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Zero-Temperature Properties of Randomly Self-Interacting Polymers

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We study the zero-temperature behavior of several simple models for randomly self-interacting polymers in one and $1+1$ dimensions. Results are based on exact enumeration and closed-form expressions.

KEY WORDS: Polymers; disordered systems; exact enumeration.

Although there has recently been considerable interest in polymers on a random lattice,(1) much less attention has been given to the case of polymers which are made up of a random sequence of monomers.(2–6) This is a problem relevant to protein folding(5,6) and to the study of polyelectrolytes.(7) In this paper we consider several simple models of such random chains, focusing particularly on the effect that the resulting random interactions between monomers have on the ground-state properties. Similar simple models have been introduced recently by other authors.(3,4)

We contrast the cases of site- and bond-disordered chains with long- and short-range interactions in one and two dimensions. Our conclusions are drawn using exact enumeration techniques, compared to exact results where possible.

We first present results for one-dimensional models and then compare them with results for a two-dimensional directed polymer. In one dimension the polymer is modeled by an L-step random walk on a line. Disorder is introduced by assigning a variable $s_i = +1$ or $s_i = -1$ (i: 1,..., L) with probabilities p and $1-p$, respectively, to, in the case of bond disorder,

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each step of the walk or, in the case of site disorder, each site separating consecutive steps of the walk. The energy of a particular configuration is

$$E = \sum_{(i,j)} V s_i s_j \tag{1}$$

For convenience we shall term the variables s_i "charges." We restrict ourselves to the case $V > 0$, corresponding to like charges repelling.

In the case of long-range interactions the sum is taken over all pairs of charges lying at the same position on the lattice. In the one-dimensional short-range case the sum is taken over those pairs that visit the same site consecutively; that is, charges separated by only one change of direction.

For each of the models considered we are interested in the quenched average of the ground-state energy $\langle E_0 \rangle$, its standard deviation σ, and the mean-square end-to-end length of the polymer $\langle R^2 \rangle$ as the length L of the walk tends to infinity. Therefore we define the exponents

$$\langle R^2 \rangle \sim L^{2\nu} \tag{2}$$

$$\langle E_0 \rangle \sim L^{\alpha} \tag{3}$$

$$\sigma^2 \equiv \langle E_0^2 \rangle - \langle E_0 \rangle^2 \sim L^{2\theta} \tag{4}$$

where the angular brackets indicate a quenched average over all possible charge assignments.

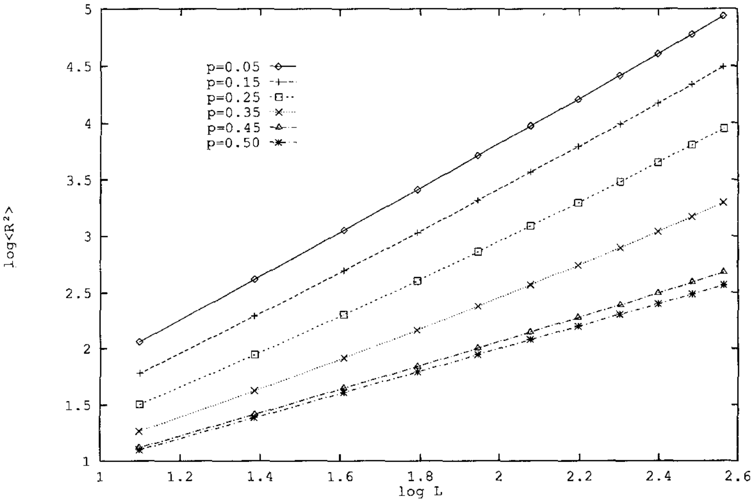

Fig. 1. Variation of the end-to-end distance squared with polymer length for the one-dimensional polymer with charges on the bonds and long-range interactions.

Numerical results were obtained by calculating the ground state exactly for all possible charge configurations of a polymer of length L for values of L up to 14. A typical set of results for the end-to-end distance of the long-ranged one-dimensional walk is shown in Fig. 1. Results for the exponents for the various cases studied are collected in Tables I–V.

