specific isomeric transi-
tions, etc.

A brief recapitulation of the DRIS model\textsuperscript{11-14} will be
presented in the next section, for self-consistency. The latter
was developed as an extension of the work of Jernigan,\textsuperscript{18}
originally developed for chains with independent bonds. The
process of configurational transitions is regarded\textsuperscript{10,14} in
the DRIS model as a discrete states, continuous time parameter
Markov process.\textsuperscript{19} The definition of stochastic weights,
configurational transition partition function and the matrix
multiplication scheme to determine transient properties will be
given in Sec. III. The mathematical approach for treating
chain dynamics parallels the one commonly used to evaluate
static properties. Similarities between the two approaches
will be emphasized throughout the development of the the-
ory for a more comprehensive presentation to the reader fa-
miliar with the RIS model. Some remarks concerning the
implications of the model on the equilibrium probabilities of
various configurations will be given in Sec. IV, which will be
followed by the conclusion.

II. DRIS MODEL

For a segment of $N$ bonds with $v$ states accessible to each
bond, the stochastics of configurational transitions are gov-
erned by the master equation\textsuperscript{10-15,18}
\begin{equation}
dP^{(N)}(\tau)/d\tau = A^{(N)}P^{(N)}(\tau)
\end{equation}
where $P^{(N)}(\tau)$ is the probability vector of order $v^N$, with
the element $P^{(N)}(\tau)$ denoting the instantaneous probability of
configuration $\{\Phi\}_a$, $A^{(N)}$ is the $v^N \times v^N$ transition matrix
whose $ab$th element ($a \neq b$) represents the rate constant for the
transition $\{\Phi\}_b \rightarrow \{\Phi\}_a$. A given configuration $\{\Phi\}_a$
is characterized by a set of $v^N$ isomeric states corresponding to
each bond. Following the assumption of single bond rotation
at a time $A^{(N)}_{ab}$ equals to zero if $\{\Phi\}_a$ and $\{\Phi\}_b$ possess
more than one bond with distinct isomeric state. Also micro-
scopic reversibility implies
\begin{equation}
A^{(N)}_{ab} = -\sum_k A^{(N)}_{kb}.
\end{equation}
The stochastic process of configurational transitions is sta-
nary, i.e., $P^{(N)}(\tau) = P^{(N)}(0)$, for all $\tau$, provided that
$P^{(N)}(0)$ obeys the equilibrium distribution of various con-
figurations. The formal solution to Eq. (1) is
\begin{equation}
P^{(N)}(\tau) = \exp(A^{(N)}\tau)P^{(N)}(0).
\end{equation}
Here $\exp(A^{(N)}\tau)$ physically represents the conditional
probability of transition between two configurations and thus
will be identified as the transition (or conditional) probabil-
ity matrix $C^{(N)}(\tau)$, according to
\begin{equation}
C^{(N)}(\tau) = \exp(A^{(N)}\tau) = B^{(N)}\exp(A^{(N)}\tau)[B^{(N)}]^{-1},
\end{equation}
where $A^{(N)}$ is the diagonal matrix of the eigenvalues $\lambda_k$,
$k = 1, v^N$, of $A^{(N)}$; $B^{(N)}$ is the matrix of the eigenvectors of
$A^{(N)}$ and $[B^{(N)}]^{-1}$ is the inverse of $B^{(N)}$. Alternately,
the time-delayed joint probability of occurrence of configura-
tions $\{\Phi\}_a$ and $\{\Phi\}_b$, with a time interval $\tau$, is given by the
$ab$th element of the time-dependent joint probability matrix
$P^{(N)}$, as
\begin{equation}
P^{(N)}_{ab}(\tau) = 1 \sum_k B^{(N)}_{ak}\exp(\lambda_k\tau)[B^{(N)}]^{-1}_{kb}P^{(N)}(0),
\end{equation}
where the subscripts indicate the corresponding elements.
For processes where the principle of detailed balance as stated
by Eq. (2) applies, all eigenvalues of $A^{(N)}$ are strictly nega-
tive with the exception of one of them, say $\lambda_1$, which is
identically equal to zero.\textsuperscript{14,19} The latter ensures the con-
vergence to equilibrium properties at long times. The corre-
sponding eigenvector and the eigenrow yield the equilibrium
probability $\{\Phi\}_a$ according to
\begin{equation}
P^{(N)}(0) = P^{(N)}(\infty) = B^{(N)}[B^{(N)}]^{-1}
\end{equation}
as may be deduced from Eq. (5). $|\lambda_i|$, for $i = 2$ to $v^N$,
represents the frequency of the $i$th mode contributing to relaxa-
tion.\textsuperscript{13-15,18}

