

# Kinematics of Polymer Chains with Freely Rotating Bonds in a Restrictive Environment. 1. Theory

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**ABSTRACT:** A mathematical formulation is developed for the study of the kinematics or geometry of motion of polymer chains with freely rotating bonds. The chains are assumed to be in a dense continuous medium constraining the spatial displacements of atoms. The basic postulate of the proposed model is that, following any perturbation of an equilibrium configuration, the atoms rearrange cooperatively in space so as to minimize their overall square displacements. This postulate is equivalent to minimizing the energy spent against the surroundings during the motion of the chain from one configuration to another. The present formulation allows for the calculation of the changes in all of the degrees of freedom of the chain, internal and external, in response to a change in the dihedral angle of an internal bond. By the use of Lagrange multipliers, the formulation may be generalized to study the results of perturbations on a chain subject to other types of external constraints, such as uniaxial deformation.

## Introduction

Local dynamics of a polymer chain above the glass transition temperature results from high-frequency torsional fluctuations about the main-chain bonds.<sup>1-3</sup> These torsional motions, imparted from the random fluctuations of the environment, are highly localized, taking place by moving only a few neighboring bonds along the chain. The evidence for such strong localization comes from kinetic studies,<sup>4,5</sup> Brownian dynamics simulations,<sup>6-8</sup> and experiments.<sup>9-11</sup> The constraints imposed by chain connectivity play a major role in controlling the kinematics of local motions. The localization mechanism is particularly important in a restrictive environment where the energy cost of moving a chain against environmental friction is relatively high. A relevant parameter controlling the motion of a chain is the sum of squares of displacements of chain atoms.<sup>5</sup> Indeed, in the case of the freely rotating chain presently adopted, neglecting inertial effects, minimization of the sum of square displacements is equivalent to the minimization of the energy spent against the surroundings during the motion of the chain from one configuration to another.

The specific aim of the present paper is to develop an efficient formalism for calculating the optimal conformational changes of a given chain, in response to a small perturbation of a dihedral angle. Once this is achieved, one may numerically integrate over several successive small steps and determine the geometry of motion of the chain over finite rotations of a bond, such as those involved in rotameric transitions among trans and gauche states. Results of such calculations for a freely rotating chain are reported in the following paper.

In a preliminary study,<sup>12</sup> the perturbation was effected in the form of a translation of one end of the chain, while the other was held fixed in space. Accordingly, the cooperative rearrangements of bond dihedral angles so as to accommodate the deformed end-to-end separation of the chain were investigated. Minimum displacement of position vectors relative to the center of gravity was assumed to occur during conformational rearrangements of the chain. This picture is reminiscent of a network

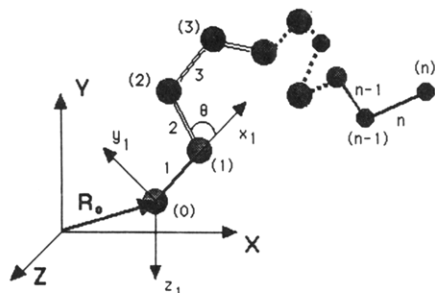
chain deforming affinely under uniaxial tension, in a restrictive medium. In the present formulation, the changes in atomic positions accompanying a rotameric transition of an internal bond are studied. Energy minimization is the fundamental criterion for the choice of a certain unique path of conformational relaxation following the given perturbation.

## Model and Assumptions

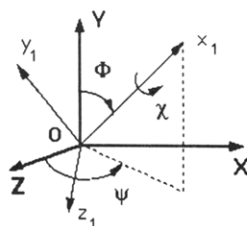
We consider a perfect tetrahedral structure of  $n$  backbone bonds, each of length  $l$ . Bond lengths and bond angles are fixed. The dihedral or torsional angle  $\varphi_i$  of bond  $i$  is assumed to take any value, in analogy to the freely rotating chain. The chain is allowed to translate or rotate in space, and coordinates of chain atoms relative to a laboratory-fixed reference frame OXYZ are observed. Thus, the total number of degrees of freedom of the chain amounts to  $n + 4$ ,  $n - 2$  of them arising from the rotations of the internal backbone bonds  $2 \leq i \leq n - 1$  and the remaining 6 associated with the absolute position and orientation of the chain.

The internal motions of the chain may be mathematically described in terms of bond-based coordinate systems. The system,  $Ox_1y_1z_1$ , affixed to the first bond, for example, is shown in Figure 1. Following the notation by Flory,<sup>13</sup> the  $x$ -axis of the  $i$ th bond-based coordinate system is chosen in the direction of the  $i$ th bond, and the  $y$ -axis is in the plane of the  $i$ th and the  $(i - 1)$ st bonds and makes an acute angle with the extension of the  $(i - 1)$ st bond. The  $z$ -axis completes a right-handed frame. Chain atoms are indexed from 0 to  $n$ .  $\mathbf{r}_i$  denotes the position vector of the  $i$ th atom along the chain relative to the local frame  $Ox_1y_1z_1$ . It will be referred to as the internal position vector in the following. The absolute position of atom  $i$  in space, on the other hand, is indicated by the vector  $\mathbf{R}_i$  connecting the origin of the frame OXYZ to the  $i$ th atom.

