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MONTE CARLO INVESTIGATION OF LATTICE MODELS OF POLYMER COLLAPSE IN FIVE DIMENSIONS

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Monte Carlo simulations, using the PERM algorithm, of interacting self-avoiding walks (ISAW) and interacting self-avoiding trails (ISAT) in five dimensions are presented which locate the collapse phase transition in those models. It is argued that the appearance of a transition (at least) as strong as a *pseudo-first-order* transition occurs in both models. The values of various theoretically-conjectured dimension-dependent exponents are shown to be consistent with the data obtained. Indeed the first-order nature of the transition is even stronger in five dimensions than four. The agreement with the theory is better for ISAW than ISAT and it cannot be ruled out that ISAT have a true first-order transition in dimension five. This latter difference would be intriguing if true. On the other hand, since simulations are more difficult for ISAT than ISAW at this transition in high dimensions, any discrepancy may well be due to the inability of the simulations to reach the true asymptotic regime.

Keywords: Interacting self-avoiding walks; interacting self-avoiding trails; polymer collapse; coil–globule transition; five dimensions.

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1. Introduction

Recently, evidence[1–3] has been presented, from the investigation of various four-dimensional lattice models, that the collapse or coil–globule transition of an isolated polymer in solution can be seen in high-dimensional models. Moreover, while being second-order, the transition elucidated seems to display many of the characteristics of a first-order transition. At first sight the importance of these findings for physical

polymers may not be apparent, but one must remember that in lower dimensions it has been well established that polymer collapse can be described by a tricritical O(0) field theory with an upper critical dimension of three.[4−6] So extending the evidence for these findings in high dimensions will eventually require a new understanding of the finite size scaling associated with the tricritical theory.

As a consequence of the above considerations, a theoretical framework has been conjectured by the present authors.[1,2] This framework keeps some aspects of the expected behavior in the infinite polymer limit and is the most likely to fit all the evidence available at present. The needed framework has been provided by re-evaluating the validity and meaning of the older collapse transition theory of Lifshitz, Grosberg and Khokhlov[7−10] in the light of modern developments and restricting this older theory to dimensions above the upper critical dimension. The phase transition, which should still be a second-order transition in the thermodynamic limit, now has finite-polymer-length scaling behavior with first-order characteristics, and so has been named a *pseudo-first-order* (PFO) transition. The proposed theory predicts also various dimension-dependent exponents while the general scenario of "false" first-order behavior should be seen in any dimension greater than three. Drawing upon Monte Carlo simulations using the PERM algorithm, we confirm here that indeed the general scenario occurs in five dimensions as well as four. Both interacting self-avoiding walks (ISAW) and interacting self-avoiding trails (ISAT) on a five-dimensional hyper-cubic lattice have been simulated. Clear bimodal distributions for the internal energy are found, which become more distinct with increasing polymer length. Indeed the first-order nature of the transition is even stronger in five dimensions than four. The agreement with the PFO theory is better for ISAW than ISAT, and we cannot rule out that ISAT (or even completely for ISAW) have a true first-order transition in the thermodynamic limit in dimension five. This latter difference would be intriguing if true though we are inclined to argue that since simulations are more difficult for ISAT than ISAW at this transition in high dimensions, any discrepancy is due to the inability of the simulations to reach the true asymptotic regime. Regardless, our results do imply that the transition is at least as strong as the PFO theory predicts and a dimensional-dependence occurs for the associated exponents. If a true thermodynamic first-order transition does occur then the tricritical theory mentioned above would need substantial revision.

We begin by summarizing the predictions of the PFO transition theory and by reviewing the previous work in four dimensions in the next section. In Sec. 3 we present the results of our simulation of five-dimensional ISAW and ISAT.