The stochastics of configurational transitions is fully descri-
bred by the time-dependent joint probability matrix
$P^{(N)}(\tau)$. Quantitative determination of $P^{(N)}(\tau)$ rests upon
the knowledge of the transition rate matrix $A^{(N)}$. In fact, as
apparent from Eqs. (5) and (6), eigenvalues and eigenfunc-
tions of the latter fix the elements of $P^{(N)}(\tau)$. The transition
rate matrix $A^{(N)}$ in turn, is constructed following a suitable
kinetic scheme for the passages between various isomeric
configurations. For chains with bonds subject to independent
rotational potentials $A^{(N)}$ may be found using the transi-
tion rate matrices $A^{(1)}$ for single bonds according to
\begin{equation}
A^{(N)} = (A^{(1)}_1 \otimes I \otimes I \otimes \cdots \otimes I) + (I \otimes A^{(1)}_2 \otimes I \otimes \cdots \otimes I)
+ \cdots + (I \otimes I \otimes I \otimes A^{(1)}_N),
\end{equation}
where $I$ is the identity matrix of order $v$ and the subscrip-
t appended to $A^{(1)}$ indicate the corresponding bond. $\otimes$
denotes the direct product.\textsuperscript{1} For pairwise interde-
pendent bonds, Eq. (7) is replaced by\textsuperscript{14}
\begin{equation}
A^{(N)} = (A^{(1)}_0 \otimes I \otimes I \otimes \cdots \otimes I) + (I \otimes A^{(1)}_2 \otimes I \otimes \cdots \otimes I)
+ \cdots (I \otimes I \otimes \cdots \otimes I \otimes A^{(1)}_N),
\end{equation}
where $A^{(1)}_0$ is the $v^2 \times v^2$ transition rate matrix for the pair
of interdependent bonds $(i,j)$, $I$ is of order $v^2$. The transition
rate matrix $A^{(1)}$ associated with independent bonds obeying
the scheme
\begin{equation}
g^- \frac{r_1}{r_2} \frac{r_2}{r_1} g^+\rightarrow
\end{equation}
is given by
\begin{equation}
A^{(1)} = \begin{bmatrix}
-2r_1 & r_2 & r_2 \\
 r_1 & -r_2 & 0 \\
 r_1 & 0 & -r_2
\end{bmatrix}.
\end{equation}
Here $r_1$ and $r_2$ are the rate coefficients associated with the
indicated transitions. Similarity transformation of $A^{(1)}$ yields

$$A = \begin{bmatrix} 0 & 0 & 0 \\ 0 & -r_2 & 0 \\ 0 & 0 & -(2r_1 + r_2) \end{bmatrix}, ~ B^{(1)} = \begin{bmatrix} 1 & 0 & 1 \\ r_1/r_2 & 1 & -1/2 \\ r_1/r_2 & -1 & -1/2 \end{bmatrix}$$

and

$$[B^{(1)}]^{-1} = \begin{bmatrix} r_2/(2r_1 + r_2) & r_2/(2r_1 + r_2) & r_2/(2r_1 + r_2) \\ 0 & 1/2 & -1/2 \\ 2r_1/(2r_1 + r_2) & -r_2/(2r_1 + r_2) & -r_2/(2r_1 + r_2) \end{bmatrix} \quad (10)$$

which may be used in Eq. (5) to evaluate the elements of $P^{(1)}(\tau)$. The latter will be employed in the following and the notation $p(\alpha; \alpha^0)$ will be used for the probability $P^{(1)}(\tau)$ of occurrence of state $\{\Phi_1\}_a = \{\alpha\}$ at time $\tau$ and $\{\Phi_1\}_a = \{\alpha^0\}$ at $\tau = 0$ for a single bond subject to independent rotational potential. Clearly $\alpha$ and $\alpha^0$ may assume the states $t$, $g^+$, and $g^-$ if the scheme $I$ is applicable, thus forming the nine elements of $P^{(1)}(\tau)$. Similarly, the symbol $p(\alpha\beta; \alpha^0\beta^0)$ will be adopted for the elements $P^{(2)}(\tau)$ of $P^{(2)}(\tau)$, bearing in mind that $\{\Phi_2\}_a = \{\alpha\beta\}$ and $\{\Phi_2\}_a = \{\alpha^0\beta^0\}$, or vice versa since $P^{(2)}(\tau)$ is symmetric. $p(\alpha\beta; \alpha^0\beta^0)$ reduces to the product $p(\alpha; \alpha^0)p(\beta; \beta^0)$ for independent bonds. This identity is obviously not applicable to pairwise interdependent bonds. In this case, $P^{(1)}(\tau)$ is found from $A^{(2)}$ which is determined with reference to two-dimensional conformational energy maps.\textsuperscript{10-15} The saddle height to be surmounted during the passage $\alpha^0\beta^0\rightarrow \alpha\beta$ is substituted for the activation energy in the Arrhenius type expression for the corresponding rate coefficient in $A^{(2)}$. The preexponential factor in the latter is left as a parameter which decreases with solvent viscosity.

