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Effect of the Excluded Volume on the Dynamics of a Polymer Chain

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ABSTRACT: The effect of the excluded volume on the dynamics of a polymer chain is studied, using a stochastic jump model introduced by Orwoll and Stockmayer. The relaxation time of the normal mode of the averaged position vectors is obtained as

$$\tau_p^{-1}=\tau_p^{(0)-1}(1-C_pz)$$

where $\tau_p^{(0)}$ is the relaxation time in the absence of the excluded volume effect, z is the usual excluded volume parameter, and C_p is a constant depending on the mode number p. The slowing down is not so large as in the computer simulation by Verdier. Further, the autocorrelation function of the normal mode of the averaged position vectors is shown to be a simple exponential function, in contrast to the nonexponential form used by Verdier. These differences are due partly to the particularity of the lattice model used by Verdier and partly to the approximations we have used.

KEY WORDS Excluded Volume Effect / Relaxation Time / Slowing Down / Freely Jointed Chain Model / Lattice Model /

A polymer molecule in solution suffers frictional as well as random forces from surrounding solvent molecules and moves irregularly. To investigate the effect of such Brownian motion on the dynamics of a polymer molecule, a bead-and-spring model was proposed by Rouse[1] in 1953 and independently by Bueche[2] in 1954. This model was improved so as to take account of the hydrodynamic interaction[3-7] and of the excluded volume effect.[5-7] In regard to the excluded volume effect, however, the theory is still not satisfactory, as will be mentioned later. On the other hand, Verdier and Stockmayer[8] presented a stochastic jump model on a cubic lattice to study the dynamics of a polymer in solution by computer simulation. Later Verdier[9] investigated this model precisely and found that in the absence of the excluded volume effect the relaxation curve of the autocorrelation function of the end-to-end distance is quite similar to that of the Rouse model. Verdier[10] confirmed this agreement by calculating numerically the autocorrelation function of the square of the normal mode of the position vectors. This agreement was also explained analytically by Iwata and Kurata[11] for the lattice model and by Orwoll and Stockmayer[12] and by Verdier[13] for the freely jointed chain. The latter model will be explained in the next section.

The effect of the excluded volume on the dynamics of a polymer is not as well understood as is the effect of the excluded volume on the equilibrium polymer configurations. The excluded volume effect on the polymer dynamics was investigated by Tschoegl[4] in the Rouse model only indirectly, through the introduction of a nongaussian distribution of the lengths between consective beads. Verdier and his coworkers[8-10,14] made a computer simulation of the dynamics of a lattice polymer by taking account of the excluded volume effect in such a way that a bead cannot make a jump into a position which is already occupied by another bead. The purpose of this paper is to investigate analytically the effect of the excluded volume on the dynamics of a polymer in solu-

tion, employing the freely jointed chain model presented by Orwoll and Stockmayer. One of the results of Verdier, *et al.*, is that the relaxation of certain correlation functions is slowed down by factors from 2 (for the number of beads $n=8$) to 20 (for $n=64$). This slowing down is fairly large. Another result is that certain correlation functions do not decay exponentially as they do in the absence of the excluded volume effect. The cause for such large slowing down for a polymer on the cubic lattice was analyzed by Hilhorst and Deutch[15] and is attributed mainly to the next-nearest-neighbor excluded volume interactions. In a freely jointed chain model the larger second-neighbor excluded volume interactions which appear in a lattice polymer can be avoided. Consequently a freely jointed chain model is more realistic than the polymer model constrained on a cubic lattice.

MASTER EQUATION AND TRANSITION PROBABILITY

Let a polymer molecule be composed of $n+1$ beads linked by n bonds. The beads are numbered from 0 to n along the chain and the position vector of the ith bead is denoted as $\boldsymbol{r}_i$. Then a configuration of the polymer is specified by a set of $n+1$ position vectors $(\boldsymbol{r}_0, \boldsymbol{r}_1, \ldots, \boldsymbol{r}_n)\equiv\{\boldsymbol{r}\}$. It is also specified by a set of n bond vectors $(\boldsymbol{b}_1, \boldsymbol{b}_2, \ldots, \boldsymbol{b}_n)\equiv\{\boldsymbol{b}\}$ defined by

$$\boldsymbol{b}_i=\boldsymbol{r}_i-\boldsymbol{r}_{i-1} \quad \text{for} \quad i=1, 2, \ldots, n \qquad (1)$$

The vector $\boldsymbol{r}_i$ is written in terms of the bond vectors as

$$\boldsymbol{r}_i=\boldsymbol{r}_0+\boldsymbol{b}_1+\boldsymbol{b}_2+\cdots+\boldsymbol{b}_i \quad \text{for} \quad i=1, 2, \ldots, n \qquad (2)$$

Both sets of vectors will be at our disposal in the following.

