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Stochastics of rotational isomeric transitions in polymer chains

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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 ν 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) model¹⁻³ 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 Ptitsyn.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 Wannier⁷ 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 (τ , $\tau + d\tau$).¹⁶ 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-

figural transition partition function will be defined for a given time τ , from the combination of the stochastic weights corresponding to various isomeric transitions accessible within the time interval τ . The matrix multiplication scheme which has proved to be a tractable means to evaluate equilibrium properties will be employed to deduce dynamic properties such as average orientational correlations, the time-dependent probability of occurrence of specific isomeric transitions, etc.

A brief recapitulation of the DRIS model^{11–14} will be presented in the next section, for self-consistency. The latter was developed as an extension of the work by Jernigan,¹⁸ originally developed for chains with independent bonds. The process of configurational transitions is regarded^{10,14} in the DRIS model as a discrete states, continuous time parameter Markov process.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 theory for a more comprehensive presentation to the reader familiar 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 ν states accessible to each bond, the stochastics of configurational transitions are governed by the master equation^{10–15,18}

$$d\mathbf{P}^{(N)}(\tau)/d\tau = \mathbf{A}^{(N)}\mathbf{P}^{(N)}(\tau) \quad (1)$$

where $\mathbf{P}^{(N)}(\tau)$ is the probability vector of order ν^N , with the element $P_a^{(N)}(\tau)$ denoting the instantaneous probability of configuration $\{\Phi\}_a$, $\mathbf{A}^{(N)}$ is the $\nu^N \times \nu^N$ 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 ν^N isomeric states corresponding to each bond. Following the assumption of single bond rotation at a time $A_{ab}^{(N)}$ equates to zero if $\{\Phi\}_a$ and $\{\Phi\}_b$ possess more than one bond with distinct isomeric state. Also microscopic reversibility implies

$$A_{aa}^{(N)} = - \sum_b A_{ba}^{(N)}. \quad (2)$$

The stochastic process of configurational transitions is stationary, i.e., $\mathbf{P}^{(N)}(\tau) = \mathbf{P}^{(N)}(0)$, for all τ , provided that $\mathbf{P}^{(N)}(0)$ obeys the equilibrium distribution of various configurations. The formal solution to Eq. (1) is

$$\mathbf{P}^{(N)}(\tau) = \exp\{\mathbf{A}^{(N)}\tau\}\mathbf{P}^{(N)}(0). \quad (3)$$

Here $\exp\{\mathbf{A}^{(N)}\tau\}$ physically represents the conditional probability of transition between two configurations and thus will be identified as the transition (or conditional) probability matrix $\mathbf{C}^{(N)}(\tau)$, according to

$$\mathbf{C}^{(N)}(\tau) = \exp\{\mathbf{A}^{(N)}\tau\} = \mathbf{B}^{(N)} \exp\{\mathbf{\Lambda}^{(N)}\tau\}[\mathbf{B}^{(N)}]^{-1}, \quad (4)$$

where $\mathbf{\Lambda}^{(N)}$ is the diagonal matrix of the eigenvalues λ_k ,

$k = 1, \nu^N$, of $\mathbf{A}^{(N)}$. $\mathbf{B}^{(N)}$ is the matrix of the eigenvectors of $\mathbf{A}^{(N)}$ and $[\mathbf{B}^{(N)}]^{-1}$ is the inverse of $\mathbf{B}^{(N)}$. Alternately, the time-delayed joint probability of occurrence of configurations $\{\Phi\}_a$ and $\{\Phi\}_b$ with a time interval τ , is given by the ab th element of the time-dependent joint probability matrix $\mathbf{P}^{(N)}$, as

$$P_{ab}^{(N)} = \sum_k B_{ak}^{(N)} \exp\{\lambda_k \tau\} [\mathbf{B}^{(N)}]_{kb}^{-1} P_b^{(N)}(0), \quad (5)$$

where the subscripts indicate the corresponding elements. For processes where the principle of detailed balance as stated by Eq. (2) applies, all eigenvalues of $\mathbf{A}^{(N)}$ are strictly negative with the exception of one of them, say λ_1 , which is identically equal to zero.^{14,19} The latter ensures the convergence to equilibrium properties at long times. The corresponding eigenvector and the eigenrow yield the equilibrium probability $\{\Phi\}_a$ according to

$$P_a^{(N)}(0) = P_a^{(N)}(\infty) = B_{a1}^{(N)} [\mathbf{B}^{(N)}]_{1b}^{-1} \quad (6)$$

as may be deduced from Eq. (5). $|\lambda_i|$, for $i = 2$ to ν^N , represents the frequency of the i th mode contributing to relaxation.^{13–15,18}