III. CONFIGURATIONAL STOCHASTICS

A. Stochastic weight matrices

For simplicity, let us first consider the statistical weight matrices for pairs of interdependent bonds in a polyethylene-like chain, i.e., a symmetrical chain with threefold rotational potential. In the absence of end effects, for a pair of bonds $(i - 1, i)$, the latter assumes the form

$$U_i = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma \Psi & \sigma \omega \\ 1 & \sigma \omega & \sigma \Psi \end{bmatrix} \quad (11)$$

Here $\sigma$ is the Boltzmann factor $\exp(-E_\sigma/RT)$ where $E_\sigma$ is the energy of the $g^+$ state in excess of the $t$ state, $\omega$ and $\Psi$ reflect the contribution of the second order interactions $E_\omega$ and $E_\Psi$ prevailing in the $g^+g^+$ and $g^+g^-$ states, respectively.

Serial multiplication of the statistical weight matrices yields the configurational partition function $Z$ according to\textsuperscript{1}

$$Z = J^* \prod_{i=2}^{N-1} U_i J \quad (12)$$

where $J^*$ and $J$ are the row and column vectors

$$J^* = \begin{bmatrix} 1 \\ 1 \end{bmatrix}, ~ J = \begin{bmatrix} 1 \\ 1 \end{bmatrix} \quad (13)$$

Our purpose is to write an analogous stochastic weight matrix $V_i$ at a given $\tau$, for the time-dependent transitions undergone by the interdependent pair of bonds $(i - 1, i)$. The elements of $V_i$ will be denoted as $u_i(\xi \eta \xi \eta^0)$. Serial multiplication of $V_i$ will yield the configurational transition partition function. As outlined in the preceding section, the DRIS model provides a means for the evaluation of the time-dependent joint probabilities $p_i(\xi \xi \eta^0 \eta^0)$ of the states $\xi \eta \eta^0 \eta^0$ and $\xi \eta$ with a time interval $\tau$ for an isolated pair of independent bonds $(i - 1, i)$. We can anticipate that the latter will be used to determine $v_i(\xi \xi \eta^0 \eta^0)$.

For an understanding of the relationship between $p_i(\xi \xi \eta^0 \eta^0)$ and $v_i(\xi \xi \eta^0 \eta^0)$, it is helpful to look back, more closely to the physical meaning of the elements of $U_i$.

The element $u_i(\xi \eta)$ of $U_i$ is defined\textsuperscript{1} by invoking the relationship

$$u_i(\xi \eta) = \exp \left( -\left[ E_i(\eta) + \Delta E_i(\xi \eta) \right]/RT \right) \quad (14)$$

Here the exponential term includes (i) the contribution to intramolecular potential from the rotation $\Phi_i$ of bond $i$, exclusively, which we denote as $E_i(\eta)$, and (ii) the nonbonded interaction which depends jointly on $\Phi_{i-1}$ and $\Phi_i$, shown as $\Delta E_i(\xi \eta)$. The former contribution is deduced\textsuperscript{1} from the single bond independent conformational behavior. The choice of $E_i(\eta)$ as the zero energy level leads to $\exp\left( -E_i(\eta)/RT \right) = 1$, $\sigma$, and $\sigma$ for the states $\eta = t, g^+$, and $g^-$, respectively. $\Delta E_i(\xi \eta)$ equates to zero for independent bonds.

The apparent equilibrium probabilities $p_i(\xi \eta)$ in an isolated pair\textsuperscript{20} of independent bonds $(i - 1, i)$ may be written in matrix notation as

$$[p_i(\xi \eta)] = z_{2i}^{-1} \begin{bmatrix} 1 & \sigma & \sigma \\ \sigma & \sigma^2 \Psi & \sigma^2 \omega \\ \sigma & \sigma^2 \Psi & \sigma^2 \omega \end{bmatrix} \quad (15)$$

with

$$z_2 = 1 + 4\sigma + 2\sigma^2(\omega + \Psi) \quad (16)$$

A general expression for $p_i(\xi \eta)$, analogous to Eq. (14) will be

$$p_i(\xi \eta) = z_2^{-1} \exp \left( -\left( E_{i-1}(\xi \eta) + E_i(\eta) \right) + \Delta E_i(\xi \eta)/RT \right) \quad (17)$$

Equation (17) may be rewritten as

\[ p_i(\xi \eta) = z_i^2 z_{i-1} p_{i-1}(\xi)p(\eta) k_i(\xi \eta) \]  

(18)

using the single bond partition function \( z_i = 1 + 2\alpha \) and the equilibrium probabilities for isolated bonds \( p_i(\eta) = z_i^{-1} \exp(-E_i(\eta)/RT) \), \( p_{i-1}(\xi) = z_i^{-1} \exp(-E_{i-1}(\xi)/RT) \). The term \( k_i(\xi \eta) \) has been substituted for \( \exp(-\Delta E_i(\xi \eta)/RT) \). The product \( z_i^2 z_{i-1}(\xi \eta) \) reduces to unity for independent bonds. Comparison of Eqs. (14) and (18) yield the following relationship between \( p_i(\xi \eta) \), \( p_{i-1}(\xi) \) and \( u_i(\xi \eta) \):

\[ u_i(\xi \eta) = (z_2 z_{i-1}) p_i(\xi \eta)/p_{i-1}(\xi) . \]  

(19)

The inclusion or omission of the proportionality constant is inconsequential since the latter is eliminated when evaluating average properties. So it may be arbitrarily set equal to 1.