The absolute location of the chain in space is specified by the position vector  $\mathbf{R}_0 = (X_0 Y_0 Z_0)^T$  of the zeroth atom in the frame OXYZ. Here the superscript T denotes the transpose. Three Euler angles shown in Figure 2 define the absolute orientation of the chain in space: the angle  $\Phi$  that the first bond makes with the  $Y$ -axis, the angle  $\psi$



**Figure 1.** An instantaneous configuration of a chain. OXYZ is the laboratory-fixed coordinate system. Bonds are numbered from 1 to  $n$ . Atom numbers are shown in parentheses. The internal motions of the chain are described in terms of bond-based coordinate systems affixed to each bond. The  $i$ th bond-based coordinate system  $O_{x_i y_i z_i}$  is chosen with the  $x_i$  axis in the direction of the  $i$ th bond. The  $y_i$ -axis is in the plane of the  $i$ th and the  $(i-1)$ st bonds and makes an acute angle with the extension of the  $(i-1)$ st bond. Only the first bond-based coordinate system is shown in the figure.  $\theta$  represents the supplemental bond angle.  $\mathbf{R}_0$  represents the position of the zeroth atom with respect to the laboratory-fixed coordinate system.  $\mathbf{R}_i$  and  $\mathbf{r}_i$  are the position vectors of the  $i$ th atom in the respective frames OXYZ and  $O_{x_i y_i z_i}$ .



**Figure 2.** Orientation of the first bond-based coordinate system relative to the laboratory-fixed coordinate system.  $\Phi$  and  $\psi$  are respectively the polar and azimuthal angles of  $\mathbf{x}_1$  in the system OXYZ.  $\chi \equiv \varphi_1$  is the rotation of the coordinate system  $O_{x_1 y_1 z_1}$  about the  $x_1$ -axis.

that the projection of the first bond on the XZ plane makes with the Z-axis, and the angle  $\chi$  of rotation of the first bond about its own axis.

According to the basic postulate adopted in the present study, in a restrictive medium which is regarded as a continuum, the conformational rearrangements of the backbone atoms succeeding an external perturbation are constrained to occur in a concerted fashion so as to preserve as much as possible the instantaneous position vectors  $\mathbf{R}_i$ . Physically, this postulate is a natural consequence of the energy minimization principle since, in the absence of energetic or enthalpic interactions, the energy change reduces to the work done by the system, which increases with the displacement of the atoms from their equilibrium positions. Assuming the chain to equilibrate prior to any conformational transition, the distortion of a given configuration is assumed to be opposed by harmonic potentials (or springlike resistance), forcing the atoms to restore their original locations. Mathematically, this requirement is satisfied by minimizing the scalar function  $S$  of the incremental changes  $\delta\mathbf{R}_i$  in position vectors

$$S \equiv (n+1)^{-1} \sum_{i=0}^n (\delta\mathbf{R}_i)^2 \quad (1)$$

The function  $S$  physically represents the mean-square displacement of atoms succeeding a perturbation of a given original configuration. For purposes of numerical computation in the following,  $\delta\mathbf{R}_i$  will be replaced by  $\Delta\mathbf{R}_i$ , which refers to small changes in  $\mathbf{R}_i$ .

In their multidimensional extension of Kramers' reaction rate theory,<sup>5</sup> Skolnick and Helfand point out that the

steepest descent path of the reaction coordinate associated with conformational transitions is a compromise between long-range and extremely short-range motions. Accordingly, the former is controlled by the cumulative square displacements of chain atoms whereas intramolecular conformational energetics determines the latter. Inasmuch as the present model chain is a freely rotating one, intramolecular energetics do not contribute to the kinetics of configurational transitions, and the above-defined  $S$  function, which is identical to eq 4.3 in ref 5, is the only remaining rate determining factor.

Constraints on valence angles and bond lengths are exactly satisfied in the freely rotating chain model presently considered. Model chains of this type are also referred to as "rigid chains", in contrast to "flexible chains" in which bond angles and valence angles are not fixed but controlled by harmonic potentials. Comparison of the equilibrium and dynamic properties of the two model chains indicates<sup>14</sup> that differences arising due to the presence of rigid constraints may be eliminated by adopting a compensating potential, originally introduced by Fixman,<sup>15</sup> based on the metric determinant of the unconstrained coordinates in the rigid model.

## Mathematical Formulation

**General Approach.** The mathematical formulation comprises two major steps: First, a computationally convenient expression is obtained for  $\Delta\mathbf{R}_i$  as a linear combination of the incremental changes in the  $n+4$  variables controlling the configurational changes of the chain. The  $n-2$  internal degrees of freedom associated with bond torsional flexibilities are represented by the dihedral angles  $\varphi_j$ ,  $2 \leq j \leq n-1$ . The external degrees of freedom are associated with the translation  $(X_0, Y_0, Z_0)$  of the first atom and rotation  $(\Phi, \psi, \chi)$  of the first bond. Hence, these six coordinates define the absolute location and orientation of a given chain configuration. As a second step, under the imposition of an external perturbation, which suppresses one or more degrees of freedom of the chain, the  $S$  function—which is composed of the additive contribution of the square displacements  $(\Delta\mathbf{R}_i)^2$  of all atoms—will be minimized with respect to all of the remaining free variables.