The stochastics of configurational transitions is fully described by the time-dependent joint probability matrix $\mathbf{P}^{(N)}(\tau)$. Quantitative determination of $\mathbf{P}^{(N)}(\tau)$ rests upon the knowledge of the transition rate matrix $\mathbf{A}^{(N)}$. In fact, as apparent from Eqs. (5) and (6), eigenvalues and eigenfunctions of the latter fix the elements of $\mathbf{P}^{(N)}(\tau)$. The transition rate matrix $\mathbf{A}^{(N)}$ 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 $\mathbf{A}^{(N)}$ may be found using the transition rate matrices $\mathbf{A}^{(1)}$ for single bonds according to¹⁸

$$\mathbf{A}^{(N)} = (\mathbf{A}_1^{(1)} \otimes \mathbf{I} \otimes \mathbf{I} \cdots \otimes \mathbf{I}) + (\mathbf{I} \otimes \mathbf{A}_2^{(1)} \otimes \mathbf{I} \cdots \otimes \mathbf{I}) + \cdots + (\mathbf{I} \otimes \mathbf{I} \otimes \mathbf{I} \cdots \otimes \mathbf{A}_N^{(1)}), \quad (7)$$

where \mathbf{I} is the identity matrix of order ν and the subscripts appended to $\mathbf{A}^{(1)}$ indicate the corresponding bond. \otimes denotes the direct product.¹ For pairwise interdependent bonds, Eq. (7) is replaced by¹⁴

$$\mathbf{A}^{(N)} = (\mathbf{A}_{12}^{(2)} \otimes \mathbf{I} \otimes \mathbf{I} \cdots \otimes \mathbf{I}) + (\mathbf{I} \otimes \mathbf{A}_{23}^{(2)} \otimes \mathbf{I} \otimes \mathbf{I} \cdots \otimes \mathbf{I}) + \cdots + (\mathbf{I} \otimes \mathbf{I} \otimes \mathbf{I} \cdots \otimes \mathbf{A}_{N-1N}^{(2)}), \quad (8)$$

where $\mathbf{A}_{ij}^{(2)}$ is the $\nu^2 \times \nu^2$ transition rate matrix for the pair of interdependent bonds (i, j) , \mathbf{I} is of order ν^2 . The transition rate matrix $\mathbf{A}^{(1)}$ associated with independent bonds obeying the scheme



is given by

$$\mathbf{A}^{(1)} = \begin{bmatrix} -2r_1 & r_2 & r_2 \\ r_1 & -r_2 & 0 \\ r_1 & 0 & -r_2 \end{bmatrix}. \quad (9)$$

Here r_1 and r_2 are the rate coefficients associated with the

indicated transitions. Similarity transformation of $\mathbf{A}^{(1)}$ yields

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

and

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

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 $P_{ab}^{(1)}(\tau)$ of occurrence of state $\{\Phi\}_a = \{\alpha\}$ at time τ and $\{\Phi\}_b = \{\alpha^0\}$ at $\tau = 0$ for a single bond subject to independent rotational potential. Clearly α and α^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 $P_{ab}^{(2)}(\tau)$ of $P^{(2)}(\tau)$, bearing in mind that $\{\Phi\}_a = \{\alpha\beta\}$ and $\{\Phi\}_b = \{\alpha^0\beta^0\}$, [or vice versa since $P^{(N)}(\tau)$ 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, $P^{(2)}(\tau)$ is found from $\mathbf{A}^{(2)}$ which is determined with reference to two-dimensional conformational energy maps.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 $\mathbf{A}^{(2)}$. 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 form¹

$$\mathbf{U}_i = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma\Psi & \sigma\omega \\ 1 & \sigma\omega & \sigma\Psi \end{bmatrix}. \quad (11)$$

Here σ is the Boltzmann factor $\exp(-E_\sigma/RT)$ where E_σ is the energy of the g^\pm state in excess of the t state, ω and Ψ reflect the contribution of the second order interactions E_ω and E_Ψ prevailing in the $g^\pm g^\mp$ and $g^\pm g^\pm$ states, respectively.