2. Review

The collapse transition describes the phase transition of an isolated polymer in dilute solution from a high temperature state, which in low dimensions is dominated by excluded volume effects, to a low temperature state dominated by the attractive

interactions between monomers so that the polymer forms a dense globule like a liquid drop. The temperature of the phase transition has been known as the θ-point and signifies a change in the scaling of the mean-square radius of gyration with polymer length N,

$$R_{g,N}^2 \sim aN^{2\nu} \quad \text{as} \quad N \to \infty \,, \tag{1}$$

such that for low temperatures $\nu = 1/d$ in dimension d. In three dimensions, for example, $\nu \approx 0.5874(2)$ at high temperatures,[11] $\nu = 1/2$ (the random walk value) at the θ-point, and $\nu = 1/3$ at low temperatures. However, the upper critical dimension of the excluded volume state is expected to be four so that in five dimensions any excluded volume state will behave, to first approximation, in the same fashion as a pure random walk and in the same fashion as the θ-point, which is expected to have an upper critical dimension of three, with $\nu = 1/2$. So in high dimensions the nature of the collapse apparently changes somewhat with a gross change between two states: a random walk or Gaussian state at high temperatures and a low temperature globular state with $\nu = 1/5$ in five dimensions.

On a deeper level, as recently shown[12] the excluded volume effects at high temperatures do not disappear altogether, and reappear as corrections-to-scaling. There is then a subtle sub-dominant difference between the excluded volume state and θ-state (which after-all is defined as the point where the excluded volume effects are cancelled out by the attractive forces between monomers). Hence, this provides a method for locating the θ-point.

If we now shift our attention to the thermodynamic limit, the application of standard mean-field theory would predict a second-order phase transition with a jump in the specific heat. For finite polymer length one may naively expect that a crossover occurs in a range of temperatures of the order of $N^{-1/2}$, that is the crossover exponent is $1/2$ regardless of dimension ($d \geq 3$).

Now, the theory[1,2,10] of the *pseudo-first-order* transition predicts also a thermo-dynamic second-order transition at a Gaussian θ-point with a jump in the specific heat. However, for finite polymer length the situation differs from the naive theory above. The size of the crossover (or rounding) region of the transition is asymp-totically small relative to the shift of the transition. Inside the crossover region the transition takes also on the characteristics of a first-order transition when con-sidered at finite polymer length, that is, if one considers the distribution of the internal energy at fixed polymer length, then a double peaked distribution occurs in the transition region that becomes sharper with increasing polymer length. In fact, a well defined latent heat can be ascribed. However, this latent heat goes to zero in the thermodynamic limit.

The consequences of the theory are that the polymer collapse transition in high dimensions is shifted below the θ-point by a temperature of the order of $O(N^{-1/(d-1)})$. Using an effective Boltzmann weight $\omega = e^{J/k_B T}$, where $-J$ is the energy associated with a single nearest-neighbor interaction for ISAW, or a single

contact for ISAT, respectively, a finite-size transition temperature[a] $\omega_{c,N}$ approaches the θ-temperature (ω_θ) as

$$\omega_{c,N} - \omega_\theta \sim \frac{s}{N^{1/(d-1)}} \tag{2}$$

for some constant s, that is, the polymer collapse *shift* exponent is $1/4$ in five dimensions. The width of the transition region $\Delta\omega$ at finite N is predicted to scale as