Following Orwoll and Stockmayer,[12] we assume that the ith bead can jump with the transition probability w_i to the new position $\boldsymbol{r}_i'$ given by

$$\boldsymbol{r}_i'=\boldsymbol{r}_{i-1}+\boldsymbol{r}_{i+1}-\boldsymbol{r}_i \quad \text{for} \quad i=1, 2, \ldots, n-1 \qquad (3a)$$

$$\boldsymbol{r}_0'=2\boldsymbol{r}_1-\boldsymbol{r}_0 \qquad (3b)$$

$$\boldsymbol{r}_n'=2\boldsymbol{r}_{n-1}-\boldsymbol{r}_n \qquad (3c)$$

(see Figure 1). This jump can also be represented in terms of bond vectors as the jump from $\boldsymbol{b}_i$, $\boldsymbol{b}_{i+1}$ to $\boldsymbol{b}_i'$, $\boldsymbol{b}_{i+1}'$; these are given by

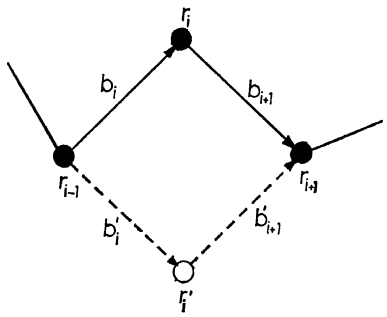

Figure 1a. The jump of the ith beads from $\boldsymbol{r}_i$ to $\boldsymbol{r}_i'$.

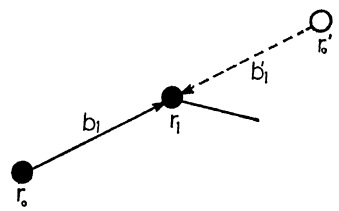

Figure 1b. The jump of a terminal bead (0th bead) from $\boldsymbol{r}_0$ to $\boldsymbol{r}_0'$.

$$\boldsymbol{b}_i'=\boldsymbol{b}_{i+1}, \quad \boldsymbol{b}_{i+1}'=\boldsymbol{b}_i \quad \text{for} \quad i=2, 3, \ldots, n-1 \qquad (4a)$$

$$\boldsymbol{b}_0'=-\boldsymbol{b}_0, \quad \boldsymbol{b}_n'=-\boldsymbol{b}_n \qquad (4b)$$

Let $P(\{\boldsymbol{r}\}, t)$ be the probability density that the configuration of the polymer is $\{\boldsymbol{r}\}$ at a time t. Then this probability density obeys the following master equation:

$$\frac{\partial P(\{\boldsymbol{r}\}, t)}{\partial t}=-\sum_{i=0}^{n} w_i P(\{\boldsymbol{r}\}, t) + \sum_{i=0}^{n} w_i' P(\boldsymbol{r}_0 \cdots \boldsymbol{r}_i' \cdots \boldsymbol{r}_n, t) \qquad (5)$$

where w_i (or w_i') is the transition probability for the jump of the ith bead from $\boldsymbol{r}_i$ to $\boldsymbol{r}_i'$ (or from $\boldsymbol{r}_i'$ to $\boldsymbol{r}_i$). The transition probability must satisfy the detailed balance condition:

$$w_i P^{\mathrm{eq}}(\{\boldsymbol{r}\})=w_i' P^{\mathrm{eq}}(\boldsymbol{r}_0 \cdots \boldsymbol{r}_i' \cdots \boldsymbol{r}_n) \qquad (6)$$

where P^{eq} is the equilibrium distribution function having the following form:

$$P^{\mathrm{eq}}(\{\boldsymbol{r}\})=\mathcal{N}\prod_{i=1}^{n}\exp\left(-\frac{3|\boldsymbol{r}_i-\boldsymbol{r}_{i-1}|^2}{2b^2}\right)\times\exp\left(-\frac{U}{k_{\mathrm{B}}T}\right) \qquad (7)$$

Here $\mathcal{N}$ is the normalization constant and b is the bond length. U is the excluded volume potential and is assumed to be the sum of the two-body-force potentials.

$$U=\sum_{i<j} u(\boldsymbol{r}_i-\boldsymbol{r}_j) \tag{8}$$

Substituting eq 7 into eq 6 and using eq 8 and 3a—3c, the detailed balance condition can be rewritten as

$$\frac{w_i'}{w_i}=\frac{\exp\left[-\frac{1}{k_BT}\sum_j u(\boldsymbol{r}_i-\boldsymbol{r}_j)\right]}{\exp\left[-\frac{1}{k_BT}\sum_j u(\boldsymbol{r}_i'-\boldsymbol{r}_j)\right]} \quad (i=0, 1, \ldots, n) \tag{9}$$