Serial multiplication of the statistical weight matrices yields the configurational partition function Z according to¹

$$Z = \mathbf{J}^* \left[\prod_{i=2}^{N-1} \mathbf{U}_i \right] \mathbf{J}, \quad (12)$$

where \mathbf{J}^* and \mathbf{J} are the row and column vectors

$$\mathbf{J}^* = [1 \ 0 \ 0]; \quad \mathbf{J} = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix}. \quad (13)$$

Our purpose is to write an analogous stochastic weight matrix \mathbf{V}_i at a given τ , for the time-dependent transitions undergone by the interdependent pair of bonds $(i-1, i)$. The elements of \mathbf{V}_i will be denoted as $v_i(\xi\eta; \xi^0\eta^0)$. Serial multiplication of \mathbf{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 $p_i(\xi\eta; \xi^0\eta^0)$ of the states $\xi^0\eta^0$ and $\xi\eta$ with a time interval τ for an isolated pair of independent bonds $(i-1, i)$. We can anticipate that the latter will be used to determine $v_i(\xi\eta; \xi^0\eta^0)$.

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

The element $u_i(\xi\eta)$ of \mathbf{U}_i is defined¹ by invoking the relationship

$$u_i(\xi\eta) = \exp\{-[E_i(\eta) + \Delta E_i(\xi\eta)]/RT\}. \quad (14)$$

Here the exponential term includes (i) the contribution to intramolecular potential from the rotation Φ_i of bond i , exclusively, which we denote as $E_i(\eta)$, and (ii) the nonbonded interaction which depends jointly on Φ_{i-1} and Φ_i , shown as $\Delta E_i(\xi\eta)$. The former contribution is deduced¹ from the single bond independent conformational behavior. The choice of $E_i(t)$ as the zero energy level leads to $\exp\{-E_i(\eta)/RT\} = 1, \sigma$, and σ 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 pair²⁰ of independent bonds $(i-1, i)$ may be written in matrix notation as

$$[p_i(\xi\eta)] = z_2^{-1} \begin{bmatrix} 1 & \sigma & \sigma \\ \sigma & \sigma^2\Psi & \sigma^2\omega \\ \sigma & \sigma^2\omega & \sigma^2\Psi \end{bmatrix} \quad (15)$$

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

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

Equation (17) may be rewritten as

$$p_i(\xi\eta) = z_1^2 z_2^{-1} p_{i-1}(\xi) p_i(\eta) k_i(\xi\eta) \quad (18)$$

using the single bond partition function $z_1 = 1 + 2\sigma$ and the equilibrium probabilities for *isolated* bonds $p_i(\eta) = z_1^{-1} \times \exp\{-E_i(\eta)/RT\}$, $p_{i-1}(\xi) = z_1^{-1} \exp\{-E_{i-1}(\xi)/RT\}$. The term $k_i(\xi\eta)$ has been substituted for $\exp\{-\Delta E_i(\xi\eta)/RT\}$. The product $z_1^2 z_2^{-1}(\xi\eta)$ 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 $u_i(\xi\eta)$

$$u_i(\xi\eta) = (z_2 z_1^{-1}) p_i(\xi\eta) / p_{i-1}(\xi). \quad (19)$$

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 $p_i(\alpha\beta; \alpha^0\beta^0)$ for the transition $\alpha^0\beta^0 \rightarrow \alpha\beta$ of the isolated pair of interdependent bonds may be written as

$$p_i(\alpha\beta; \alpha^0\beta^0) = p_{i-1}(\alpha; \alpha^0) p_i(\beta; \beta^0) k_i(\alpha\beta; \alpha^0\beta^0), \quad (20)$$