The error bars were obtained by comparing different straight line fits to the data. In some cases it was possible to derive a closed form for the ground-state energy and end-to-end distance and hence find exact or very accurate values for the exponents. This provided a check for the numerical calculations. We discuss results for each of the different models in turn.

One-Dimensional Chain with Long-Range Interactions and Charges on the Bonds

We first consider the one-dimensional chain with long-range interactions with the charges on the bonds. For this problem it is possible to derive a closed-form expression for the ground-state energy and its variance and an exact expression for the end-to-end distance squared. Our argument consists of finding a minimum of the functional form of the energy for a given set of charges and then showing that there is at least one possible walk which satisfies the minimization. The result agrees order by order with the exact enumeration results. The advantage of obtaining closed forms for the thermodynamic quantities is that for very small amounts of computing time it is possible to obtain values for very long polymers. This gives essentially exact results and provides an important check on whether the exact enumerations have reached the asymptotic regime.

Consider a polymer made up of n positive and m negative charges. Of these charges let n_k positive and m_k negative charges lie on each bond k. The total energy of the polymer is

$$E = -\frac{V}{2}\sum_k \left[(n_k + m_k) - (n_k - m_k)^2\right] \tag{5}$$

$$= -\frac{V}{2}\left[n + m - \sum_k (n_k - m_k)^2\right] \tag{6}$$

For a given charge distribution the second term in this expression must be minimized to achieve the ground state. Assuming that the number of positive charges is greater than the number of negative charges, the lowest energy arises when $(n_k - m_k)$ is either 0 or 1, with the fewest possible number of terms $n_k - m_k = 1$. The ground-state energy is then simply proportional to the excess number of positive charges over negative ones, giving

$$E_0 = -\frac{V}{2}[n+m-(n-m)] = -Vm \tag{7}$$

or, more generally,

$$E_0 = -V\min(m,n) \tag{8}$$

It is possible to find at least one state which satisfies these conditions: that in which all the positively charged links go to the right and all the negatively charged links to the left. Thus this is indeed an achievable ground-state energy.

Averaging over all possible sets of charges gives

$$\langle E_0\rangle = -\sum_{m=0}^{L}[V\min(L-m,m)]\frac{L!}{m!\,(L-m)!}p^m(1-p)^{L-m} \tag{9}$$

$$\langle E_0^2\rangle = \sum_{m=0}^{L}[V\min(L-m,m)]^2\frac{L!}{m!\,(L-m)!}p^m(1-p)^{L-m} \tag{10}$$

from which the standard deviation σ^2 follows immediately.

A bond k visited an even number of times will have as many links going to the right as the left and therefore will add nothing to the end-to-end distance, whereas a bond visited an odd number of times will add one unit to the end-to-end distance. It follows from the above that the number of bonds visited an odd number of times [that is, those where $(n_k-m_k)^2=1$] is $|n-m|$. Hence the end-to-end distance for a given ground-state distribution is $|n-m|$, and

$$\langle R^2\rangle = \sum_{m=0}^{L}(2m-L)^2\frac{L!}{m!\,(L-m)!}p^m(1-p)^{L-m} \tag{11}$$

This is just the expression for an asymmetric random walk, that is, a biased walk with a probability p of going in one direction and a probability $1-p$ of going in the opposite direction. Performing the sum in Eq. (11) explicitly gives

$$\langle R^2\rangle = (2p-1)^2L^2 + 4p(1-p)L \tag{12}$$

The results from the closed-form expressions (9) and (10) are summarized in Table I. Results for $\langle E_0\rangle$ and $\langle E_0^2\rangle$ can be calculated numerically to high accuracy and show that the model is self-averaging ($\alpha=1$) and has a value of $\theta=1/2$ for all values of p. It can be seen directly from Eq. (12) that for $p=1/2$, $\nu=1/2$, but for all other values of p, $\nu=1$.

