Pseudo-First-Order Transition in Interacting Self-avoiding Walks and Trails

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Abstract

The coil-globule transition of an isolated polymer has been well established to be a second-order phase transition described by a standard tricritical O(0) field theory. We present Monte-Carlo simulations of interacting self-avoiding walks and interacting self-avoiding trails in four dimensions which provide compelling evidence that the approach to this (tri)critical point is dominated by the build-up of first-order-like singularities masking the second-order nature of the coil-globule transition.

Key words: first-order transition, critical point, tricritical point, scaling theory, interacting self-avoiding walks, interacting self-avoiding trails, polymer collapse, coil-globule transition
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Much work has been done on polymer collapse models in the physically important dimensionalities two and three. In addition to general tri-critical scaling theory, results from conformal field theory and exactly solvable models have given a thorough understanding of the polymer collapse transition, leaving but a few open questions. At the upper critical dimension $d_u = 3$ results from field-theoretical work and simulations also confirm the tri-critical scaling behaviour [1–3].

Until recently [4], polymer collapse above the upper critical dimension has attracted little attention, presumably because it was generally accepted that it is described by standard mean field theory and therefore should be of little interest. However, our work in [5–7] uncovers a surprisingly interesting scenario.

Mean-field theory is generally applicable to second-order phase transitions above their upper critical dimension, and so is believed to provide an adequate description of the approach to such critical points. One type of transition where mean-field theory should hold are tri-critical points [8] for dimension $d > 3$. The region around a tri-critical point in general dimension is described by

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crossover scaling forms, where quantities depending on two relevant parameters can be essentially described by functions of a single scaling combination of those two parameters.

The application of the mean-field theory of a tricritical point to 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 $\alpha = 0$. 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 expect pure mean-field behaviour with a crossover exponent of 1/2 [9].

On the other hand, for $d > 3$ Sokal [10] has pointed out that the alternative method of analysing collapse which has been shown to be equivalent to the field theoretic approach, namely the continuum Edwards model, has difficulties: in fact, an analysis of the Edwards model shows that the crossover exponent is given by $\phi_E = 2 - d/2$, which for $d = 4$ gives $\phi_E = 0$! In passing we note here that the same analysis predicts the shift of the θ-point, defined say via the universal ratio of the radius of gyration to the end-to-end distance equalling its Gaussian value, should scale as $N^{-(d/2-1)}$ so $\psi_E = (d/2-1) \neq \phi_E$. This difference between the shift and the crossover exponent implies that strict crossover scaling has broken down. Of course, the theoretical fact that the swollen phase should also be Gaussian for $d > 4$ does raise the suspicion that the analysis of the Edwards model for polymer collapse may be subtle for $d > 3$.

To consider such issues, we have simulated 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. (For obvious reasons it is not sufficient to model the collapse by simply weakening the self-avoidance, as this allows for the possibility of an unphysical buildup of density in small spacial regions.)

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 [11].

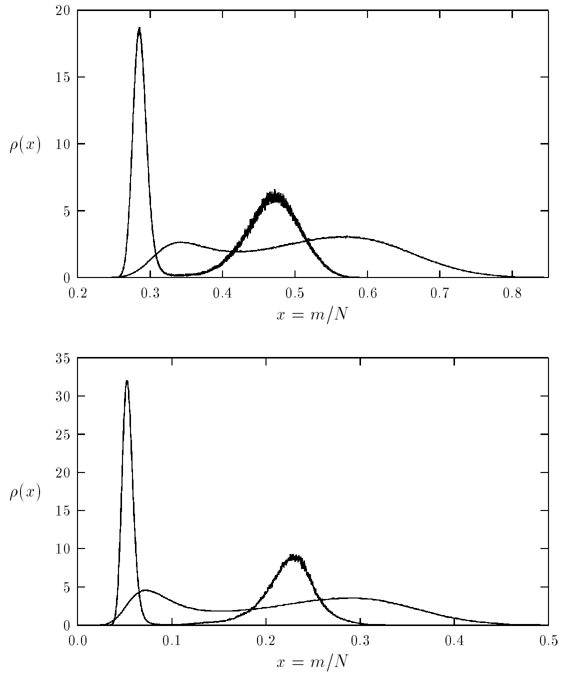

Fig. 1. *Internal energy density distributions for interacting self-avoiding walks at lengths 2048 and 16384 (above) and interacting self-avoiding trails at lengths 512 and 4096 (below) on the four-dimensional hyper-cubic lattice, at their respective transition temperatures. The more highly peaked distribution is associated with the longer respective length (Figures 11 from [5] and 7 from [7]).*

