1 Polymer Collapse in High Dimensions: Monte Carlo Simulation of Lattice Models

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Summary. We present Monte Carlo simulations of the coil-globule transition for interacting self-avoiding walks (ISAW) and interacting self-avoiding trails (ISAT) on the hyper-cubic lattice in four and five dimensions, performed with the PERM algorithm. We find that the second-order nature of the coil-globule transition is masked by *pseudo-first-order* behaviour, i.e. the build-up of first-order-like singularities due to strong finite-size corrections to scaling.

Key words: interacting self-avoiding walks, interacting self-avoiding trails, polymer collapse, coil-globule transition, theta-point, pseudo-first-order transition

It is widely accepted that polymer collapse is a second-order phase transition described by a standard tri-critical O(0) field theory [1, 2, 3], supported by evidence from simulations [4, 5, 6]. Above the upper critical dimension $d_u = 3$, a mean-field analysis of polymer collapse predicts that at the transition point the polymer actually behaves as if it were a random walk. In the thermodynamic limit, one expects a weak transition with a jump in the specific heat (i.e. the specific heat exponent α equals zero). For finite polymer length there is no sharp transition for an isolated polymer and so this mean-field transition is rounded and shifted. In four and higher dimensions one may therefore expect pure mean-field behaviour with a crossover exponent $\phi = 1/2$ [1].

However, a more detailed theoretical framework predicts a rather different scenario [7, 8]. This framework is based on an extended self-consistent mean-field theory of Lifshitz, Grosberg and Khokhlov [9, 10, 11, 12], which takes into account the contribution to the free energy coming from a well-defined surface of the globule in the collapsed phase. In the thermodynamic limit, the surface contribution vanishes and one recovers some aspects of the expected behaviour in the infinite polymer limit. The phase transition, which should still be a second-order transition in the thermodynamic limit, now has finite-polymer-length scaling behaviour with first-order characteristics, and so has been named a *pseudo-first-order* (PFO) transition. The proposed theory also predicts various dimension-dependent exponents while the general scenario

of 'false' first-order behaviour should be seen in any dimension greater than three.

Support for the validity of this theoretical approach comes from simulations of two lattice models of polymer collapse. The first is the canonical model of interacting self-avoiding walk (ISAW), where one associates an attractive interaction with non-consecutive nearest-neighbour interactions of a self-avoiding walk. The model of interacting self-avoiding trails (ISAT) is yet another plausible lattice model of polymer collapse, with self-avoidance restricted to bonds and attractive interaction incorporated via contacts. There is some evidence that while self-avoiding trails are in the same universality class as self-avoiding walks the corresponding interacting models may have different scaling at their collapse points. For instance, simulations on the square lattice show that there are logarithmic corrections to scaling at the ISAT θ-point [13].

Using PERM, a clever generalisation of a kinetic growth algorithm [5], we have simulated interacting self-avoiding walks and interacting self-avoiding trails on the hyper-cubic lattice in four [7, 14] and five dimensions [15]. The implications for collapse scaling is discussed in detail in [8]. PERM is based on the Rosenbluth-Rosenbluth method [16], in which samples are generated by growing configurations kinetically. Additionally, it overcomes the exponential "attrition" and re-weighting needed in this approach by a combination of enrichment and pruning strategies. It turns out that PERM is highly efficient for simulations of polymers near the θ-point.

The main result of our simulations is that in all four cases considered we find a θ-scaling region and additionally a collapse transition region distinct from the θ-point scaling region.

In four dimensions, the θ-point scaling region is simply the region in which the polymer behaves like a random walk. In five dimensions, we must use a more subtle argument, as the swollen phase has now the same dominant scaling behaviour as we expect at the θ-point. As recently shown [17] the excluded volume effects at high temperatures do not disappear altogether, and reappear as corrections-to-scaling. There is now a subtle sub-dominant difference between the excluded volume state and θ-state, which can be used for locating the θ-point.

