Analysis of Monte Carlo results on the kinetics of lattice polymer chains with excluded volume*

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Monte Carlo calculations by Verdier *et al.* on the kinetics of polymer chains on a lattice have shown a large increase of relaxation times in the presence of excluded volume restrictions, i.e., when two beads of the chain cannot occupy the same lattice site. We show that these long relaxation times must be attributed to the specific choice of the kinetics rather than to the intrinsic nature of the excluded volume interaction. A simplified analytic model which preserves the essential characteristics of the kinetics of Verdier's model reproduces qualitatively the Monte Carlo results for the realxation of the squares of the Rouse coordinates.

I. INTRODUCTION

The influence of excluded volume on the dynamics of polymer chains in solution is much less well understood than the influence of excluded volume on equilibrium polymer configurations. The simplest model of a polymer where the excluded volume effect can be investigated is the representation of a polymer chain of $N+1$ units as a random path of N steps on a simple cubic lattice. The $N+1$ occupied lattice sites on the path are the polymer "beads," and the excluded volume interaction imposes the condition that no two beads of the chain can occupy the same lattice site (see Figs. 1 and 2).

In recent years, in an extremely valuable series of papers,[1–4] Verdier and co-workers have examined a stochastic generalization of this model where the Brownian motion of the polymer beads is simulated by a kinetic scheme for the jumps of single beads. Since the stochastic time evolution cannot be solved analytically, Verdier has turned to extensive Monte Carlo computer simulations. The computer simulations show that the dynamic lattice model without excluded volume behaves remarkably similarly to the predictions of the Rouse model, which is the simplest model for polymer motion in the absence of excluded volume.[5–7] This agreement has been explained analytically by Iwata and Kurata,[8] by Orwoll and Stockmayer,[9] and by Verdier.[10]

However, the Monte Carlo calculations on lattice chains with excluded volume show a very different behavior. It is found that the relaxation of equilibrium correlation functions related to the over-all chain shape is slowed down by factors ranging from 2 for $N=7$ to 20 for chains with $N=63$. Furthermore, certain correlation functions which decay exponentially in the absence of excluded volume become strongly nonexponential in the presence of excluded volume restrictions.

To our knowledge, these important computer "experiments" on the dynamics of chains with excluded volume have not been interpreted. In this paper we take a first step toward explaining these results. In Sec. II we analyze the kinetics of the stochastic model employed by Verdier in the Monte Carlo simulation. We argue that the influence of excluded volume, as introduced by Verdier, should change the time scale for relaxation from the N^2 dependence found without excluded volume to at least N^3. One of our major conclusions is that this strong slowing-down effect is due to the particular choice of kinetics adopted by Verdier rather than to the intrinsic nature of the excluded volume interaction. By "intrinsic nature" of the excluded volume interaction, we mean the interaction between beads at large distances (measured along the chain), which arises owing to the folding back of the chain. There are many kinetic schemes that are consistent with the correct excluded volume restrictions on polymer configurations; Verdier has selected a kinetic scheme that results in particularly strong slowing down.

In Sec. III a simple model is constructed that contains the features that in Sec. II were found to be essential in Verdier's model. The N^3 time scale is built into the model, which is then used to test further characteristics of the computer results. Mathematically, this simplified model is closely related to the "tube model" introduced by De Gennes in a different context.[11] It can be solved analytically, and we show that it leads to relaxation curves which exhibit the same characteristics as those found in the Monte Carlo studies.

II. VERDIER'S MODEL FOR RELAXATION OF LATTICE POLYMERS

A. Description of the stochastic model

We number the beads along the chain from 0 to N, and denote by $\mathbf{r}_n$ the position of the nth bead. It is convenient to set the lattice constant equal to unity and to choose $\mathbf{r}_n$ to have integer coordinates $r_{n\alpha}(\alpha = x, y, z)$.

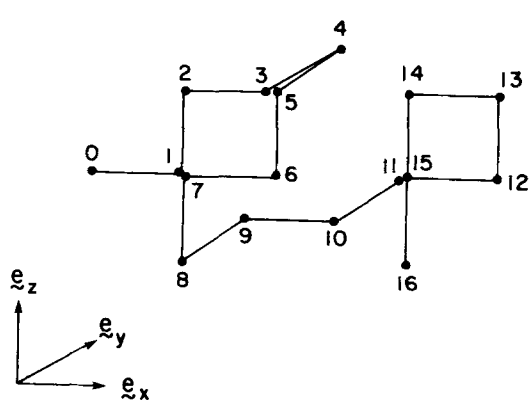

FIG. 1. Lattice polymer chain of length $N=16$ without excluded volume. Beads occupying the same lattice site have been drawn as distinct dots for clarity.

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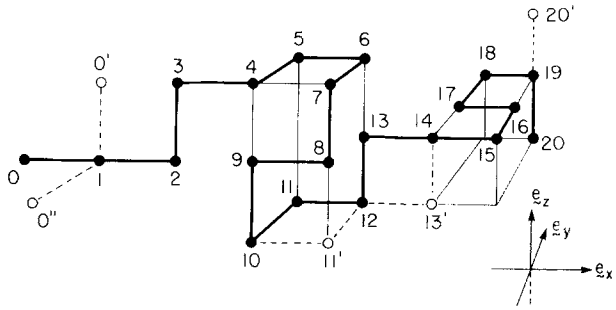

FIG. 2. Lattice polymer chain of length $N=20$ with excluded volume. To suggest perspective a few extra lines have been drawn. The extrema in this chain are listed in Table I. Some examples of allowed flips are those of bead 11 to position 11′, of bead 13 to 13′, of 0 to 0′ or 0″, and of 20 to 20′. Disallowed are, e.g., flips of bead 3, due to excluded volume interaction with 9, and of 6, due to excluded volume interaction with 4. The effects of flips on the extrema may be illustrated by the following examples. The flip $11 \rightarrow 11'$ transforms the x minimum (9,10,11) into (9,10) and the y minimum (7,8,9,10) into (7,8,9,10,11). The flip $0 \rightarrow 0'$ creates the z minimum (1,2), which "enters" the chain. The flip $0 \rightarrow 0''$ does not exchange the extrema. The flip $10 \rightarrow 20'$ destroys the z maximum (13,14,15,16,17,18,19), which "leaves" the chain.

The stochastic time dependence of the chain configuration in Verdier's computer studies is generated according to the following rules.[1-4,12]

A bead is picked at random and its position $\mathbf{r}_n$ on the lattice is determined. This bead is then "flipped" with probability f_n from its position $\mathbf{r}_n$ to the new position

$$\mathbf{r}_n' \equiv \mathbf{r}_{n-1} + \mathbf{r}_{n+1} - \mathbf{r}_n \tag{2.1}$$

(see Fig. 2). Note that if the chain segments $\mathbf{r}_n - \mathbf{r}_{n-1}$ and $\mathbf{r}_{n+1} - \mathbf{r}_n$ are perpendicular, the nth bead flips to the diagonally opposite corner of the square determined by these segments in three-dimensional space. Clearly, a flip preserves the chain structure, i.e., the $(n+1)$th and $(n-1)$th beads remain nearest neighbors of the nth bead on the lattice. If a terminal bead is picked, it is moved with probability f_0 (or f_N) to a different position $\mathbf{r}_0'$ (or $\mathbf{r}_N'$), randomly selected from among the several positions which it can occupy while preserving the chain structure.