In analogy to the above analysis, the time-dependent joint probability \( p_i(\alpha \beta; \alpha' \beta') \) for the transition \( \alpha' \beta' \rightarrow \alpha \beta \) of the isolated pair of interdependent bonds may be written as

\[ p_i(\alpha \beta; \alpha' \beta') = p_{i-1}(\alpha; \alpha') p_i(\beta \beta') k_i(\alpha \beta; \alpha' \beta'), \]  

(20)

where the deviation from independent bond statistics is accounted for by the correction term \( k_i(\alpha \beta; \alpha' \beta') \) characteristic of the transition \( \alpha' \beta' \rightarrow \alpha \beta \) undergone by the pair of bonds \((i-1, i)\). The corresponding stochastic weight reads

\[ v_i(\alpha \beta; \alpha' \beta') = p_i(\beta \beta') k_i(\alpha \beta; \alpha' \beta') \]  

(21)

\[ = p_i(\alpha \beta; \alpha' \beta')/p_{i-1}(\alpha; \alpha'). \]  

(22)

Equation (20) is the dynamic counterpart of Eq. (18) of equilibrium statistics. It should be recalled that \( p_{i-1}(\alpha; \alpha') \) represents an element of the joint probability matrix \( P^{(1)}(\tau) \) for the single bond \((i-1)\). The latter is easily found by inserting Eq. (10) into Eq. (5). A similar operation starting from \( A^{(2)} \) instead of \( A^{(1)} \), yields the elements \( p_i(\alpha \beta; \alpha' \beta') \) of \( P^{(2)}(\tau) \). Thus, Eq. (22) is conveniently used to determine the elements of the stochastic weight matrix \( V_i(\tau) \) corresponding to bonds \((i-1, i)\). It should be noted that \( V_i(\tau) \) depends on the time interval \( \tau \) chosen. At \( \tau = 0 \), it reduces to \( U_i \) (apart from the constant factor \( z_2 z_{i-1}^{-1} \)), as may be seen by inserting the identities \( p_i(\alpha \beta; \alpha' \beta') = p_i(\alpha' \beta') \) and \( p_{i-1}(\alpha; \alpha') = p_{i-1}(\alpha') \) at \( \tau = 0 \), into Eq. (22).

Let us consider the simplest case of \( v = 2 \) states \( \alpha \) and \( \beta \) accessible to each bond in a given pair. \( V_i(\tau) \) will be defined as

\[ V_i(\tau) = \begin{bmatrix} v_i(\alpha \alpha; \alpha \alpha) & v_i(\alpha \alpha; \alpha \beta) & v_i(\alpha \beta; \alpha \alpha) & v_i(\alpha \beta; \alpha \beta) \\ v_i(\beta \alpha; \alpha \beta) & v_i(\alpha \beta; \beta \beta) & v_i(\beta \beta; \alpha \beta) & v_i(\beta \beta; \beta \beta) \\ v_i(\beta \alpha; \beta \beta) & v_i(\beta \beta; \alpha \beta) & v_i(\alpha \beta; \beta \beta) & v_i(\beta \beta; \beta \beta) \\ v_i(\beta \beta; \beta \beta) & v_i(\beta \beta; \beta \beta) & v_i(\beta \beta; \beta \beta) & v_i(\beta \beta; \beta \beta) \end{bmatrix}. \]  

(23)

Thus, as shown by the above dashed lines, \( V_i(\tau) \) is divided into \( v^2 \) submatrices of size \( v \times v \), each representing the stochastic weights for the transitions to a given final state.

**B. Transition partition function and a priori probabilities**

The transition partition function \( Z_r \) for a chain of \( n \) bonds, with \( v \) states accessible to each bond, is defined as the serial product of the stochastic weight matrices according to

\[ Z_r = J^T \prod_{i=0}^{N-1} V_i(\tau) J, \]  

(24)

where \( J = \text{col}(1, 1, \cdots, 1) \), \( J^T = \text{row}(1, 1, \cdots, 1) \). \( V_2(\tau) \) is the diagonal matrix defined as

\[ V_2(\tau) = \begin{bmatrix} v_2(\alpha \alpha) & & & \\ & v_2(\alpha \beta) & & \\ & & \ddots & & \\ & & & v_2(\nu \nu) \end{bmatrix}. \]  

(25)

Here \( v_2(\alpha \beta) \) may conveniently be replaced by \( p(\alpha \beta) \) inasmuch as the stochastic behavior of bond 2 is not affected by the first bond and \( V_1(\tau), i = 3, N - 1 \) is the \( v^2 \times v^2 \) stochastic weight matrix for bonds \((i-1, i)\), with the structure given by Eq. (23) for the simple case of \( v = 2 \). The adaptation of Eq. (23) to \( v = 2 \) is straightforward. It should be noted that, the rotations of the terminal bonds are not included in Eq. (24), as they do not affect the internal configurational transitions.