If we put

$$w_i=\alpha\exp\left[-\frac{1}{k_BT}\sum_j u(\boldsymbol{r}_i'-\boldsymbol{r}_j)\right] \quad \text{for } i=1, 2, \ldots, n-1 \tag{10a}$$

$$w_0=\gamma\exp\left[-\frac{1}{k_BT}\sum_j u(\boldsymbol{r}_0'-\boldsymbol{r}_j)\right] \tag{10b}$$

$$w_n=\gamma\exp\left[-\frac{1}{k_BT}\sum_j u(\boldsymbol{r}_n'-\boldsymbol{r}_j)\right] \tag{10c}$$

the detailed balance condition is satisfied, where α and γ are assumed as constants independent of the position vectors. The choice of the form of eq 10a—10c is not unique and thus α or γ may depend on the position vectors, provided that the detailed balance condition is satisfied. We can take into account the hydrodynamic interaction by considering α as a proper function of bond vectors.[12] But we exclude this possibility. If $u(\boldsymbol{r}_i'-\boldsymbol{r}_j)$ is the hard-core potential with the diameter a, that is

$$u(\boldsymbol{r}_i'-\boldsymbol{r}_j)=\infty \quad \text{for} \quad |\boldsymbol{r}_i'-\boldsymbol{r}_j|<a \tag{11a}$$

and

$$u(\boldsymbol{r}_i'-\boldsymbol{r}_j)=0 \quad \text{for} \quad |\boldsymbol{r}_i'-\boldsymbol{r}_j|\geq a \tag{11b}$$

eq 10a becomes

$$w_i=0 \quad \text{for} \quad |\boldsymbol{r}_i'-\boldsymbol{r}_j|<a \tag{12a}$$

and

$$w_i=\alpha \quad \text{for} \quad |\boldsymbol{r}_i'-\boldsymbol{r}_j|\geq a \tag{12b}$$

This implies that the transition probability is zero if the ith bead jumps to a position which is already occupied by any other bead, and the transition probability is a constant α if the ith bead jumps to a position which is vacant. In this way the direct effect of the excluded volume on the motion of the beads is taken into account.

We rewrite the transition probabilities given by eq 10a—10c into more tractable forms by introducing the Mayer's f-function:

$$\exp\left[-\frac{1}{k_BT}u(\boldsymbol{r}_i'-\boldsymbol{r}_j)\right]=1+f(\boldsymbol{r}_i'-\boldsymbol{r}_j) \tag{13}$$

Substituting eq 13 into eq 10a and assuming that f is small, we obtain

$$w_i=\alpha[1+\sum_j f(\boldsymbol{r}_i'-\boldsymbol{r}_j)] \tag{14}$$

The Mayer's f-function is approximated by

$$f(\boldsymbol{r}_i'-\boldsymbol{r}_j)=-v\delta(\boldsymbol{r}_i'-\boldsymbol{r}_j) \tag{15}$$

Here v is the excluded volume, given by

$$v=\frac{4\pi a^3}{3}\left(1-\frac{\Theta}{T}\right), \tag{16}$$

where Θ is the Flory temperature. From eq 14 and 15 we obtain the final form of the transition probability:

$$w_i=\alpha[1-v\sum_j \delta(\boldsymbol{r}_i'-\boldsymbol{r}_j)] \quad (i=1, 2, \ldots, n-1) \tag{17a}$$

and

$$w_0=\gamma[1-v\sum_j \delta(\boldsymbol{r}_0'-\boldsymbol{r}_j)] \tag{17b}$$

$$w_n=\gamma[1-v\sum_j \delta(\boldsymbol{r}_n'-\boldsymbol{r}_j)] \tag{17c}$$

EQUATIONS OF MOTION FOR THE AVERAGED POSITION VECTORS

The equations of motion for the averaged position vectors defined by

$$\boldsymbol{q}_k\equiv\langle\boldsymbol{r}_k\rangle=\int \mathrm{d}\{\boldsymbol{r}\}\boldsymbol{r}_k P(\{\boldsymbol{r}\}, t) \tag{18}$$

are obtained from eq 5 by multiplying by $\boldsymbol{r}_k$ and integrating over all possible configurations. Since the terms for $i\neq k$ in the summation vanish, we obtain

$$\frac{\mathrm{d}\boldsymbol{q}_k}{\mathrm{d}t}=-\langle w_k(-\boldsymbol{r}_{k-1}+2\boldsymbol{r}_k-\boldsymbol{r}_{k+1})\rangle \tag{19a}$$

for $k=1, 2, \ldots, n-1$ and

$$\frac{d\boldsymbol{q}_0}{dt}=-2\langle w_0(\boldsymbol{r}_0-\boldsymbol{r}_1)\rangle \tag{19b}$$

$$\frac{d\boldsymbol{q}_n}{dt}=-2\langle w_n(\boldsymbol{r}_n-\boldsymbol{r}_{n-1})\rangle \tag{19c}$$

where use is made of eq 3a—3c.