In the kinetic model without excluded volume, one sets all f_n equal to 1. In the model with excluded volume, one has $f_n = 0$ if the site $\mathbf{r}_n'$ is already occupied by another bead of the chain, and $f_n = 1$ otherwise (see Fig. 2 for examples).

The process of picking a bead at random and deciding whether or not it moves to a new position is called a bead cycle. After completion of a bead cycle, a new one can begin according to the same rules. To make the connection with real time t, we may consider a bead cycle as a (successful or unsuccessful) attempt by a solvent molecule to change the position of a polymer bead. Assuming that all beads suffer the same number of collisions with solvent molecules per unit time, we are led to identify a bead cycle with $(N+1)^{-1}$ unit of time. Hence, in the case without excluded volume, where all bead cycles are successful, each bead flips with frequency 1. In the presence of excluded volume this frequency is lowered.

Verdier has undertaken Monte Carlo calculations on this model for chains with lengths up to $N=63$. He has considered equilibrium time correlation functions of such quantities as the square of the end-to-end distance $\mathbf{R}_N$,[1-3] and the squares of the Rouse coordinates $\mathbf{u}_p$.[4] The Rouse coordinates are those linear combinations of the bead positions $\mathbf{r}_n$ which decay purely exponentially in the Rouse model,[5,7] and it is of interest to see how their decay is affected by excluded volume.

B. Analysis of the stochastic model

In order to analyze the kinetics described in the preceding subsection, we introduce some new terminology. We shall call the vector $\mathbf{a}_n \equiv \mathbf{r}_n - \mathbf{r}_{n-1}$ the nth bond vector of the chain. A chain configuration is then specified by the N bond vectors $\mathbf{a}_1, \mathbf{a}_2, \ldots, \mathbf{a}_N$. Each bond vector $\mathbf{a}_n$ has one of the six values $\pm\mathbf{e}_x$, $\pm\mathbf{e}_y$, $\pm\mathbf{e}_z$, where $\mathbf{e}_\alpha$ is the unit vector in the α direction ($\alpha = x, y, z$). A flip of the nth bead ($n = 1, 2, \ldots, N-1$) evidently interchanges the nth and the $(n+1)$th bond.

Hence, the kinetics may be viewed as a diffusion of bonds along the chain, a picture already put forward by De Gennes[13] and others.[14-16] Only a flip of one of the two end beads can destroy a bond while creating a new one in its place. The new bond may then diffuse into the chain.

In chains without excluded volume there are no restrictions on the bead flips. All bonds have the same probability per unit time to move one step along the chain in either direction. Hence each single bond performs a random walk along the chain with step size 1 and step frequency 2 (as there are always two bead flips possible which change the position of a bond). Since the average bond has to travel $\sim N$ steps before being destroyed at either chain end, it will take a time $\tau \sim N^2$ before it leaves the chain and is replaced by a random one. As the end to end distance $\mathbf{R}_N = \sum_{n=1}^{N} \mathbf{a}_n$ is just the sum of all bonds, it will also decay on time scale N^2. This is the well-known result of the Rouse model,[7] which is reproduced by Monte Carlo studies of lattice chains without excluded volume.[2,3]

In the presence of excluded volume the situation is different. The configurations $(\mathbf{a}_1, \ldots, \mathbf{a}_N)$ cannot be arbitrary, but are restricted by the $N(N+1)/2$ excluded volume conditions

$$\sum_{m=n}^{n'} \mathbf{a}_m \neq 0, \qquad 1 \leq n < n' \leq N. \tag{2.2}$$

We shall see that these conditions, in conjunction with the kinetics of only single bead flips selected by Verdier, result in certain crucial constraints on the chain motion. We identify these constraints as the dominant factor in the slowing down observed in the computer simulations. These constraints apply to subchains formed by a sequence of beads, say $(n, n+1, \ldots, n+k)$, that all lie in the same plane with fixed α coordinate, while the α coordinates of the immediately adjacent

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TABLE I. Extrema with their coordinates in the chain of Fig. 2. It is assumed that the 0th bead is located at the origin. The densities ρ_α are in this case given by $\rho_x=\frac{4}{20}=0.2$, $\rho_y=\frac{2}{20}=0.1$, $\rho_z=\frac{3}{20}=0.15$.

Nature of extremum	Location	Coordinate
x maximum	(6, 7, 8)	$x=4$
x maximum	(15, 16)	$x=7$
x minimum	(9, 10, 11)	$x=3$
x minimum	(17, 18)	$x=6$
y maximum	(5, 6)	$y=1$
y minimum	(7, 8, 9, 10)	$y=0$
z maximum	(3, ···, 7)	$z=1$
z maximum	(13, ···, 19)	$z=0$
z minimum	(10, 11, 12)	$z=-1$

beads $(n-1)$ and $(n+k+1)$ are both lower or both higher (see Fig. 2 and Table I). We shall call such a subchain an α minimum or an α maximum. Mathematically, a subchain $(n, n+1, \ldots, n+k)$ with $1 \leq n < n+k \leq N-1$ and $k=1, 2, \ldots$ is called an α extremum if

(i) $\mathbf{a}_l \neq \pm \mathbf{e}_\alpha$ for $l=n+1, n+2, \ldots, n+k$,

(ii) $\mathbf{a}_n = -\mathbf{a}_{n+k+1} = \mathbf{e}_\alpha$ or $\mathbf{a}_n = -\mathbf{a}_{n+k+1} = -\mathbf{e}_\alpha$.

Evidently, α maxima and α minima cannot overlap and must alternate along the chain. The average density ρ_α of α extrema on the chain and the average number m_α of beads in an extremum may be estimated from randomly drawn configurations. We roughly estimate $m_\alpha \simeq 3$ and $\rho_\alpha \simeq 0.12$/unit length, both independent of α.

From the basic rules of motion of the chain, one can deduce that the time-dependent behavior of the α extrema is subject to a number of (mostly self-evident) rigorous constraints (see Fig. 2):

(1) Owing to bead flips, the number of beads in a given α extremum may grow or decrease by one at a time, but can never become less than two.

(2) Extrema cannot disappear or be created except at the chain ends due to flips of the beads 0 and N.

(3) Extrema can move along the chain, but α maxima and α minima (with the same α) cannot pass each other (nor even overlap), thus always staying disjoint and maintaining their alternating order along the chain.

(4) The α coordinate of an α extremum is conserved while it moves along the chain.

(5) A given bond $\mathbf{e}_\alpha$ (or $-\mathbf{e}_\alpha$) initially located between an α minimum and an α maximum remains located between these same extrema during their motion along the chain.

To establish (1) it suffices to realize that an α extremum of two beads $n-1$ and n implies a local chain configuration $\mathbf{a}_{n-1}$, $\mathbf{a}_n$, $\mathbf{a}_{n+1}$ with $\mathbf{a}_{n-1} = \pm \mathbf{e}_\alpha$, $\mathbf{a}_n \neq \pm \mathbf{e}_\alpha$, and $\mathbf{a}_{n+1} = \mp \mathbf{e}_\alpha$. In this configuration, flips of the beads $n-1$ and n are forbidden owing to excluded volume interaction with their second nearest neighbors $n+1$ and $n-1$, respectively. This is illustrated in Figs. 3(a) and 3(b) for a two-dimensional case. Constraints (2) and (3) mean that the α extrema can be considered as separate entities randomly moving along the chain with a hard core repulsion between them. It should be noted that extrema belonging to different coordinates α and α' may overlap as well as pass each other. Constraint (4) is of crucial importance. It means that an α extremum on its random motion along the chain "forces" the beads that it passes to occupy lattice sites with its own α coordinate. Therefore, at any time t, the α coordinate of a given bead is equal to the coordinate of the α extrema in which the bead is contained, or lies between the α coordinates of the α extrema between which the bead lies. Since a long chain contains a large number of α extrema ($\sim \rho_\alpha N$ for each α), it suffices to know the locations of the α extrema on the chain, as well as their α coordinates, to reconstruct the shape of the chain over distances $\gtrsim 1/\rho_\alpha$.