$$\Delta\omega \sim \frac{w}{N^{(d-2)/(d-1)}} \tag{3}$$

for some constant w, that is, the polymer collapse *crossover* exponent is $3/4$ in five dimensions. Hence as mentioned above the size of the crossover region is asymptotically small relative to the shift of the transition. Over the width of the transition there is a rapid change in the internal energy that scales as $O(N^{-1/(d-1)})$: the important point here of course is that this tends to zero for infinite length so the effect of the peak in the specific heat is scaled away for N large, leaving a finite jump in the thermodynamic limit. Just as important, as mentioned above, is to consider the full distribution of internal energy $\rho_{\omega,N}(E)$ as a function of temperature ω and polymer length N. For any ω below ω_θ (high temperatures), and those well above $\omega_{c,N}$ (low temperatures), one expects the distribution of internal energy to look like a single-peaked distribution centered close to the thermodynamic limit value: a Gaussian distribution is expected around the peak with variance $O(N^{-1/2})$. In fact, this picture should be valid for all temperatures outside the range $[\omega_{c,N} - O(N^{-(d-2)/(d-1)}), \omega_{c,N} + O(N^{-(d-2)/(d-1)})]$. When this region is entered one expects to see a double-peaked distribution as in a first-order transition region. For any temperature in this region there should be two peaks in the internal energy distribution separated by a gap δU of the order of $O(N^{-1/(d-1)})$. Each peak should be of Gaussian type with individual variances again of the order of $O(N^{-1/2})$. Defining the "interfacial tension" as the height of the minimum between the two peaks relative to the height of the maxima (at an appropriately chosen temperature, at which both peaks are of equal height), this scaling implies an exponential decrease of the interfacial tension in $N(\Delta U)^2$, i.e., as $\exp(-\text{const } N^{(d-3)/(d-1)})$. Hence as N increases the peaks will become more and more distinct and relatively sharper but the peak positions will be getting closer together. Hence this scenario has been referred to as a *pseudo*-first-order transition. If there were a real first-order transition then the distance between the peaks should converge to a nonzero constant. On the other hand the transition is *not* a conventional second-order phase transition with a well defined limit distribution of the internal energy that is simply bimodal.

In previous work the above scenario has been established for the lattice models of self-avoiding walks[1,2] interacting via nearest neighbor attractive potentials on the

[a]For the sake of ease of expression in this section we will use the word "temperature" to mean the effective Boltzmann weight.

four-dimensional hyper-cubic lattice and self-avoiding trails (lattice paths that are bond-avoiding but not site-avoiding)[3] interacting via site contact potentials on the same lattice. The first-order nature was well established with a reasonable fit to the shift and crossover exponents found. The latent heat was, if anything, larger than expected though it was shown to be decreasing, as expected, with increasing polymer length (two different measures of the latent heat were compared for the sake of consistency).

In this work we have considered both self-avoiding walks and trails interacting as described above on five-dimensional hyper-cubic lattices. This allows us to, firstly, confirm that the above results were not peculiar to four dimensions, and, secondly, to attempt to confirm the dimensional-dependence of the shift and crossover of the transition, namely that the shift becomes larger and the crossover sharper as the dimension is increased. Expecting these results however means that while the transition will be easier to see, it will be more difficult to simulate because of the inherent difficulty in computer simulation of any first-order like transition.

3. Results

We have simulated ISAW and ISAT on a five-dimensional hyper-cubic lattice using the Pruned-Enriched Rosenbluth Method (PERM), a clever generalization of a simple kinetic growth algorithm.[13,14] The PERM builds upon the Rosenbluth–Rosenbluth method,[15] in which walks/trails are generated by simply growing an existing walk/trail kinetically, but overcomes the exponential "attrition" and reweighting is needed in this approach by a combination of enrichment and pruning strategies. Our implementation here directly extends our previous ISAW and ISAT work.[1−3]

Each run had a maximum length $N_{\max}$ set and while individual runs gave information about shorter lengths we collected data from independent runs at some shorter lengths to guarantee statistical independence. For ISAW, simulations were conducted with the maximum lengths $N_{\max}$ set to 256, 384, 512, 768, 1024, 1536, and 2048, and for ISAT, simulations were conducted with the maximum lengths $N_{\max}$ set to 64, 96, 128, 192, 256, 384, and 512. The values of ω were chosen to cover double the width of the collapse region. For this, we estimated the approximate position and width of the specific heat peak at each $N_{\max}$ with an initial simulation and then ran extended simulations at five temperatures around the peak position covering this range.

To locate the θ-point, we ran many closer spaced simulations for ISAW in the range of ω from 1.1 to 1.2 at length $N_{\max} = 16\,384$, and for ISAT in the range of ω from 1.26 to 1.32 at length $N_{\max} = 16\,384$. At each fixed ω, we generated 10^8 configurations of maximal length. To illustrate the computational effort, the generation of a sample of size 10^8 at length $N_{\max} = 16\,384$ took several months CPU time on a 1.3 GHz Pentium-3 Xeon.