Substituting the transition probabilities given by eq 17a—17c, eq 19a—19c can be written as

$$\frac{d\boldsymbol{q}_k}{dt}=-\alpha(-\boldsymbol{q}_{k-1}+2\boldsymbol{q}_k-\boldsymbol{q}_{k+1}) +\alpha v\sum_j\langle\delta(\boldsymbol{r}_k'-\boldsymbol{r}_j)(-\boldsymbol{r}_{k-1}+2\boldsymbol{r}_k-\boldsymbol{r}_{k+1})\rangle \tag{20a}$$

for $k=1, 2, \ldots, n-1$ and

$$\frac{d\boldsymbol{q}_0}{dt}=-2\gamma(\boldsymbol{q}_0-\boldsymbol{q}_1) +2\gamma v\sum_j\langle\delta(\boldsymbol{r}_0'-\boldsymbol{r}_j)(\boldsymbol{r}_0-\boldsymbol{r}_1)\rangle \tag{20b}$$

$$\frac{d\boldsymbol{q}_n}{dt}=-2\gamma(\boldsymbol{q}_n-\boldsymbol{q}_{n-1}) +2\gamma v\sum_j\langle\delta(\boldsymbol{r}_n'-\boldsymbol{r}_j)(\boldsymbol{r}_n-\boldsymbol{r}_{n-1})\rangle \tag{20c}$$

Now we put

$$\boldsymbol{I}_j=\langle\delta(\boldsymbol{r}_k'-\boldsymbol{r}_j)(-\boldsymbol{r}_{k-1}+2\boldsymbol{r}_k-\boldsymbol{r}_{k+1})\rangle \tag{21}$$

which is equal to

$$\boldsymbol{I}_j=\langle\delta(\boldsymbol{b}_{j+1}+\boldsymbol{b}_{j+2}+\cdots+\boldsymbol{b}_{k-1}+\boldsymbol{b}_{k+1})(\boldsymbol{b}_k-\boldsymbol{b}_{k+1})\rangle \tag{22a}$$

for $j<k$ and

$$\boldsymbol{I}_j=\langle\delta(\boldsymbol{b}_k+\boldsymbol{b}_{k+2}+\cdots+\boldsymbol{b}_{j-1}+\boldsymbol{b}_j)(\boldsymbol{b}_k-\boldsymbol{b}_{k+1})\rangle \tag{22b}$$

for $j>k$.

Introducing the integral representation of the δ-function

$$\delta(\boldsymbol{b})=\int\frac{d\boldsymbol{k}}{(2\pi)^3}e^{i\boldsymbol{k}\cdot\boldsymbol{b}} \tag{23}$$

we have for $j<k$

$$\boldsymbol{I}_j=\int\frac{d\boldsymbol{k}}{(2\pi)^3}\langle\exp[i\boldsymbol{k}\cdot(\boldsymbol{b}_{j+1} +\boldsymbol{b}_{j+2}+\cdots+\boldsymbol{b}_{k-1}+\boldsymbol{b}_{k+1})](\boldsymbol{b}_k-\boldsymbol{b}_{k+1})\rangle \tag{24}$$

If we may assume as a first approximation that there are no correlations between bond vectors, this can be rewritten as

$$\boldsymbol{I}_j=\int\frac{d\boldsymbol{k}}{(2\pi)^3}\langle\exp(i\boldsymbol{k}\cdot\boldsymbol{b}_{j+1})\rangle\langle\exp(i\boldsymbol{k}\cdot\boldsymbol{b}_{j+2})\rangle\cdots \langle\exp(i\boldsymbol{k}\cdot\boldsymbol{b}_{k-1})\rangle \times[\langle\exp(i\boldsymbol{k}\cdot\boldsymbol{b}_{k+1})\rangle\langle\boldsymbol{b}_k\rangle-\langle\exp(i\boldsymbol{k}\cdot\boldsymbol{b}_{k+1})\boldsymbol{b}_{k+1}\rangle] \tag{25}$$

The characteristic function $\langle\exp(i\boldsymbol{k}\cdot\boldsymbol{b})\rangle$ in the above expression is approximately calculated as the characteristic function of a Gaussian distribution function with the average $\langle\boldsymbol{b}\rangle=\boldsymbol{b}'$ and the variance $\langle(\boldsymbol{b}-\boldsymbol{b}')^2\rangle=\langle\boldsymbol{b}^2\rangle-\boldsymbol{b}'^2\simeq b^2$, if $\boldsymbol{b}'^2\ll\langle\boldsymbol{b}^2\rangle=b^2$. Thus

$$\langle\exp(i\boldsymbol{k}\cdot\boldsymbol{b})\rangle=\exp\left(-\frac{b^2}{b}\boldsymbol{k}^2+i\boldsymbol{k}\cdot\boldsymbol{b}'\right) \tag{26}$$

and

$$\langle\exp(i\boldsymbol{k}\cdot\boldsymbol{b})\boldsymbol{b}\rangle=\left(\boldsymbol{b}'+\frac{b^2}{3}i\boldsymbol{k}\right)\exp\left(-\frac{b^2}{b}\boldsymbol{k}^2+i\boldsymbol{k}\cdot\boldsymbol{b}'\right) \tag{27}$$