C. Relaxation with excluded volume

We wish to determine, as a function of the chain length N, the time scale on which the end-to-end distance decays. This is, as before, the time needed for the average bond to diffuse over a distance N or, by

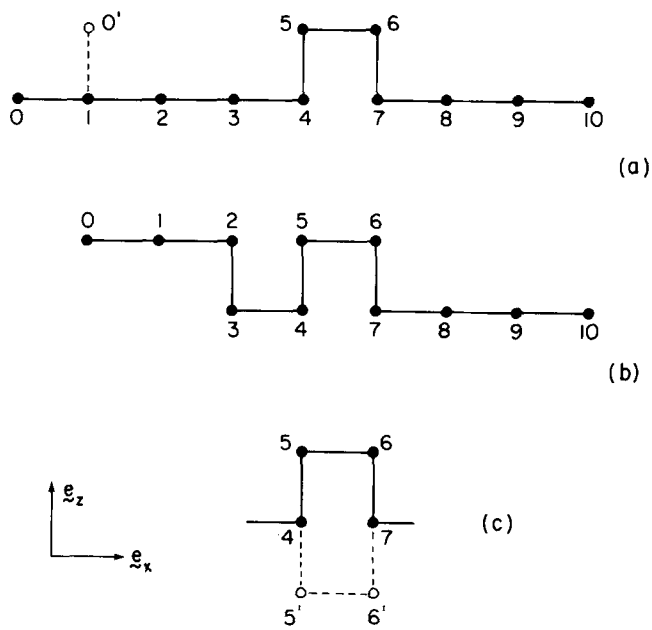

FIG. 3. Lattice polymer chain of length $N=10$ with excluded volume, for simplicity drawn in the xz plane. (a) Bead 0 is chosen as the origin of the coordinate system. The only extremum contained in the chain is the z maximum (5, 6), with coordinate $z=1$. This maximum may increase in length (e.g., by successive flips of beads 4, 7, ···) or be displaced (e.g., by successive flips of 4, 6, 3, 5, 2, 4). However, it cannot disappear unless it diffuses towards a chain end. The flip $0 \rightarrow 0'$ creates the z minimum (1, 2, 3, 4) with coordinate $z=0$. If subsequently the beads 1 and 2 flip, this minimum takes the position (3, 4) as shown in (b). (b) The z extrema with coordinates 0 and 1, located at (3, 4) and (5, 6), respectively, cannot pass each other. They act as two random walkers with a hard core repulsion. (c) The situation would be fundamentally different if the kinetics would allow for "double flips" of the type ($5 \rightarrow 5'$, $6 \rightarrow 6'$). In such a case the extrema and their coordinates would no longer be conserved. In Verdier's model it is the next nearest neighbor excluded volume interaction between 5 and 7, and between 6 and 4, which is responsible for the conservation of the extrema and their coordinates.

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constraint (5), the time needed for the average α extremum to diffuse over a distance N. The random motion of the extrema along the chain is of course coupled to the complete chain configuration $(\mathbf{a}_1, \mathbf{a}_2, \ldots, \mathbf{a}_N)$. So far our discussion has been rigorous. We shall now assume that each α extremum may be considered as a random walker on a line of length $\sim N$, performing steps of size ~ 1 with frequency ~ 1, and subject only to the condition that it cannot pass its neighboring random walkers. At the chain ends random walkers may diffuse out of the chain and new ones randomly enter so as to keep the average random walker density at its value ρ_α. This approximation ignores, apart from certain inessential details, the intrinsic (long range) effect of the excluded volume interaction, i.e., the possibility that owing to folding back of the chain two extrema at large separation measured along the chain may still interact. The effect of this interaction is that certain otherwise possible moves of the extrema are blocked, and hence it tends to increase the time needed for chain relaxation. Our picture of random walkers will therefore lead to an underestimation of the relaxation time.

Since each walker is confined between its two neighbors, its steps are not random but (negatively) correlated. To find the relaxation time it therefore no longer suffices to consider just one random walker, as we did in the case without excluded volume. Instead, we must consider the collective translational motion along the chain of all random walkers. We can characterize this motion by a variable

$$k_\alpha(t) = (N\rho_\alpha)^{-1} \sum_i k_i^\alpha(t) , \tag{2.3}$$

where i runs through all random walkers, and $k_i^\alpha(t)$ denotes the displacement along the chain of the ith random walker from its position at an initial time $t=0$. For convenience we shall imagine here that random walkers which leave the chain at one end enter at the same time at the other end. Whenever a neighboring pair of random walkers i and $i+1$ blocks each other, both the possibility for a step to the left $(k_{i+1} \to k_{i+1} - 1)$ and the possibility for a step to the right $(k_i \to k_i + 1)$ are lost. The changes in $k_\alpha(t)$ therefore always have equal probability to be negative or positive. The individual changes in $k_\alpha(t)$ will be of order N^{-1} because of the factor $(N\rho_\alpha)^{-1}$ appearing in the expression for the collective displacement. The frequency of changes in $k_\alpha(t)$ is of order N because this collective variable is the sum of N individual variables, each changing with frequency 1. Hence the root mean square displacement $d(t)$ of $k_\alpha(t)$ is given by

$$d(t) \sim N^{-1}(Nt)^{1/2} = (N^{-1}t)^{1/2} . \tag{2.4}$$

Owing to the inability of the random walkers to pass each other, the displacement of each individual random walker is equal to $k_\alpha(t)$, the displacement of the collective coordinate, if we disregard local fluctuations. Hence Eq. (2.4) also represents the root mean square displacement of a single random walker which represents an extremum; in the absence of the excluded volume constraint this identification is not possible. Thus the excluded volume condition associated with the constraints (1)–(5) above enters by the identification of the motion of a typical random walker with the motion of the collective coordinate $k_\alpha(t)$.

It follows from Eq. (2.4) that the time t_N needed for an extremum to diffuse over a distance $d(t_N) \sim N$ is proportional to N^3. We conclude that the relaxation time of the end-to-end distance, and of any other quantity related to the over-all shape of the chain, should therefore also be proportional to (at least) N^3. Table II shows that the Monte Carlo results obtained by Verdier[2,4] indeed satisfy this relation. Deviations from the exponent 3 are positive rather than negative and should be attributed to the intrinsic (long range) excluded volume interaction.

It should be realized that our picture of random walkers with nearest neighbor interactions is based upon the constraints (1)–(5), produced by the single-flip kinetics together with the next nearest neighbor excluded volume restriction. It does not account for the extra slowing-down effect to be expected from what we have called the intrinsic excluded volume interaction. Nevertheless it explains the larger part of the slowing down found in Verdier's computer experiments.