We computed statistics for $R_{e,N}^2$, the average square of the end-to-end distance, and for $R_{m,N}^2$, the average square of the mean distance of the internal sites of the walk from the end points for an N-step walk respectively trail, the partition function Z_N, the internal energy U_N and specific heat C_N. Moreover, we generated the distribution of the number of interactions at $N_{\max}$. The distributions obtained at various temperatures were then combined using the multiple histogram method.[16] Error bars were computed as previously described.[1,3]

As indicated above, recent evidence[12] has shown that the corrections to scaling in the swollen phase in five dimensions lead to a scaling of the size of the polymer as

$$R_N^2 \sim dN(1 + cN^{-1/2} + O(N^{-1}))\tag{4}$$

and to a scaling of the partition function as

$$Z_N \sim a\mu^N(1 + bN^{-1/2} + O(N^{-1}))\,.\tag{5}$$

We argued in Ref. 12 that the source of the $N^{-1/2}$ corrections is the excluded volume effect. Therefore, these should disappear at the θ-point. Hence, one method to locate the θ-point is to find where such corrections vanish. Figure 1 shows that the $N^{-1/2}$ corrections vanish near $\omega = 1.13$ for the end-to-end distance of ISAW. Figure 2 shows the scaling of $Z_N/Z_{N/2}^2$ for ISAW, which as a consequence of Eq. (5), scales as $a^{-1}(1 - b(\sqrt{2} - 1)N^{-1/2} + O(N^{-1}))$. Again, we find that the correction to scaling vanishes near $\omega = 1.13$. The consistency of the two estimates is a validation of our method. From our data, we estimate the location of the ISAW θ-point to be $\omega_\theta = 1.130(5)$. For ISAT, we obtain analogously a θ-point estimate of $\omega_\theta = 1.29(2)$.

At this point it is intriguing to note that the PERM algorithm is most efficient at, or near, the θ-point. If one could indeed use this efficiency criterion to locate the θ-point, this would, for example, lead to a very precise estimate of 1.1305(10) for the θ-point of ISAW.
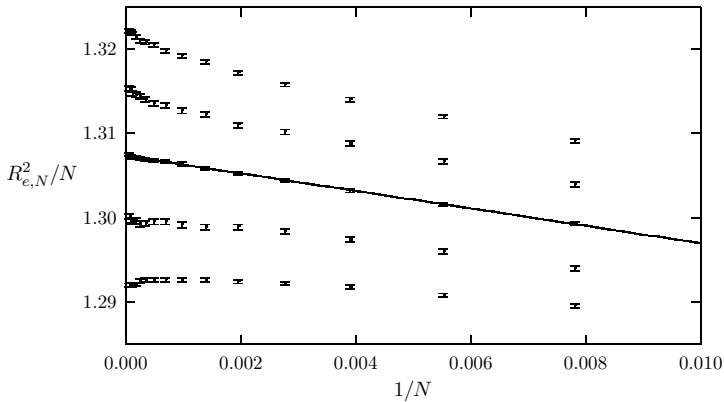

Fig. 1. $R_{e,N}^2/N$ versus $1/N$ in the θ-region with $\omega = 1.120, 1.125, 1.130, 1.135, 1.140$ from top to bottom. The linear fit for $\omega = 1.130$ indicates a clear $1/N$-correction.
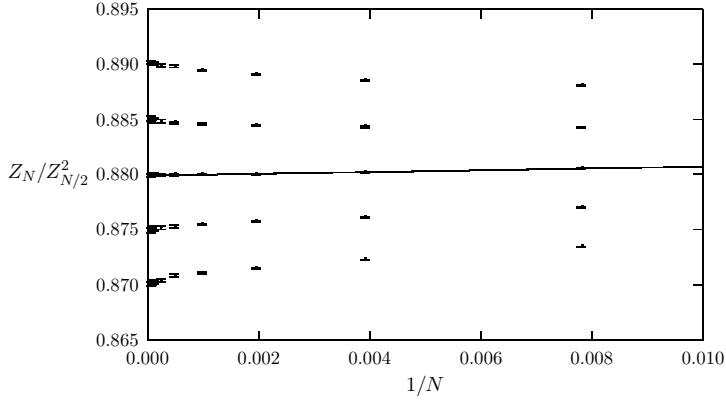
Fig. 2. $Z_N/Z_{N/2}^2$ versus $1/N$ in the θ-region with $\omega = 1.120,\ 1.125,\ 1.130,\ 1.135,\ 1.140$ from bottom to top. The linear fit for $\omega = 1.130$ indicates a clear $1/N$-correction.