where the deviation from independent bond stochastics is accounted for by the correction term $k_i(\alpha\beta; \alpha^0\beta^0)$ charac-

teristic of the transition $\alpha^0\beta^0 \rightarrow \alpha\beta$ undergone by the pair of bonds $(i-1, i)$. The corresponding stochastic weight reads

$$v_i(\alpha\beta; \alpha^0\beta^0) = p_i(\beta; \beta^0) k_i(\alpha\beta; \alpha^0\beta^0) \quad (21)$$

$$= p_i(\alpha\beta; \alpha^0\beta^0) / p_{i-1}(\alpha; \alpha^0). \quad (22)$$

Equation (20) is the dynamic counterpart of Eq. (18) of equilibrium statistics. It should be recalled that $p_{i-1}(\alpha; \alpha^0)$ represents an element of the joint probability matrix $\mathbf{P}^{(1)}(\tau)$ for the single bond $(i-1)$. The latter is easily found by inserting Eq. (10) into Eq. (5). A similar operation starting from $\mathbf{A}^{(2)}$ instead of $\mathbf{A}^{(1)}$, yields the elements $p_i(\alpha\beta; \alpha^0\beta^0)$ of $\mathbf{P}^{(2)}(\tau)$. Thus, Eq. (22) is conveniently used to determine the elements of the stochastic weight matrix $\mathbf{V}_i(\tau)$ corresponding to bonds $(i-1, i)$. It should be noted that $\mathbf{V}_i(\tau)$ depends on the time interval τ chosen. At $\tau = 0$, it reduces to \mathbf{U}_i (apart from the constant factor $z_2 z_1^{-1}$), as may be seen by inserting the identities $p_i(\alpha\beta; \alpha^0\beta^0) = p_i(\alpha\beta)$ and $p_{i-1}(\alpha; \alpha^0) = p_{i-1}(\alpha)$ at $\tau = 0$, into Eq. (22).

Let us consider the simplest case of $\nu = 2$ states α and β accessible to each bond in a given pair. $\mathbf{V}_i(\alpha)$ will be defined as

$$\mathbf{V}_i(\tau) = \begin{bmatrix} v_i(\alpha\alpha; \alpha\alpha) & v_i(\alpha\alpha; \alpha\beta) & v_i(\alpha\beta; \alpha\alpha) & v_i(\alpha\beta; \alpha\beta) \\ v_i(\alpha\alpha; \beta\alpha) & v_i(\alpha\alpha; \beta\beta) & v_i(\alpha\beta; \beta\alpha) & v_i(\alpha\beta; \beta\beta) \\ v_i(\beta\alpha; \alpha\alpha) & v_i(\beta\alpha; \alpha\beta) & v_i(\beta\beta; \alpha\alpha) & v_i(\beta\beta; \alpha\beta) \\ v_i(\beta\alpha; \beta\alpha) & v_i(\beta\alpha; \beta\beta) & v_i(\beta\beta; \beta\alpha) & v_i(\beta\beta; \beta\beta) \end{bmatrix}. \quad (23)$$

Thus, as shown by the above dashed lines, $\mathbf{V}_i(\tau)$ is divided into ν^2 submatrices of size $\nu \times \nu$, 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_τ for a chain of n bonds, with ν states accessible to each bond, is defined as the serial product of the stochastic weight matrices according to

$$Z_\tau = \mathbf{J}^T \left[\prod_{i=2}^{N-1} \mathbf{V}_i(\tau) \right] \mathbf{J}, \quad (24)$$

where $\mathbf{J} = \text{col}(1, 1, \dots, 1)$, $\mathbf{J}^T = \text{row}(1, 1, \dots, 1)$, $\mathbf{V}_2(\tau)$ is the diagonal matrix defined as

$$\mathbf{V}_2(\tau) = \begin{bmatrix} v_2(\alpha; \alpha) & & & \\ & v_2(\alpha; \beta) & & \\ & & \ddots & \\ & & & v_2(\nu; \nu) \end{bmatrix}. \quad (25)$$