Alternately, \( Z_r \) may be found from

\[ Z_r = J^T \prod_{i=0}^{N-1} V_i(\tau) J \]  

(26)

where \( V_i(\tau) \) is now identical in form to \( V_i(\tau) \) for \( i = 2, N - 1 \), with the adoption of \( k_i(\alpha \beta; \alpha' \beta') = 1 \). This more convenient notation will be preferred in the following. Equation (26) of chain dynamics is equivalent to Eq. (12) of chain statistics.

The matrix multiplication of Eq. (24) [or (26)] generates the required sum of products

\[ Z_r = \sum \cdots \sum [v_2(\alpha \alpha) v_3(\alpha \beta; \beta \beta) v_4(\beta \beta; \beta \beta) \cdots], \]  

(27)

where the summation is performed over all possible initial states \( \alpha \beta; \gamma \delta; \cdots \) and final states \( \alpha, \beta, \gamma, \cdots \) for bonds whose ordinal numbers are indicated by the subscripts. Using Eq. (22), Eq. (27) may be written in terms of the elements of \( P^{(1)}(\tau) \) and \( P^{(1)}(\tau) \) as

\[ Z_r = \sum \cdots \sum [p_3(\alpha \beta; \alpha' \beta')/p_2(\beta \beta)] \times \cdots [p_{N-1}(\nu \nu)/p_1(\mu \mu)] \]  

(28)

It should be noted that the definition of \( V_i(\tau) \) according to Eq. (23) ensures the juxtaposition in the above series of the stochastic weight with identical initial and final states \( \beta \) for the common bond, as required by chain connectivity.
The term in brackets in Eq. (28) represents the stochastic weight \( \Omega(\Phi_b; \Phi_s) \) of the joint occurrence of the two configurations \( \{\Phi_b\} = \{\alpha \beta \gamma \delta \cdots\} \) and \( \{\Phi_s\} = \{\alpha \beta^* \delta \cdots\} \) characterized by the isomeric states of the \( N - 2 \) internal bonds, i.e.,

\[
\Omega(\Phi_b; \Phi_s) = \left( \frac{p_3(\alpha \beta \gamma \delta \cdots)}{p_3(\alpha \beta \gamma \delta \cdots)} \right) \times \frac{\prod_{j=1}^{N-1} \hat{V}_j (\tau)}{\prod_{j=1}^{N-1} \hat{V}_j (\tau)}.
\]

(29)

Consequently, the \textit{a priori} probability \( p^* = p^* (\Phi_b; \Phi_s) \) of the transition \( \{\Phi_b\} \rightarrow \{\Phi_s\} \) at time \( \tau \) is

\[
p^* (\Phi_b; \Phi_s) = \Omega(\Phi_b; \Phi_s) / Z. \tag{30}
\]

In analogy with the conventional treatment of equilibrium statistics, it is possible to determine the \textit{a priori} probabilities of specific isomeric \textit{transitions} at a given time, along the chain. For instance, the \textit{a priori} probability \( p^*(tg^+ \rightarrow t) \) of the joint occurrence of state \( t \) at time \( \tau \) and \( g^+ \) at \( \tau = 0 \), for bond \( j \), will be

\[
p^*(tg^+) = Z^{-1} \left[ J \left[ \prod_{j=0}^{N-1} V_j (\tau) \right] \times \hat{V}_j (\tau) \prod_{j=0}^{N-1} V_j (\tau) J \right]. \tag{31}
\]

where \( \hat{V}_j (\tau) \) is the stochastic weight matrix where all elements \( v_j (\alpha \beta \gamma \delta \cdots) \) with \( \beta \neq \beta^* \), \( \gamma \neq \gamma^* \), \( \delta \neq \delta^* \), \( \cdots \), \( \tau \), \( \tau \) are equated to zero. This device retains precisely those terms meeting the condition \( g^+ \rightarrow t \) in the sum of stochastic weights \( \Omega(\Phi_b; \Phi_s) \) over all transitions of the chain, at a given time \( \tau \). Similarly, the \textit{a priori} probability of a specific joint event, say \( (g^- \tau) \) at \( \tau = 0 \) and \( g^+ \tau \) at \( \tau = \tau \), for the pair of bonds \( (j-1, j) \) may be found, using Eq. (31), but now equating all elements of \( \hat{V}_j \) to zero, with the exception of \( v_j (g^- \tau g^+ \tau) \).