Substituting eq 26 and 27 into eq 25 we obtain

$$\boldsymbol{I}_j=\int\frac{d\boldsymbol{k}}{(2\pi)^3}\exp\left[-\frac{(k-j)b^2}{b}\boldsymbol{k}^2+i\boldsymbol{k}\cdot(\boldsymbol{b}'_{j+1}+\boldsymbol{b}'_{j+2}+\cdots+\boldsymbol{b}'_{k-1}+\boldsymbol{b}'_{k+1})\right] \times\left[\boldsymbol{b}_k'-\left(\boldsymbol{b}'_{k+1}+\frac{b^2}{3}i\boldsymbol{k}\right)\right] \tag{28}$$

Performing the integral over $\boldsymbol{k}$ and neglecting the higher order terms of $\boldsymbol{b}'$, $\boldsymbol{I}_j$ becomes the following:

$$\begin{aligned}\boldsymbol{I}_j&=\left(\frac{3}{2\pi b^2}\right)^{3/2}\frac{1}{(k-j)^{3/2}}\left[\boldsymbol{b}_k'-\boldsymbol{b}'_{k+1} +\frac{1}{k-j}(\boldsymbol{b}'_{j+1}+\boldsymbol{b}'_{j+2}+\cdots+\boldsymbol{b}'_{k-1}+\boldsymbol{b}'_{k+1})\right]\\ &=\left(\frac{3}{2\pi b^2}\right)^{3/2}\frac{1}{(k-j)^{3/2}}\left[-\boldsymbol{q}_{k-1}+2\boldsymbol{q}_k-\boldsymbol{q}_{k+1} +\frac{1}{k-j}(\boldsymbol{q}_{k-1}+\boldsymbol{q}_{k+1}-\boldsymbol{q}_k-\boldsymbol{q}_j)\right]\end{aligned} \tag{29}$$

In a similar manner we obtain $\boldsymbol{I}_j$ for $j>k$:

$$\boldsymbol{I}_j=\left(\frac{3}{2\pi b^2}\right)^{3/2}\frac{1}{(j-k)^{3/2}}\left[-\boldsymbol{q}_{k-1}+2\boldsymbol{q}_k-\boldsymbol{q}_{k+1} +\frac{1}{j-k}(\boldsymbol{q}_{k-1}+\boldsymbol{q}_{k+1}-\boldsymbol{q}_k-\boldsymbol{q}_j)\right] \tag{30}$$

Using eq 22a, 22b, 29, and 30, eq 20a—20c are given as follows:

$$\begin{aligned}\frac{1}{\alpha}\frac{d\boldsymbol{q}_k}{dt}&=-(-\boldsymbol{q}_{k-1}+2\boldsymbol{q}_k-\boldsymbol{q}_{k+1})\\ &\quad-\beta\left[(a_k-b_k)\boldsymbol{q}_{k-1}-(2a_k-b_k)\boldsymbol{q}_k+(a_k-b_k)\boldsymbol{q}_{k+1}\right.\\ &\quad\left.+\sum_{j=0}^{k-2}\frac{\boldsymbol{q}_j}{(k-j)^{5/2}}+\sum_{j=k+2}^{n}\frac{\boldsymbol{q}_j}{(j-k)^{5/2}}\right]\end{aligned} \tag{31a}$$

$$\frac{1}{\gamma}\frac{d\boldsymbol{q}_0}{dt}=-2(\boldsymbol{q}_0-\boldsymbol{q}_1)-2\beta\Big[(d_1-c_1)\boldsymbol{q}_0+(c_1-2d_1)\boldsymbol{q}_1+\sum_{j=2}^{n}\frac{\boldsymbol{q}_j}{j^{5/2}}\Big] \tag{31b}$$

$$\frac{1}{\gamma}\frac{d\boldsymbol{q}_n}{dt}=-2(\boldsymbol{q}_n-\boldsymbol{q}_{n-1})-2\beta\Big[(d_2-c_2)\boldsymbol{q}_n+(c_2-2d_2)\boldsymbol{q}_{n-1}+\sum_{j=0}^{n-2}\frac{\boldsymbol{q}_j}{(n-j)^{5/2}}\Big] \tag{31c}$$

where

$$\beta=v\left(\frac{3}{2\pi b^2}\right)^{3/2} \tag{32}$$

and a_k, b_k, c_1, d_1, c_2, and d_2 are given by

$$a_k=\sum_{j=0}^{k-2}\frac{1}{(k-j)^{3/2}}+\sum_{j=k+2}^{n}\frac{1}{(j-k)^{3/2}}\simeq 2\left(\sqrt{2}-\frac{1}{k^{1/2}}-\frac{1}{(n-k)^{1/2}}\right) \tag{33a}$$