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 $\mathbf{V}_i(\tau)$, $i = 3, N-1$ is the $\nu^2 \times \nu^2$ stochastic weight matrix for bonds $(i-1, i)$, with the structure given by Eq. (23) for the simple case of $\nu = 2$. The adaptation of Eq. (23) to $\nu > 2$ 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_τ may be found from

$$Z_\tau = \mathbf{J}^* \left[\prod_{i=2}^{N-1} \mathbf{V}_i(\tau) \right] \mathbf{J} \quad (26)$$

where $\mathbf{V}_2(\tau)$ is now identical in form to $\mathbf{V}_i(\tau)$ for $i = 2, N-1$, with the adoption of $k_2(\alpha\beta; \alpha^0\beta^0) = 1$. 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

$$Z_\tau = \sum \sum \cdots \sum [v_2(\alpha; \alpha^0) v_3(\alpha\beta; \alpha^0\beta^0) v_4(\beta\gamma; \beta^0\gamma^0) \cdots], \quad (27)$$

where the summation is performed over all possible initial states $\alpha^0, \beta^0, \gamma^0, \dots, \nu^0$ and final states $\alpha, \beta, \gamma, \dots, \nu$ for bonds whose ordinal numbers are indicated by the subscripts. Using Eq. (22), Eq. (27) may be written in terms of the elements of $\mathbf{P}^{(2)}(\tau)$ and $\mathbf{P}^{(1)}(\tau)$ as

$$Z_\tau = \sum \sum \cdots \sum \left[p_3(\alpha\beta; \alpha^0\beta^0) [p_4(\beta\gamma; \beta^0\gamma^0) / p_3(\beta; \beta)] \right. \\ \left. \times \cdots [P_{N-1}(\mu\nu; \mu^0\nu^0) / p_{N-2}(\mu; \mu^0)] \right]. \quad (28)$$

It should be noted that the definition of $\mathbf{V}_i(\tau)$ according to Eq. (23) ensures the juxtaposition in the above series of the stochastic weight with identical initial and final states for the common bond, as required by chain connectivity.

The term in brackets in Eq. (28) represents the stochastic weight $\Omega\{\Phi_b; \Phi_a\}$ of the joint occurrence of the two configurations $\{\Phi\}_a = \{\alpha^0\beta^0\gamma^0\delta^0\cdots\}$ and $\{\Phi\}_b = \{\alpha\beta\gamma\delta\cdots\}$ characterized by the isomeric states of the $N-2$ internal bonds, i.e.,

$$\Omega\{\Phi_b; \Phi_a\} = \{p_3(\alpha\beta; \alpha^0\beta^0)[p_4(\beta\gamma; \beta^0\gamma^0)/p_3(\beta; \beta^0)] \times [p_5(\gamma\delta; \gamma^0\delta^0)/p_4(\gamma; \gamma^0)] \cdots\}. \quad (29)$$

Consequently, the *a priori* probability $p^*\{\Phi_a; \Phi_b\}$ of the transition $\{\Phi\}_a \rightarrow \{\Phi\}_b$ at time τ is

$$p^*\{\Phi_a; \Phi_b\} = \Omega\{\Phi_a; \Phi_b\}/Z_\tau. \quad (30)$$

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

$$p_j^*(t; g^+) = Z_\tau^{-1} \left[\mathbf{J}^T \left[\prod_{i=2}^{j-1} \mathbf{V}_i(\tau) \right] \times \mathbf{V}_j^*(\tau) \left[\prod_{i=j+1}^{N-1} \mathbf{V}_i(\tau) \right] \mathbf{J} \right], \quad (31)$$

where $\mathbf{V}_j^*(\tau)$ is the stochastic weight matrix where all elements $v_j(\alpha\beta; \alpha^0\beta^0)$ with $\beta^0, \beta \neq g^+, t$ are equated to zero. This device retains precisely those terms meeting the condition $g^+ \rightarrow t$ in the sum of stochastic weights $\Omega\{\Phi_a; \Phi_b\}$ over all transitions of the chain, at a given time τ .

Similarly, the *a priori* probability of a specific joint event, say (g^+t) at $\tau=0$ and (g^-g^+) at time τ , for the pair of bonds $(j-1, j)$ may be found, using Eq. (31), but now equating all elements of \mathbf{V}_j^* to zero, with the exception of $v_j(g^-g^+; g^+t)$.