The average number of bonds which undergo the transition \( g^+ \rightarrow t \), for instance, within the time interval \( \tau \) will be

\[
\langle n(tg^+) \rangle = (N - 2) p^*(tg^+) = (N - 2) \sum_{j=0}^{N-1} p^*(tg^+). \tag{32}
\]

The summation of Eq. (33) may be readily computed by the matrix generation method described in Ref. 1 for the equivalent static probabilities. Here the stochastic weight matrices replace the statistical weight matrices. Thus,

\[
p^*(\xi; \gamma) = (N - 2) Z^{-1} J \left[ \prod_{j=0}^{N-1} \hat{V}_j (\xi; \gamma) \right] J \tag{34}
\]

where

\[
\hat{V}_j (\xi; \gamma) = \begin{bmatrix} V_j (\tau) & V_j (\tau) \\ V_j (\tau) & V_j (\tau) \end{bmatrix}, \tag{35}
\]

\[
J^* = \begin{bmatrix} 1 & 0 & \cdots & 0 \\ 0 & 1 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & 1 \end{bmatrix}, \tag{36}
\]

Here \( J^* \) and \( J \) are row and column vectors of order \( 2^N \). \( V_j^*(\tau) \) is obtained from \( V_j (\tau) \) by striking all elements except those of column \( (\xi; \gamma) \) for bond \( j \), as already defined in Eq. \( (31) \). Similarly the time dependent \textit{a priori} probability \( p^* (\alpha \beta \xi \gamma \eta) \) of the pair transition \( \xi \gamma \eta \rightarrow \alpha \beta \), within a time interval \( \tau \) or the average number \( \langle n(\alpha \beta \xi \gamma \eta) \rangle \) of pairs of bond that have undergone this transition may be found from

\[
p^* (\alpha \beta \xi \gamma \eta) = \langle n(\alpha \beta \xi \gamma \eta) \rangle / (N - 3) \tag{37}
\]

\[
= (N - 3)^{-1} Z^{-1} J \left[ \prod_{j=0}^{N-1} \hat{V}_j (\alpha \beta \xi \gamma \eta) \right] J, \tag{38}
\]

where \( \hat{V}_j (\alpha \beta \xi \gamma \eta) \) through Eq. (35), has all elements equal to zero with the exception of \( v_j (\alpha \beta \xi \gamma \eta) \).

The extension of the formulation to calculate the analysis of the time-dependent occurrence of any type of conformational transition for any length of sequence is straightforward. It is sufficient to perform averages by striking suitable elements of the stochastic weight matrices, as illustrated by Eq. (31) for the simplest case of single bond transition.

C. Average transient properties

Let \( f_i (\alpha; \alpha^*) \) be a time-dependent function of the transition \( \alpha^* \rightarrow \alpha \) undergone by the \( i \)th bond. Its average \( \langle f_i (\tau) \rangle \) over all configurational transitions of the chain at time \( \tau \) may be found from

\[
\langle f_i (\tau) \rangle = Z^{-1} J \left[ \prod_{j=0}^{N-1} V_j (\tau) \right] F_i \left[ \prod_{j=0}^{N-1} V_j (\tau) \right] J, \tag{39}
\]

where \( F_i \) is the diagonal matrix

\[
F_i = \begin{bmatrix} f(\alpha; \alpha) & \cdots & \cdots \\ \cdots & f(\alpha; \alpha) & \cdots \\ \cdots & \cdots & f(\alpha; \alpha) \end{bmatrix}. \tag{40}
\]

of the values of the function \( f_i (\alpha; \alpha^*) \) the several isomeric transitions of bond \( i \). Similarly the average of the product of \( k \) such transient functions of consecutive bond rotations is obtained by interdigitating the \( F \)'s with the appropriate \( V(\tau) \)’s, i.e.,

\[
\langle f_i f_{i+1} \cdots f_{i+k} \rangle = Z^{-1} J \left[ \prod_{j=0}^{N-1} V_j (\tau) \right] \left[ \prod_{j=0}^{k} V_j F_i \right] \left[ \prod_{j=0}^{N-1} V_j (\tau) \right] J. \tag{41}
\]

Here the time arguments of \( V_i (\tau) \) are omitted for brevity.

Local orientational motions depend in fact on the transition of several consecutive bonds. A quantitative measure of such motions would be the orientational autocorrelation function (OACF) associated with a vectorial quantity \( m \) rigidly affixed to the chain. The latter is defined as

\[
\langle m(0) \cdot m(\tau) \rangle \text{ where the angular brackets indicate the ensemble average over all possible initial and final configurations. Suppose \( m^0 \) is the fixed representation of \( m(\tau) \) in the local (\( i + 1 \))th bond-based frame where it is rigidly embedded. In the simplest case where the orientational motion of \( m \)}

