Self-Avoiding Random Walk with Multiple Site Weightings and Restrictions

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We introduce a new class of models for polymer collapse, given by random walks on regular lattices which are weighted according to multiple site visits. A Boltzmann weight ω_l is assigned to each $(l+1)$-fold visited lattice site, and self-avoidance is incorporated by restricting to a maximal number K of visits to any site via setting $\omega_l = 0$ for $l \geq K$. In this Letter we study this model on the square and simple cubic lattices for the case $K = 3$. Moreover, we consider a variant of this model, in which we forbid immediate self-reversal of the random walk. We perform simulations for random walks up to $n = 1024$ steps using FLATPERM, a flat histogram stochastic growth algorithm. We find evidence that the existence of a collapse transition depends sensitively on the details of the model and has an unexpected dependence on dimension.

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Introduction.—The transition of a flexible macromolecular chain from a random-coil conformation to a globular compact form, called the coil-globule transition, has been a subject of extensive theoretical and experimental studies [1]. Generally, polymers in a good solvent are modeled by random walks with short-range repulsion (excluded volume). Polymers undergoing a coil-globule transition are then modeled by adding an additional short-range attraction. The canonical lattice model [2,3] for this transition is given by interacting self-avoiding walks (ISAWs), in which self-avoiding random walks on a lattice are weighted according to the number of nearest-neighbor contacts.

From the point of view of continuum models, the drawback of an ISAW is that it contains two different kind of interactions (on-site and nearest-neighbor). In this Letter, we introduce a different class of lattice models for polymer collapse, which has only on-site interactions. This is in spirit similar to the Domb-Joyce model [4], in which a random walk is weighted according to the number of multiple visits of lattice sites.

It has generally been accepted that a model of a polymer in a good solvent based on static random-walk configurations with either a finite site repulsion, as in the Domb-Joyce model, or an infinite site (and/or bond) repulsion, as in the self-avoiding walk or trail models, agree and are accurate for universal features, in both discrete and continuum models. Furthermore, it is generally assumed that the addition of short-range attraction, say between nearest-neighbor sites on a lattice, should describe the coil-globule transition. The collapsed globule is a liquidlike bubble and the transition is expected to be second-order [5] in all dimensions with an upper critical dimension of three. If some stiffness is added to the system the collapsed globule can be frozen and the transition is expected to be first order [6], at least in three dimensions; how this depends on the dimension is not known.

However, an investigation of our new class of models reveals that not only the strength of the coil-globule transition, but also its very existence, depends sensitively on details of the model.

The class of models and the algorithm.—We consider n-step random walks $\xi = (\vec{\xi}_0, \vec{\xi}_1, \ldots, \vec{\xi}_n)$ on a lattice. The number of visits to each site $\vec{x}$ induces a density ϕ_ξ on the lattice sites $\vec{x}$ via

$$\phi_\xi(\vec{x}) = \sum_{i=0}^{n} \delta_{\vec{\xi}_i,\vec{x}}. \tag{1}$$

Interpreting the density $\phi = \phi_\xi$ as a field induced by a particular random-walk configuration ξ, we denote the energy of the field as $E(\phi)$. In the Domb-Joyce model, the energy functional is given by

$$E_{\mathrm{DJ}}(\phi) = a\sum_{\vec{x}} \phi(\vec{x}) + b\sum_{\vec{x}} \phi^2(\vec{x}). \tag{2}$$

The first term in this expression is simply related to the length n of the random walk, as

$$\sum_{\vec{x}} \phi(\vec{x}) = n + 1, \tag{3}$$

so that a is related to a chemical potential. For $b = 0$ we have a pure random walk, while for $b < 0$ the model is weakly self-avoiding. The case $b > 0$ leads to an extremely collapsed phase, which is dominated by configurations occupying a few lattice sites with very high density. Thus, while this model is capable of modelling the swollen polymer regime, further terms in the energy functional need to be taken into consideration to model "realistic" polymer collapse.

Generalizing Eq. (2), we write the energy for a given configuration ξ as

$$E(\xi) = E(\phi_\xi) = \sum_{\vec{x}} f[\phi(\vec{x})]. \tag{4}$$

In Eq. (2), $f(t)$ is simply the quadratic polynomial $f(t) = at + bt^2$, and any particular choice of $f(t)$ gives an alternative to the Domb-Joyce model.