**Changes in Internal Position Vectors.** The internal position vectors  $\mathbf{r}_i$ , for  $1 \leq i \leq n$ , are written as

$$\mathbf{r}_i = (\mathbf{E} + \mathbf{T}_1 + \mathbf{T}_1\mathbf{T}_2 + \mathbf{T}_1\mathbf{T}_2\mathbf{T}_3 + \dots + \mathbf{T}_1\mathbf{T}_2\dots\mathbf{T}_{i-1})\ell \quad (2)$$

where  $\ell$  is the bond vector  $(l \ 0 \ 0)^T$  and  $\mathbf{E}$  is the identity matrix of order 3. The transformation matrix  $\mathbf{T}_i$  for expressing vectorial or tensorial quantities of the bond-based frame  $O_{i+1 x_{i+1} y_{i+1} z_{i+1}}$  in their representation in frame  $O_{i x_i y_i z_i}$  reads

$$\mathbf{T}_i = \begin{bmatrix} \cos \theta & \sin \theta & 0 \\ \sin \theta \cos \varphi_i & -\cos \theta \cos \varphi_i & \sin \varphi_i \\ \sin \theta \sin \varphi_i & -\cos \theta \sin \varphi_i & -\cos \varphi_i \end{bmatrix} \quad (3)$$

where  $\theta$  is the supplement of the fixed tetrahedral bond angle. The torsional angle  $\varphi_i = 0^\circ$  leading to the planar geometry of the three bonds  $i-1$ ,  $i$ , and  $i+1$  defines the trans (t) state.  $\pm 120^\circ$  rotations with respect to the trans state are referred to as the gauche<sup>±</sup> ( $g^\pm$ ) states.<sup>13</sup> In the interest of simplifying the presentation, we include a fictitious zeroth bond by the aid of which it becomes possible to define the torsional state  $\varphi_1$  of the first bond. Thus, the set of dihedral angles is enlarged to include the rotation of the first bond; i.e.,  $\varphi_j$  varies in the range  $1 \leq j \leq n-1$  and the external rotation  $\chi$  is identified with  $\varphi_1$ .

Inasmuch as we are primarily interested in the change in bond torsional angles, in response to a rotameric jump of an internal bond, it is expedient to express first the incremental change in the position vector  $\Delta \mathbf{R}_i$  as a function of the change in dihedral angles  $\Delta \varphi_j$ ,  $1 \leq j \leq n-1$ . Using the partial derivatives of  $\mathbf{r}_i$  with respect to the bond torsional angles, the incremental changes  $\Delta \mathbf{r}_i$  for small  $\Delta \varphi_j$ ,  $j < i$ , may be written as a linear combination of  $\Delta \varphi_j$  as

$$\Delta \mathbf{r}_i = \mathbf{A} \mathbf{T}_1 (\mathbf{E} + \mathbf{T}_2 + \mathbf{T}_2 \mathbf{T}_3 + \dots + \mathbf{T}_2 \mathbf{T}_3 \dots \mathbf{T}_{i-1}) \ell \Delta \varphi_1 + \mathbf{T}_1 \mathbf{A} \mathbf{T}_2 (\mathbf{E} + \mathbf{T}_3 + \mathbf{T}_3 \mathbf{T}_4 \dots + \mathbf{T}_3 \mathbf{T}_4 \dots \mathbf{T}_{i-1}) \ell \Delta \varphi_2 + \mathbf{T}_1 \mathbf{T}_2 \mathbf{A} \mathbf{T}_3 (\mathbf{E} + \mathbf{T}_4 + \mathbf{T}_4 \mathbf{T}_5 + \dots + \mathbf{T}_4 \mathbf{T}_5 \dots \mathbf{T}_{i-1}) \ell \Delta \varphi_3 + \dots + \mathbf{T}_1 \mathbf{T}_2 \mathbf{T}_3 \dots \mathbf{T}_{i-2} \mathbf{A} \mathbf{T}_{i-1} \ell \Delta \varphi_{i-1} \quad (4)$$

Here  $i$  varies in the range  $2 \leq i \leq n$ , and the partial derivative  $\partial \mathbf{T}_j / \partial \varphi_j$  has been replaced as

$$\partial \mathbf{T}_j / \partial \varphi_j = \mathbf{A} \mathbf{T}_j \equiv \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix} \mathbf{T}_j \quad (5)$$

It is noted that eq 4 is exact in the limit of differential changes in position vectors and dihedral angles. The integrated form in terms of gradients of position vectors and dihedral angles presented in eq 4 is applicable to the case of small changes in those variables only. Thus, a change in dihedral angle of about  $120^\circ$ , which occurs during transitions from one rotational isomeric state to another in real chains, will be approximated by a succession of small-amplitude steps ( $< 3^\circ$ ) in the required direction. It is noted that a constant torsional velocity path for the rotameric transition of a given bond does not necessarily yield minimum energy dissipation upon integration. However, the approach is rigorously exact in the limit of infinitesimally small step size.