The location of the collapse transition $\omega_{c,N}$ was found by considering the peak of the specific heat curves. For both ISAW and ISAT it is observed that the specific heat curves display a divergent specific heat peak and a small transition region of the collapse well separated from the θ-region, see Fig. 3. As we shall see below the region where the specific heat is large is also the region where the distribution of the internal energy is bimodal, with different peaks of this distribution dominant at each end of the temperature range. This indicates that a first-order like transition occurs in this region.

The collapse region is clearly shifted away from the θ-region at finite lengths but moves towards the θ-region as length increases. Assuming there exists a single transition in the thermodynamic limit we now argue that the collapse point and the θ-point must coalesce as N becomes very large. Equation (2) predicts that $N^{1/4}(\omega_{c,N} - \omega_\theta)$ should approach a constant. Using our θ-point estimates, this quantity is plotted in Fig. 4 and indeed is almost a constant over the range of simulated lengths with a small linear correction in $N^{-3/4}$ (the chosen scale is due to the fact that we expect further analytic corrections to scaling in $\omega_{c,N}$). An analogous plot using the four-dimensional value for the shift exponent shows clear curvature. Our data is then consistent with the dimensional-dependence of the shift exponent predicted in Eq. (2).

As Eq. (3) predicts that the width $\Delta\omega$ of the transition decreases as $N^{-3/4}$, Fig. 4 shows also the N-dependence of $N^{3/4}\Delta\omega$. While $\Delta\omega$ decreases even faster than to be expected for even a first-order transition, an asymptotic scaling of $N^{-3/4}$ as predicted by the PFO theory is not inconsistent with the data.

As mentioned above, the character of the transition becomes apparent if one plots the internal energy density distribution (rescaled density of interactions) at the finite-size collapse transition temperature, $\omega_{c,N}$. Figure 5 shows the emergence of a bimodal distribution for both ISAW and ISAT. As lengths increase, the distributions
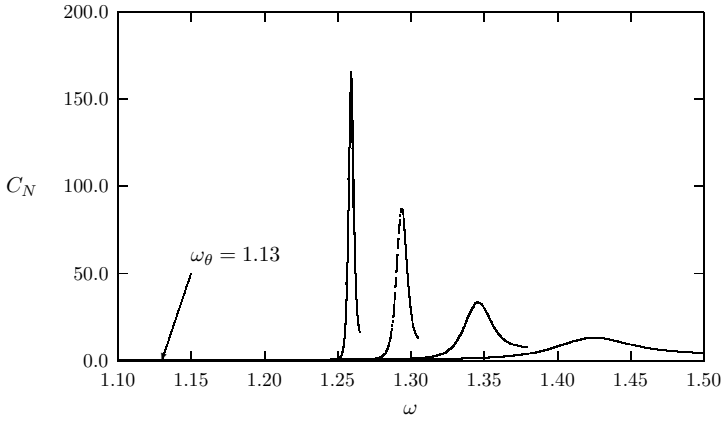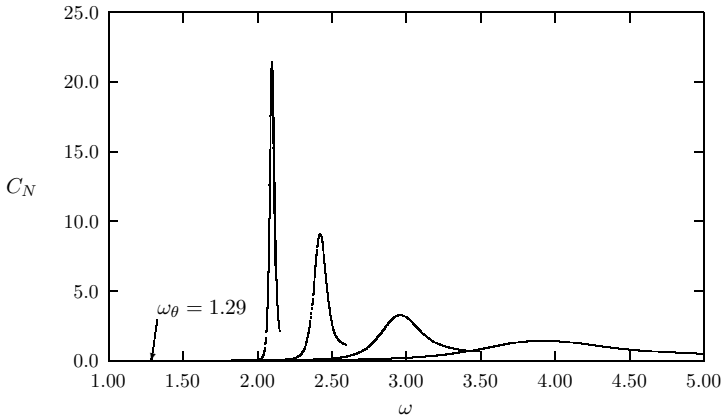
Fig. 3.   Specific heat C_N versus ω for (a) ISAW at lengths 256, 512, 1024, and 2048 and (b) ISAT at lengths 64, 128, 256, and 512 from right to left respectively, using the multi-histogram method.