Restricting to a maximal number K of visits to any site incorporates self-avoidance. Choosing $K = 1$ gives self-avoiding walks, and for $K > 1$ we obtain a model with $K - 1$ parameters. To be precise, we choose f to be given by $f(0) = f(1) = 0$,

$$f(2) = \varepsilon_1, \qquad f(3) = \varepsilon_2, \qquad \ldots, \qquad f(K) = \varepsilon_{K-1}, \tag{5}$$

and $f(t) = \infty$ for $t > K$. Thus, each l-fold visited site contributes ε_{l-1} to the energy of a configuration.

The canonical partition function is given by

$$Z_n(\beta) = \sum_{|\xi|=n+1} e^{-\beta E(\xi)}, \tag{6}$$

where the sum extends over all random-walk configurations with n steps, i.e., $n + 1$ sites. Writing

$$\vec{\varepsilon} = (\varepsilon_1, \ldots, \varepsilon_{K-1}) \quad \text{and} \quad \vec{m} = (m_1, \ldots, m_{K-1}) \tag{7}$$

where m_l denotes the number of sites which are occupied by $l + 1$ monomers, the energy can be written as

$$E(\vec{m}) = \sum_{i=1}^{K-1} \varepsilon_i m_i = \vec{\varepsilon} \cdot \vec{m}. \tag{8}$$

This enables us to write the partition function Eq. (6) as

$$Z_n(\beta) = \sum_{\vec{m}} C_{n,\vec{m}} e^{-\beta E(\vec{m})} = \sum_{\vec{m}} C_{n,\vec{m}} e^{\vec{\beta}\cdot\vec{m}} \tag{9}$$

where $C_{n,\vec{m}}$ denotes the density of states, and $\vec{\beta} = (\beta_1, \ldots, \beta_{K-1})$ are generalized temperature parameters, given by $\beta_l = -\beta\varepsilon_l$. In other words, $(l + 1)$-fold visited sites carry a Boltzmann weight $\omega_l = e^{\beta_l}$, with $\omega_0 = 1$ and $\omega_l = 0$ for $l \geq K$.

The density of states is estimated directly by the FLATPERM algorithm (see below for a description). Any averaged quantity Q over the set of parameters $\vec{m}$ for a given length n is calculated by

$$\langle Q \rangle_n(\vec{\beta}) = \frac{\sum_{\vec{m}} Q_{n,\vec{m}} C_{n,\vec{m}} e^{\vec{\beta}\cdot\vec{m}}}{\sum_{\vec{m}} C_{n,\vec{m}} e^{\vec{\beta}\cdot\vec{m}}}. \tag{10}$$

For our simulations, we restrict ourselves to $K = 3$, i.e., we only allow twofold and threefold visits to any site, so that we have two free parameters β_1 and β_2.

We consider two variants of the model which differ in the underlying set of random walks used. For the first variant, we include all simple random-walk configurations, whereas for the second variant, we only include simple random walks without immediate self-reversal. For this reason, we call the first variant RA for "reversal allowed", and the second variant RF for "reversal forbidden". Clearly, RF configurations form a subset of RA configurations. An example of a configuration of the RA model is shown in Fig. 1 for the case of a square lattice. We shall consider both models in two dimensions on the square lattice and in three dimensions on the simple cubic lattice, so that we have a total of four models, which we denote by RA2, RA3, RF2, and RF3.

We have simulated these four models using the FLATPERM algorithm [7]. The power of this algorithm is the ability to sample the density of states uniformly with respect to a chosen parametrization, so that the whole parameter range is accessible from one simulation.

The natural parameters for this problem are m_1 and m_2. The algorithm directly estimates the density of states C_{n,m_1,m_2} for all $n \leq n_{\max}$ and any value of m_1 and m_2. From this, we can then calculate all interesting quantities using Eq. (10). As we need to store the full density of states, we only perform simulations up to a maximal length of $n_{\max} = 256$.