$$b_k=\sum_{j=0}^{k-2}\frac{1}{(k-j)^{5/2}}+\sum_{j=k+2}^{n}\frac{1}{(j-k)^{5/2}}\simeq\frac{2}{3}\left(\frac{1}{\sqrt{2}}-\frac{1}{k^{3/2}}-\frac{1}{(n-k)^{3/2}}\right) \tag{33b}$$

$$c_1=\sum_{j=2}^{n}\frac{1}{j^{3/2}}\simeq 2\left(\frac{1}{\sqrt{2}}-\frac{1}{n^{1/2}}\right) \tag{33c}$$

$$d_1=\sum_{j=2}^{n}\frac{1}{j^{5/2}}\simeq\frac{2}{3}\left(\frac{1}{2\sqrt{2}}-\frac{1}{n^{3/2}}\right) \tag{33d}$$

$$c_2=\sum_{j=0}^{n-2}\frac{1}{(n-j)^{3/2}}=c_1 \tag{33e}$$

$$d_2=\sum_{j=0}^{n-2}\frac{1}{(n-j)^{5/2}}=d_1 \tag{33f}$$

Here we replaced the summation by the integral. These equations can be written in a vector notation:

$$\frac{1}{\alpha}\frac{d\boldsymbol{q}}{dt}=-(\mathbf{A}+\beta\mathbf{B})\boldsymbol{q} \tag{34}$$

where

$$\boldsymbol{q}=\begin{bmatrix}\boldsymbol{q}_0\\ \boldsymbol{q}_1\\ \vdots\\ \boldsymbol{q}_n\end{bmatrix}\qquad \mathbf{A}=\begin{bmatrix}1&-1&0&0&&&\\ -1&2&-1&0&&&\\ 0&-1&2&-1&&&\\ &&&\ddots&\ddots&&\\ &&&&-1&2&-1\\ &&&&0&-1&1\end{bmatrix} \tag{35}$$

and the elements of $\mathbf{B}$ are given by

$$\mathbf{B}_{00}=d_1-c_1,\qquad \mathbf{B}_{01}=(c_1-2d_1),$$
$$\mathbf{B}_{0j}=\frac{1}{j^{5/2}}\quad(2\le j\le n),$$
$$\mathbf{B}_{kk}=b_k-2a_k\quad(1\le k\le n-1),$$
$$\mathbf{B}_{kk-1}=\mathbf{B}_{kk+1}=a_k-b_k\quad(1\le k\le n-1),$$
$$\mathbf{B}_{kj}=\frac{1}{(k-j)^{5/2}}\quad(0\le j\le k-2,\ j+2\le k\le n-1),$$
$$\mathbf{B}_{kj}=\frac{1}{(j-k)^{5/2}}\quad(k+2\le j\le n,\ 1\le k\le j-2),$$
$$\mathbf{B}_{nn}=d_1-c_1,\qquad \mathbf{B}_{nn-1}=c_1-2d_1,$$
$$\mathbf{B}_{nj}=\frac{1}{(n-j)^{5/2}}\quad(0\le j\le n-2), \tag{36}$$

RELAXATION TIME

We define the normal mode of the averaged position vectors by

$$\boldsymbol{u}=\mathbf{Q}^{-1}\boldsymbol{q} \tag{37}$$

where $\boldsymbol{u}$ is a $(n+1)\times 1$ column matrix whose p th elements is the p th normal mode $\boldsymbol{u}_p$ and $\mathbf{Q}$ is a $(n+1)\times(n+1)$ matrix which diagonalizes the matrix $\mathbf{A}+\beta\mathbf{B}$ in eq 34. Then the relaxation time of the p th normal mode is given by

$$\tau_p^{-1}=\alpha\lambda_p \tag{38}$$

and

$$\boldsymbol{u}_p(t)=\boldsymbol{u}_p(0)\exp(-t/\tau_p) \tag{39}$$

where λ_p is the p th eigenvalue of the eigenvalue equation

$$(\mathbf{A}+\beta\mathbf{B})\boldsymbol{a}=\lambda\boldsymbol{a} \tag{40}$$

We can solve eq 40 by a perturbation method, assuming that β is small. The eigenvalue and eigenvectors of the matrix $\mathbf{A}$ are obtained exactly and are given by

$$\lambda_p^{(0)}=4\sin^2\frac{p\pi}{2(n+1)}\quad p=0,\ 1,\ \ldots,\ n \tag{41}$$

and

$$\mathbf{Q}_{pk}^{(0)}=\left(\frac{2}{n+1}\right)^{1/2}\cos\frac{(k+1/2)p\pi}{n+1}\qquad k=0,\ 1,\ \ldots,\ n \tag{42}$$