We emphasize that it is easy to imagine modified kinetic models in which the excluded volume interaction does not lead to the constraints (1)–(5). One example of such a modified model is obtained by allowing in Verdier's model, in addition to the single-bead transitions, an elementary transition of the "crankshaft" type [see Fig. 3(c)]. The possibility of crankshaft transitions removes the constraints (1)–(5) upon which our discussion of this section is based. If Verdier's model is so modified, we have no reason to expect a decay on time scale N^3, but would rather expect to see the much subtler effect of the intrinsic excluded volume interaction.

III. AN EQUIVALENT MODEL

In the preceding analysis we have aimed to capture the essential characteristics of the single-flip kinetic model of lattice polymers with excluded volume. We expect that even a simplified model which preserves these characteristics should reproduce the qualitative features of the Monte Carlo calculations. To investigate this, we adopt a model closely related to one introduced by De Gennes in a different context.[11]

TABLE II. Values of the decay times $\tau(A)/N^3$, defined by $C(A; \tau(A)N/^3\pi^2\theta) = e^{-1}$, as found by Verdier (values for $A = \mathbf{u}_p^2$ as given by Table IV of Ref. 4, and values for $A = \mathbf{R}_N^2$ extracted from Fig. 1 of Ref. 2. The times are expressed as multiples of 10^{-3} real time units [or $10^{-3}(N+1)$ bead cycles]. According to the theory of Sec. II, $\tau(A)/N^3$ for fixed A should tend to a constant as $N \to \infty$. Deviations from such behavior should be attributed to the "intrinsic" excluded volume and increase as N gets larger.

N	$N^{-3}\tau(\mathbf{R}_N^2)$	$N^{-3}\tau(\mathbf{u}_1^2)$	$N^{-3}\tau(\mathbf{u}_2^2)$
15	5.2	9.1	3.6
31	5.4	10.3	3.8
63	6.1	16.1	4.5

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Let $\mathbf{r}(\nu)$ with $0 \leq \nu \leq N$ be a continuous polymer chain with units chosen such that

$$\mathbf{a}^2(\nu) = (\partial \mathbf{r}/\partial \nu)^2 = 1 . \tag{3.1}$$

Then the chain length is

$$\int_0^N d\nu \, |\mathbf{a}(\nu)| = \int_0^N d\nu \sqrt{\left(\frac{\partial \mathbf{r}}{\partial \nu}\right)^2} = N . \tag{3.2}$$

The Rouse coordinates are given by

$$\begin{aligned} \mathbf{u}_p &= \frac{1}{N} \int_0^N d\nu \cos \frac{\pi p \nu}{N} \mathbf{r}(\nu) \\ &= -\frac{1}{\pi p} \int_0^N d\nu \sin \frac{\pi p \nu}{N} \mathbf{a}(\nu), \qquad p = 1, 2, \ldots \end{aligned} \tag{3.3}$$

The end-to-end distance $\mathbf{R}_N$ is expressed as

$$\mathbf{R}_N = \mathbf{r}(N) - \mathbf{r}(0) = \int_0^N d\nu \, \mathbf{a}(\nu) . \tag{3.4}$$

Before passing to the kinetics we shall define the equilibrium statistics of the chain. We have seen that the excluded volume effect that we wish to describe influences Verdier's results mainly through the *kinetic* properties of his model: the excluded volume kinetics was shown to modify the relaxation time by a factor $\sim N$, whereas it is known that in equilibrium the averages of squared end-to-end distance[1-3,17] and the squared Rouse coordinates[18] are modified by factors of only $\sim N^{1/5}$. Hence we incur only a minor error if we employ for $\mathbf{a}(\nu)$ the probability measure for a chain without excluded volume. This measure is obtained as

$$P[\mathbf{a}(\nu)] = \lim_{b \to 0} \lim_{\mathbf{a}^b \to \mathbf{a}} P^b[\mathbf{a}^b] , \tag{3.5}$$

where $\mathbf{a}^b \equiv (\mathbf{a}_1^b, \mathbf{a}_2^b, \ldots, \mathbf{a}_{N/b}^b)$ is a chain of length N on a simple cubic lattice with lattice constant b, and

$$\begin{aligned} P^b[\mathbf{a}^b] &= \prod_{n=0}^{N/b} p^b(\mathbf{a}_n^b) , \\ p^b(\mathbf{a}_n) &= \tfrac{1}{6}(\delta_{a_{nx},b} + \delta_{a_{nx},-b})\delta_{a_{ny},0}\delta_{a_{nz},0} \\ &\quad + \tfrac{1}{6}(\delta_{a_{ny},b} + \delta_{a_{ny},-b})\delta_{a_{nz},0}\delta_{a_{nx},0} \\ &\quad + \tfrac{1}{6}(\delta_{a_{nz},b} + \delta_{a_{nz},-b})\delta_{a_{nx},0}\delta_{a_{ny},0} . \end{aligned} \tag{3.6}$$

From Eq. (3.6) one easily finds the equilibrium correlation

$$\begin{aligned} &\langle a_{n\alpha}^b \rangle^b = 0 , \\ &\langle a_{n\alpha}^b a_{m\alpha'}^b \rangle^b = \tfrac{1}{3}\delta_{\alpha\alpha'}\delta_{nm} , \end{aligned} \tag{3.7}$$

whence we have for the continuous chain

$$\begin{aligned} &\langle a_\alpha(\nu) \rangle = 0 , \\ &\langle a_\alpha(\nu) a_{\alpha'}(\mu) \rangle = \tfrac{1}{3}\delta_{\alpha\alpha'}\delta(\nu - \mu) . \end{aligned} \tag{3.8}$$

In an analogous way we find the four point correlation function, which will be needed in the sequel,

$$\begin{aligned} \langle a_\alpha(\nu) a_\alpha(\nu') a_\beta(\mu) a_\beta(\mu') \rangle &= \tfrac{1}{9}\delta(\nu - \nu')\delta(\mu - \mu') \\ &\quad + \tfrac{1}{9}\delta_{\alpha\beta}[\delta(\nu - \mu)\delta(\nu' - \mu') + \delta(\nu - \mu')\delta(\nu' - \mu)] \\ &\quad + \tfrac{1}{9}[\delta_{\alpha\beta} - 1]\delta(\nu - \nu')\delta(\mu - \mu')\delta(\nu - \mu) \end{aligned} \tag{3.9}$$

From Eqs. (3.3), (3.4), (3.8), and (3.9) we find the equilibrium values of the squares and fourth powers of the end-to-end length and the Rouse coordinates.

$$\begin{aligned} &\langle \mathbf{R}_N^2 \rangle = N , \\ &\langle (\mathbf{R}_N^2)^2 \rangle = \tfrac{5}{3}N^2 + \mathcal{O}(N) , \\ &\langle \mathbf{u}_p^2 \rangle = N/(2\pi^2 p^2) , \\ &\langle (\mathbf{u}_p^2)^2 \rangle = 5N^2/(12\pi^4 p^4) + \mathcal{O}(N) . \end{aligned} \tag{3.10}$$

