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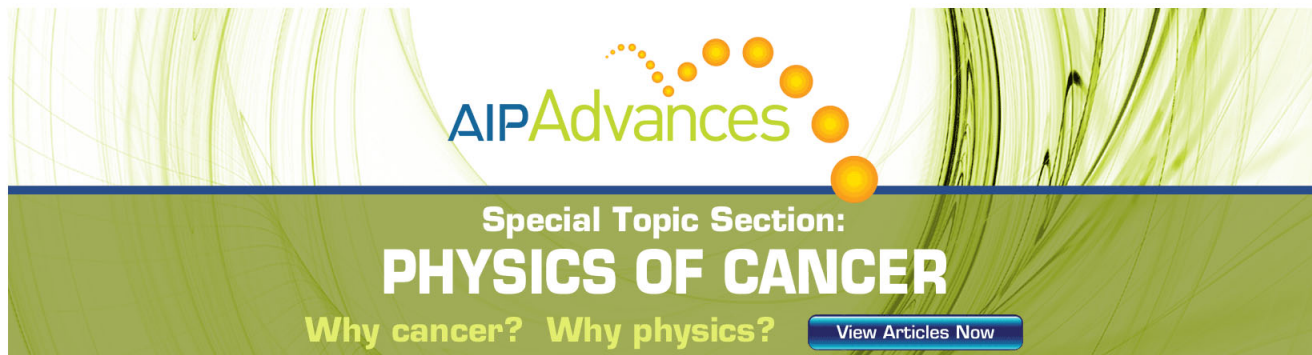
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## Structural modes of a polymer in the repton model

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Using extensive computer simulations, the behavior of the structural modes—more precisely, the eigenmodes of a phantom Rouse polymer—are characterized for a polymer in the three-dimensional repton model and are used to study the polymer dynamics at time scales well before the tube renewal. Although these modes are not the eigenmodes for a polymer in the repton model, we show that numerically the modes maintain a high degree of statistical independence. The correlations in the mode amplitudes decay exponentially with  $(p/N)^2 A(t)$ , in which  $p$  is the mode number,  $N$  is the polymer length, and  $A(t)$  is a single function shared by all modes. In time, the quantity  $A(t)$  causes an exponential decay for the mode amplitude correlation functions for times  $< 1$ ; a stretched exponential with an exponent  $1/2$  between times  $1$  and  $\tau_R \sim N^2$ , the time-scale for diffusion of tagged reptons along the contour of the polymer; and again an exponential decay for times  $t > \tau_R$ . Having assumed statistical independence and the validity of a single function  $A(t)$  for all modes, we compute the temporal behavior of three structural quantities: the vectorial distance between the positions of the middle monomer and the center-of-mass, the end-to-end vector, and the vector connecting two nearby reptons around the middle of the polymer. Furthermore, we study the mean-squared displacement of the center-of-mass and the middle repton, and their relation with the temporal behavior of the modes.

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### I. INTRODUCTION: POLYMER REPTATION AND THE REPTON MODEL

The dynamics of a coarse-grained polymer has two extremes in polymer physics. One extreme features the phantom Rouse model,<sup>1,2</sup> wherein the polymer is described as a chain of beads serially connected by harmonic springs. A polymer in the phantom Rouse model does not feel its surroundings and not even itself. Comprised of  $N + 1$  beads with spatial locations  $\vec{r}_i$  ( $i = 0, 1, \dots, N$ ), a polymer of length  $N$  in the Rouse model lends itself to a complete analysis of its dynamics in terms of the eigenmodes indexed by  $p$  ( $p = 0, 1, \dots, N$ ), correspondingly called the Rouse modes, whose amplitudes are given by

$$\vec{X}_p(t) = \frac{1}{N+1} \sum_{i=0}^N \cos[\alpha_p(i+1/2)] \vec{r}_i(t), \quad (1)$$

in which  $\alpha_p = p\pi/(N+1)$ . The other extreme features Rubinstein's repton model,<sup>3</sup> which describes the dynamics of a highly restricted polymer, in which the only dynamical freedom is a mechanism known as *reptation*,<sup>2,4</sup> a snakelike motion in which stored length travels back and forth along the polymer, and can be created and annealed only at the polymer ends. In the repton model, the polymer is composed of mobile points, called reptons, residing in the cells of a lattice, connected by bonds. A configuration of the polymer in the repton model in two dimensions is shown in Fig. 1. The

neighboring reptons can reside either in the same cell or in the adjacent cells. The configuration of the polymer contour in space, defined by the serially connected cells occupied by the reptons, is that of a random walk and is not allowed to undergo any change, other than by the motion of one of its ends. Each repton, except the end ones, is therefore constrained to move along the contour of the polymer. The repton model is extensively discussed and illustrated in the literature.<sup>5,6</sup> Duke has extended the repton model to study gel electrophoresis,<sup>7</sup> by adding an electric field which acts on the charged reptons; also this model has been studied extensively.<sup>6,8,9</sup> A highly efficient simulation approach of the repton model was developed and based on bit-operations;<sup>8</sup> the present paper uses this approach as well.

In this paper, we characterize the analogs of the Rouse modes for a polymer consisted of  $N + 1$  reptons in the repton model in three spatial dimensions, having denoted the spatial locations of the reptons by  $\vec{r}_i$  ( $i = 0, 1, \dots, N$ ), as in Eq. (1). Henceforth, these are simply referred to as the *modes*. They are not the eigenmodes of the polymer in the repton model. We express several dynamical variables for the polymer in terms of the modes. We verify the time-correlations of the modes and these dynamical variables by high-precision computer simulations.

In the simulations the repton positions are the natural variables. For theoretical analysis; however, the distance between successive reptons, or the “link variables,” defined as

$$\vec{y}_i = \vec{r}_i - \vec{r}_{i-1} \quad \text{for } i = 0, \dots, N, \quad (2)$$

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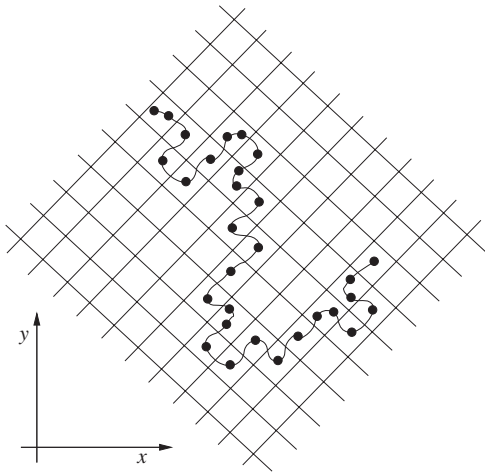


FIG. 1. A two-dimensional lattice representation of the repton model. The polymer is represented by points (reptons), that reside in the cells of the lattice and are connected by bonds. The rules governing this model are described in the text.

are a more convenient choice. By construction, the link variables are either a unit vector or zero. In the former case, the link is taut, while in the latter case the link is slack and it represents an element of “stored length.” The motion of the polymer can be viewed as diffusion of stored length along the chain (instead of the movements of the individual reptons).