$\Delta \mathbf{r}_i$  may be written in compact notation as a linear combination of  $\Delta \varphi_j$ ,  $1 \leq j \leq i-1$ , as

$$\Delta \mathbf{r}_i = \sum_{j=1}^{i-1} \mathbf{a}_{ij} \Delta \varphi_j \quad (6)$$

$$= \sum_{j=1}^{n-1} H(j,i) \mathbf{a}_{ij} \Delta \varphi_j \quad (7)$$

where  $H(j,i)$  is defined as

$$H(j,i) = 1 \quad j < i \\ = 0 \quad j \geq i \quad (8)$$

and, for each  $i$  in the range  $2 \leq i \leq n$ ,  $\mathbf{a}_{ij}$  is a  $3 \times 1$  vector given by

$$\mathbf{a}_{ij} \equiv \left[ \prod_{k=0}^{j-1} \mathbf{T}_k \right] \mathbf{A} \mathbf{T}_j \begin{bmatrix} \mathbf{E} & 0 \end{bmatrix} \left[ \prod_{k=j+1}^{i-1} \mathbf{G}_k \right] \begin{bmatrix} \ell \\ 1 \end{bmatrix} \quad (9)$$

Here,  $\mathbf{T}_0$  is defined as the identity matrix of order 3, and  $\mathbf{G}_j$  is the generator matrix given by

$$\mathbf{G}_j = \begin{bmatrix} \mathbf{T}_j & \ell \\ 0 & 1 \end{bmatrix} \quad (10)$$

It is noted that a computationally efficient expression for the intermediate position vector  $\mathbf{r}_i$  is

$$\mathbf{r}_i = [\mathbf{E} \quad 0] \left[ \prod_{k=1}^{i-1} \mathbf{G}_k \right] \begin{bmatrix} \ell \\ 1 \end{bmatrix} \quad (11)$$

**Changes in Absolute Position Vectors.**  $\Delta \mathbf{r}_i$  differs from  $\Delta \mathbf{R}_i$  by the rotations  $\Delta \Phi$  and  $\Delta \psi$  of the first bond and

the translation  $\mathbf{R}_0$  of the first atom, which have not been considered so far. Thus,  $\Delta \mathbf{r}_i$  represents the incremental change in the position vectors  $\mathbf{r}_i$ , corresponding to the intermediate chain configuration with  $\Delta \Phi = \Delta \psi = 0^\circ$  and  $\Delta \mathbf{R}_0 = 0$ . The passage to the set of position vectors  $\mathbf{R}_i$  is through

$$\mathbf{R}_i = \mathbf{T}(\psi) \mathbf{T}(\Phi) \mathbf{r}_i + \mathbf{R}_0 \quad (12)$$

Here the transformation matrices  $\mathbf{T}(\psi)$  and  $\mathbf{T}(\Phi)$  are respectively

$$\mathbf{T}(\psi) = \begin{bmatrix} \sin \psi & 0 & -\cos \psi \\ 0 & 1 & 0 \\ \cos \psi & 0 & \sin \psi \end{bmatrix} \quad (13)$$

and

$$\mathbf{T}(\Phi) = \begin{bmatrix} \sin \Phi & -\cos \Phi & 0 \\ \cos \Phi & \sin \Phi & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (14)$$

From eq 12,  $\Delta \mathbf{R}_i$  is readily written as

$$\Delta \mathbf{R}_i = \mathbf{T}(\psi) \mathbf{T}(\Phi) \Delta \mathbf{r}_i + \mathbf{T}(\psi) \mathbf{T}'(\Phi) \mathbf{r}_i \Delta \Phi + \mathbf{T}'(\psi) \mathbf{T}(\Phi) \mathbf{r}_i \Delta \psi + \Delta \mathbf{R}_0 \quad (15)$$

for small incremental changes in  $\mathbf{r}_i$ ,  $\Phi$ , and  $\psi$ . Here the primes indicate the derivatives with respect to the arguments. By inserting eq 6 into eq 15, we obtain the following expression for  $\Delta \mathbf{R}_i$  in terms of the  $n+4$  variables ( $\Delta \varphi_i$ ,  $1 \leq i \leq n-1$ ,  $\Delta \psi$ ,  $\Delta \Phi$ , and  $\Delta \mathbf{R}_0$ ) of the problem:

$$\Delta \mathbf{R}_i = \mathbf{T}(\psi) \mathbf{T}(\Phi) \left[ \sum_{j=1}^{n-1} H(j,i) \mathbf{a}_{ij} \Delta \varphi_j \right] + \mathbf{T}(\psi) \mathbf{C} \mathbf{T}(\Phi) \mathbf{r}_i \Delta \psi + \mathbf{T}(\psi) \mathbf{T}(\Phi) \mathbf{B} \mathbf{r}_i \Delta \Phi + \Delta \mathbf{R}_0 \quad i = 1, n \quad (16)$$

Here  $\mathbf{T}'(\Phi)$  and  $\mathbf{T}'(\psi)$  have been replaced by  $\mathbf{T}(\Phi) \mathbf{B}$  and  $\mathbf{T}(\psi) \mathbf{C}$ , respectively, and the matrices  $\mathbf{B}$  and  $\mathbf{C}$  are

$$\mathbf{B} \equiv \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad \mathbf{C} \equiv \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{bmatrix} \quad (17)$$