Fixing one of the parameters β_1 and β_2 reduces the size the histogram, and enables us to perform simulations of larger systems. Fixing β_2, say, the algorithm directly estimates a partially summed density of states

$$\bar{C}_{n,m_1}(\beta_2) = \sum_{m_2} C_{n,m_1,m_2} e^{\beta_2 m_2}. \tag{11}$$

In this way, we can simulate lengths up to $n_{\max} = 1024$ at specifically chosen parameters β_1 or β_2. Any averaged quantity $\langle Q \rangle_n$ is now calculated by using a suitably modified version of relation (10).

Results.—For all four models we find SAW behavior in the case of repulsion (i.e. $\beta_1, \beta_2 < 0$). Here, singly visited sites dominate, and the polymer is swollen, as is clearly evident from the scaling of the mean-squared end-to-end distance.

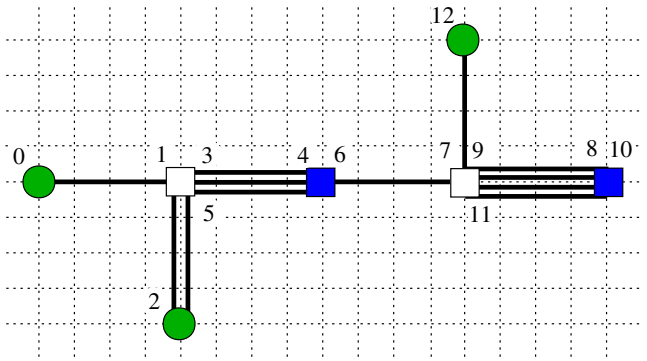

FIG. 1 (color online). Example of a 12-step walk on the square lattice with self-reversal allowed (RA). A filled circle [light gray (green online)] denotes the presence of a single monomer; filled squares [dark gray (blue online)], two; and empty squares (white), three monomers. The numbers denote the sequence of monomers.

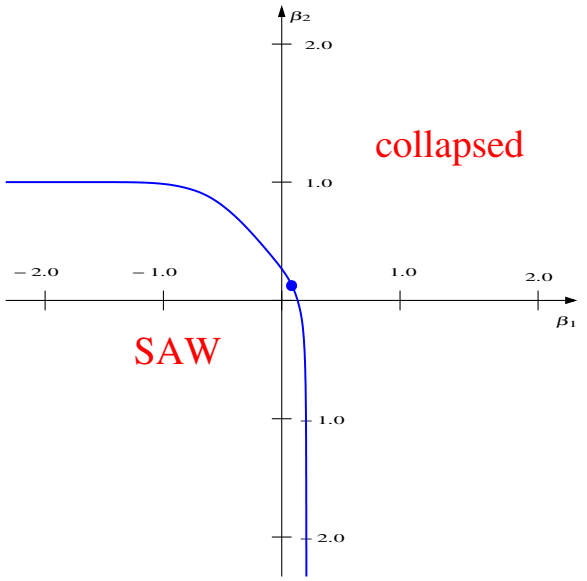

FIG. 2 (color online). Model RF3 with two different phase transitions. On varying β_2 at fixed negative β_1, there is one type of transition (possibly first order), and on varying β_1 at fixed negative β_2, there is another. The dot represents the point at which the type of transition changes.

When $\beta_2 \ll 0 \ll \beta_1$, doubly visited sites should dominate, and when $\beta_1 \ll 0 \ll \beta_2$, triply visited sites should dominate. Our simulations confirm this, as well.

We now turn to the question of phase transitions between these regimes. Naively one would expect to find coil-globule transitions from the swollen phase to the collapsed region. Moreover, for β_1, $\beta_2 \gg 0$, there is competition between doubly visited and triply visited sites, along with the possibility of a further transition.

We have investigated this scenario in detail for all four models.

Model RF3.—For random walks with forbidden reversal on the simple cubic lattice (RF3), we find clear evidence of two different phase transitions, leading to the phase diagram sketched in Fig. 2. We cannot precisely locate the point where the two phase transition lines meet; however, it is likely that this point is located in the first quadrant.