Few exact results are known for the repton model, all concerning the asymptotic time regime, governed by the overall diffusion constant  $D$  of the polymer. It was already proposed by Rubinstein,<sup>3</sup> that  $D$  scales as  $N^{-2}$ . Later it was found by van Leeuwen and Kooiman<sup>10</sup> that in the repton model on a  $d$ -dimensional hypercubic lattice,  $D = 1/[(2d + 1)N^2]$ . This result was shown to be exact by Prähofer and Spohn<sup>11</sup> and by Widom and Al-Lehyani.<sup>12</sup> In this paper, we study the repton model on a cubic lattice. For reasons of computational efficiency, the rates for extraction and retraction of the ends are modified to obtain a dimensionality independent density of stored length, tuned to that of the one-dimensional model, so that  $D = 1/(3N^2)$ . We are specifically interested in the polymer dynamics over intermediate time regimes, for which, so far, only simulations can reveal the behavior.

Before the diffusive regime is reached, the repton model has various distinct time regimes. First, at very short times  $t < 1$ , the dynamics is governed by individual hops of reptons, which are spatially separated. Next, there is one intermediate regime  $1 < t < \tau_R \sim N^2$ , where  $\tau_R$  is the time at which the fluctuations in the density of stored lengths decay. This is followed by a second intermediate regime  $\tau_R < t < \tau_d \sim N^3$ , where  $\tau_d$  is the well-known tube-renewal time after which the initial information on the chain has been forgotten.

Our basic quantity of interest is the equilibrium correlation function,

$$C_{pq}(t) \equiv \langle \vec{X}_p(t) \cdot \vec{X}_q(0) \rangle, \quad (3)$$

in the above time regimes, where the angular brackets denote an average over the equilibrium ensemble of polymer conformations. More specifically, we put the middle monomer at  $t = 0$  at the origin. Then a polymer configuration can be build

up from independent link variables  $\vec{y}_i$ . The link may be taut or slack, with probabilities  $2/3$  and  $1/3$ . A taut link variable may assume one of the six possibilities corresponding to the six directions on the cubic lattice, each with equal weight.

Since, the modes are not eigenmodes of the polymer in the repton model, they do not decay exponentially in time. In Sec. II, we show that the cross-correlation functions for  $p \neq q$  vanish for  $t = 0$  and remain small at later times. In Sec. III, we study the autocorrelation functions  $C_{pp}(t)$ . These autocorrelations are found to decay exponentially at short times  $t < 1$  and at long times  $t > \tau_R$ , but in the intermediate regime  $1 < t < \tau_R$  they decay as stretched exponentials in time, with exponent  $1/2$ . In all these regimes, the exponent has a power-law dependence on mode number  $p$  and polymer length  $N$ . In Sec. IV, using the mode amplitude autocorrelation functions  $C_{pp}(t)$  and neglecting cross-correlations, we reconstruct other time-dependent correlation functions, in particular, those of the vector between the positions of the middle repton and the center-of-mass, the end-to-end vector, and a spatial vector connecting two nearby reptons around the middle repton. We compare these analytical results with direct computer simulations. In Sec. V, we evaluate the mean-squared displacement of the center-of-mass and of the middle repton in the above time regimes, and compare them with direct computer simulations. We end the paper with a discussion in Sec. VI.

## II. BEHAVIOR OF CORRELATIONS BETWEEN DIFFERENT MODES

For phantom chains in the Rouse model, the modes as defined in Eq. (1) are strictly independent and orthogonal, i.e., the correlations  $C_{pq}(t)$  as defined in Eq. (3) are 0 for all times, if  $p \neq q$ . This property is part of the motivation why in the study of the dynamics of a polymer, it is very convenient to express the quantities of interest in amplitudes of the structural modes. In this section, we will show analytically that at  $t = 0$ , also in the repton model the same structural modes are orthogonal. We will also show that correlations between even modes  $p$  and odd modes  $q$  are strictly 0 at all times. Next, with computer simulations, we will show that for time  $t > 0$  cross-correlations between the modes  $p \neq q$ , in which  $p$  and  $q$  are both even or both odd, start to develop.

### A. Behavior of $C_{pq}(0)$

First, we turn to the correlation functions  $C_{pq}(t)$  for time  $t = 0$ , which only require the evaluation of equilibrium averages. For this purpose it is convenient to provide the relation between the mode amplitudes and the link variables which have the simple equilibrium averages,

$$\langle \vec{y}_j \vec{y}_k \rangle = \mathbf{I}(\rho/d) \delta_{jk}, \quad (4)$$

where  $\mathbf{I}$  is the unity tensor and  $\rho$  is the equilibrium density of the taut links, which equals  $\rho = 2/3$  in our simulations.