is prescribed by the rotation of the single bond \(i\), the OACF reduces to
\[
\langle \mathbf{m}(0) \cdot \mathbf{m}(\tau) \rangle = m_0^\nu \left( T_i(0) T_i^\nu(\tau) m_0 \right)^0, \tag{42}
\]
where \(T_i\) is the transformation matrix which expresses \(m\) in the \(i\)th bond-based local frame. The time argument follows from the torsional angle of bond \(i\), which is a time-dependent variable. Eq. (42) may be regarded as the internal OACF of \(m(\tau)\) as observed from the frame of the preceding bond. The average over all configurational transitions may be computed by using a mathematical method devised by Gotlib,\(^8\) Birshstein and Pitsyn,\(^5\) Hoeve,\(^2\) Lifson,\(^3\) and Nagai,\(^4\) for evaluating \(T_i\) in equilibrium statistics. Accordingly, we can define a pseudodiagonal matrix \(\|S_i\|\) of order \(3\nu^2\) as
\[
\|S_i\| = \begin{bmatrix}
T_i^\nu(\alpha) T_i(\alpha) \\
T_i^\nu(\alpha) T_i(\beta) \\
T_i^\nu(\nu) T_i(\nu)
\end{bmatrix}.
\tag{43}
\]
By following exactly the same arguments as those developed for equilibrium statistics,\(^3\) it can be shown that the average quantity in Eq. (42) is given by
\[
\langle T_i^\nu(0) T_i(\tau) \rangle = Z_0^{-1} (J^* \otimes I_3) \left\{ \sum_{\nu = 1}^{N-1} V_i(\tau) \otimes I_3 \right\} \times \left[ \prod_{k = \tau + 1}^{N-1} V_k(\tau) \otimes I_3 \right] J \otimes I_3. \tag{44}
\]
The matrix \(V_i(\tau) \otimes I_3\|S_i\|\) in Eq. (43) consists of block elements of the form \(v_i(\mathbf{a}_i \mathbf{a}_i^0) T_i^\nu(\mathbf{b}^0) T_i(\mathbf{b})\), thus associating each transition with the corresponding stochastic weight. Similarly, the OACF which depends on the rotations of the pair of bonds \((i-1, i)\) may be found using the same formula as Eq. (43), provided that \(V_i(\tau) \otimes I_3\|S_i\|\) is defined as the matrix of block elements \(v_i(\mathbf{a}_i \mathbf{a}_i^0) T_i^\nu(\mathbf{b}^0) T_i(\mathbf{b})\), \((\mathbf{a}_i \mathbf{a}_i^0) T_{i-1}^\nu(\alpha) T_i(\beta)\).

If, alternately, the OACF depends on the simultaneous rotations of \(k\) bonds preceding bond \((i + 1)\), Eq. (42) is replaced by
\[
\langle \mathbf{m}(0) \cdot \mathbf{m}(\tau) \rangle = m_0^\nu \left( \prod_{k = 1}^{i} T_i(0) \right)^T \times \left( \prod_{k = i}^{N-1} T_i(\tau) \right) m_0^0. \tag{45}
\]
An expression analogous to Eq. (44) for the average quantity in the right-hand side of Eq. (45) is not obtainable due to the non commutativity of the matrices. Instead, a double summation over the initial and final states available to the \(k\) moving bonds yields the required OACF as
\[
\langle \mathbf{m}(0) \cdot \mathbf{m}(\tau) \rangle = Z_0^{-1} (m_0^0)^T \sum_{x \in \mathbf{X}} \Omega \left\{ \mathbf{X}_i \mathbf{X}_i \right\} T^\nu(\mathbf{X}_i) T(\mathbf{X}_i) m_0^0, \tag{46}
\]
where \(\Omega \left\{ \mathbf{X}_i \mathbf{X}_i \right\}\) is the stochastic weight for the transition \(\{\mathbf{X}_i \mathbf{X}_i \} \rightarrow \{\mathbf{X}_i \mathbf{X}_i \}\), \(T(\mathbf{X}_i)\) represents the product of transformation matrices in serial order for the \(k\) initial torsional angles in \(\{\mathbf{X}_i \mathbf{X}_i \}\), \(Z_0\) is the transition partition function for the mobile segment of \(k\) bonds.

IV. REMARKS

The time-dependent probability \(p_i(\alpha \beta ; \alpha_0 \beta_0^0)\) of the transition from state \(\alpha \beta \beta_0^0\) at \(\tau = 0\) to the state \(\alpha \beta \beta_0^0\) at time \(\tau\), for the interdependent pair of bonds \((i-1, i)\) is assumed to result from three contributions, as formulated by Eq. (20). (i) the independent stochastics of bond \((i-1)\) accounted for by the term \(p_{i-1}(\alpha \beta \alpha_0^0)\) readily obtainable by inserting Eqs. (6) and (10) into Eq. (5). (ii) the independent stochastics of bond \(i\), represented by \(p_i(\beta \beta \beta_0^0)\), and (iii) a deviation from independent stochastics due to the coupling of the two bonds to give rise to secondary effects perturbing independent dynamics. The latter assumes a distinct value for each specific transition and may be indirectly obtained from \(P(i, \tau)\) and \(P(i, \tau)\) which are in turn found from the respective transition rate matrices \(A(i)\) and \(A(i)\), as outlined in Sec. II. For pairs subject to independent rotational potentials \(k_i(\alpha \beta^0 \beta_0^0) = 1\) and the stochastic weight \(\Omega \left\{ \mathbf{X}_i \mathbf{X}_i \right\}\) simplifies to the product \(p_2(\alpha \beta \alpha_0^0)p_2(\beta \beta \beta_0^0)\). Otherwise, the adoption of the pair stochastic weights, according to Eq. (22), as follows from the above formulation of \(p_i(\alpha \beta \alpha_0^0)\), leads to Eq. (29). It is clear that the division by \(p_{i-1}(\alpha \beta \alpha_0^0)\) automatically avoids the double counting of the independent transitions of bond \(i-1\), in the serial multiplication of pair stochastic weights.