This substitution will prove useful in the evaluation of the square displacement of position vectors  $(\Delta \mathbf{R}_i)^2$ , which will be summed up to form the  $S$  function, following eq 1. A concise expression for  $(\Delta \mathbf{R}_i)^2$  obtained after a few algebraic manipulations is

$$(\Delta \mathbf{R}_i)^2 = \begin{bmatrix} \Delta \mathbf{r}_i \\ \Delta \psi \\ \Delta \Phi \\ \Delta \mathbf{R}_0 \end{bmatrix}^T \times \begin{bmatrix} 1 & & & & \\ \mathbf{D} \mathbf{r}_i & \dots & & & \\ \mathbf{B} \mathbf{r}_i & \mathbf{D} \mathbf{r}_i \cdot \mathbf{D} \mathbf{r}_i & \dots & & \\ \mathbf{T}(\psi) \mathbf{T}(\Phi) & \mathbf{T}(\psi) \mathbf{T}(\Phi) \mathbf{D} \mathbf{r}_i & \mathbf{B} \mathbf{r}_i \cdot \mathbf{B} \mathbf{r}_i & & \\ & & & & 1 \end{bmatrix} \times \begin{bmatrix} \Delta \mathbf{r}_i \\ \Delta \psi \\ \Delta \Phi \\ \Delta \mathbf{R}_0 \end{bmatrix} \quad (18)$$

where square matrix on the right-hand side is symmetric and the matrix  $\mathbf{D}$  is defined as

$$\mathbf{D} = \mathbf{T}(\Phi)^T \mathbf{C} \mathbf{T}(\Phi) \quad (19)$$

**Minimization of the Cumulative Square Displacements.** The minimization of the cumulative square displacements  $\sum_i (\Delta \mathbf{R}_i)^2$  with respect to differential changes in various degrees of freedom is performed by equating

the partial derivatives of  $S$  with respect to (i)  $\Delta\varphi_m$ , where  $1 \leq m \leq n-1$ , (ii)  $\Delta\psi$  and  $\Delta\Phi$ , and (iii)  $\Delta\mathbf{R}_0$  to zero.

We first consider derivatives with respect to changes in dihedral angles, which using eq 18 may be written as

$$\frac{1}{2} \frac{\partial S}{\partial \Delta\varphi_m} = \sum_{i=1}^n \Delta\mathbf{r}_i \frac{\partial \Delta\mathbf{r}_i}{\partial \Delta\varphi_m} + \sum_{i=1}^n \frac{\partial}{\partial \Delta\varphi_m} (\mathbf{D}\mathbf{r}_i \cdot \Delta\mathbf{r}_i) \Delta\psi + \sum_{i=1}^n \frac{\partial}{\partial \Delta\varphi_m} (\mathbf{B}\mathbf{r}_i \cdot \Delta\mathbf{r}_i) \Delta\Phi + \left( \mathbf{T}(\psi)\mathbf{T}(\Phi) \sum_{i=1}^n \frac{\partial \Delta\mathbf{r}_i}{\partial \Delta\varphi_m} \right) \cdot \Delta\mathbf{R}_0 = 0 \quad (20)$$

Using the expression

$$\frac{\partial \Delta\mathbf{r}_i}{\partial \Delta\varphi_m} = \mathbf{a}_{im} H(m, i) \quad (21)$$

which follows from eq 7, and the definition

$$u_{mj} = \sum_{i=2}^n \mathbf{a}_{im} H(m, i) \cdot \mathbf{a}_{ij} H(j, i) \quad (22)$$

eq 20 reduces to

$$\frac{1}{2} \frac{\partial S}{\partial \Delta\varphi_m} = \sum_{j=1}^{n-1} u_{mj} \Delta\varphi_j + \sum_{i=2}^n H(m, i) (\mathbf{a}_{im} \cdot \mathbf{D}\mathbf{r}_i) \Delta\psi + \sum_{i=2}^n H(m, i) (\mathbf{a}_{im} \cdot \mathbf{B}\mathbf{r}_i) \Delta\Phi + \sum_{i=2}^n H(m, i) (\mathbf{T}(\psi)\mathbf{T}(\Phi) \mathbf{a}_{im} \cdot \Delta\mathbf{R}_0) = 0 \quad (23)$$

This equality is representative of a set of  $n-1$  equations, comprising the derivatives with respect to each  $\Delta\varphi_m$ ,  $1 \leq m \leq n-1$ . If a given rotation  $\Delta\varphi_s$  is imposed on a particular bond  $s$ , eq 23 becomes for each  $m$

$$\left[ \sum_{\substack{j=1 \\ j \neq s}}^{n-1} u_{mj} \Delta\varphi_j \right] + p_m \Delta\psi + w_m \Delta\Phi + \mathbf{v}_m \cdot \Delta\mathbf{R}_0 = -u_{ms} \Delta\varphi_s \quad (24)$$

Here the substitutions

$$p_m \equiv \sum_{i=2}^n H(m, i) (\mathbf{a}_{im} \cdot \mathbf{D}\mathbf{r}_i) \quad (25)$$

$$w_m \equiv \sum_{i=2}^n H(m, i) (\mathbf{a}_{im} \cdot \mathbf{B}\mathbf{r}_i) \quad (26)$$

and

$$\mathbf{v}_m \equiv \mathbf{T}(\psi)\mathbf{T}(\Phi) \sum_{i=2}^n H(m, i) \mathbf{a}_{im} \quad (27)$$

are used for conciseness.