We express the position of the  $i$ -th repton with respect to that of the middle repton  $\vec{r}_{N/2}$  [for simplicity we take  $N$  even all throughout this paper; if one is interested in odd  $N$  polymers, one can take as a reference point  $\vec{r}_m = \frac{1}{2}(\vec{r}_{(N-1)/2} + \vec{r}_{(N+1)/2})$ , which has the same symmetry] and

the link variables as

$$\begin{aligned}\vec{r}_j &= \vec{r}_{N/2} + \sum_{i=N/2+1}^j \vec{y}_i, \quad \text{for } (j > N/2), \\ \vec{r}_j &= \vec{r}_{N/2} - \sum_{i=j+1}^{N/2} \vec{y}_i \quad \text{for } (j < N/2).\end{aligned}\quad (5)$$

In the summations to come we will use the following relation for  $p \neq 0$ :

$$\sum_{j=k}^N \cos[\alpha_p(j + 1/2)] = -\frac{\sin(\alpha_p k)}{2s_p}, \quad (6)$$

with  $s_p = \sin(\alpha_p/2)$ . Note that Eq. (6) yields 0 for  $k = 0$ . This implies that the middle repton location  $\vec{r}_{N/2}$  in Eq. (5) does not contribute in the mode amplitude expression for  $p \neq 0$ . Thus, using Eq. (5), and further, upon interchanging the summations over  $j$  and  $k$ , for  $p \neq 0$ , we have

$$\vec{X}_p = -\frac{1}{2(N+1)s_p} \sum_{k=1}^N \sin(\alpha_p k) \vec{y}_k. \quad (7)$$

Equation (7) cannot be applied to the center-of-mass mode  $p = 0$  as  $s_0 = 0$ . For  $p = 0$ , with the help of Eq. (5), the corresponding formula becomes

$$\vec{X}_0 = \vec{r}_{N/2} + \frac{1}{N+1} \left[ \sum_{j=1}^{N/2} j (\vec{y}_{N+1-j} - \vec{y}_j) \right]. \quad (8)$$

While the mode amplitudes for  $p \neq 0$  are expressed solely in terms of the link (or structural) variables, the center-of-mass mode needs an additional (translational) coordinate  $\vec{r}_{N/2}$ .

Equation (7) can be inverted using the relation,

$$\sum_{k=1}^N \sin(\alpha_p k) \sin(\alpha_q k) = \frac{N+1}{2} \delta_{pq}, \quad (9)$$

and its inverse

$$\sum_{p=1}^N \sin(\alpha_p k) \sin(\alpha_p l) = \frac{N+1}{2} \delta_{kl}. \quad (10)$$

These results lead us to the inverse relation for the link variables in terms of the mode amplitudes,

$$\vec{y}_k = -4 \sum_{p=1}^N s_p \sin(\alpha_p k) \vec{X}_p. \quad (11)$$

Equation (11) reveals that the mode amplitudes for  $p \neq 0$  and the link variables are fully equivalent since they can be transformed into each other.

From the expression (8) and the average (4) it follows that the mode amplitudes for  $p \neq 0$  and  $q \neq 0$  are orthogonal for  $t = 0$  with the inner product,

$$C_{pq}(0) = \frac{\rho}{8(N+1)s_p^2} \delta_{pq}. \quad (12)$$

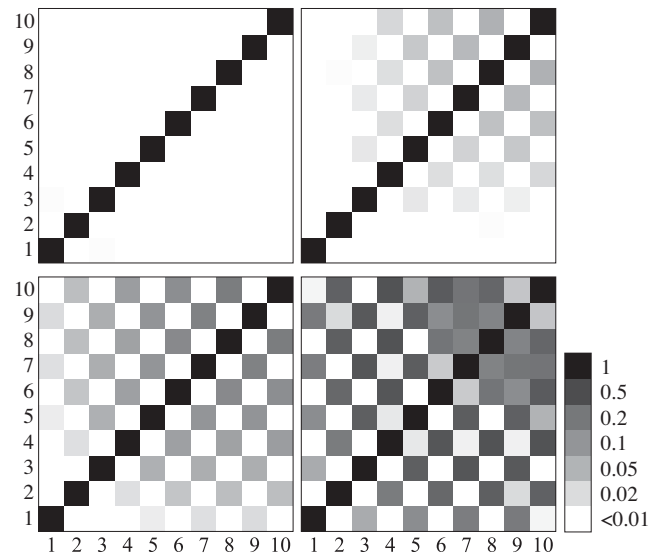


FIG. 2. Checkerboard plot for  $\eta_{pq}(t)$  for  $N = 400$  at four different times; upper left:  $t = 0$ , upper right:  $t = 8,000$ , lower left:  $t = 64,000$ , and lower right  $t = 10^6$ . The data are manually symmetrized around the diagonal. The grayscale used is shown in the scale bar.

## B. Behavior of $C_{pq}(t)$ for $p, q > 0$ and $t > 0$

In Fig. 2 we plot the normalized cross-correlation,

$$\eta_{pq}(t) = C_{pq}(t) / \sqrt{C_{pp}(t)C_{qq}(t)}, \quad (13)$$

for a number of  $p$  and  $q$  and several times. In the upper-left panel one observes the absence of cross-correlations for  $t = 0$ , as derived in Eq. (12). The next clear observation in Fig. 2 is the absence of cross-correlations between the even and odd modes. This is a consequence of the inversion symmetry of the polymer chain: inversion is a renumbering of the reptons from  $N$  to 0 and the inversion of the link variables, or notationally,

$$\vec{y}_i \leftrightarrow -\vec{y}_{N-i+1}. \quad (14)$$

The amplitudes of the even modes are invariant under this operation, while the odd mode amplitudes change sign. Since the dynamical evolution commutes with the inversion operation, the symmetry of the even mode amplitudes and the change of sign for the odd mode amplitudes are preserved under time evolution. In the lower-right panel the inversion symmetry appears to be violated for larger  $p$  and  $q$ , but this is actually a consequence of the numerical inaccuracy of the simulation data, which is magnified once the normalizations involved in  $\eta_{pq}$  become very small.

Figure 2 also reveals that for  $t > 0$ ,  $C_{pq}(t)$  is no longer strictly proportional to  $\delta_{pq}$ . Nevertheless, the off-diagonal correlation functions are small in comparison to the diagonal ones.

## III. BEHAVIOR OF $C_{pp}(t)$

For the properties for  $C_{pp}(t)$  we can anticipate the following behavior:

- (i) At short times  $t < 1$ , reptons typically make zero or one move, and the movements of individual reptons



are uncorrelated. In an earlier work on lattice polymers with exactly the same equilibrium properties as in the repton model, but less restricted dynamics,<sup>13</sup> we found that the decay of the structural modes in this short-time regime was characterized by  $C_{pp}(t) = C_{pp}(0) \exp[-A_1 p^2 t / N^2]$ , for some constant  $A_1$ . Since the moves allowed in the repton model are a finite fraction of the moves in this earlier work, we expect the same behavior to hold, be it with a modified value of the parameter  $A_1$ .