We now turn to the time dependence of the chain. We shall consider the bond vector $\mathbf{a}(\nu)$ as the sum of its three Cartesian projections $\mathbf{a}_\alpha(\nu)$, and imagine that the vectors $\mathbf{a}_\alpha(\nu)$ perform diffusive motion along the chain. The time-dependent chain configuration will be denoted by $\mathbf{r}(\nu, t)$. Let the local minima and maxima of the function $r_\alpha(\nu, t)$ occur at $\ldots, \nu_i^\alpha(t), \nu_{i+1}^\alpha(t), \nu_{i+2}^\alpha(t), \ldots$. An essential characteristic of Verdier's model is that these extrema move while conserving their extremal values, i.e.,

$$r_\alpha(\nu_i^\alpha(t), t) = r_\alpha(\nu_i^\alpha(0), 0) \quad \text{for all } t , \tag{3.11}$$

and while conserving their order, i.e.,

$$\cdots < \nu_i^\alpha(t) < \nu_{i+1}^\alpha(t) < \cdots \quad \text{for all } t . \tag{3.12}$$

The simplest way to incorporate the properties (3.11) and (3.12) into our model is to postulate that in a time t all bond vectors $\mathbf{a}_\alpha(\nu)$ diffuse over the same distance $k_\alpha(t)$, which was defined in Sec. II. Hence we have the kinetic equation

$$\begin{aligned} \mathbf{a}_\alpha(\nu, t) &= \mathbf{a}_\alpha(\nu - k_\alpha(t), 0) \\ &\equiv \mathbf{a}_\alpha(\nu - k_\alpha(t)), \qquad \text{with } k_\alpha(0) = 0 . \end{aligned} \tag{3.13}$$

This kinetic equation neglects fluctuations in the relative distances between the positions of the $\mathbf{a}_\alpha(\nu)$, which we believe not to be essential. Equation (3.13) expresses that the bond vector $\mathbf{a}_\alpha(\nu - k_\alpha(t))$, located at $\nu - k_\alpha(t)$ at time zero, has diffused to ν at time t, its path being given by $\nu - k_\alpha(t) + k_\alpha(t')$, with t' in the interval $[0, t]$.

Of course the equation ceases to be valid when the bond vector $\mathbf{a}_\alpha(\nu - k_\alpha(t))$ diffuses out of the chain, i.e., if $\nu - k_\alpha(t) + k_\alpha(t')$ is not between 0 and N for some t' in the interval $[0, t]$. In this case $\mathbf{a}_\alpha(\nu, t)$ is equal to some vector $\mathbf{b}_\alpha(\nu - k_\alpha(t))$ which has entered the chain after the initial time to replace $\mathbf{a}_\alpha(\nu - k_\alpha(t))$. We now supplement Eq. (3.13) with the postulate that the vectors $\mathbf{b}_\alpha(\nu)$ are uncorrelated to the original ones $\mathbf{a}_\alpha(\nu)$, present at $t = 0$. This postulate is clearly consistent with the equilibrium statistics without excluded volume defined above. A vector $\mathbf{b}_\alpha(\nu)$ may of course again diffuse out of the chain, but we shall not introduce a new symbol for the vector by which it is replaced. For our future calculations it suffices to know that it is uncorrelated to the $\mathbf{a}_\alpha(\nu)$. This completes the definition of our simplified model.

In 1971, De Gennes introduced a model for the wormlike motion of a polymer in a dense solution or melt.[11] The model defined above reduces to De Gennes' model in its mathematical formulation if we require that $k_x(t) = k_y(t) = k_z(t)$.[19] The physical contents of the two models differ, however, considerably. The role of the "gas of defects" in Ref. 11 is played by the α extrema. The N^3 time scale in Ref. 11 arises from diffusion under

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the influence of a friction proportional to the chain length N; in the present case it arises from the hard core interaction between the $N\rho_\alpha$ diffusing α extrema. The role of the exterior polymer network which prevents sideways movements of the polymer considered by De Gennes is replaced, for each Cartesian coordinate separately, by the second nearest neighbor excluded volume interaction between the beads of the polymer itself. No longer does the chain $\mathbf{r}(\nu)$ move through a tube in $\mathbf{r}$ space, but instead each of its three components $r_\alpha(\nu)$ moves through a tube in r_α, ν space.

We shall compute the equilibrium correlation function $\langle a_\alpha(\mu,0)a_\alpha(\nu,t)\rangle$ as a path integral by averaging over all initial chain configurations $\mathbf{a}(\mu,0)$ and all possible time evolutions $k_\alpha(t)$. Thus, employing Eq. (3.13), we have

$$\langle a_\alpha(\mu,0)a_\alpha(\nu,t)\rangle = \int'_{k_\alpha(0)=0} \mathfrak{D}[k_\alpha(t)]\langle a_\alpha(\mu,0)a_\alpha(\nu-k_\alpha(t),0)\rangle, \tag{3.14}$$

where the prime reminds us of the restriction that paths $\nu + k_\alpha(t')$, with $0 \le t' \le t$, that lead from ν across the ends of the chain, will result in the replacement of the bond $\mathbf{a}_\alpha(\nu)$ by a random bond $\mathbf{b}_\alpha(\nu)$.

For the following it is useful to introduce this restriction in an explicit mathematical form. Accordingly, we replace Eq. (3.13) by

$$\begin{aligned}\mathbf{a}_\alpha(\nu,t) &= \mathbf{a}_\alpha(\nu-k_\alpha(t),0) \quad \text{for } \Theta_N^\alpha[t,\nu-k_\alpha(t)]=1\\ &= \mathbf{b}_\alpha(\nu-k_\alpha(t)) \quad \text{for } \Theta_N^\alpha[t,\nu-k_\alpha(t)]=0,\end{aligned} \tag{3.15}$$

where the step function $\Theta_N^\alpha[t,\nu]$ is defined by

$$\begin{aligned}\Theta_N^\alpha[t,\nu] &= 1 \text{ if } 0<\nu+k_\alpha(t')<N \text{ for } 0\le t'\le t,\\ &= 0 \text{ otherwise}.\end{aligned} \tag{3.16}$$

Thus the step function keeps the value unity until the bond vector $\mathbf{a}_\alpha(\nu)$ initially present at ν diffuses to the end of the chain and is replaced by a random bond $\mathbf{b}_\alpha(\nu)$. If we use the mathematical expression for the randomness of $\mathbf{b}_\alpha(\nu)$, viz.,

$$\langle a_\alpha(\mu,0)b_\alpha(\nu)\rangle = 0, \tag{3.17}$$

the correlation function Eq. (3.14) may be expressed as

$$\begin{aligned}\langle a_\alpha(\mu,0)a_\alpha(\nu,t)\rangle = &\int_{k_\alpha(0)=0} \mathfrak{D}[k_\alpha(t)]\Theta_N^\alpha[t,\nu-k_\alpha(t)]\\ &\times\langle a_\alpha(\mu,0)a_\alpha(\nu-k_\alpha(t),0)\rangle.\end{aligned} \tag{3.18}$$

Use of Eq. (3.8) permits us to rewrite Eq. (3.18) as

$$\begin{aligned}\langle a_\alpha(\mu,0)a_\alpha(\nu,t)\rangle &= \frac{1}{3}\int_{k_\alpha(0)=0} \mathfrak{D}[k_\alpha(t)]\Theta_N^\alpha[t,\nu-k_\alpha(t)]\delta(\mu-\nu+k_\alpha(t))\\ &= \frac{1}{3}\int_{\substack{k_\alpha(0)=0\\ k_\alpha(t)=\nu-\mu}} \mathfrak{D}[k_\alpha(t)]\Theta_N^\alpha[t,\mu] \equiv G_{\nu\mu}^{(N)}(t).\end{aligned} \tag{3.19}$$

The quantity $G_{\nu\mu}^{(N)}(t)$ has the physical interpretation of a probability that a bond initially at μ diffuses to ν in time t [with $0<\mu,\nu<N$] without having passed either of the two points $\nu=0$ and $\nu=N$. A subscript α has been suppressed on $G^{(N)}$, since this quantity will be the same for all α.