However, we also find a collapse transition region shifted away from and distinct to the θ-point scaling region. The nature of this collapse is most strikingly seen in the internal energy density distribution near the collapse transition, as shown in Figures 1.1 and 1.2. We find a distinct double peak distribution for the internal energy, which becomes *more* pronounced as the chain length is increased. This would seem to suggest a first-order transition. A closer analysis suggests, however, that the distance of the peaks starts to decrease with increasing system size, which would indicate a vanishing latent heat in the thermodynamic limit.

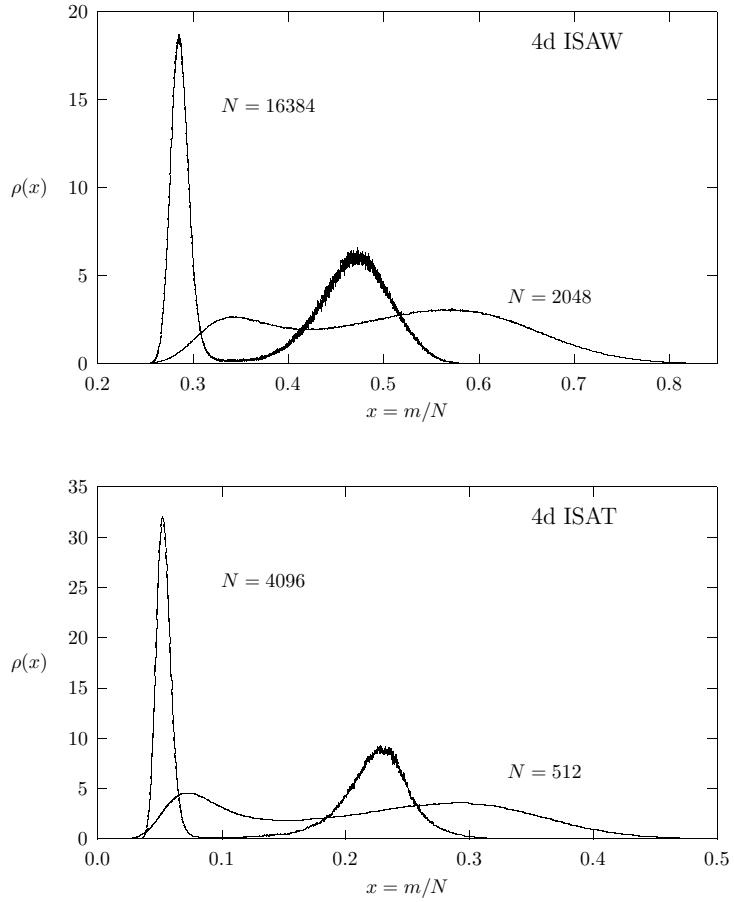

Fig. 1.1. Internal energy density distributions for interacting self-avoiding walks at lengths 2048 and 16384 (above) and interacting self-avoiding trails at lengths 512 and 4096 (below) on the four-dimensional hyper-cubic lattice, at their respective transition temperatures. The more highly peaked distribution is associated with the longer respective length.

In summary, we find that there is a rather dramatic breakdown of the simple crossover scaling for the case of the coil-globule transition of an isolated polymer.

These findings turn out to be consistent with PFO theory. For example, when considering the distribution of internal energy for d-dimensional interacting polymers as a function of polymer length N, PFO theory predicts a collapse region in which one expects to see a double peaked distribution as