- (ii) In the regime  $t > 1$ , reptons have the time to attempt multiple moves. Right after a repton has moved in the “upstream” direction, the reverse “downstream” move is guaranteed to be possible, while another “upstream” move requires the presence of another slack link upstream, and therefore has a significant probability to be ruled out. Hence, the nature of the dynamics changes at  $t \sim 1$ . From a curvilinear perspective, the motion changes from ordinary diffusion to “single-file diffusion,” in which the squared curvilinear displacement increases  $\sim \sqrt{t}$ . Continuity of the curves near  $t \sim 1$  then leads to an expected behavior  $C_{pp}(t) = C_{pp}(0) \exp[-A_2 p^2 \sqrt{t} / N^2]$ .
- (iii) Slack links can move freely up and down the chain, in unit steps, without constraints. This diffusive behavior along the chain with a curvilinear diffusion constant of  $\sim 1$ , combined with the polymer length  $\sim N$ , yields a characteristic time scale  $\tau_R \sim N^2$  beyond which the distribution of slack links becomes statistically independent. Without such correlations, the curvilinear dynamics ceases to be anomalous and becomes ordinary diffusion once more. Continuity of all curves around  $\tau_R$  then yields  $C_{pp}(t) = C_{pp}(0) \exp[-A_3 p^2 t / N^3]$ . The data reveal that  $A_1$ ,  $A_2$ , and  $A_3$  are all of  $O(1)$ .

Having combined (i–iii), we present the simulation data for several  $p$  and  $N$  values in Fig. 3. The data collapse confirms that for  $t < 1$ ,

$$C_{pp}(t) = C_{pp}(0) \exp[-A_1 p^2 t / N^2], \quad (15)$$

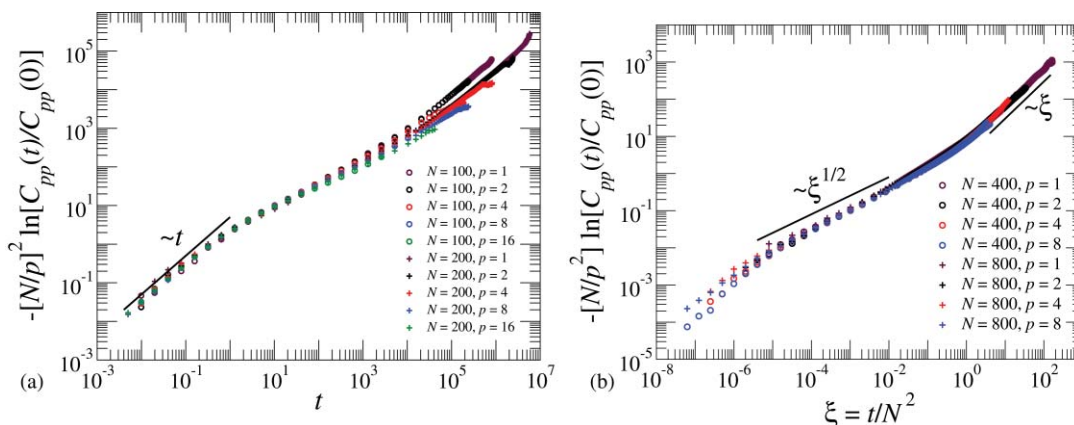


FIG. 3. Behavior of  $C_{pp}(t)$  for  $t > 0$ . (a) For  $t < 1$ ,  $C_{pp}(t) = C_{pp}(0) \exp[-A_1 p^2 t / N^2]$  for some constant  $A_1$  of magnitude  $O(1)$ . (b) For  $1 < t < \tau_R \sim N^2$ ,  $C_{pp}(t) = C_{pp}(0) \exp[-A_2 p^2 t^{1/2} / N^2]$ , while for  $t > \tau_R$ ,  $C_{pp}(t) = C_{pp}(0) \exp[-A_3 p^2 t / N^3]$ , with  $A_2$  and  $A_3$  also of magnitude  $O(1)$ .

for some constant  $A_1$  of magnitude  $O(1)$ . Further, for  $1 < t < \tau_R \sim N^2$ ,

$$C_{pp}(t) = C_{pp}(0) \exp[-A_2 p^2 t^{1/2} / N^2], \quad (16)$$

while for  $t > \tau_R$ ,

$$C_{pp}(t) = C_{pp}(0) \exp[-A_3 p^2 t / N^3]. \quad (17)$$

Having combined Eqs. (15)–(17), we see that  $C_{pp}(t)$  is expressed in general terms as  $C_{pp}(0) \exp[-(p/N)^2 A(t)]$  with a time-dependent quantity  $A(t)$ ; which we will encounter in the coming sections. At short and long times, this function  $A(t)$  is linear in time, with at short times a length-independent prefactor  $A_1$  and at long times a prefactor  $A_3/N$ , inversely proportional to polymer length; in the intermediate regime  $1 < t < \tau_R \sim N^2$ , the function  $A(t)$  increases proportional to  $\sqrt{t}$ , with a length-independent prefactor  $A_2$ . Note that at all times  $A(t)$  is independent of the mode number  $p$ .

#### IV. THREE STRUCTURAL QUANTITIES IN TERMS OF MODE AMPLITUDES

All structural quantities, which can be expressed in terms of the link variables, are also expressible in terms of the mode amplitudes. In Sec. III, we obtained an approximate description of the behavior in time of the mode amplitudes: we neglect cross-correlations at all times and assume that a single function  $A(t)$  determines the autocorrelation of all mode amplitudes. In this section, we will confront this approximate description with direct simulations. For this purpose, we consider three such structural variables: the vector  $\vec{S}_0$  between the center-of-mass and the middle repton, the polymer end-to-end vector  $\vec{S}_1$ , and the vector  $\vec{S}_2$  connecting the two reptons next to the middle repton.