Table I. Enumeration and Exact Results for a One-Dimensional Polymer with Charges on the Bonds and Long-Range Interactions

p	θ	"exact" θ	α	"exact" α	ν	Exact ν
0.05	0.51 ± 0.03	0.50	1.0 ± 0.001	1.00	1.01 ± 0.05	1.00
0.15	0.51 ± 0.03	0.50	1.02 ± 0.03	1.00	0.99 ± 0.05	1.00
0.25	0.60 ± 0.05	0.50	1.01 ± 0.03	1.00	0.87 ± 0.05	1.00
0.35	0.68 ± 0.05	0.50	1.1 ± 0.2	1.00	0.61 ± 0.05	1.00
0.45	0.56 ± 0.05	0.50	1.2 ± 0.2	1.00	0.53 ± 0.05	1.00
0.50	0.50 ± 0.05	0.50	1.2 ± 0.3	1.00	0.48 ± 0.05	0.50

Extrapolated results from the exact enumerations are also given in Table I for comparison. This comparison gives some handle on the accuracy of the exact enumeration for models where no closed-form expressions are available. α agrees with the exact value to within the error bars and θ shows broad agreement but with error bars suggested by the data too small. ν shows a slow crossover from 1 to 1/2 as would be expected from the form of Eq. (12). The data showed some odd/even parity effects, which affected the determination of the results to varying degrees.

Equation (12) implies that for large L, $\langle R^2 \rangle$ obeys the scaling form

$$\langle R^2 \rangle \sim L^{2\nu} G(|p-1/2| L^{\phi}) \tag{13}$$

with $\nu = \phi = 1/2$ and $G(x) = 1 + 4x^2$. This scaling form is consistent with the idea that for $p \neq 1/2$ we will have, on large length scales, the behavior of $p = 1$.

One-Dimensional Chain with Long-Range Interactions and Charges on the Sites

Again considering long-range interactions, but with the charges now on the sites, we have not been able to find closed-form expressions for the thermodynamic variables, but have to rely on exact enumeration data. Results are listed in Table II. The numerical data are not as good as for the case with the charges on the bonds, but the evidence is that here, too, the ground-state energy is extensive ($\alpha = 1$) for all values of $p \gtrsim 0.15$. We believe that the anomalous result for $p = 0.05$ is simply a consequence of the limited length of the polymer chains considered, and that here, too, the system is likely to be self-averaging. To obtain a nonzero result for the ground-state energy, it is necessary to have at least two neighboring positive charges, which occurs with a probability too small to give sensible numerical results. Results for the variance are not precise, but are consistent with a value $\theta = 1/2$ for all p.

