

# LOCAL-JUMP MODELS FOR CHAIN DYNAMICS\*†

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## ABSTRACT

A previously developed simple stochastic model for the rate of conformational change in freely-jointed chains is extended to a wider class of local processes, and to chains containing atoms or links of several kinds. The long-time relaxation spectrum in every case is just the same as that given by the more familiar beads-and-springs model, but the short-time behaviour depends in more detail on chain structure.

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## INTRODUCTION

The main purpose of this article is to illustrate and extend a treatment of chain dynamics which offers conceptual alternatives to and perhaps physical advantages over the familiar bead-and-spring models for chain diffusion which are recalled under the names of Rouse<sup>1</sup>, Bueche<sup>2</sup>, Kargin and Slonimsky<sup>3</sup>, Zimm<sup>4</sup> and others. It is shown that the slow time-dependent behaviour of a flexible chain molecule is phenomenologically invariant to the fine details of its molecular structure; but that for short times or high frequencies the individual structural features can and must lead to differences in relaxation behaviour.

In previous papers<sup>5,6</sup> a simple stochastic model for chain diffusion was described. The most elementary version deals with a freely-jointed chain, there being no correlations in the directions of neighbouring links, and the local jump process was of a specially simple and restricted kind. Models were also treated which provide correlations between nearest-neighbour links, and it was further shown that a certain kind of kinetic bias could also be introduced without altering the nature of the results. In this paper, while outlining the general nature of the model and recalling some of the earlier results<sup>5,6</sup>, the treatment is extended to a broader class of local processes and to chains whose elements need not all show equiprobable tendencies to relaxation.

It should be mentioned that somewhat related studies have been published by Monnerie and Geny<sup>7</sup>, by Iwata and Kurata<sup>8</sup>, by Verdier<sup>9</sup> and by Anderson<sup>10</sup>.

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## BASIC MODEL

The close connection between the problem of random flights and the process of diffusion has long been known<sup>11</sup>, and it is thus a natural temptation to contemplate models in which the translational, rotational and deformational motions of chain molecules result from repeated local segmental rearrangements distributed randomly along the chain backbone<sup>12</sup>. It appears that G. W. King<sup>13</sup> first suggested the possibility of studying such articulated chain motion by means of computer simulation, but it was Verdier<sup>14</sup> who first carried out such a programme to some incisive degree. Since one of Verdier's principal purposes was and has remained<sup>15</sup> the investigation of the dynamic effects of excluded volume interactions (non-intersecting restrictions for lattice chains), no simple analytical approach was feasible. The elementary results to be described here owe their simplicity to the abandonment of any attempts to treat chains with excluded volume. For further ease, we also ignore any hydrodynamic interactions between chain segments.

Let a simple chain molecule consist of  $N + 1$  beads, joined by  $N$  bonds each of the same length  $l$ . Number the beads from 0 to  $N$  and the bonds from 1 to  $N$ . The direction of the bond from bead  $(i - 1)$  to bead  $i$  is described by the unit vector  $\sigma_i$ . If the spatial position of the zeroth bead is  $r_0$ , then the location and conformation of the molecule is specified by the set of  $N + 1$  vectors  $r_0, \sigma_1, \sigma_2, \dots, \sigma_N$ .

To vary the chain conformation, beads are allowed to move one at a time. For interior beads ( $i \neq 0$  or  $N$ ) the motion of bead  $i$  consists of a jump or 'flip' whereby the vectors  $\sigma_i$  and  $\sigma_{i+1}$  are changed to new values  $\sigma'_i$  and  $\sigma'_{i+1}$ . Terminal beads would require a different specification, but here we are content to deal only with long chains and thus do not trouble with end effects. We shall thus ignore translational motions. A complete treatment can be found elsewhere<sup>5,9</sup>.

Let the probability density in the  $\sigma$ -space that the chain at time  $t$  has the conformation  $\{\sigma_1, \sigma_2, \dots, \sigma_N\} \equiv \{\sigma^N\}$  be designated by  $p(\sigma^N, t)$ . We must now formulate a kinetic or 'master' equation for the rate of change of this probability density. The nature of the treatment, though differing in trivial details, is inspired by and similar to that of Glauber<sup>16</sup> for spin relaxation on a linear Ising lattice. In the present example we shall ignore correlations between neighbouring bond vectors, so that the basic jump process for bead  $i$  depends only on the state of its two bonds to the adjacent beads. Let the conditional probability per unit time that a pair of adjacent bond vectors  $\sigma'_i$  and  $\sigma'_{i+1}$  rotate through an angle  $\phi$  to the new conformation  $\sigma_i, \sigma_{i+1}$  be denoted by  $w_i(\sigma'_i, \sigma'_{i+1} | \sigma_i, \sigma_{i+1})$ . The time evolution of the conformational probability density then follows the master equation