### A. Structural variables $\vec{S}_0$ , $\vec{S}_1$ , and $\vec{S}_2$ expressed in terms of the modes amplitudes

The distance  $\vec{S}_0$  between the center-of-mass and the middle repton, defined in Eq. (8), is given by

$$\vec{S}_0 = \vec{R}_0 - \vec{r}_{N/2} = \frac{1}{N+1} \left[ \sum_{j=1}^{N/2} j (\vec{y}_{N+1-j} - \vec{y}_j) \right], \quad (18)$$

in terms of the link variables. Its mean-squared equilibrium-average follows from Eq. (4) as

$$\langle S_0^2 \rangle = \frac{\rho N(N+2)}{12(N+1)}. \quad (19)$$

Having expressed the link variables in terms of the mode amplitudes further yields the expression,

$$\vec{S}_0 = 2 \sum_{p=2,4,\dots}^N (-1)^{p/2} \vec{X}_p. \quad (20)$$

Similarly, the end-to-end vector  $\vec{S}_1$  of the polymer is expressed as

$$\vec{S}_1 = \vec{r}_N - \vec{r}_0 = \sum_{k=1}^N \vec{y}_k, \quad (21)$$

in terms of the link variables. Its mean-squared equilibrium-average is given by

$$\langle S_1^2 \rangle = \rho N, \quad (22)$$

and the expression of  $\vec{S}_1$  in terms of the mode amplitudes takes the form,

$$\vec{S}_1 = -4 \sum_{p=1,3,\dots}^N c_p \vec{X}_p, \quad (23)$$

with  $c_p = \cos(\alpha_p/2)$ .

Note that the end-to-end vector is a special case of the vector between two arbitrary reptons  $m$  and  $n$ ,

$$\vec{r}_m - \vec{r}_n = \sum_{k=n+1}^m \vec{y}_k. \quad (24)$$

For a characteristic case, we consider the vector  $\vec{S}_2$  between the two reptons next to the middle repton as our third structural variable, i.e.,

$$\vec{S}_2 = \vec{r}_{N/2+1} - \vec{r}_{N/2-1}, \quad (25)$$

with the mean-squared equilibrium-average,

$$\langle S_2^2 \rangle = 2\rho; \quad (26)$$

$\vec{S}_2$  is related to the mode amplitudes as

$$\vec{r}_{N/2+1} - \vec{r}_{N/2-1} = -8 \sum_{p=1}^N \sin(p\pi/2) c_p s_p \vec{X}_p. \quad (27)$$

We summarize the expressions of  $\vec{S}_0$ ,  $\vec{S}_1$  and  $\vec{S}_2$  [Eqs. (20), (23), and (27)] in the form,

$$\vec{S}_i = \sum_{p=1}^N S_{p,i} \vec{X}_p. \quad (28)$$

The equilibrium averages can also be evaluated via the averages of the mode amplitudes, as provided in Eq. (12). This leads one to the evaluation of sums of the type,

$$\langle S_i^2 \rangle = \frac{\rho}{8(N+1)} \sum_{p=1}^N (S_{p,i}/s_p)^2, \quad (29)$$

which can be found in Ref. 14.

Although the mode amplitudes for  $p \neq 0$  are equivalent to the link variables, one must realize that the domains of possible values are quite different. The domain of possible  $\vec{y}_j$  consists of  $2d+1 = 7$  values for each  $j$  in three dimensions ( $d=3$ ), whereas the domain of possible values of the  $\vec{X}_p$  is complicated. Each  $\vec{X}_p$  assumes  $(2d+1)^N$  values (multiplicities included) and the possibilities are inter-related.

### B. Dynamical properties of the structural variables $\vec{S}$

Whereas the equilibrium averages of structural properties are easily evaluated using the link variables, their time-dependent correlations have to be evaluated through the use of temporal behavior of the correlations in the mode amplitudes.

Using the general form Eq. (28), we find, for the correlators, that

$$\langle \vec{S}_i(t) \cdot \vec{S}_i(0) \rangle = \sum_{p,q=1}^N S_{p,i} S_{q,i} C_{pq}(t). \quad (30)$$

For the time-dependent  $C_{pq}(t)$ , we use the approximation discussed in Sec. III, leaving out the cross-correlations and employing for the diagonal terms the generic form,

$$\begin{aligned} C_{pp}(t) &= C_{pp}(0) \exp[-(p/N)^2 A(t)] \\ &= \frac{\rho}{8(N+1)s_p^2} \exp[-(p/N)^2 A(t)]. \end{aligned} \quad (31)$$

In other words,

$$\langle \vec{S}_i(t) \cdot \vec{S}_i(0) \rangle = \frac{8\rho}{N+1} \sum_{p=1}^N (S_{p,i}/s_p)^2 \exp[-(p/N)^2 A(t)]. \quad (32)$$

We note that  $t=0$  values are given as sums over the ratios  $(S_{p,i}/s_p)^2$ , which are most easily evaluated through their relation with the link variable representation.

For the finite chains that we consider here, numerical evaluation of the sums presents no problems. The behavior can be generally characterized by three regimes.

1. The initial regime, in which  $A(t)$  remains of order unity and all terms in the sum over  $p$  participate. In this regime the deviation from the initial value is proportional to  $A(t)$ .
2. The intermediate regime from  $1 \leq t \leq \tau_R$ , where  $A(t)$  grows as  $\sqrt{t}$  with time. Then the small  $p$  modes contribute to the sum, but the exponential effectively cuts the sum off at a value of  $p \sim N/\sqrt{A(t)}$ .
3. The asymptotic regime, starting from the Rouse time  $\tau_R$ . Then  $A(t)$  is of order  $1/N$  and the sum is effectively

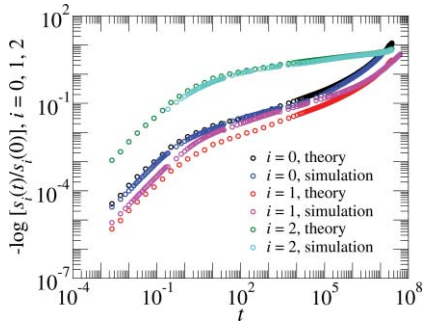


FIG. 4. The correlation functions  $s_i(t) = (\vec{S}_i(t) \cdot \vec{S}_i(0)) / \langle S_i^2 \rangle$  for  $i = 0, 1$ , and  $2$ .

restricted to its first term with exponentially small corrections for the other  $p$ .

In order to check the approximation (32) we performed computer simulations for chains with length  $N = 400$ , and stored at regular times the instantaneous values for the structural variables  $\vec{S}_0$ ,  $\vec{S}_1$ , and  $\vec{S}_2$ . These observables show a dynamical behavior with variations spanning over many decades. For practical purposes, we therefore performed independent simulations with  $n_{\Delta t} = 1, 10^2, 10^4, 10^6$ , or  $10^7$  elementary moves between successive measurements, corresponding to time steps of  $\Delta t = n_{\Delta t} / (N + 1)$ . For each time step, we generated 64 sets of  $10^5$  measurements. The results of these independent simulations were then combined into a single curve in Fig. 5 (see also the next paragraph), which occasionally shows little “hiccup” at the times where the results of independent simulations are joined together.