It should be noted that a slightly different approximate expression of the form
\[
p^* \{\mathbf{X}_i \mathbf{X}_i \} = p_2(\alpha \beta \alpha_0^0) q_4(\beta \gamma \beta \gamma^0) q_4(\gamma \alpha \rho \rho^0) \cdots \tag{46}
\]
with
\[
q_4(\beta \gamma \beta \gamma^0) = p_4(\beta \gamma \beta \gamma^0) / \sum \gamma' p_4(\beta \gamma' \beta \gamma^0) \tag{47}
\]
was adopted in previous work for the probability of the transition \(\{\mathbf{X}_i \mathbf{X}_i \} = \{\alpha \beta \beta_0^0 \beta_0^0 \cdots \} \rightarrow \{\mathbf{X}_i \mathbf{X}_i \} = \{\alpha \beta \gamma \gamma \cdots \}\). The probabilities given by Eq. (46) are normalized. The main approximation in Eq. (46) is that pair probabilities associated with interdependent isolated pairs of bonds are adopted, therein ignoring any effect which would lead to different values depending on the serial order of the pair. That a slightly distinct \textit{a priori} probability of transition corresponds to each bond (or pair of bonds) is clearly shown in the rigorous formulation of Sec. II. Nevertheless, Eq. (46) is a simple expression which may conveniently be used as a first order approximation.

It is important to note that the equilibrium probabilities indirectly obtained by the DRIS formalism, by summing, for example, \(\Omega \left\{ \mathbf{X}_i \mathbf{X}_i \right\}\) over the final states \(\{\mathbf{X}_i \mathbf{X}_i \}\), are identical to those independently obtainable by the conventional RIS model of equilibrium statistics. In fact, the adoption of an expression of the form of Eq. (29) was motivated by the desire to reproduce, at \(\tau = 0\), some equilibrium probabilities as those predicted by the RIS model. Alternately, calculation performed by adopting time periods \(\tau\), significantly
large compared to the time range \((10^{-10} \text{ s})\) of local relaxational motions, verify that \(P(\infty) = P(0)\).

V. CONCLUSION

A time-dependent transition partition function is introduced in the present mathematical formulation of configurational stochastics. The latter is found from the sum of the stochastic weights associated with all possible types of configurational transitions at a given time \(\tau\).

A given transition \((\Phi)_{\alpha} \rightarrow (\Phi)_{\beta}\) is assigned a stochastic weight \(\Omega(\Phi_{\alpha}; \Phi_{\beta})\) according to Eq. (29). This equation rests upon the fundamental approximation of chain statistics and dynamics of a Markov chain of pairwise dependent bonds. Thus, the approach may be regarded as representative of an idealized chain unperturbed by any dynamic or static effect of long-range nature or of intermolecular character.

The theory allows for the determination of the probabilistic occurrence of specific configurational transitions in polymeric segments. A recent application of the model was to assess the fraction of segments undergoing structural changes to excimer-favoring conformations as a function of time.\(^{23,24}\) For flexible segments of about 10–15 bonds, a practical method of estimating the time-dependent probability of occurrence of a given transition would be to evaluate the corresponding stochastic weight from Eq. (29) and divide by the transition partition function defined by Eq. (24).

The matrix multiplication scheme employed in the present study has its origins in classical treatments of equilibrium problems.\(^7,^{25}\) It has proved to be highly versatile and powerful to investigate polymer statistics. A future development of the present study may be in the direction of the formulation of generator matrices to compute average transient properties, in analogy to the well-established methods\(^9\) of equilibrium statistics.

\(^7\) H. A. Kramers, and G. H. Wannier, Phys. Rev. 60, 252, 263 (1941).
\(^8\) E. Ising, Z. Phys. 31, 253 (1925).
\(^15\) I. Bahar, B. Erman, L. Monnerie, Macromolecules (in press).
\(^20\) The terminology of apparent probabilities for isolated pairs is used to distinguish from the a priori probabilities which are found by rigorous matrix multiplication procedures (Ref. 1) and which differ according to the exact location of the pair in question, along the chain.