The differentiation of  $S$  with respect to the changes in the external orientational degrees of freedom  $\Delta\psi$  and  $\Delta\Phi$  leads to the following expressions:

$$\frac{1}{2} \frac{\partial S}{\partial \Delta\psi} = \sum_{m=1}^{n-1} p_m \Delta\varphi_m + \sum_{i=0}^n (\mathbf{D}\mathbf{r}_i \cdot \mathbf{D}\mathbf{r}_i) \Delta\psi + \sum_{i=0}^n (\mathbf{D}\mathbf{r}_i \cdot \mathbf{B}\mathbf{r}_i) \Delta\Phi + [\mathbf{T}(\psi)\mathbf{T}(\Phi) \sum_{i=0}^n \mathbf{D}\mathbf{r}_i] \cdot \Delta\mathbf{R}_0 = 0 \quad (28)$$

and

$$\frac{1}{2} \frac{\partial S}{\partial \Delta\Phi} = \sum_{m=1}^{n-1} w_m \Delta\varphi_m + \sum_{i=0}^n (\mathbf{B}\mathbf{r}_i \cdot \mathbf{B}\mathbf{r}_i) \Delta\Phi + \sum_{i=0}^n (\mathbf{B}\mathbf{r}_i \cdot \mathbf{D}\mathbf{r}_i) \Delta\psi + [\mathbf{T}(\psi)\mathbf{T}(\Phi) \sum_{i=0}^n \mathbf{B}\mathbf{r}_i] \cdot \Delta\mathbf{R}_0 = 0 \quad (29)$$

Finally, the derivatives of  $S$  with respect to the components  $\Delta X_0$ ,  $\Delta Y_0$ , and  $\Delta Z_0$  of the translation vector  $\Delta\mathbf{R}_0$  yield three equalities which, in compact notation, read

$$\frac{1}{2} \frac{\partial S}{\partial \Delta\mathbf{R}_0} = \sum_{m=1}^{n-1} \mathbf{v}_m \Delta\varphi_m + [\mathbf{T}(\psi)\mathbf{T}(\Phi) \sum_{i=0}^n \mathbf{D}\mathbf{r}_i] \Delta\psi + [\mathbf{T}(\psi)\mathbf{T}(\Phi) \sum_{i=0}^n \mathbf{B}\mathbf{r}_i] \Delta\Phi + (n+1) \Delta\mathbf{R}_0 = 0 \quad (30)$$

In analogy to eq 24, eqs 28–30 may be readily written in nonhomogeneous form for a fixed change  $\Delta\varphi_s$ , as

$$\sum_{\substack{m=1 \\ m \neq s}}^{n-1} p_m \Delta\varphi_m + \sum_{i=0}^n (\mathbf{D}\mathbf{r}_i \cdot \mathbf{D}\mathbf{r}_i) \Delta\psi + \sum_{i=0}^n (\mathbf{D}\mathbf{r}_i \cdot \mathbf{B}\mathbf{r}_i) \Delta\Phi + [\mathbf{T}(\psi)\mathbf{T}(\Phi) \sum_{i=0}^n \mathbf{D}\mathbf{r}_i] \cdot \Delta\mathbf{R}_0 = -p_s \Delta\varphi_s \quad (31)$$

$$\sum_{\substack{m=1 \\ m \neq s}}^{n-1} w_m \Delta\varphi_m + \sum_{i=0}^n (\mathbf{B}\mathbf{r}_i \cdot \mathbf{B}\mathbf{r}_i) \Delta\Phi + \sum_{i=0}^n (\mathbf{B}\mathbf{r}_i \cdot \mathbf{D}\mathbf{r}_i) \Delta\psi + [\mathbf{T}(\psi)\mathbf{T}(\Phi) \sum_{i=0}^n \mathbf{B}\mathbf{r}_i] \cdot \Delta\mathbf{R}_0 = -w_s \Delta\varphi_s \quad (32)$$

and

$$\sum_{\substack{m=1 \\ m \neq s}}^{n-1} \mathbf{v}_m \Delta\varphi_m + [\mathbf{T}(\psi)\mathbf{T}(\Phi) \sum_{i=0}^n \mathbf{D}\mathbf{r}_i] \Delta\psi + [\mathbf{T}(\psi)\mathbf{T}(\Phi) \sum_{i=0}^n \mathbf{B}\mathbf{r}_i] \Delta\Phi + (n+1) \Delta\mathbf{R}_0 = -\mathbf{v}_s \Delta\varphi_s \quad (33)$$

respectively. The set of  $(n+3)$  equations represented by eq 24 and eqs 31–33 are conveniently organized in matrix notation as

$$\begin{bmatrix} \mathbf{Q}_1 & \mathbf{Q}_2 \\ \mathbf{Q}_2^T & \mathbf{Q}_4 \end{bmatrix} \begin{bmatrix} \Delta\varphi \\ \Delta\mathbf{X} \end{bmatrix} = \begin{bmatrix} \Delta\varphi^0 \\ \Delta\mathbf{X}^0 \end{bmatrix} \quad (34)$$