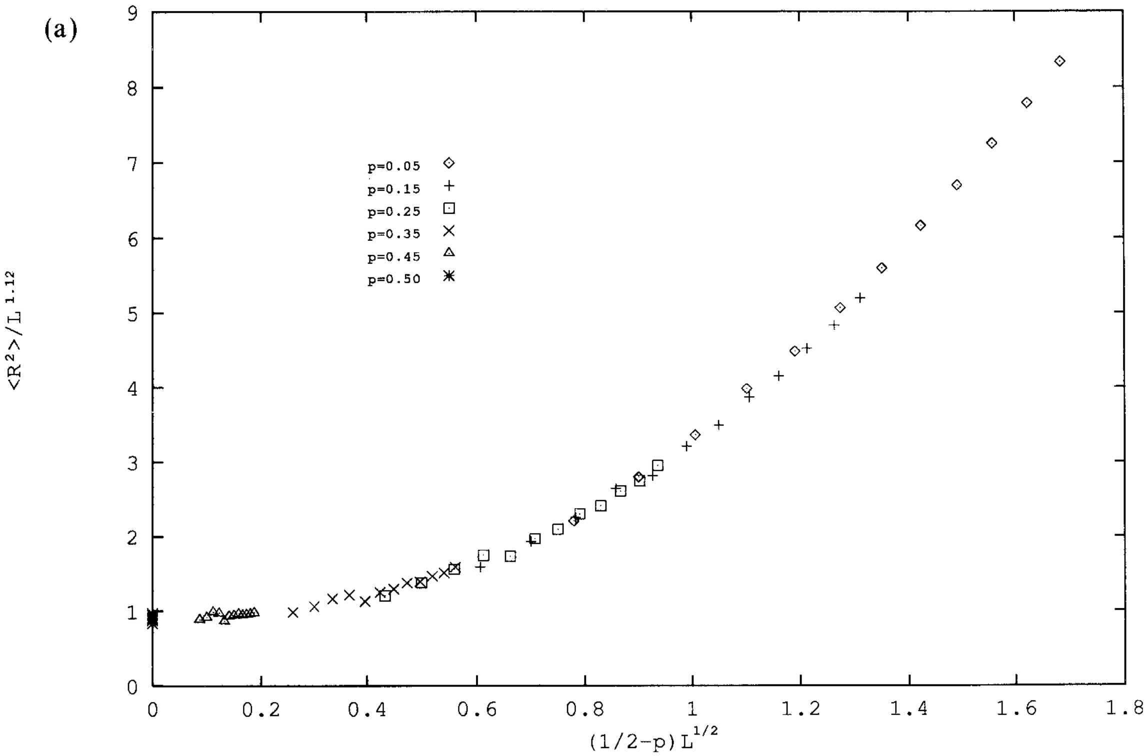

Fig. 2. (a) Scaling function $G(x)$ showing data collapse for the end-to-end distance squared of a polymer with charges on the sites and long-range interactions. (b) Log–log plot of $G(x)$ showing the large-x behavior. The straight line shown has slope 1.76.

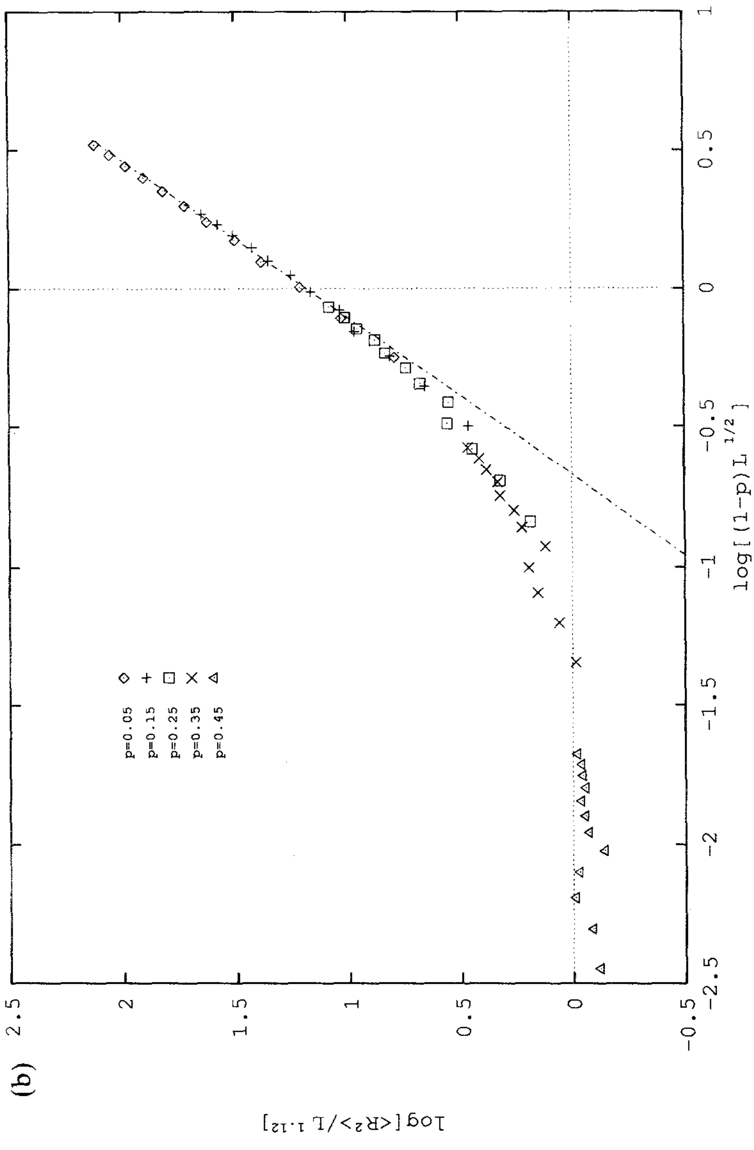

Fig. 2. *(Continued)*

Table II. Enumeration Results for a One-Dimensional Polymer with Charges on the Sites and Long-Range Interactions