In Fig. 4, we plot the measured value of the correlators for  $N = 400$  and the calculated values from Eq. (32). The agreement is very good for  $i = 0$  and  $i = 2$ ; for  $i = 1$  the calculated values are about a factor of two smaller than the measured values in the intermediate range. Given the very wide range in time and values of these correlators the correspondence is still impressive. Since the main approximation is the neglect of the cross-correlations in the structural modes, this is indirect proof that although the number of cross-correlations is very large, the main contribution comes from the autocorrelations.

## V. MEAN-SQUARED DISPLACEMENT OF CENTER-OF-MASS AND MIDDLE REPTON

Beyond the dynamical behavior of structural properties of the polymer, the dynamical behavior of its position is also of interest. Two key observables, that characterize this, are the mean-squared displacement of the center-of-mass and of the middle repton.

We performed computer simulations of polymers with length  $N = 100, 200, 400$ , and  $800$  and stored at regular times the positions of the middle repton and the center-of-mass. For each length, we performed independent simulations in which the time between updates of the positions was  $n_{\Delta t} = 1, 10^2, 10^4, 10^6$ , or  $10^7$  elementary moves, corresponding to time differences of  $\Delta t = n_{\Delta t} / N$ . For each length and

time difference, we performed 64 simulations of  $10^5$  time steps each.

We first show the results for the mean-squared displacement of the center-of-mass and the middle repton of the polymer, and then we discuss how the two are related.

The computer simulations show that the mean-squared displacement of the center-of-mass of the polymer behaves as follows:

$$\begin{aligned} & \langle [\vec{X}_0(t) - \vec{X}_0(0)]^2 \rangle \\ & \equiv \langle \Delta_{\text{cm}}^2(t) \rangle \sim \begin{cases} t/N & t \lesssim 1 \\ t^{1/2}/N & 1 \lesssim t \lesssim \tau_R \sim N^2 \\ t/N^2 & t \gtrsim \tau_R \end{cases} \quad (33) \end{aligned}$$

The data corresponding to Eq. (33) are shown in Fig. 5.

For the mean-squared displacement of the middle repton we find from the simulations,

$$\begin{aligned} & \langle [\vec{r}_{N/2}(t) - \vec{r}_{N/2}(0)]^2 \rangle \\ & \equiv \langle \Delta_{N/2}^2(t) \rangle \sim \begin{cases} t & t \lesssim 1 \\ t^{1/4} & 1 \lesssim t \lesssim \tau_R \sim N^2 \\ \sqrt{t/N} & \tau_R \lesssim 1 \lesssim \tau_d \sim N^3 \\ t/N^2 & t > \tau_d \end{cases} \quad (34) \end{aligned}$$

The data corresponding to Eq. (34) are shown in Fig. 6. Note that the microscopic formulation for the mean-squared displacement of the middle monomer is that of a generalized Langevin equation.<sup>15</sup>

The two mean-squared displacements are related in the following manner:

$$\begin{aligned} \langle \Delta_{\text{cm}}^2(t) \rangle - \langle \Delta_{N/2}^2(t) \rangle &= 2\langle \vec{r}_{N/2}(t) \cdot [\vec{S}_0(t) - \vec{S}_0(0)] \rangle \\ &+ \langle [\vec{S}_0(t) - \vec{S}_0(0)]^2 \rangle, \quad (35) \end{aligned}$$

since  $\vec{S}_0$  is the vectorial distance between the center-of-mass and the middle repton. The last term in Eq. (35) can be related to a structural correlation function using the relation,

$$\langle S_0^2(t) \rangle = \langle S_0^2(0) \rangle. \quad (36)$$

This equality holds because the structural distribution is not affected by the position of the middle repton at  $t = 0$ . So we may evaluate this terms as

$$\langle [\vec{S}_0(t) - \vec{S}_0(0)]^2 \rangle = 2[\langle S_0^2 \rangle - \langle \vec{S}_0(t) \cdot \vec{S}_0(0) \rangle]. \quad (37)$$

The correlator of  $\vec{S}_0$  has been worked out in Sec. IV B and the equilibrium value in Eq. (19).

The first term (35), being a cross-correlation between a translational and a structural variable, cannot be computed using the structural modes only. It is interesting to remark that

$$\langle \vec{r}_{N/2}(t) \cdot [\vec{S}_0(t) + \vec{S}_0(0)] \rangle = 0, \quad (38)$$

since the sum  $\vec{S}_0(t) + \vec{S}_0(0)$  is time-reversal invariant, while  $\vec{r}_{N/2}(t)$  changes sign under time reversal. We have verified that the simulations obey this consequence of time-reversal



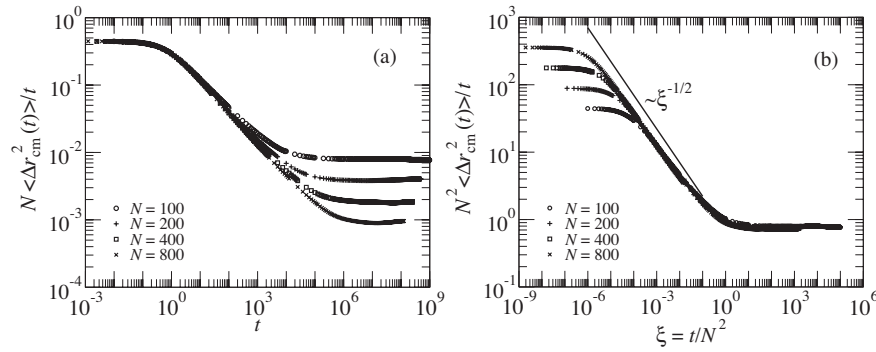


FIG. 5. Behavior of the mean-squared displacement of the center-of-mass,  $\langle \Delta r_{\text{cm}}^2(t) \rangle$ . (a) For  $t < 1$ ,  $\langle \Delta r_{\text{cm}}^2(t) \rangle \sim t/N$ . (b) For  $1 < t < \tau_R \sim N^2$ ,  $\langle \Delta r_{\text{cm}}^2(t) \rangle \sim \sqrt{t}/N$ , while for  $t > \tau_R$ ,  $\langle \Delta r_{\text{cm}}^2(t) \rangle \sim t/N^2$ .