We compute the somewhat more general quantity $G_{\nu\mu}^{(M)}(t)$, needed for later purposes, by recognizing from the analysis of the previous section that $k_\alpha(t)$ will make jumps of size N^{-1} with frequency N. Thus, in the continuous limit the probability $\Pi(\nu,t)$ for a displacement $k_\alpha(t)=\nu$ may be determined from the diffusion equation

$$\frac{\partial\Pi(\nu,t)}{\partial(Nt)} = \theta\frac{\partial^2\Pi(\nu,t)}{\partial(N\nu)^2}, \tag{3.20}$$

where θ is a constant of order N^0.

From the definition of $G_{\nu\mu}^{(M)}(t)$ we see that it may be obtained as the solution of Eq. (3.20) for $0\le\nu\le M$ with initial condition $\Pi(\nu,0)=\delta(\nu-\mu)$ and boundary conditions $\Pi(0,t)=\Pi(M,t)=0$. The boundary conditions absorb any bond which has diffused to a chain end.[11] We obtain

$$G_{\nu\mu}^{(M)}(t) = \frac{2}{M}\sum_{k=1,3,\ldots}\sin\frac{\pi k\nu}{M}\sin\frac{\pi k\mu}{M}\exp(-\pi^2k^2\theta t/NM^2). \tag{3.21}$$

This determines the pair correlation function (3.19). By a similar but somewhat more complicated analysis (see Appendix A), we find for the four point time correlation function

$$\begin{aligned}\langle a_\alpha(\nu,0)a_\alpha(\nu',0)a_\beta(\mu,t)a_\beta(\mu',t)\rangle &= \tfrac{1}{9}[\delta(\nu-\nu')\delta(\mu-\mu')\{1+(\delta_{\alpha\beta}-1)G_{\mu\nu}^{(N)}(t)\}\\ &+\delta_{\alpha\beta}\{\delta(\nu-\nu'-\mu+\mu')G_{\mu\nu}^{(N+\mu-\mu')}(t)\\ &+\delta(\nu-\nu'+\mu-\mu')G_{\mu\nu'}^{(N+\mu-\mu')}(t)\}], \quad (\mu\le\mu').\end{aligned} \tag{3.22}$$

The expression for $\mu>\mu'$ is obtained by interchanging μ and μ' as well as ν and ν'. This four point correlation function is required for the calculation of some of the correlation functions of interest mentioned below. The probabilities $G^{(M)}(t)$ with $M<N$ enter as a consequence of the fact that $\mathbf{a}_\beta(\mu)$ and $\mathbf{a}_\beta(\mu')$ perform coherent random motion along the chain. The correlation (3.22) is destroyed as soon as either of the two bond vectors passes a chain end. Hence the effective available chain length for a pair of bonds a distance $|\mu-\mu'|$ apart is only $N-|\mu-\mu'|$.

We shall be concerned with certain equilibrium time correlation functions that have been computed by Verdier. The definition of the correlation function of a dynamical quantity A is

$$C(A;t) = \frac{\langle AA(t)\rangle - \langle A\rangle^2}{\langle A^2\rangle - \langle A\rangle^2}. \tag{3.23}$$

If A is a vector, the products in Eq. (3.23) should be read as dot products. Using the results obtained above and neglecting terms of order N^{-1}, we obtain for our simplified model the following correlation functions:

$$C(\mathbf{R}_N;t) = N^{-1}\int_0^N d\nu\int_0^N d\nu' G_{\nu\nu'}^{(N)}(t), \tag{3.24a}$$

$$C(\mathbf{R}_N^2;t) = 2N^{-2}\int_0^N d\mu\int_0^{N-\mu} d\nu\int_0^{N-\mu} d\nu' G_{\nu\nu'}^{(N-\mu)}(t), \tag{3.24b}$$

$$C(\mathbf{u}_p;t) = 2\pi^2p^2N^{-1}\int_0^N d\nu\int_0^N d\nu' U_\nu^p U_{\nu'}^p G_{\nu\nu'}^{(N)}(t), \tag{3.24c}$$

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$$C(\mathbf{u}_p^2;t) = 8\pi^4 p^4 N^{-2} \int_0^N d\mu \int_0^{N-\mu} d\nu \int_0^{N-\mu} d\nu' \times U_\nu^p U_{\nu'}^p U_{\nu+\mu}^p U_{\nu'+\mu}^p G_{\nu\nu'}^{(N-\mu)}(t), \quad (3.24d)$$

where

$$U_\nu^p = \frac{1}{\pi p} \sin\frac{\pi p \nu}{N}. \quad (3.25)$$

For the correlation functions of the vector quantities Eqs. (3.24a) and (3.24c) we find, employing Eq. (3.21), the results

$$C(\mathbf{R}_N;t) = \frac{8}{\pi^2} \sum_{k=1,3,\ldots} \exp(-k^2\tau)/k^2, \quad (3.26)$$

$$C(\mathbf{u}_p;t) = \exp(-p^2\tau), \quad (3.27)$$

where $\tau = (\pi^2\theta N^{-3}t)$. The result Eq. (3.26) is identical to that found by De Gennes.[11]

For the correlation functions of the squared quantities Eq. (3.24b) and (3.24d), we find (see Appendix B)

$$C(\mathbf{R}_N^2;t) = \frac{8}{\pi^2} \sum_{k=1,3,\ldots} \frac{1}{k^2} \int_1^\infty d\xi \frac{\exp(-\xi k^2\tau)}{\xi^2}, \quad (3.28)$$

$$C(\mathbf{u}_p^2;t) = \frac{8}{\pi^2} \sum_{k=1,3,\ldots} \frac{1}{k^2} \int_1^\infty d\xi \frac{\cos^2\pi p \xi^{-1/2}}{[1-(k/2p)^2\xi]^2} \frac{\exp(-\xi k^2\tau)}{\xi^2}. \quad (3.29)$$

Computer results for $C(\mathbf{u}_p^2;t)$ with $p = 1, 2, \ldots, 7$ have been obtained for times such that $1 = C(\mathbf{u}_p^2;0) \gtrsim C(\mathbf{u}_p^2;t) > 0.1$, for chains of length up to $N = 63$ (see Fig. 2 of Ref. 4). The corresponding time region is $\tau \lesssim 1$. An approximate evaluation of (3.29) in this time region (see Appendix C) leads to the curves shown in Fig. 4.

We first note that the chain length dependence of our model may be absorbed entirely in the time scale. Since our chain is a continuous one, its behavior is expected to be similar to that of lattice chains with large N. We observe the following similarities between our results and the Monte Carlo results (Fig. 2 of Ref. 4):

(1) The initial decay of $C(\mathbf{u}_p^2;t)$ is faster as p increases. In fact, an initial time expansion of Eq. (3.29) gives[20] $C(\mathbf{u}_p^2;t) = 1 - 2p^2\tau + 4p^2\tau^2 - \cdots$, so that the initial decay is proportional to p^{-2}. This agrees quantitatively with Table IV of Ref. 4.

(2) After the initial decay there is a changeover to a slow decay, with the same slope for all p.

(3) As p gets large, the asymptotic decay curves tend to a limiting curve.