become dominated by two sharp and well-separated peaks. The values of the minima and maxima of the distribution are different by three orders of magnitude for the largest lengths. As ω is increased through the transition region the density distribution switches from the peak located at a small value of contacts to the peak located at a larger value of contacts, corresponding to a sudden change in the internal energy. In the collapsed phase, the width of the peak is much wider than in the swollen phase, implying a larger specific heat. It is this difference between the swollen and collapsed phases' specific heats that will eventually become the thermodynamic second-order jump. The rapid first-order like switch between two peaks in the distribution becomes more pronounced at larger polymer lengths since the depth of the "valley" between the two peaks becomes relatively larger.
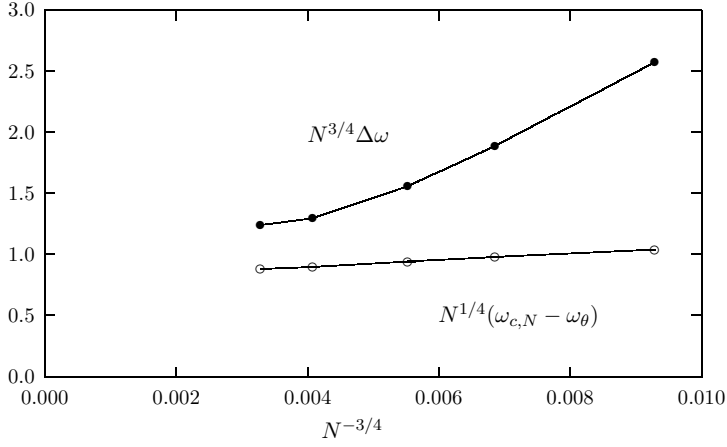
(a)
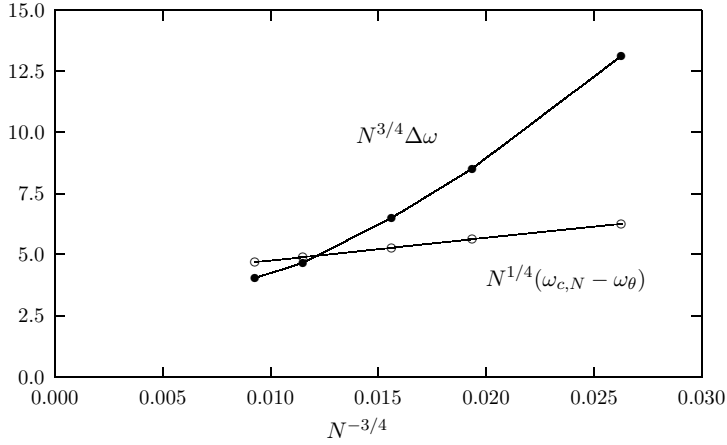
(b)

Fig. 4.   Scaling of the transition: shift and width of the collapse region. Shown are the scaling combinations $N^{1/4}(\omega_{c,N} - \omega_\theta)$ and $N^{3/4}\Delta\omega$ versus $N^{-3/4}$ for (a) ISAW and (b) ISAT.