Here  $\mathbf{Q}_1$  is the symmetric matrix of order  $n-2$

$$\mathbf{Q}_1 \equiv$$

$$\begin{bmatrix} u_{11} & u_{12} & \dots & u_{1,s-1} & u_{1,s+1} & \dots & u_{1,n-2} & u_{1,n-1} \\ u_{21} & u_{22} & \dots & u_{2,s-1} & u_{2,s+1} & \dots & u_{2,n-2} & u_{2,n-1} \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ u_{n-1,1} & u_{n-1,2} & \dots & \dots & \dots & \dots & \dots & u_{n-1,n-1} \end{bmatrix} \quad (35)$$

$\mathbf{Q}_2$  is defined as

$$\mathbf{Q}_2 \equiv \begin{bmatrix} \bar{p}_1 & w_1 & \mathbf{v}_1^T \\ p_2 & w_2 & \mathbf{v}_2^T \\ \dots & \dots & \dots \\ p_{s-1} & w_{s-1} & \mathbf{v}_{s-1}^T \\ p_{s+1} & w_{s+1} & \mathbf{v}_{s+1}^T \\ \dots & \dots & \dots \\ p_{n-1} & w_{n-1} & \mathbf{v}_{n-1}^T \end{bmatrix} \quad (36)$$

and  $\mathbf{Q}_4$  is the  $5 \times 5$  symmetric matrix

$$\mathbf{Q}_4 \equiv \begin{bmatrix} \sum_{i=0}^n \mathbf{D}\mathbf{r}_i \mathbf{D}\mathbf{r}_i & \dots & \dots \\ \sum_{i=0}^n \mathbf{D}\mathbf{r}_i \mathbf{B}\mathbf{r}_i & \sum_{i=0}^n \mathbf{B}\mathbf{r}_i \mathbf{B}\mathbf{r}_i & \dots \\ \mathbf{T}(\psi)\mathbf{T}(\Phi) \sum_{i=0}^n \mathbf{D}\mathbf{r}_i & \mathbf{T}(\psi)\mathbf{T}(\Phi) \sum_{i=0}^n \mathbf{B}\mathbf{r}_i & (n+1)\mathbf{E} \end{bmatrix} \quad (37)$$

with

$$\Delta\varphi \equiv$$

$$\text{col} [\Delta\varphi_1 \ \Delta\varphi_2 \ \Delta\varphi_3 \ \dots \ \Delta\varphi_{s-1} \ \Delta\varphi_{s+1} \ \dots \ \Delta\varphi_{n-2} \ \Delta\varphi_{n-1}] \quad (38)$$

$$\Delta\mathbf{X} \equiv \text{col} [\Delta\psi \ \Delta\Phi \ \Delta X_0 \ \Delta Y_0 \ \Delta Z_0] \quad (39)$$

$$\Delta\varphi^0 \equiv$$

$$-\text{col} [u_{1s} \ u_{2s} \ \dots \ u_{s-1,s} \ u_{s+1,s} \ \dots \ u_{n-2,s} \ u_{n-1,s}] \Delta\varphi_s \quad (40)$$

$$\Delta\mathbf{X}^0 \equiv -\text{col} [p_s \ w_s \ \mathbf{v}_s^T] \Delta\varphi_s \quad (41)$$

Here col denotes the column. Equation 34 is solved for the unknowns  $\Delta\varphi$  and  $\Delta\mathbf{X}$  by inverting the square matrix on the left-hand side and inserting the result in

$$\begin{bmatrix} \Delta\varphi \\ \Delta\mathbf{X} \end{bmatrix} = \begin{bmatrix} \mathbf{Q}_1 & \mathbf{Q}_2 \\ \mathbf{Q}_2^T & \mathbf{Q}_4 \end{bmatrix}^{-1} \begin{bmatrix} \Delta\varphi^0 \\ \Delta\mathbf{X}^0 \end{bmatrix} \quad (42)$$

Here the superscript  $-1$  indicates the inverse of the matrix. Thus, the optimal changes in the dihedral angles and in the absolute location and orientation of the chain segment accompanying the torsional motion of any internal bond  $s$  are computed from eq 42. It should be noted that eq 42 presents the unique solution for a particular internal configuration. The set of torsional angles characterizing that particular configuration is implicitly present in the formulation through the intermediate position vectors  $\mathbf{r}_i$ . To extract information on the mechanism of the local relaxation phenomenon in general, a sufficiently large number of Monte Carlo chains with a variety of initial configurations needs to be generated.