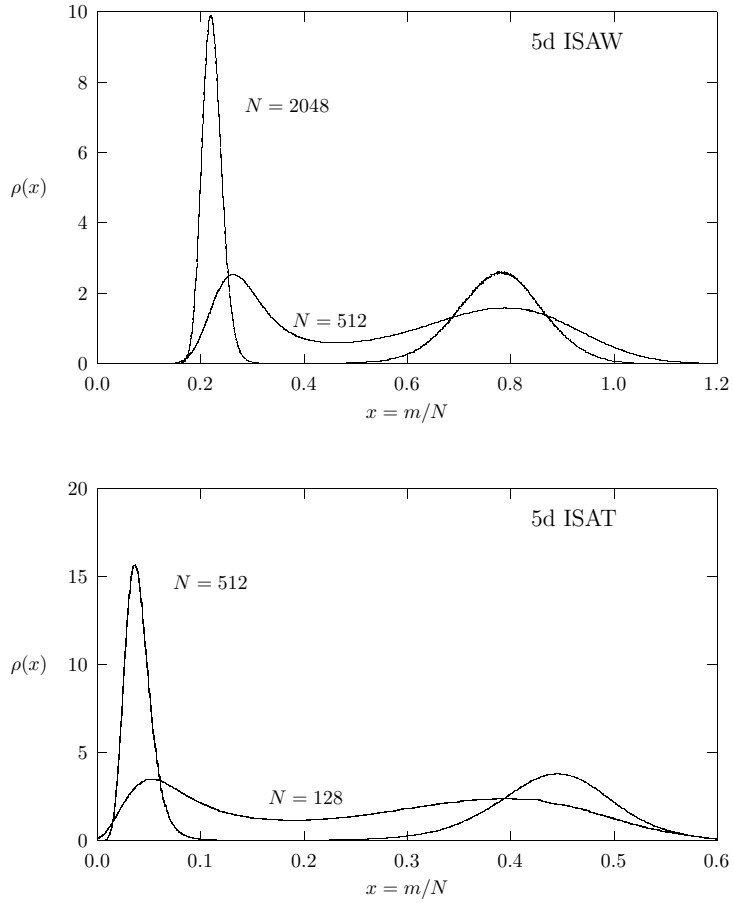

Fig. 1.2. Internal energy density distributions for interacting self-avoiding walks at lengths 512 and 2048 (above) and interacting self-avoiding trails at lengths 128 and 512 (below) on the five-dimensional hyper-cubic lattice, at their respective transition temperatures. The more highly peaked distribution is associated with the longer respective length.

in a first-order transition region. There should be two peaks in the internal energy distribution separated by a gap of the order of $O(N^{-1/(d-1)})$, with each peak being of Gaussian type with individual variances of the order of $O(N^{-1/2})$. As N increases the peaks will become more and more distinct and relatively sharper but the peak positions will be getting closer together. This is why this scenario has been termed a *pseudo*-first-order transition. If there were a real first-order transition then the distance between the peaks

should converge to a non-zero 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.

Comparing the data for interacting trails and walks in more detail, we note further that the bimodal distribution emerges for trails at much shorter configurations than for walks, so that the peaks in the distribution for trails at length $N = 512$ are already more pronounced than the peaks in the distribution for walks at length $N = 2048$, which is is due to the smaller effective excluded volume in ISAT as compared to ISAW.

Similarly, when comparing the data for four and five dimensions, we note that the bimodal distribution emerges in five dimensions at much shorter configurations than in four dimensions. The reason for this is that the bimodality is caused by the surface contribution to the finite size free energy. As dimensionality increases, so does the relative proportion of globule surface to volume.

A closer look at the distribution for ISAT in five dimensions in Figure 1.2 shows that the distance between the peaks does not decrease at the simulated system sizes. However, as collapsed trails of length $N = 512$ in five dimensions have diameters of less than four lattice spacings, it is likely that the asymptotic scaling regime, in which typical length scales are much larger than the lattice spacing, has not yet been reached.

In summary, we have discussed the results of large scale Monte Carlo simulations of interacting self-avoiding walks and trails on the hyper-cubic lattice in four and five dimensions. The data was compared to the predictions of a pseudo first-order transition. The transition was found to be stronger for ISAT than for ISAW and stronger in five than four dimensions.

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