Continuing with the scaling predictions from the PFO theory, a suitably defined finite-size latent heat, ΔU, should tend to zero as $N^{-1/4}$ in the thermodynamic limit. One possible measure of this latent heat is given by the product of specific heat peak $C_N(\omega_{c,N})$ and specific heat peak width $\Delta\omega$, and another is given by the distance δU of the peaks in the bimodal internal energy distribution. Figure 6 shows the behavior of both of these quantities for ISAW and ISAT. As in four dimensions, one again notices that even at the longest lengths there is considerable discrepancy between the two quantities plotted, so that one needs to be cautious in the interpretation of the scaling behavior. However the ISAW data at the largest
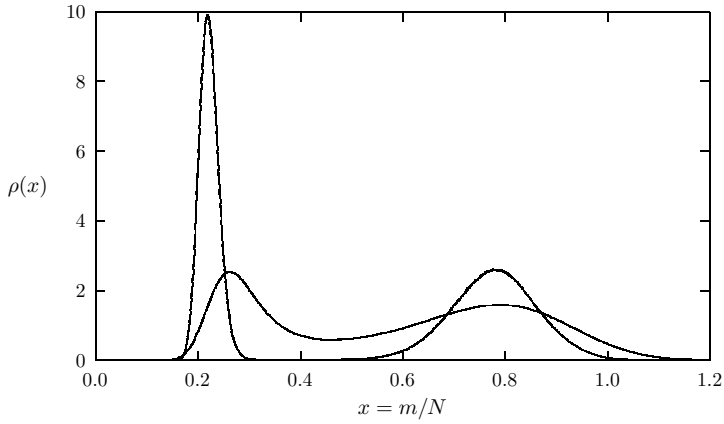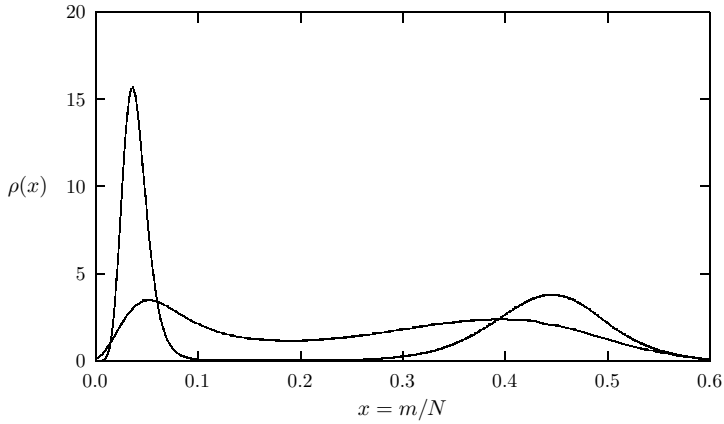
Fig. 5.   Internal energy density distributions at $\omega_{c,N}$ (a) for ISAW at lengths 512 and 2048 and (b) for ISAT at lengths 128 and 512. The more highly-peaked distributions are associated with larger lengths.

lengths is beginning to show a consistent decrease in the latent heat. For ISAT only one measure is so behaved. This difficulty is also evident in Fig. 7, where the interfacial tension between the two peaks is shown. For a true first-order transition this quantity should decrease exponentially in N, whereas the PFO theory predicts an exponential decrease in $N^{1/2}$. The ISAW data is consistent with an exponential decrease in $N^{1/2}$, and so with the PFO hypothesis, while there is significant curvature in Fig. 7 for the ISAT data. In fact the ISAT data is most consistent with a decrease in the interfacial tension exponentially in N, and so with the hypothesis of a true first-order transition. We also note that the interfacial tension
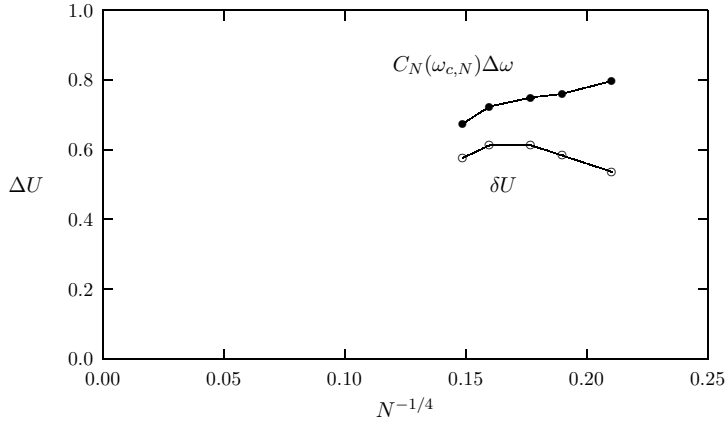
(a)
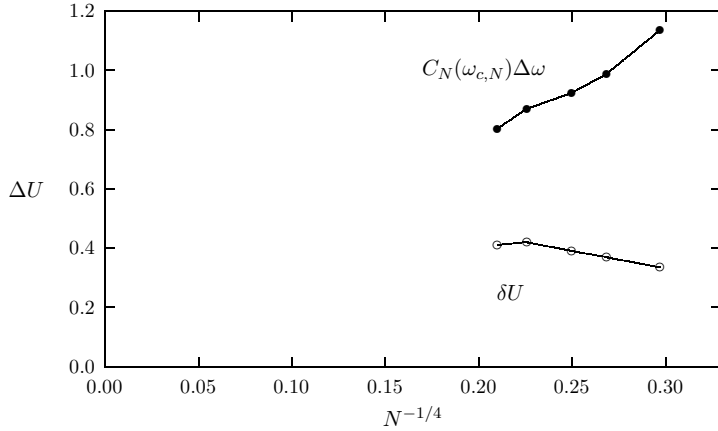
(b)