We have analyzed these two phase transitions from simulations at $\beta_1 = -1.0$ and $\beta_2 = -1.0$, respectively. Figure 3 shows fluctuations in m_1 along $\beta_2 = -1.0$ and fluctuations in m_2 along $\beta_1 = -1.0$. In both cases, there is a buildup of fluctuations as the system size increases. The transition at fixed $\beta_2 = -1.0$ is stronger than the transition at fixed $\beta_1 = -1.0$. While the latter transition is second order, the former appears to be first order. It may be the case that the latter transition is of the same type as ISAW collapse in three dimensions. The first-order character of the former transition is supported by the fact that the distribution of m_2 near the transition shows a weak bimodality; see Fig. 4. An investigation of the scaling behavior

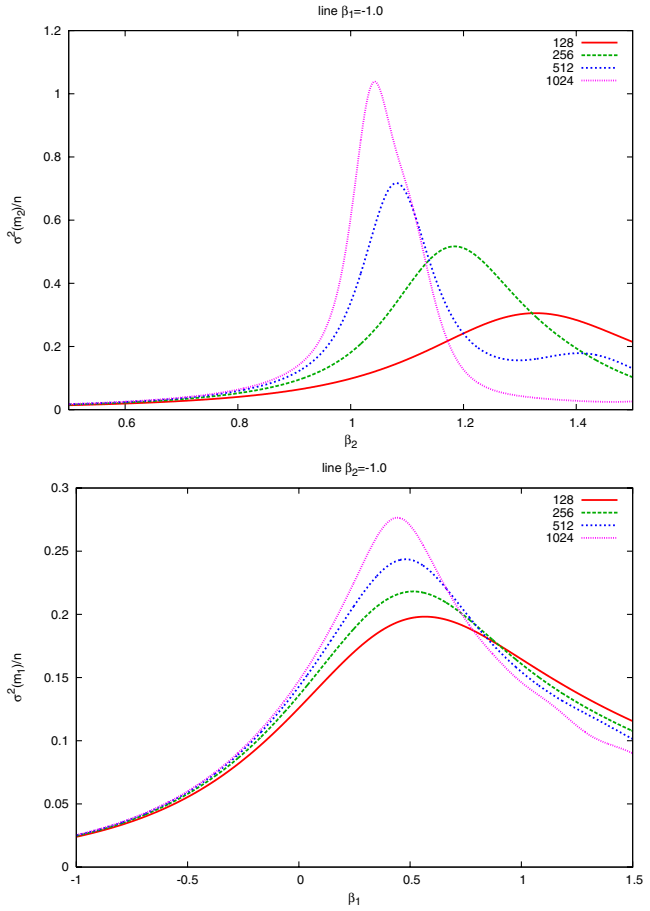

FIG. 3 (color online). Fluctuations in m_2 at $\beta_1 = -1.0$ (top) and in m_1 at $\beta_2 = -1.0$ (bottom) for model RF3.

of the mean-squared end-to-end distance supports these conclusions.

There is no indication of any collapse-collapse transition in the first quadrant joining up with the point at which the type of the collapse transition changes.

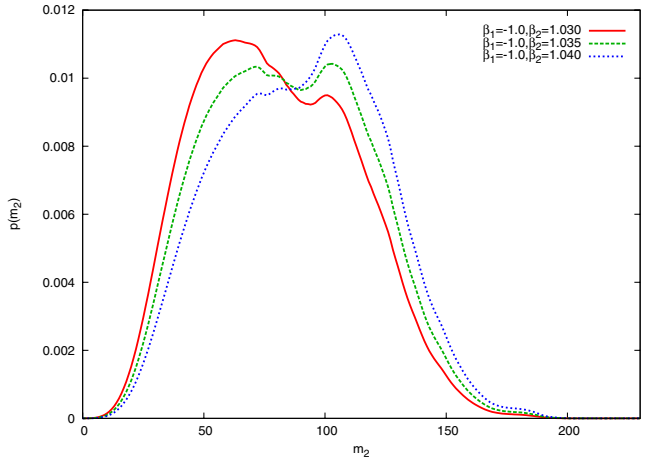

FIG. 4 (color online). Distribution of m_2 at $\beta_2 = -1.0$ near the phase transition for model RF3 at $n = 1024$.