invariance. We therefore have

$$\langle \vec{r}_{N/2}(t) \cdot [\vec{S}_0(t) - \vec{S}_0(0)] \rangle = -2 \langle \vec{r}_{N/2}(t) \cdot \vec{S}_0(0) \rangle. \quad (39)$$

It is clear that the right-hand side of Eq. (39) is negative because the middle repton has a tendency to move in the direction of the instantaneous position of the center-of-mass. It is worth noting that this tendency has a persistent effect on the value of the correlation function. Similarly, it can be shown that the center-of-mass also has a tendency to move toward the middle repton! This means that a reptating polymer experiences more than only internal forces—indeed, part of the forces a reptating polymer experiences originate from the dynamical constraints that prevent the polymer from moving sideways; giving rise to the phenomenon that mode  $p = 0$  is *not* independent from the other nonzero modes. In Fig. 7, we show simulation results for the first term in the left-hand side of Eq. (35). Note that the correlation function saturates asymptotically to a value close to  $N/9$ .

Let us now remark here that the  $t^{1/4}$  behavior of the middle repton is a consequence of two separate aspects of the middle repton's motion: (i) that the middle repton simply moves along the backbone of the polymer (curvilinear motion). For  $t \lesssim 1$  the middle repton moves diffusively along the backbone of the polymer. For  $1 \lesssim t \lesssim \tau_R \sim N^2$  its motion corresponds to that of single-file diffusion, which yields the curvilinear mean-squared displacement of the middle repton  $\langle \Delta u_{N/2}^2(t) \rangle_c$ , where the subscript “c” denotes an average for a given initial polymer configuration, increasing in time

as  $t^{1/2}$ . For  $\tau_R \lesssim t \lesssim \tau_d \sim N^3$  the motion of the middle repton becomes diffusive along the backbone, and its curvilinear motion becomes diffusive in time, i.e., increases  $\sim t/N$ , and beyond  $\tau_R$  the backbone of the polymer is completely renewed in physical space. (ii) The backbone configuration of the polymer, from one end to the other, is that of a random walk in physical space. Hence, the real-space mean-squared displacement of the middle repton  $\langle \Delta r_{N/2}^2(t) \rangle$  averaged over all polymer configurations equals  $\sqrt{\langle \Delta u_{N/2}^2(t) \rangle_c}$ ; i.e.,  $\langle \Delta r_{N/2}^2(t) \rangle \sim t^{1/4}$  for  $1 \lesssim t \lesssim \tau_R$ , and then  $\sim \sqrt{t/N}$  for  $\tau_R \lesssim t \lesssim \tau_d$ .

Given the above discussion, one can relate the mean-squared displacements of the middle repton and the center-of-mass in the following manner. First, we ignore the end-effects, i.e., assume that the motion of all the reptons progress along the polymer backbone, which is fixed in space. Second, for a given backbone of the polymer fixed in space we imagine an interior repton  $i$  of the polymer at  $t = 0$ . After time  $t$ , the repton would have moved to a different location on the backbone, which was occupied by another repton  $j$  at  $t = 0$ : clearly,  $j$  is a function of  $i$  and  $t$ , i.e.,  $j \equiv j_i(t)$ . In fact, the real-space displacement  $\Delta \vec{r}_i(t)$  for repton  $i$  is then written as, using Eq. (2),

$$\Delta \vec{r}_i(t) = \sum_{k=i}^{j_i(t)} \vec{y}_k(0). \quad (40)$$

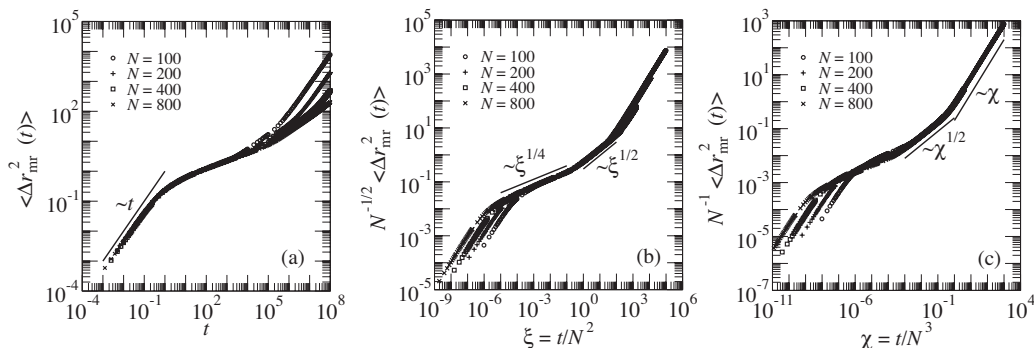


FIG. 6. Behavior of the mean-squared displacement of the middle repton,  $\langle \Delta r_{N/2}^2(t) \rangle$ . (a) For  $t < 1$ ,  $\langle \Delta r_{N/2}^2(t) \rangle \sim t$ . (b) For  $1 < t < \tau_R \sim N^2$ ,  $\langle \Delta r_{N/2}^2(t) \rangle \sim t^{1/4}$ . (c) For  $\tau_R < t < \tau_c$ ,  $\langle \Delta r_{N/2}^2(t) \rangle \sim \sqrt{t/N}$ , and for  $t > \tau_c$ ,  $\langle \Delta r_{N/2}^2(t) \rangle \sim t/N^2$ .

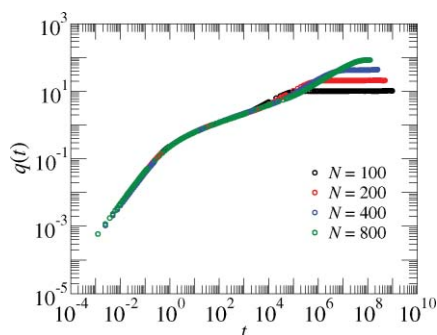


FIG. 7. The cross-correlation function  $q(t) = -\langle \vec{r}_{N/2}(t) \cdot [\vec{S}_0(t) - \vec{S}_0(0)] \rangle$ .