### Discussion and Concluding Remarks

For a chain subject to constrained motion, the equation of motion of the  $i$ th atom reads<sup>16,17</sup>

$$\zeta \mathbf{v}_i = -\nabla_i(U + kT \ln \psi) + \mathbf{P}_i \quad (43)$$

where  $\zeta$  is the friction coefficient,  $\mathbf{v}_i$  is the velocity of the  $i$ th atom,  $\psi$  is the probability distribution function, and  $U$  is the potential energy including hindrances to internal torsional rotations and the external resistance.  $\mathbf{P}_i$  is a constraining force arising from hard potentials associated with constant bond length and bond angles in the case of the freely rotating chain model. In the present zero temperature approximation, contributions from the distribution function drop out of eq 43. The holonomic constraints described by  $\mathbf{P}_i$  are implicitly accounted for in the mathematical formalism developed in the present study. Inasmuch as no conformational barrier to torsional rotations takes place in a freely rotating chain model, the potential  $U$  contains the effect of environmental frictional

resistance only, which is proportional to  $S$  given by eq 1. In the high-friction regime, eq 43 sets the velocity of each atom to the total force on that atom divided by the friction coefficient. A constrained equation of motion emerges from eq 43 if the minimized  $S$  is used in  $U$ . Inasmuch as the final state rather than the time evolution was of interest in the present work, the resulting constrained equation has not been elaborated upon, but only the optimal state succeeding an imposed rotameric transition has been determined.

The set of equations 34–41 corresponds to the case of conformational rearrangements accompanying a well-defined rotation  $\Delta\varphi_s$  imposed on bond  $s$ . However, the mathematical formalism presented above is readily adaptable to the process of conformational transitions subject to other types of restraining or modulating external effects as well. For the case of incremental translations of chain ends, which may be implemented upon uniaxial deformation of network chains, for example, the constraint of fixed displacement of the chain ends is compiled by the introduction of three Lagrange multipliers,  $\lambda_x$ ,  $\lambda_y$ , and  $\lambda_z$ , for the terminal atom. The ascribed displacement of the zeroth atom is asserted by the proper choice of the vector  $\Delta\mathbf{R}_0$ . The problem therefore reduces to the minimization of  $S$  in the presence of the Lagrange multipliers as<sup>12</sup>

$$\partial[S - \lambda \cdot (\Delta\mathbf{R}_n - \Delta\mathbf{R}_{n,\text{ext}})] / \partial\Delta\varphi_m = 0 \quad (44)$$

Here  $\Delta\mathbf{R}_{n,\text{ext}}$  represents the externally imposed displacement of the terminal atom of the chain, and the Lagrange multipliers are conveniently written as  $\lambda = [\lambda_x \ \lambda_y \ \lambda_z]^T$ . The solution of the above set of  $(n-1)$  homogeneous equations, for  $m$  in the range  $1 \leq m \leq n-1$ , together with the three identities in

$$\Delta\mathbf{R}_{n,\text{ext}} = \Delta\mathbf{R}_n = \sum_{j=1}^{n-1} \mathbf{a}_{nj} \Delta\varphi_j + \Delta\mathbf{R}_0 \quad (45)$$

yields the  $(n+2)$  unknowns,  $\Delta\varphi_m$  with  $1 \leq m \leq n-1$ ,  $\lambda_x$ ,  $\lambda_y$ , and  $\lambda_z$ , for the particular case of  $\Delta\psi = \Delta\Phi = 0$ . Incorporation of the rigid body rotations given by the Euler angles  $\Delta\psi$  and  $\Delta\Phi$  is readily achieved by the use of eq 16 for  $\Delta\mathbf{R}_n$  and the consideration of two additional equations, obtained by differentiating the term in brackets in eq 44 with respect to  $\Delta\psi$  and  $\Delta\Phi$ .

In the analysis of internal motions of long chains, the vector  $\Delta\mathbf{X}$  accounting for the external motion according to eq 39 may be safely neglected. In this case, the problem reduces to the solution of the simpler equation

$$\Delta\varphi = \mathbf{Q}_1^{-1} \Delta\varphi^0 \quad (46)$$

where  $\mathbf{Q}_1$ ,  $\Delta\varphi$ , and  $\Delta\varphi^0$  are defined in eqs 35, 38, and 40, respectively.

Inasmuch as the above theory is a first-order approximation applicable to differential changes only, in either external or internal degrees of freedom, the incremental changes  $\Delta\varphi_s$  in the rotational states have to be selected sufficiently small to avoid any nonlinear response. The occurrence of a nonlinear response, if any, may be monitored by observing the magnitude of the  $S$  function during a particular conformational rearrangement. An abrupt change in the latter is indicative of a major, large-amplitude change in the spatial distribution of atoms, which is beyond the range of the applicability of the theory. Incremental changes  $\Delta\varphi_s$  of 0.05 rad have proven to be compatible with the present mathematical framework, as presented in the following paper. For  $\Delta\varphi_s \leq 0.05$  rad, the evolution of the dihedral angles of relevant bonds exhibits

closely the same pattern as a function of  $\varphi_s$ , and hence the adoption of smaller size steps is unnecessary.

In the present work, the kinematics of a segment succeeding a rotameric transition of a given bond was emphasized. However, not only the accommodation of the segment accompanying a complete isomeric jump but the coupled or concerted small-amplitude oscillatory motions—to minimize the energy dissipation under the constraints of chain connectivity and environmental resistance—are also described by the present mathematical model. Those highly correlated motions may be particularly important in the vicinity of the glass transition temperature where free volume limitations hinder large-amplitude rotations and superposition of fast librational motions predominantly operate in local relaxation.<sup>18-21</sup>

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