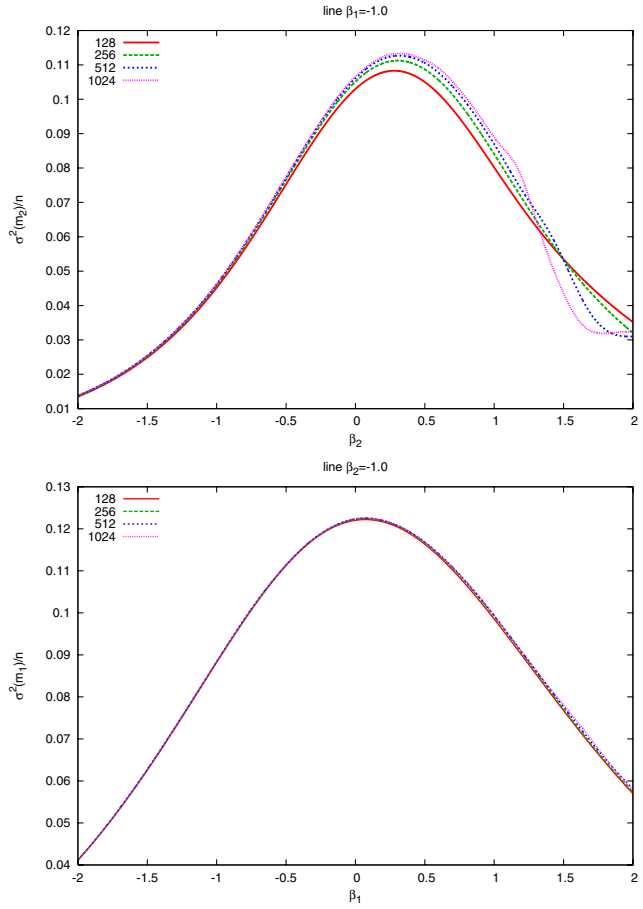

FIG. 5 (color online). Fluctuations in m_2 at $\beta_1 = -1.0$ (top) and in m_1 at $\beta_2 = -1.0$ (bottom) for model RA2, showing convergence to smooth thermodynamic functions.

Model RA2.—We now consider random walks with allowed reversal on the square lattice (RA2), since it provides the largest contrast with RF3. Surprisingly, for RA2, we do not find *any* indication of a phase transition, but merely a smooth crossover. Figure 5 shows fluctuations in m_1 along $\beta_2 = -1.0$ and fluctuations in m_2 along $\beta_1 = -1.0$. In both cases, there is a smooth crossover, and no buildup of fluctuations as the system size increases. There could, of course, still be a weak transition. However, an investigation of the scaling behavior of the mean-squared end-to-end distance supports the conclusion of no transitions. At the three points $(\beta_1, \beta_2) = (-1.0, -1.0)$, $(-1.0, 1.0)$, and $(1.0, -1.0)$, we find clear evidence for self-avoiding walk scaling behavior. We conclude that RA2 is in the self-avoiding walk universality class for all values of β_1 and β_2.

So it would seem that changing the dimension and allowing for reversals has removed the phase transition altogether. This is unexpected.

Models RA3/RF2.—Our analysis of the two remaining models shows that these in some way interpolate between RF3 and RA2. Random walks with allowed reversal on the simple cubic lattice (RA3) and random walks with forbidden reversal on the square lattice (RF2) show behavior similar to each other.

For negative values of β_1, we find a transition from a swollen to a collapsed phase upon increasing β_2. However, for negative values of β_2, we cannot decide whether there exists a very weak phase transition (the specific heat exponent α may be negative) or a simple crossover. An analysis of the mean-squared end-to-end distance scaling is inconclusive.

Conclusion.—In conclusion, we have introduced and simulated various new models of polymer collapse in two and three dimensions. We have found evidence that the type and very existence of the transition depends crucially on subtle aspects of the underlying lattice model, in particular, on whether the random walk contains immediate reversals or not. There is also a greater dependence on dimension than one might expect. There is clearly need for further work to be done to understand these intriguing results. If backed up, these results will surely challenge the current theoretical framework of our understanding of polymer collapse.

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