Fig. 6.   Scaling of the latent heat ΔU for (a) ISAW and (b) ISAT: our two measures of ΔU, $C_N(\omega_{c,N})\Delta\omega$ and peak distance δU are plotted versus $N^{-1/4}$.

is comparatively larger for ISAT than for ISAW, a fact already found in the four-dimensional simulations.[3,17] While this results in a stronger transition for ISAT at shorter lengths, the first-order nature of this transition makes it more difficult to simulate ISAT than ISAW at equal lengths.

In this paper we have discussed the results of large scale Monte Carlo simulations of interacting self-avoiding walks and trails on the hyper-cubic lattice in five dimensions. The data was compared to the predictions of a pseudo first-order transition. The best comparison with the theory came from the shift of the finite size transition temperature which clearly showed a exponent difference from previous four-dimensional simulations. The strength of the transition was found to be even
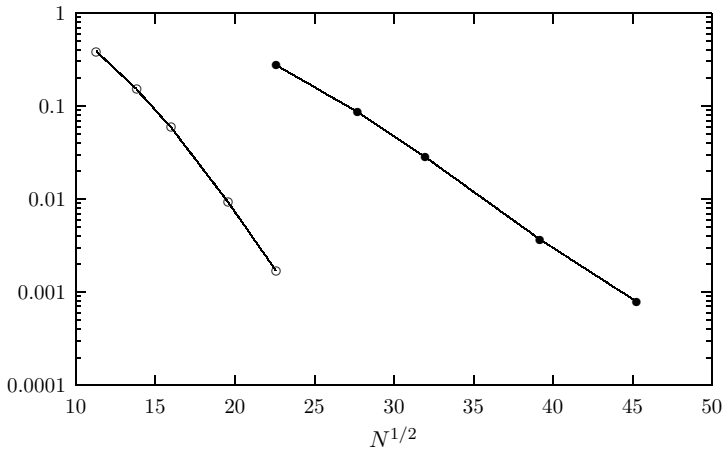
Fig. 7.   "Interfacial tension" for ISAW ($\bullet$) and ISAT ($\circ$): plotted is the height of the minimum between the two peaks relative to the height of the maxima (at an appropriately chosen temperature, at which both peaks are of equal height). The logarithm of this quantity should scale as $-N(\Delta U)^2 \sim -N^{1/2}$. The ISAW data fall consistently on a straight line, and so are compatible with this hypothesis, whereas the ISAT data do not.

stronger in five than four dimensions. The difficulty that follows from this implies that further simulations in even higher dimensions would not be profitable at this stage. While the ISAW data was reasonably in agreement with the PFO theory for all the quantities calculated the ISAT data showed a distribution of internal energy that is consistent with a true first-order transition. We argue though that this is due to the simulations not reaching the asymptotic regime as demonstrated by the inconsistency of various measures of the latent heat. To progress further with present hardware one needs a new algorithm that will both cope with the first-order-like bimodality of the internal energy distribution and, at the same time, be an efficient algorithm in the simulation of collapsed configurations of polymers.

Acknowledgments

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