Hence, in their main characteristics the Monte Carlo data agree very well with our results, and we expect the agreement would improve if N were larger in the simulation. At this time no Monte Carlo data are available on $C(\mathbf{u}_p;t)$. We expect from Eq. (3.27) that the behavior of this quantity in Verdier's model will be close to exponential.

Equations (3.26) and (3.28) determine the decay curves for $\mathbf{R}_N^2$ and $\mathbf{R}_N$, which were also obtained by computer simulation.[2,3] Our curves show the same infinite slope at $t = 0$ as those in Fig. 1 of Ref. 3. However, asymptotically we have $C(\mathbf{R}_N;t) \sim e^{-\tau}$ and $C(\mathbf{R}_N^2;t) \sim e^{-\tau}/\tau$, in contrast to the asymptotic relation $C(\mathbf{R}_N^2;t) \sim [C(\mathbf{R}_N;t)]^m$ with $m \approx 5$, found by Verdier.[3] We have no explanation for this disagreement.

IV. CONCLUSION

We have attempted to interpret Verdier's Monte Carlo results on the Brownian motion of an $(N+1)$ bead lattice polymer with excluded volume. In Sec. II we analyzed the kinetic scheme employed in the computer simulations. It was shown that this scheme, in conjunction with the excluded volume interaction between beads that are second nearest neighbors on the chain, imposes certain rigorous constraints on the chain motion. These constraints can be formulated as conservation laws for extrema in the chain (with respect to each of the Cartesian coordinates $\alpha = x, y, z$) and for the α coordinate of each α extremum. An approximate equivalence with a system of one-dimensional random walkers is used to estimate the time scale on which the over-all chain shape decays. This time scale is argued to be proportional to at least N^3, as opposed to the N^2 dependence found without excluded volume. Verdier's computer simulations indeed show that excluded volume leads to slowing down with at least a factor N.

In Sec. III we set up an analytically soluble model whose kinetics contains the same characteristics that were identified as essential to Verdier's model. Our model has the N^3 time scale built in, but it can be used to test further details of Verdier's results. It appears to give a good explanation for the shapes of the relaxation curves of the squared Rouse coordinates at large N.

We conclude that our analysis has successfully determined the dominant cause for the slowing down observed in chains with excluded volume. A second important conclusion is that this slowing down, viz., by a factor $\sim N$, is due to the specific properties of the kinetic scheme chosen by Verdier, which leads to severe constraints on the chain motion. In our analysis the "intrinsic" excluded volume interaction between beads at

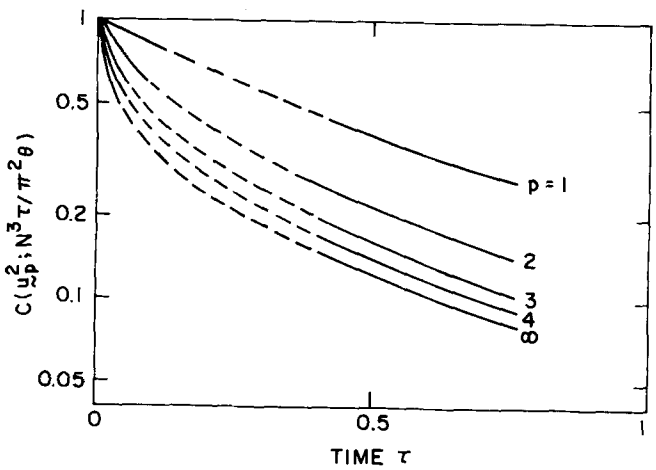

FIG. 4. Relaxation curves $C(\mathbf{u}_p^2;t)$ of the squared Rouse coordinates according to Eq. (3.29) as approximated by Eqs. (C7) and (C10). The time variable is $\tau = \pi^2\theta N^{-3}t$.

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distances >2 along the chain could be neglected. This interaction is expected to cause only a further, but much weaker, slowing down.

It is easy to imagine modified kinetic schemes [see, e.g., Fig. 3(c)], consistent with the same equilibrium properties of excluded volume chains, in which the second nearest neighbor excluded volume does not lead to the above mentioned constraints on the chain motion. In such a case there is no reason to expect slowing down by as much as a factor N; one would rather expect to see the much subtler effect of excluded volume interaction between distant beads of the chain.

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APPENDIX A:

Using Eqs. (3.15), (3.16), and the fact that any correlation linear in $b_\beta(\mu)$ vanishes, we get

$$\langle a_\alpha(\nu,0)a_\alpha(\nu',0)a_\beta(\mu,t)a_\beta(\mu',t)\rangle = \int_{k_\beta(0)=0} \mathfrak{D}[k_\beta(t)]\{\Theta_N^\beta[t;\mu-k_\beta(t)]\Theta_N^\beta[t;\mu'-k_\beta(t)]\langle a_\alpha(\nu)a_\alpha(\nu')a_\beta(\mu-k_\beta(t))a_\beta(\mu'-k_\beta(t))\rangle$$
$$+(1-\Theta_N^\beta[t;\mu-k_\beta(t)])(1-\Theta_N^\beta[t;\mu'-k_\beta(t)])\langle a_\alpha(\nu)a_\alpha(\nu')b_\beta(\mu)b_\beta(\mu')\rangle\}\,. \tag{A1}$$

We now employ the relation

$$\Theta_N^\alpha[t;\nu]\Theta_N^\alpha[t;\nu'] = \Theta_{N-|\nu-\nu'|}^\alpha[t;\min(\nu,\nu')]\,, \tag{A2}$$

which follows directly from the definition of Θ_N^α.

With Eq. (A2) and the explicit expressions for the correlation functions, Eq. (A1) becomes, for $\mu \le \mu'$,

$$\langle a_\alpha(\nu,0)a_\alpha(\nu',0)a_\beta(\mu,t)a_\beta(\mu',t)\rangle$$
$$=\frac{1}{9}\int_{k_\beta(0)=0}\mathfrak{D}[k_\beta(t)]\{\Theta^\beta_{N+\mu-\mu'}[t;\mu-k_\beta(t)](\delta(\nu-\nu')\delta(\mu-\mu')+\delta_{\alpha\beta}\delta(\nu-\mu+k_\beta(t))\delta(\nu'-\mu'+k_\beta(t))$$
$$+\delta_{\alpha\beta}\delta(\nu-\mu'+k_\beta(t))\delta(\nu'-\mu+k_\beta(t))+(\delta_{\alpha\beta}-1)\delta(\nu-\nu')\delta(\nu-\mu+k_\beta(t))\delta(\nu'-\mu'+k_\beta(t)))$$
$$+(1-2\Theta_N^\beta[t;\mu-k_\beta(t)]+\Theta^\beta_{N+\mu-\mu'}[t;\mu-k_\beta(t)])\delta(\nu-\nu')\delta(\mu-\mu')\}$$
$$=\frac{1}{9}\int_{k_\beta(0)=0}\mathfrak{D}[k_\beta(t)]\delta(\nu-\nu')\delta(\mu-\mu')+\tfrac{1}{9}\delta_{\alpha\beta}\int_{\substack{k_\beta(0)=0\\k_\beta(t)=\mu-\nu}}\mathfrak{D}[k_\beta(t)]\Theta^\beta_{N+\mu-\mu'}[t;\nu]\delta(\nu'-\mu'-\nu+\mu)$$
$$+\tfrac{1}{9}\delta_{\alpha\beta}\int_{\substack{k_\beta(0)=0\\k_\beta(t)=\mu-\nu'}}\mathfrak{D}[k_\beta(t)]\Theta^\beta_{N+\mu-\mu'}[t;\nu']\delta(\nu-\mu'-\nu'+\mu)+\tfrac{1}{9}(\delta_{\alpha\beta}-1)\int_{\substack{k_\beta(0)=0\\k_\beta(t)=\mu-\nu}}\mathfrak{D}[k_\beta(t)]\Theta_N^\beta[t;\nu]\delta(\nu-\nu')\delta(\mu-\mu')$$
$$=\tfrac{1}{9}[\delta(\nu-\nu')\delta(\mu-\mu')\{1+(\delta_{\alpha\beta}-1)G_{\mu\nu}^{(N)}(t)\}+\delta_{\alpha\beta}\{\delta(\nu-\nu'-\mu+\mu')G_{\mu\nu}^{(N+\mu-\mu')}(t)+\delta(\nu-\nu'+\mu-\mu')G_{\mu\nu'}^{(N+\mu-\mu')}(t)\}]\,. \tag{A3}$$