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

$$\langle n(t; g^+) \rangle = (N-2)p^*(t; g^+), \quad (32)$$

where $p^*(t; g^+)$ is the *a priori* probability of the transition $g^+ \rightarrow t$ averaged over all possible configurational changes of the internal bonds, according to

$$p^*(t; g^+) = (N-2)^{-1} \sum_{j=2}^{N-1} p_j^*(t; g^+). \quad (33)$$

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,

$$p^*(\xi; \eta) = (N-2)^{-1} Z_\tau^{-1} \mathbf{J}^* \left[\prod_{j=2}^{N-1} \hat{\mathbf{V}}_j(\xi; \eta) \right] \mathbf{J}, \quad (34)$$

where

$$\hat{\mathbf{V}}_j(\xi; \eta) \equiv \begin{bmatrix} \mathbf{V}_j(\tau) & \mathbf{V}_j^*(\tau) \\ 0 & \mathbf{V}_j(\tau) \end{bmatrix}, \quad (35)$$

$$\mathbf{J}^* = [\mathbf{J}^* \ 0 \ 0 \cdots 0]$$

$$\mathbf{J} = \text{col}(0, 0, \cdots, 0, \mathbf{J}). \quad (36)$$

Here \mathbf{J}^* and \mathbf{J} are row and column vectors of order $2\nu^2$. $\mathbf{V}_j^*(\tau)$ is obtained from $\mathbf{V}_j(\tau)$ by striking all elements except those of column $(\xi; \eta)$ for bond j , as already defined in Eq.

(31). Similarly the time dependent *a priori* probability $p^*(\alpha\beta; \xi\eta)$ of the pair transition $\xi\eta \rightarrow \alpha\beta$, within a time interval τ or the average number $\langle n(\alpha\beta; \xi\eta) \rangle$ of pairs of bond that have undergone this transition may be found from

$$p^*(\alpha\beta; \xi\eta) = \langle n(\alpha\beta; \xi\eta) \rangle / (N-3), \quad (37)$$

$$= (N-3)^{-1} Z_\tau^{-1} \mathbf{J}^* \left[\prod_{j=2}^{N-1} \hat{\mathbf{V}}_j(\alpha\beta; \xi\eta) \right] \mathbf{J}, \quad (38)$$

where $\mathbf{V}_j^*(\tau)$ in $\hat{\mathbf{V}}_j(\alpha\beta; \xi\eta)$, through Eq. (35), has all elements equal to zero with the exception of $v_j(\alpha\beta; \xi\eta)$.

The extension of the formulation to the analysis of the time-dependent occurrence of any type of configurational 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 $f_i(\alpha; \alpha^0)$ be a time-dependent function of the transition $\alpha^0 \rightarrow \alpha$ undergone by the i th bond. Its average $\langle f_i(\tau) \rangle$ over all configurational transitions of the chain at time τ may be found from

$$\langle f_i(\tau) \rangle = Z_\tau^{-1} \mathbf{J}^* \left[\prod_{j=2}^{i-1} \mathbf{V}_j(\tau) \right] \mathbf{V}_i(\tau) \mathbf{F}_i \left[\prod_{m=i+1}^{N-1} \mathbf{V}_m(\tau) \right] \mathbf{J}, \quad (39)$$

where \mathbf{F}_i is the diagonal matrix

$$\mathbf{F}_i = \begin{bmatrix} f(\alpha; \alpha) & & & & \\ & f(\alpha; \beta) & & & \\ & & \ddots & & \\ & & & \ddots & \\ & & & & f(v; v) \end{bmatrix} \quad (40)$$

of the values of the function $f_i(\alpha; \alpha^0)$ 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 \mathbf{F} 's with the appropriate $\mathbf{V}(\tau)$ s, i.e.,

$$\langle f_i f_{i+1} \cdots f_{i+k} \rangle = Z_\tau^{-1} \mathbf{J}^* \left[\prod_{j=2}^{i-1} \mathbf{V}_j \right] \left[\prod_{n=i}^{i+k} \mathbf{V}_n \mathbf{F}_n \right] \left[\prod_{m=i+k+1}^{N-1} \mathbf{V}_m \right] \mathbf{J}. \quad (41)$$