$$\begin{aligned} \partial p(\sigma^N, t) / \partial t = & - \sum_i \int \int p(\sigma^N, t) w_i(\sigma_i, \sigma_{i+1} | \sigma'_i, \sigma'_{i+1}) d\sigma'_i d\sigma'_{i+1} \\ & + \sum_i \int \int p(\sigma_1, \dots, \sigma'_i, \sigma'_{i+1}, \dots, \sigma_N, t) w_i(\sigma'_i, \sigma'_{i+1} | \sigma_i, \sigma_{i+1}) d\sigma_i d\sigma_{i+1} \quad (1) \end{aligned}$$

This is simply an expression of the fact that the rate of change of configuration of the bond vectors in time is the difference between the rates of creation and annihilation.

At equilibrium we have the condition

$$p(\sigma_1, \dots, \sigma'_i, \sigma'_{i+1}, \dots, \sigma_N, \infty) w_i(\sigma'_i, \sigma'_{i+1} | \sigma_i, \sigma_{i+1}) = p(\sigma^N, \infty) w_i(\sigma_i, \sigma_{i+1} | \sigma'_i, \sigma'_{i+1}) \quad (2)$$

Also, at equilibrium the probability density  $p(\sigma^N, \infty)$  for a freely-jointed chain must be a constant, having the same value for all possible sets of the bond vectors. Thus equation 2 shows that

$$w_i(\sigma'_i, \sigma'_{i+1} | \sigma_i, \sigma_{i+1}) = w_i(\sigma_i, \sigma_{i+1} | \sigma'_i, \sigma'_{i+1}) \quad (3)$$

Now let us describe the local jump process more precisely as a rotation of bead  $i$  about an axis passing through beads  $i - 1$  and  $i + 1$ . The old and new bond vectors are then connected by the relations

$$\sigma'_i = \sigma_i \cos^2 \frac{1}{2}\phi + \sigma_{i+1} \sin^2 \frac{1}{2}\phi + (\sigma_i \times \sigma_{i+1}) \sin \phi / \sqrt{2(1 + \sigma_i \cdot \sigma_{i+1})} = f(\sigma_i, \sigma_{i+1}, \phi) \quad (4)$$

$$\sigma'_{i+1} = \sigma_i \sin^2 \frac{1}{2}\phi + \sigma_{i+1} \cos^2 \frac{1}{2}\phi - (\sigma_i \times \sigma_{i+1}) \sin \phi / \sqrt{2(1 + \sigma_i \cdot \sigma_{i+1})} = f(\sigma_{i+1}, \sigma_i, \phi) \quad (5)$$

If the flip rate for rotations through angle  $\phi$  to within  $d\phi$  is expressed as  $\alpha g(\phi) d\phi$ , we then have

$$w_i(\sigma_i, \sigma_{i+1} | \sigma'_i, \sigma'_{i+1}) = \alpha \int_{-\pi}^{\pi} \delta(\sigma'_i - f(\sigma_i, \sigma_{i+1}, \phi)) \delta(\sigma'_{i+1} - f(\sigma_{i+1}, \sigma_i, \phi)) g(\phi) d\phi \quad (6)$$

It is seen that equation 3 is consistent with equation 6 provided that  $g(\phi)$  is an even function, as of course is also necessary on physical grounds.

To extract simple results from the master equation it is convenient, as earlier<sup>5,6</sup>, to work with the average values of bond vectors. Let

$$q_j(t) \equiv \langle \sigma_j(t) \rangle = \int \dots \int \sigma_j p(\sigma^N, t) d\sigma_1 \dots d\sigma_N \quad (7)$$

To evaluate the time-dependence of this quantity, multiply the master equation 1 by  $\sigma_j(t)$  and integrate over all configuration space. Since  $\sigma_j$  may only be reoriented by rotation along with either  $\sigma_{i-1}$  or  $\sigma_{i+1}$ , we obtain the following general expression:

$$\begin{aligned} dq_j/dt = & -q_j \iint w_{j-1}(\sigma_{j-1}, \sigma_j | \sigma'_{j-1}, \sigma'_j) d\sigma'_{j-1}, d\sigma'_j \alpha \\ & - q_j \iint w_j(\sigma_j, \sigma_{j+1} | \sigma'_j, \sigma'_{j+1}) d\sigma'_j d\sigma'_{j+1} \\ & + \int \dots \int d\sigma_1 \dots d\sigma_N \iint \sigma_j p(\sigma_1, \dots, \sigma'_{j-1}, \sigma'_j, \dots, \sigma_N, t) \\ & \times w_{j-1}(\sigma'_{j-1}, \sigma'_j | \sigma_{j-1}, \sigma_j) d\sigma'_{j-1} d\sigma'_j + \int \dots \int d\sigma_1 \dots d\sigma_N \iint \sigma_j \\ & \times p(\sigma_1, \dots, \sigma'_j, \sigma'_{j+1}, \dots, \sigma_N, t) w_j(\sigma'_j, \sigma'_{j+1} | \sigma_j, \sigma_{j+1}) d\sigma'_j d\sigma'_{j+1} \end{aligned} \quad (8)$$

Now using equation 6 for the jump probabilities, and making use of the fact that  $g(\phi)$  is an even function, we find

$$dq_j/dt = -\alpha'(2q_j - q_{j-1} - q_{j+1}) \quad (9)$$

where

$$\alpha' = \alpha \int_{-\pi}^{\pi} g(\phi) \sin^2(\frac{1}{2}\phi) d\phi \quad (10)$$

or in matrix form

$$d\mathbf{q}/dt = -\alpha' A\mathbf{q} \quad (11)$$

in which  $\mathbf{q}$  is a column matrix with the  $q_j$  as elements and  $A$  is the familiar<sup>1</sup> square matrix with elements 2 on the diagonal,  $-1$  just off diagonal, and zero otherwise. This matrix is diagonalized by the transformation  $Q^{-1}AQ = A$ , where

$$Q_{jp} = (2/N)^{1/2} \sin(jp\pi/N) \quad (12)$$

and the eigenvalues of  $A$  are

$$\lambda_p = 4 \sin^2(p\pi/2N) \quad (13)$$

The normal coordinates  $\xi_p(t)$ , as defined by the orthogonal transformation  $\xi = Q\mathbf{q}$ , thus relax exponentially with relaxation times

$$\tau_p = 1/\alpha'\lambda_p \quad (14)$$

in exact mimicry of the bead-and-spring model results<sup>1</sup>. In our earlier work, the flip process had been restricted completely to  $180^\circ$  rotations, i.e. to  $g(\phi) = \delta(\phi \pm \pi)$ , which gives  $\alpha' = \alpha$  in equations 10; but now we see that any mixture of rotation processes will produce the same behaviour. At another extreme, for example, we could pass to the diffusion limit by making  $g(\phi)$  sharply peaked around the origin, which would lead to  $\alpha' = \alpha\langle\phi^2\rangle/4$ .

Although we have avoided direct consideration of the displacement of the chain as a whole, it is easy to relate the model parameters to the translational diffusion coefficient  $D_t$  of the chain. The mean square displacement per unit time of the centre of mass as a result of repeated flip processes, taken over an equilibrium ensemble, is

$$\sum_{i=0}^N \langle w_i(\Delta\mathbf{r}_i)^2 \rangle_{\text{eq}} / (N+1)^2 = 6D_t \quad (15)$$

in which the displacement of bead  $i$  at a flip is

$$\Delta\mathbf{r}_i = l(\sigma'_i - \sigma_i) \quad (16)$$

Performing the calculation, and neglecting the trivial difference between  $N$  and  $N+1$ , we get

$$D_t = \alpha' l^2 / 3N \quad (17)$$

Since the equilibrium mean-square end-to-end displacement of the freely-jointed chain is just

$$\langle r^2 \rangle = Nl^2 \quad (18)$$

the slower relaxation times, i.e. those for which  $p \ll N$ , may be expressed in the form

$$\lambda_p = \langle r^2 \rangle / 3D_t \pi^2 p^2 \quad (19)$$

which is exactly the same as the Rouse result<sup>1</sup>, in terms of the observable quantities  $\langle r^2 \rangle$  and  $D_t$ . The force constants of Hookean springs and the

friction constants of the beads do not appear, any more than do the flip rates of individual bond lengths of our freely-jointed chain model. The two models are both unreal in many ways; but for large scale motions, such that the precise details of chain structure are much smaller than the wavelengths of the low low- $p$  normal coordinates, these unrealities are invisible. As an analogous case we may cite the Debye theory of crystal heat-capacity, which works well for low temperatures where the only important vibrational modes of the crystal are those with wavelengths many times the atomic separations.