p	θ	α	ν
0.05	0.4 ± 0.1	0.5 ± 0.05	0.99 ± 0.05
0.15	0.6 ± 0.1	1.0 ± 0.1	0.99 ± 0.05
0.25	0.7 ± 0.1	1.0 ± 0.1	0.97 ± 0.05
0.35	0.7 ± 0.1	1.0 ± 0.1	0.77 ± 0.05
0.45	0.5 ± 0.1	1.1 ± 0.2	0.58 ± 0.05
0.50	0.5 ± 0.1	1.1 ± 0.2	0.56 ± 0.05

Somewhat surprisingly, the exact enumeration result for the end-to-end distance when $p = 1/2$ is $\nu = 0.56$, which differs from the value of 1/2 obtained when the charges are on the bonds. It is interesting that Kantor and Kardar, considering a similar site problem, but with a Gaussian distribution of charges, find $\nu = 0.574 > 1/2$.(3)

The situation is less clear for the case when $p \neq 1/2$. However, comparing the results of the exact enumeration to that for the bond-disordered case, it would appear at least plausible that $\nu = 1$ away from $p = 1/2$ for the site-disordered case as well. In the bond-disordered case the transition from $\nu = 1/2$ to $\nu = 1$ occurs because at $p = 1/2$ the numbers of positive and negative charges balance on average, giving rise to a compact structure, whereas for $p \neq 1/2$ there is an excess of one species over the other, which gives rise to a tail, proportional in length to this excess and therefore, in turn, proportional to the length of the polymer. It would seem reasonable to assume that a similar mechanism arises in the site-disordered case.

Further support for this behavior comes from a scaling analysis of the data. The above arguments imply that Eq. (13) should still hold with $\nu = 0.56$, and possibly a different value of ϕ. One expects that for $x \to \infty$, $G(x) \to x^{\psi}$ with $\psi\phi + 2\nu = 2$. Figure 2a shows the data plotted as $\langle R^2 \rangle / L^{2\nu}$ versus $(1/2 - p) L^{1/2}$, for different values of p and L. We see that the data collapse fairly well, and note particularly that the results for $p = 1/2$ fall close to a point, implying that, to within numerical errors, $\nu = 0.56$. In Fig. 2b we show the log–log plot of these data. The data become asymptotically linear with slope $\psi = 1.76$, giving good agreement with the scaling assumption and thus strengthening the conclusion that for $p \neq 1/2$, $\nu = 1$.

One-Dimensional Chain with Short-Range Interactions

The exact enumeration data are given for the short-range one-dimensional problems for the bond- and site-disordered cases in Tables III and IV, respectively.

Table III. Enumeration and Exact Results for a One-Dimensional Polymer with Charges on the Bonds and Short-Range Interactions

p	θ	"exact" θ	α	"exact" α	ν	Exact ν
0.05	0.60 ± 0.05	0.50	1.14 ± 0.05	1.00	1.01 ± 0.05	1.00
0.15	0.60 ± 0.05	0.50	1.16 ± 0.05	1.00	0.99 ± 0.05	1.00
0.25	0.64 ± 0.05	0.50	1.20 ± 0.05	1.00	0.87 ± 0.05	1.00
0.35	0.62 ± 0.05	0.50	1.20 ± 0.05	1.00	0.61 ± 0.05	1.00
0.45	0.50 ± 0.07	0.50	1.20 ± 0.05	1.00	0.53 ± 0.05	1.00
0.50	0.50 ± 0.07	0.50	1.20 ± 0.05	1.00	0.50 ± 0.05	0.50

In the bond-disordered case it is clear that the end-to-end distance behaves like that of an anisotropic random walk [$\langle R^2 \rangle$ given by Eq. (12)], since the polymer can minimize its energy by changing direction each time there is a change in the sign of the charges. Once an initial direction is selected, one species of charge will correspond to stepping to the right, and the other to the left, giving $\nu = 1/2$ for $p = 1/2$ and $\nu = 1$ otherwise. This is not the case for the site-disordered problem, as the polymer folds in such a way as to bring into contact charges which are next nearest neighbors on the chain. This property appears to depress the value of the exponent, possibly giving rise to a subdiffusive value for ν, at least for $p = 1/2$.