Here the time arguments of $\mathbf{V}_i(\tau)$ 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 \mathbf{m} rigidly affixed to the chain. The latter is defined as $\langle \mathbf{m}(0) \cdot \mathbf{m}(\tau) \rangle$ where the angular brackets indicate the ensemble average over all possible initial and final configurations. Suppose \mathbf{m}^0 is the fixed representation of $\mathbf{m}(\tau)$ in the local $(i+1)$ th bond-based frame¹ where it is rigidly embedded. In the simplest case where the orientational motion of \mathbf{m}

is prescribed by the rotation of the single bond i , the OACF reduces to

$$\langle \mathbf{m}(0) \cdot \mathbf{m}(\tau) \rangle = \mathbf{m}^{0T} \langle \mathbf{T}_i^T(0) \mathbf{T}_i(\tau) \rangle \mathbf{m}^0, \quad (42)$$

where \mathbf{T}_i is the transformation matrix¹ which expresses \mathbf{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 $\mathbf{m}(\tau)$ 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,²¹ Birshtein and Ptitsyn,⁶ Hoeve,²² Lifson,⁴ and Nagai,⁵ for evaluating $\langle \mathbf{T}_i \rangle$ in equilibrium statistics. Accordingly, we can define a pseudodiagonal matrix $\|\mathbf{S}_i\|$ of order $3\nu^2$ as

$$\|\mathbf{S}_i\| = \begin{bmatrix} \mathbf{T}_i^T(\alpha) \mathbf{T}_i(\alpha) & & \\ & \mathbf{T}_i^T(\alpha) \mathbf{T}_i(\beta) & \\ & & \ddots \\ & & & \mathbf{T}_i^T(\nu) \mathbf{T}_i(\nu) \end{bmatrix}. \quad (43)$$

By following exactly the same arguments as those developed for equilibrium statistics,¹ it can be shown that the average quantity in Eq. (42) is given by

$$\begin{aligned} \langle \mathbf{T}_i^T(0) \mathbf{T}_i(\tau) \rangle &= \mathbf{Z}_\tau^{-1} (\mathbf{J}^* \otimes \mathbf{I}_3) \left[\prod_{j=2}^{i-1} \mathbf{V}_j(\tau) \otimes \mathbf{I}_3 \right] \\ &\quad \times [\mathbf{V}_i(\tau) \otimes \mathbf{I}_3] \|\mathbf{S}_i\| \\ &\quad \times \left[\prod_{k=i+1}^{N-1} \mathbf{V}_k(\tau) \otimes \mathbf{I}_3 \right] (\mathbf{J} \otimes \mathbf{I}_3). \end{aligned} \quad (44)$$

The matrix $\mathbf{V}_i(\tau) \otimes \mathbf{I}_3 \|\mathbf{S}_i\|$ in Eq. (43) consists of block elements of the form $v_i(\alpha\beta; \alpha^0\beta^0) \mathbf{T}_i^T(\beta^0) \mathbf{T}_i(\beta)$, 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 $\mathbf{V}_i(\tau) \otimes \mathbf{I}_3 \|\mathbf{S}_i\|$ is defined as the matrix of block elements $v_i(\alpha\beta; \alpha^0\beta^0) \mathbf{T}_i^T(\beta^0) \mathbf{T}_{i-1}^T(\alpha^0) \mathbf{T}_{i-1}(\alpha) \mathbf{T}_i(\beta)$.