where $\mathbf{Q}_{pk}^{(0)}$ is the k th component of the eigenvector $\boldsymbol{a}_p^{(0)}$. Then the eigenvalues of eq 40

can be obtained:

$$\lambda_p=\lambda_p^{(0)}+\beta \boldsymbol{a}_p^{(0)\mathrm{T}}\cdot\mathbf{B}\cdot\boldsymbol{a}_p^{(0)} + \beta^2 \sum_{p\neq p'} \frac{\boldsymbol{a}_p^{(0)\mathrm{T}}\cdot\mathbf{B}\cdot\boldsymbol{a}_{p'}^{(0)}\boldsymbol{a}_{p'}^{(0)\mathrm{T}}\cdot\mathbf{B}\cdot\boldsymbol{a}_p^{(0)}}{\lambda_p^{(0)}-\lambda_{p'}^{(0)}}+\cdots \quad (43)$$

where the superscript T denotes the transpose of the eigenvector.

We calculate the first order term of β in eq 43:

$$\lambda_p^{(1)}=\beta\boldsymbol{a}_p^{(0)\mathrm{T}}\cdot\mathbf{B}\cdot\boldsymbol{a}_p^{(0)}=\beta\sum_{k=0}^{n}\sum_{j=0}^{n}\mathrm{Q}_{pk}^{(0)}\mathrm{B}_{kj}\mathrm{Q}_{jp}^{(0)} = -\beta\frac{(p\pi)^2}{n^{3/2}}C_p \quad (44)$$

where $n\gg 1$ is assumed and eq 36 and 42 are used. C_p is given by

$$C_p=\frac{8}{3}\frac{1}{(p\pi)^2}\left[2(1-(-1)^p)+2\pi p^{1/2}S(2p\pi) -\frac{5\sqrt{2}\pi}{2}p^{1/2}S(p\pi)+\sqrt{2}\pi^2p^{3/2}C(p\pi)\right] \quad (45)$$

where

$$S(x)=\int_0^x\frac{\sin t}{(2\pi t)^{1/2}}\mathrm{d}t\,, \qquad C(x)=\int_0^x\frac{\cos t}{(2\pi t)^{1/2}}\mathrm{d}t \quad (46)$$

Fixman also derived the same form for C_p as given by eq 45 in the theory of the Rouse model with the excluded volume effect (eq 76 in ref 6). The relaxation time for the slow mode given by eq 38 becomes, up to the first order of β:

$$\tau_p^{-1}=\tau_p^{(0)-1}(1-C_pz) \quad (47)$$

where

$$\tau_p^{(0)-1}=\alpha\left(\frac{p\pi}{n}\right)^2 \quad (48)$$

is the relaxation time for the slow mode in the absence of the excluded volume effect and

$$z=v\left(\frac{3}{2\pi b^2}\right)^{3/2}n^{1/2} \quad (49)$$

α can be related to the translational diffusion constant D[12] by

$$D=\frac{\alpha b^2}{3(n+1)} \quad (50)$$

From the Einstein relation $D=k_\mathrm{B}T/(n+1)\zeta$, α can also be written as

$$\alpha=\frac{3k_\mathrm{B}T}{\zeta b^2} \quad (51)$$

Table I. Values of C_p for the mode numbers p from 1 to 6

p	C_p
1	1.516
2	1.170
3	0.993
4	0.878
5	0.796
6	0.733

where ζ is a frictional constant. If eq 51 is substituted into eq 48, $\tau_p^{(0)}$ gives the relaxation time of the Rouse model.

From eq 47 it is found that the relaxation time for the slow mode can be expanded in powers of the excluded volume parameter z at least up to the first order. Since $C_p>0$, the relaxation time becomes larger in the presence of the excluded volume effect than in its absence. The cause of this slowing down is that jumps into the positions occupied already by other beads are forbidden because of the excluded volume restriction.

The numerical values of C_p are shown in Table I for the values of p from 1 to 6. Since the value for smaller p is always larger than the value for larger p, the effects of the excluded volume are larger for the slow modes than for the fast modes. The ratio of the slowest relaxation time τ_1 to the fastest relaxation time τ_n becomes

$$\tau_1/\tau_n\simeq n^2(1-C_1z)^{-1}>n^2 \quad (52)$$

which means that the width of the spectrum of the relaxation time is broader in the presence of the excluded volume effect than in its absence. The relaxation function $H(\tau)$, when τ_p is regarded as a continuous function of p for large n, is given by

$$H(\tau)=-ck_\mathrm{B}T(\mathrm{d}\ln\tau/\mathrm{d}p)^{-1} \quad (53)$$

where c is the polymer concentration. From eq 47, 45, and 53 this function is approximately given, in the case $z\ll 1$, by

$$H(\tau)\simeq\frac{ck_\mathrm{B}Tn}{2\pi}\tau^{-1/2}\left(1-\frac{\sqrt{2}}{3}\left(\frac{\pi}{n}\right)^{1/2}z\tau^{1/4}\right) \quad (54)$$