In the bond-disordered case the ground-state energy is given by

$$E_0 = -V \sum_k (n_k - 1) = -VL + VN_k \tag{14}$$

when n_k is the number of monomers on bond k, and $N_k = \sum_k 1$, the number of visited bonds. It can then be seen that

$$\langle E_0 \rangle = -VL + V\langle N_k \rangle \tag{15}$$

$$\sigma^2 = V^2[\langle N_k^2 \rangle - \langle N_k \rangle^2] \tag{16}$$

Table IV. Enumeration Results for a One-Dimensional Polymer with Charges on the Sites and Short-Range Interactions

p	θ	α	ν
0.05	0.54 ± 0.05	1.0 ± 0.1	0.85 ± 0.05
0.15	0.63 ± 0.05	1.1 ± 0.1	0.61 ± 0.1
0.25	0.66 ± 0.05	1.2 ± 0.1	0.47 ± 0.1
0.35	0.65 ± 0.05	1.23 ± 0.08	0.43 ± 0.1
0.45	0.56 ± 0.05	1.26 ± 0.07	0.42 ± 0.1
0.50	0.53 ± 0.05	1.26 ± 0.07	0.31 ± 0.1

N_k represents a characteristic length scale for the polymer, and therefore we would expect it to scale in the same manner as the other characteristic length scales, that is, $\langle N_k \rangle \sim L^{1/2}$ for $p = 1/2$ and $\langle N_k \rangle \sim L$ for $p \neq 1/2$. This then implies, when substituted back into Eq. (15), that $\langle E_0 \rangle \sim L$ for all p.

The polymer configurations for this problem are the same as for a simple random walk in one dimension with an imposed drift. It is therefore to be expected that any fluctuation in the size of the polymer would be the same as for the case with no drift, $p = 1/2$. This then implies that $\sigma^2 \sim L$.

These results give that for the short-range bond-disordered problem we again have that $\alpha = 1$ and $\theta = 1/2$. We were not able to find similar arguments for the site-disordered case, but it is possible to say that the ground-state energy must lie between 0 and $-VL$, since there can be no more than L interactions in any configuration. This imposes the restriction that $0 \leqslant \alpha \leqslant 1$. The numerical results suggest a higher value for α, but it would seem reasonable that here, too, the ground-state energy is self-averaging ($\alpha = 1$).

Two-Dimensional Directed Polymer with Short-Range Interactions

It is of interest to compare our results for one-dimensional chains to those for a simple two-dimensional model. We consider a self-avoiding random walk on a square lattice which is directed in that steps in the negative x direction are not allowed, as shown in Fig. 3. Charges are assigned to the bonds and every pair of nonconsecutive steps which fall in the same row but in adjacent columns are allowed to interact with the energy defined by Eq. (1).

Results for the directed polymer are given in Table V. As for the one-dimensional models with short-range interactions, our numerical results suggest that the model is not self-averaging, but as the number of interactions is again bounded above by L, $\alpha \leqslant 1$. There is no evidence for a collapse transition: v_x and v_y decrease smoothly with p, indicating, as expected, that the polymer is becoming more compact. It is interesting to note that the ratio of $v_y/v_x = \zeta$ is close to 2/3 for all values of p. This is the exponent that would be expected for a directed polymer in a random environment.(8) Within numerical accuracy, $\theta = \zeta$, whereas for the directed polymer in a random environment $\theta = 2\zeta - 1$.(1,8) It would be of great interest to understand these relations better.