Thereafter, in terms of the link variables  $\{\vec{y}_k\}$ s, the real-space displacement of the center-of-mass for this polymer in time  $t$  is given by

$$\Delta \vec{r}_{\text{cm}}(t) = \frac{1}{(N+1)} \sum_{i=1}^{N+1} \Delta \vec{r}_i(t) = \frac{1}{(N+1)} \sum_{i=1}^{N+1} \sum_{k=i}^{j_i(t)} \vec{y}_k(0). \quad (41)$$

Third, as we observe that for  $1 \lesssim t \lesssim \tau_R$ ,  $\langle \Delta r_i^2(t) \rangle_c \sim t^{1/2}$ , it becomes clear that  $|j_i(t) - i| \sim t^{1/4}$ , meaning that in Eq. (41) each *distinct*  $\vec{y}_k(0)$  appears  $\sim t^{1/4}$  times. With  $\langle \vec{y}_{k_1}(0) \cdot \vec{y}_{k_2}(0) \rangle = \delta_{k_1 k_2}$ , this implies that  $\langle r_{\text{cm}}^2(t) \rangle \sim \sqrt{t}/N$ . Note that this argument can be used again to show that  $\langle r_{\text{cm}}^2(t) \rangle \sim t/N$  for  $t \lesssim 1$  and also that  $\langle r_{\text{cm}}^2(t) \rangle \sim t/N^2$  for  $\tau_R \lesssim t \lesssim \tau_d$ . Indeed, as for the pure time behavior is concerned, this argument shows that for a general reptation motion of a polymer, if the real-space mean-squared displacement of the middle repton increases in time as  $t^\alpha$  for some  $\alpha$ , then the real-space mean-squared displacement of the center-of-mass has to increase in time as  $t^{2\alpha}/N$ .

## VI. DISCUSSION

By extensive simulations we have established scaling properties of the structural modes for a polymer in the repton model. It turns out that their autocorrelation functions can be written as a function of the scaling variable  $p/N$ , where  $p$  is the mode number and  $N$  is the length of the chain, and a function  $A(t)$  which is shared by all modes. This latter function causes exponential decay at short times  $t < 1$  and long times  $t > \tau_R \sim N^2$ , and causes an intermediate regime of stretched exponential decay.

Although the notion of structural modes stems from a freely moving polymer, held together by harmonic forces, it also turns out to be useful for the dynamics in the repton model, for which the chain is restricted to move along its contour. The reasons are, apart from the above-mentioned scaling properties, the following:

1. The structural modes form a complete basis for the structural quantities, i.e., any linear function of the link variables can be written as a superposition of structural modes.
2. The equal-time correlations between the structural modes are strictly orthogonal and they preserve this orthogonality to a high degree for correlations at different

times. So for practical purposes cross-correlations between structural modes may be ignored.

3. This orthogonality allows to write the correlations in time between structural quantities as a sum over the autocorrelation functions of the structural modes.
4. The motion of the center-of-mass is correlated with that of the middle monomer. This stems from the fact that a reptating polymer experiences more than only internal forces—part of the forces a reptating polymer experiences originate from the dynamical constraints that prevent the polymer from moving sideways. The effect of this correlation is captured in the phenomenon that mode  $p = 0$  is *not* independent from the other nonzero modes.

The mean-squared displacement of the center-of-mass shows also changes in its behavior at the same crossover times  $t \sim 1$  and  $t = \tau_R \sim N^2$ : from an initially diffusive regime in which it grows as  $t/N$  similar to a free Rouse chain, via an intermediate regime with anomalous diffusion in which it grows as  $\sqrt{t}/N$ , to an asymptotic regime with reentrant diffusive behavior where it grows as  $t/N^2$ .

The asymptotic regime of the mean-squared displacement of the middle repton equals that of the center-of-mass, as it should to preserve integrity of the chain, but this regime is only entered after the tube renewal time  $\tau_d \sim N^3$ . It has an initially diffusive regime in which it grows linearly with time, also similar to the free Rouse chain. In contrast to the center-of-mass, it shows however two intermediate regimes in which it grows as  $t^{1/4}$  and  $\sqrt{t}/N$ , respectively. We have presented arguments that for general reptation motion of a polymer, a real-space mean-squared displacement of the middle repton scaling as  $t^\alpha$  for some  $\alpha$  must be accompanied by a mean-squared displacement of the center of mass increasing in time as  $t^{2\alpha}/N$ .

Finally, we note that the most interesting and revealing aspect of the mode analysis presented in this paper is the interplay between the translational degree of freedom and the structural degree of freedom, i.e., the cross-correlation between the position of the middle repton and the vector connecting the center-of-mass and the middle repton.

<sup>1</sup>M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon, Oxford, 2003) (reprinted).

<sup>2</sup>M. Doi, *Introduction to Polymer Physics* (Oxford University Press, New York, 2001) (reprinted).

<sup>3</sup>M. Rubinstein, *Phys. Rev. Lett.* **59**, 1946 (1987).

<sup>4</sup>P. G. de Gennes, *J. Chem. Phys.* **55**, 572 (1971).

<sup>5</sup>B. Widom, J. L. Viovy, and A. D. Defontaine, *J. Phys. (France) I* **1**, 1759 (1991).

<sup>6</sup>J. M. J. van Leeuwen and A. Drzewinski, *Phys. Rep.* **475**, 53 (2009).

<sup>7</sup>T. A. J. Duke, *Phys. Rev. Lett.* **62**, 2877 (1989).

<sup>8</sup>G. T. Barkema, J. F. Marko, and B. Widom, *Phys. Rev. E* **49**, 5303 (1994); M. E. J. Newman and G. T. Barkema, *Phys. Rev. E* **56**, 3468 (1997).

<sup>9</sup>A. B. Kolomeisky and A. Drzewinski, *J. Chem. Phys.* **120**, 7784 (2004).

<sup>10</sup>J. M. J. van Leeuwen and A. Kooiman, *Physica A* **184**, 79 (1992).

<sup>11</sup>M. Prähofer and H. Spohn, *Physica A* **233**, 191 (1996).

<sup>12</sup>M. Widom and I. Al-Lehyani, *Physica A* **244**, 510 (1997).

<sup>13</sup>D. Panja and G. T. Barkema, *J. Chem. Phys.* **131**, 154903 (2009).

<sup>14</sup>E. R. Hanson, *A Table of Series and Products* (Prentice-Hall, Englewood Cliffs, NJ, 1975), p. 267.

<sup>15</sup>D. Panja, *J. Stat. Mech.* P06011 (2010).