A much more elegant formulation has been offered by Iwata<sup>8</sup>, who considers more general local conformational rate processes in more realistic chains. After a 'coarse-graining' operation on his basic master equation, he obtains, for sufficiently slow motions, precisely the diffusion equation of the bead-and-spring model. Thus the physically-based assertions of the previous paragraph can apparently be substantiated quite generally.

### HETEROGENEOUS CHAINS

When we abandon the long-time region of the relaxation spectrum and proceed to higher frequencies, any of the models previously described begins to display features that depend on the structural details assumed. In this region, local-jump models would appear on physical grounds to be more attractive than beads and springs. It was shown earlier<sup>5,6</sup> that at high frequencies the existence of correlations between neighbouring links, i.e. a departure from the strict freedom of the freely-jointed chain, causes systematic deviations from the bead-and-spring relaxation spectrum. We now briefly discuss local-jump models for heterogeneous chains, again finding agreement with Rouse behaviour at long times but systematic differences at short times.

As an elementary example, we consider a freely-jointed chain of two regularly alternating kinds of atoms, with the structure ... ABABAB ... All  $N$  bonds have the same length  $l$ , but the two kinds of atoms can have different jump rates,  $\alpha$  and  $\beta$  respectively. Ignoring end effects, we can proceed as before and find for even-numbered bonds

$$d\mathbf{q}_{2j}/dt = -(\alpha + \beta)\mathbf{q}_{2j} + \beta\mathbf{q}_{2j-1} + \alpha\mathbf{q}_{2j+1} \quad (20)$$

and for odd-numbered bonds

$$d\mathbf{q}_{2j+1}/dt = -(\alpha + \beta)\mathbf{q}_{2j+1} + \alpha\mathbf{q}_{2j} + \beta\mathbf{q}_{2j+2} \quad (21)$$

To find the relaxation times, we can imitate closely the procedure for finding the vibrational frequencies of a linear diatomic lattice<sup>17,18</sup>. The problem differs only in the appearance of first rather than second time-derivatives. Assume solutions of the form:

$$\mathbf{q}_{2j} = A_2 e^{-\lambda(\alpha+\beta)t} e^{-2jik} \quad (22)$$

$$\mathbf{q}_{2j+1} = A_1 e^{-\lambda(\alpha+\beta)t} e^{-(2j+1)ik} \quad (23)$$

where  $k = \pi p/N$  with integral  $p$ , and  $i^2 = -1$ . Substitution into the relaxation equations 20 and 21 leads to two linear equations in the amplitudes

$A_1$  and  $A_2$ . The condition for a non-trivial solution is that the determinant of the coefficients of  $A_1$  and  $A_2$  shall vanish, and this leads to the relation

$$(1 - \lambda)^2 = 1 - 4\theta(1 - \theta) \sin^2 k \quad (24)$$

where  $\theta = \alpha/(\alpha + \beta)$ . This equation possesses two solutions for  $\lambda$ , and thus the  $\lambda(k)$  curve will have two branches, in exact analogy to the acoustical and optical branches of the lattice-vibration problem. It is easy to verify that for the special case  $\alpha = \beta$  the two branches coalesce and the earlier results of equations 13 and 14 are recovered. The greater the disparity between  $\alpha$  and  $\beta$ , the greater the gap in time scale between the slow and fast branches of the relaxation spectrum, as could be seen by generating numerical examples.

The longest relaxation times, obtained when  $k \ll 1$ , are specifically given by

$$\tau_p = \{(\alpha + \beta)/2\alpha\beta\} \{N^2/\pi^2 p^2\} \quad (25)$$

and we see that if one kind of atom is much more sluggish than the other (e.g.  $\beta \ll \alpha$ ), the slowest chain motions are limited by the slowest backbone motions. This result is more comforting than surprising.

The method used earlier for the homogeneous chain to evaluate the translational diffusion coefficient  $D$ , does not lend itself to the present case, and we shall not pursue this question further in this paper.

The general method of Brillouin<sup>18</sup> may be followed in treating chains of any backbone complexity, provided the structure be periodic. A Rouse-type spectrum always obtains for long times, and is clearly a consequence just of the linear connectivity of the chain.

## CONCLUSION

The results displayed in the present paper are little more than didactic exercises. We believe, however, that models of this type can lead to more realistic results than beads and springs in the treatment of short-time relaxation processes, and we hope to confirm this belief in later work.

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- <sup>11</sup> See, for example, S. Chandrasekhar, *Rev. Mod. Phys.* **15**, 1 (1943).
- <sup>12</sup> It is tempting to call this a 'centipede' model, but that would be inaccurate because in the stochastic model the segments move in no unique or specified order.

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