In summary, this paper presents results for the ground-state properties of one- and two-dimensional randomly interacting polymer systems, the

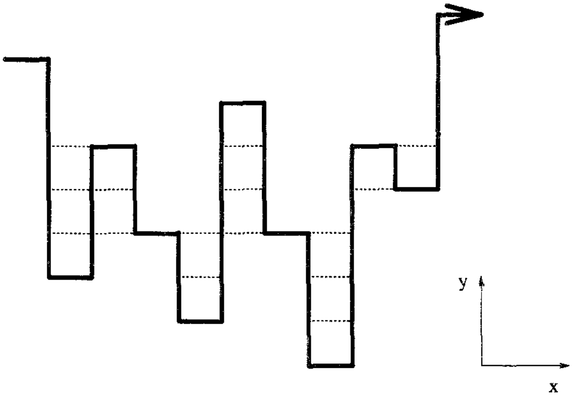

Fig. 3. A directed polymer on a square lattice. The dashed lines show the nearest neighbor interactions.

ground-state energy $\langle E_0 \rangle$, its variance σ^2, and the squared end-to-end distance of the polymer $\langle R^2 \rangle$. The results obtained are sensitive to the details of the underlying model.

For a one-dimensional model with charges on the bonds we have obtained exact expressions for σ^2, $\langle E_0 \rangle$, and $\langle R^2 \rangle$ for the case where the interactions are long-range and for $\langle R^2 \rangle$ for short-range interactions. Other results follow from scaling arguments and exact enumerations. It is important to caution that, where exact results are available for comparison, it is apparent that it can be difficult to reach the asymptotic regime. It was possible to overcome this difficulty for the long-ranged site problem by finding appropriate scaling variables.

A result which needs particular emphasis is that $\nu \neq 1/2$ for $p = 1/2$ for models with charges on the sites in one dimension.

Table V. Enumeration Results for a Directed Polymer with Short-Range Interactions

p	θ	α	ν_y	ν_x	ν_y/ν_x
0.05	0.68 ± 0.05	1.22 ± 0.08	0.66 ± 0.06	0.99 ± 0.05	0.67
0.15	0.71 ± 0.05	1.26 ± 0.1	0.66 ± 0.06	0.96 ± 0.05	0.69
0.25	0.71 ± 0.05	1.26 ± 0.1	0.62 ± 0.05	0.90 ± 0.05	0.69
0.35	0.70 ± 0.05	1.27 ± 0.1	0.55 ± 0.05	0.83 ± 0.08	0.66
0.45	0.67 ± 0.05	1.31 ± 0.1	0.50 ± 0.05	0.80 ± 0.1	0.63
0.50	0.67 ± 0.05	1.31 ± 0.1	0.50 ± 0.05	0.80 ± 0.1	0.63

NOTE ADDED IN PROOF

We would like to thank Dr. F. Igloi for bringing to our notice that the sums in Equations (9) and (10) may be performed using the central limit theorem and approximating the binomial distribution by a Gaussian:

$$\frac{L!}{m!(L-m)!}\,p^m q^{L-m} \simeq \frac{1}{(2\pi Lpq)^{1/2}} \exp\left[-\frac{(m-Lp)^2}{2Lpq}\right]$$

The sums in (9) and (10) may then be treated as integrals, giving the following results

$$\begin{aligned}
\langle E_0\rangle &= L\min(p, 1-p) + O(1) && p \neq 1/2\\
\langle E_0\rangle &= \frac{L}{2}\left\{1-\frac{1}{\sqrt{\pi/2\,L}}\right\} && p = 1/2\\
\langle E_0^2\rangle &= L^2[\min(p, 1-p)]^2 + Lp(1-p) && p \neq 1/2\\
\langle E_0^2\rangle &= \left(\frac{L}{2}\right)^2\left\{1-\frac{2}{\sqrt{\pi/2\,L}}+\frac{1}{L}\right\} && p = 1/2
\end{aligned}$$

It then follows that

$$\begin{aligned}
\sigma^2 &= Lp(1-p) && p \neq 1/2\\
\sigma^2 &= \frac{L}{4}\left(1+\frac{2}{\pi}\right) && p = 1/2
\end{aligned}$$

Hence $\langle E_0\rangle \sim L$ and $\sigma^2 \sim L$ in agreement with the numerical results.

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