In deriving this, use was made of the approximation $C_p\simeq(8\sqrt{2}/3)C(p\pi)/p^{1/2}$ which is valid

Table II. Ratios $\tau_p/\tau_p^{(0)}$ for various p and n

p	n			
	64	32	16	8
1	2.64	1.78	1.45	1.28
2	1.92	1.51	1.32	1.20
3	1.67	1.40	1.26	1.17
4	1.56	1.34	1.22	1.15
5	1.48	1.30	1.20	1.13
6	1.43	1.27	1.18	1.12

Table III. Ratios $\tau_p/\tau_p^{(0)}$ by Verdier

p	n			
	64	32	16	8
1	21.0	6.13	2.62	1.34
2	21.7	8.75	4.08	2.79
3	19.5	7.23	3.96	2.12
4	15.5	5.91	2.90	1.97
5	13.2	4.90	2.79	1.19
6	10.5	4.31	2.08	1.23

for $p>1$ and also the fact that $C(p\pi)\simeq 0.5$ irrespective of p for $p>1$. The slope of the graph $\ln H(\tau)$ *vs.* $\ln\tau$ becomes

$$\frac{\mathrm{d}\ln H(\tau)}{\mathrm{d}\ln\tau}=-\frac{1}{2}-\frac{\sqrt{2}}{3}\left(\frac{\pi}{n}\right)^{1/2}z\tau^{1/4} \qquad (55)$$

where $-1/2$ is the value in the absence of the excluded volume effect and agrees with the value of the Rouse model for the free draining case. The second term of eq 55 is the correction in the presence of the excluded volume effect; this term decreases the slope. This means that the excluded volume effect has an effect similar to the hydrodynamic interaction, which also decreases the slope.

In Table II the ratios of the relaxation time τ_p in the presence of the excluded volume effect to the relaxation time $\tau_p^{(0)}$ in its absence are shown for the number of beads $n=8$, 16, 32, and 64 and for the mode numbers p from 1 to 6. These values are calculated from eq 47 assuming a hard core excluded volume potential and $a/b=1/3$, in other words $\beta=0.0512$. In Table III the same ratios calculated by Verdier[10] by Monte Carlo computer simulations are shown. From these Tables II and III it is clear that our calculation does not show such a large slowing down as does the Monte Carlo calculation. One of the reasons for this disagreement is the particularity of the lattice model employed by Verdier. As pointed out by Hilhorst *et al.*,[15] the large slowing down in Verdier's computation is mainly due to the second-nearest-neighbor excluded volume interaction. In the freely jointed chain model, the effect of the second-nearest-neighbor excluded volume interaction on the slowing down does not become so large as in the lattice model.

The autocorrelation function of the normal modes $\boldsymbol{u}_p$, which is defined by

$$f(\boldsymbol{u}_p,\boldsymbol{u}_p)=\frac{\langle\boldsymbol{u}_p(0)\cdot\boldsymbol{u}_p(t)\rangle}{\langle\boldsymbol{u}_p^{\,2}\rangle} \qquad (56)$$

becomes

$$f(\boldsymbol{u}_p,\boldsymbol{u}_p)=\exp(-t/\tau_p) \qquad (57)$$

where use is made of eq 39. Thus the autocorrelation function of normal modes $\boldsymbol{u}_p$ is a simple exponential type. The origin of this fact is the linear approximation with respect to the averaged bond vector $\boldsymbol{b}'$, which permits the existence of normal modes even in the presence of the excluded volume effect. In Verdier's results[10] the relaxation curve for this autocorrelation function is supposed to be nonexponential, although it is not calculated explicitly. This disagreement comes from the linear approximation. If we do not use this approximation, we will obtain nonlinear equations for the averaged position vectors, which will lead to a nonexponential relaxation curve.

CONCLUSION

We have derived the relaxation time of the normal mode of the averaged position vectors of beads in the presence of the excluded volume effect under the assumptions: (1) the excluded volume v is not too large, (2) the system is not too far from equilibrium, and (3) the equations of motion for the averaged position vectors can be linearized. One of the results obtained is that for a suitable choice of parameter β the relaxation of the normal mode of the averaged position vectors of beads is slowed down by factors from 1.1 for $n=8$ to 2.6 for $n=64$. The autocorrelation function of the normal

mode of the averaged position vectors of the beads, however, decays exponentially, as in the case of the Rouse model, without the excluded volume effect. This is contrary to Verdier's computer experiments. These differences are considered to be due to the particularity of the lattice model employed by Verdier and the approximation we have used. A freely jointed chain model is considered more realistic, as mentioned already in the Introduction.

In a similar way it will be possible to discuss the intrinsic viscosity of freely jointed chain with the excluded volume effect. This problem is now under study.

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