It is easily shown that for $\mu>\mu'$ the correct expression is obtained by interchanging μ and μ' as well as ν and ν'.

APPENDIX B

Substituting Eqs. (3.21) and (3.25) in Eqs. (3.24c) and (3.24d) and performing the integrals over ν and ν' leads to

$$C(\mathbf{R}_N^2;t) = 16\pi^{-2}N^{-2}\sum_{k=1,3,\ldots}\frac{1}{k^2}\int_0^N d\mu\,\mu\exp[-(N/\mu)^2k^2\tau]\,, \tag{B1}$$

$$C(\mathbf{u}_p^2;t) = 16\pi^{-2}N^{-2}\sum_{k=1,3,\ldots}\frac{1}{k^2}\times\int_0^N d\mu\,\mu\frac{\cos^2(\pi p\mu/N)}{[1-(kN/2p\mu)^2]^2}\exp[-(N/\mu)^2k^2\tau]\,. \tag{B2}$$

The results (3.28) and (3.29) are obtained by changing to the variable of integration $\xi=(N/\mu)^2$.

APPENDIX C

For times $\tau \gtrsim 0.2$ the $k=1$ term dominates the integral (3.29), which may then be written

$$C(\mathbf{u}_p^2;t) \simeq \frac{8}{\pi^2}\int_1^\infty d\xi\,\rho_p(\xi)\,e^{-\xi\tau}\,, \tag{C1}$$

$$\rho_p(\xi) = \frac{\cos^2\pi p\xi^{-1/2}}{\xi^2[1-\xi/4p]^2}\,. \tag{C2}$$

The main contribution to this integral, for $\tau \gtrsim 0.2$, comes from the region $1<\xi\le 4$. The squared cosine causes $\sim \frac{1}{2}p$ oscillations of the integrand in this ξ region. For large p the oscillations become dense, and we may replace $\cos^2\pi p\xi^{-1/2}$ by its average $\frac{1}{2}$. Thus we find the limiting curve

$$C(\mathbf{u}_\infty^2;t) \simeq \frac{4}{\pi^2}[e^{-\tau}-\tau E_1(\tau)]\,, \tag{C3}$$

where $E_1(\tau)$ is the exponential integral.

For general p we note that, with $\xi_{pl}=16p^2/(4p-l)^2$, we have

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$$\cos^2 \pi p \xi_{pl}^{-1/2} = \begin{cases} 1 & \text{for } l = 0, 4, \ldots, 4p-4 \\ \frac{1}{2} & \text{for } l = 1, 3, \ldots, 4p-1 \\ 0 & \text{for } l = 2, 6, \ldots, 4p-2 . \end{cases} \quad \text{(C4)}$$

We approximate the density of decay times $\rho_p(\xi)$ by a sum of step functions, each of which is nonzero only in a region with $\cos^2 \pi p \xi_{pl}^{-1/2} > \frac{1}{2}$, i.e., we take

$$\rho_p(\xi) \simeq \sum_{l=0}^{p-1} u_{pl}(\xi) \quad \text{(C5)}$$

with

$$u_{p0}(\xi) = \rho_p(1) \equiv \rho_{p0} \qquad \text{for } 1 \leq \xi \leq \xi_{p1}$$
$$u_{pl}(\xi) = \rho_p(\xi_{p,4l}) \equiv \rho_{pl} \qquad \text{for } \xi_{p,4l-1} \leq \xi \leq \xi_{p,4l+1}$$
$$(l = 1, 2, \ldots, p-1)$$
$$u_{pl}(\xi) = 0 \quad \text{else } (l = 0, 1, \ldots, p). \quad \text{(C6)}$$

With Eqs. (C2), (C5), and (C6), the integration in Eq. (C1) can be performed and gives, for $\tau \gtrsim 0.2$,

$$C(\mathbf{u}_p^2; t) \simeq \frac{8}{\pi^2} \frac{1}{\tau} \sum_{l=0}^{p-1} \rho_{pl} [e^{-\tau \xi_{p,4l-1}} - e^{-\tau \xi_{p,4l+1}}] . \quad \text{(C7)}$$

For $p = 1$ we approximate the density of decay times $\rho_1(\xi)$ more precisely by

$$\rho_1(\xi) = u_0(\xi) + u_1(\xi),$$
$$u_0(\xi) = \begin{cases} \rho_1(1) & \text{for } 1 \leq \xi \leq \xi_1 \\ 0 & \text{otherwise,} \end{cases} \quad \text{(C8)}$$
$$u_1(\xi) = \begin{cases} \rho_1(\xi_2) & \text{for } \xi_1 \leq \xi \leq \xi_3 \\ 0 & \text{otherwise,} \end{cases}$$

with ξ_i chosen such that $\cos^2 \pi \xi_i^{-1/2} = i/4$ for $i = 1, 2, 3$, i.e.,

$$\xi_1 = \tfrac{36}{25}, \qquad \xi_2 = \xi_{11} = \tfrac{16}{9}, \qquad \xi_3 = \tfrac{9}{4} . \quad \text{(C9)}$$

The integral is again easily calculated and gives, for $\tau \gtrsim 0.2$,

$$C(\mathbf{u}_1^2; t) \simeq \frac{8}{\pi^2} \frac{1}{\tau} \left[\tfrac{16}{9} e^{-\tau} - \tfrac{145\,751}{115\,200} e^{-(36/25)\tau} - \tfrac{1}{2} (\tfrac{81}{80})^2 e^{-(9/4)\tau} \right] . \quad \text{(C10)}$$

In Fig. 4 we have employed Eq. (C10) for $p = 1$ and Eq. (C7) for $p > 1$, as well as the initial-time expansion $C(\mathbf{u}_p^2; t) = 1 - 2p^2\tau + 4p^2\tau^2 - \cdots$. Although the approximations (C5) and (C8) are somewhat arbitrary, other approximations give very similar results.

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[19] In the lattice model each bead flip causes the interchange of two bond vectors. Hence we have the relation $\sum_\alpha k_\alpha(t) = 0$ for all t. However, this coupling between the coordinates does not enter into our calculations, and is not inconsistent with random motion of each $k_\alpha(t)$ separately.
[20] Use, e.g., obvious modifications of formulas 1.421.3 and 1.423 of I. S. Gradshteyn and I. M. Ryzhik, *Tables of Integrals, Series, and Products* (Academic, New York, 1965).

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