If, alternately, the OACF depends on the simultaneous rotations of k bonds preceding bond $(i+1)$, Eq. (42) is replaced by

$$\begin{aligned} \langle \mathbf{m}(0) \cdot \mathbf{m}(\tau) \rangle &= \mathbf{m}^{0T} \left\langle \left[\prod_{j=i-k+1}^i \mathbf{T}_j(0) \right]^T \right. \\ &\quad \times \left. \left[\prod_{j=i-k+1}^i \mathbf{T}_j(\tau) \right] \right\rangle \mathbf{m}^0. \end{aligned} \quad (45)$$

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

$$\begin{aligned} \langle \mathbf{m}(0) \cdot \mathbf{m}(\tau) \rangle &= \mathbf{Z}_\tau^{-1} (\mathbf{m}^0)^T \left[\sum_{\mathbf{a}} \sum_{\mathbf{b}} \Omega\{\Phi_{\mathbf{a}}; \Phi_{\mathbf{b}}\} \mathbf{T}^T\{\Phi_{\mathbf{b}}\} \mathbf{T}\{\Phi_{\mathbf{a}}\} \right] \mathbf{m}^0, \end{aligned} \quad (46)$$

where $\Omega\{\Phi_{\mathbf{a}}; \Phi_{\mathbf{b}}\}$ is the stochastic weight for the transition

$\{\Phi_{\mathbf{b}}\} \rightarrow \{\Phi_{\mathbf{a}}\}$, $\mathbf{T}\{\Phi_{\mathbf{b}}\}$ represents the product of transformation matrices in serial order for the k initial torsional angles in $\{\Phi_{\mathbf{b}}\}$, \mathbf{Z}_τ is the transition partition function for the mobile segment of k bonds.

IV. REMARKS

The time-dependent probability $p_i(\alpha\beta; \alpha^0\beta^0)$ of the transition from state $\alpha^0\beta^0$ at $\tau = 0$ to the state $\alpha\beta$ at time τ , 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 $p_{i-1}(\alpha; \alpha^0)$ readily obtainable by inserting Eqs. (6) and (10) into Eq. (5), (ii) the independent stochastics of bond i , represented by $p_i(\beta; \beta^0)$, 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 $\mathbf{P}^{(2)}(\tau)$ and $\mathbf{P}^{(1)}(\tau)$ which are in turn found from the respective transition rate matrices $\mathbf{A}^{(2)}$ and $\mathbf{A}^{(1)}$, as outlined in Sec. II. For pairs subject to independent rotational potentials $k_i(\alpha\beta; \alpha^0\beta^0) = 1$ and the stochastic weight $\Omega\{\Phi_{\mathbf{a}}; \Phi_{\mathbf{b}}\}$ simplifies to the product $p_2(\alpha; \alpha^0) p_3(\beta; \beta^0) \cdots$. Otherwise, the adoption of the pair stochastic weights, according to Eq. (22), as follows from the above formulation of $p_i(\alpha\beta; \alpha^0\beta^0)$, leads to Eq. (29). It is clear that the division by $p_{i-1}(\alpha; \alpha^0)$ 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

$$p^*\{\Phi_{\mathbf{a}}; \Phi_{\mathbf{b}}\} = p_3(\alpha\beta; \alpha^0\beta^0) q_4(\beta\gamma; \beta^0\gamma^0) q_5(\gamma\sigma; \gamma^0\sigma^0) \cdots \quad (46)$$

with

$$q_4(\beta\gamma; \beta^0\gamma^0) = p_4(\beta\gamma; \beta^0\gamma^0) / \sum_{\gamma'} \sum_{\gamma''} p_4(\beta\gamma; \beta^0\gamma^0) \quad (47)$$

was adopted in previous work for the probability of the transition $\{\Phi_{\mathbf{b}}\} = \{\alpha^0\beta^0\gamma^0\sigma^0 \cdots\} \rightarrow \{\Phi_{\mathbf{a}}\} = \{\alpha\beta\gamma\sigma \cdots\}$. 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 *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, $\Omega\{\Phi_{\mathbf{a}}; \Phi_{\mathbf{b}}\}$ over the final states $\{\Phi_{\mathbf{a}}\}$, 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 $\tau = 0$, same equilibrium probabilities as those predicted by the RIS model. Alternately, calculation performed by adopting time periods τ , significantly

large compared to the time range (10^{-10} 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 τ .

A given transition $\{\Phi\}_b \rightarrow \{\Phi\}_a$ is assigned a stochastic weight $\Omega\{\Phi_a; \Phi_b\}$ 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 methods⁹ of equilibrium statistics.

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