Using PERM, a clever generalisation of a kinetic growth algorithm [2], we have simulated interacting self-avoiding walks and interacting self-avoiding trails on the four-dimensional hyper-cubic lattice [5,7], and report on the implications for collapse scaling in [6]. PERM builds upon the Rosenbluth-Rosenbluth method [12], in which configurations are generated by simply growing an existing configuration kinetically but overcomes the exponential "attrition" and re-weighting needed

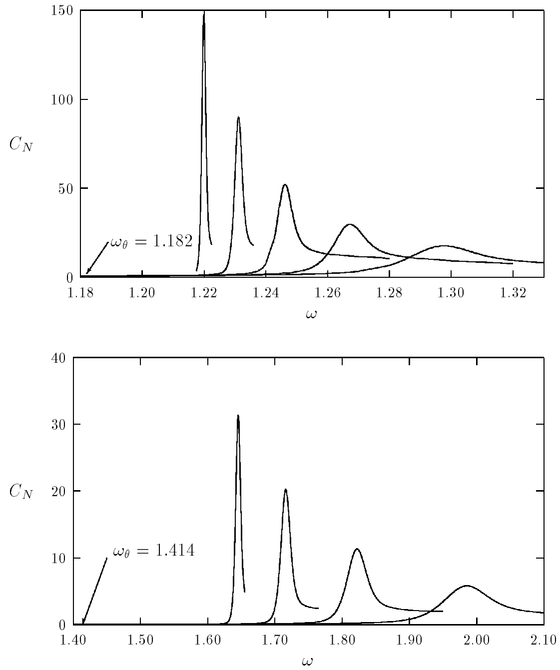

Fig. 2. *Specific heat C_N versus ω for interacting self-avoiding walks at lengths 1024, 2048 , 4096, 8192 and 16384 (above) and for interacting self-avoiding trails at lengths 512, 1024, 248, and 4096 (below) on the four-dimensional hyper-cubic lattice. (Figures 9 from [5] and 5 from [7]).*

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.

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. It is likely that the build up of the tri-critical point is through the forming of singularities that have more in common with a (non-critical) first-order transition! However, this can be explained by a different kind of mean-field approach (not starting with an explicitly tri-critical Landau functional); moreover, the region around the tri-critical point needs to be described by more complex scaling forms. This second issue is in fact separate from the first-order nature of the scaling approach: we speculate that this behaviour is intimately related to the general description of systems where mean-field theory is used, so may have more general applicability.

The main evidence for this scenario stems from the internal energy density distribution near the collapse transition, which is shown in Figure 1. The character of that transition is particularly intriguing; 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. If this were the case there would be a delta function peak forming in the specific heat but we find that while a peak is indeed forming it does not seem to be growing linearly with the size of the polymer, see Figure 2. Moreover, there is a θ-point scaling region distinct from the collapse transition (the location of which is indicated in Figure 2), a scenario which is incompatible with a first-order transition.

Fortunately there is a (suitably extendable) theoretical framework that is consistent with the evidence we present. This framework was explained in a paper by Khokhlov [13] who applied the mean-field approach of Lifshitz, Grosberg and Khokhlov [14–16] to arbitrary dimensions. This theory is based on a phenomenological free energy in which the competition between a bulk free energy of a dense globule and its surface tension drive the transition. Until recently [17] the consequences of this surface free energy were largely ignored in the polymer literature.

The implications of this theory for polymer collapse above the upper critical dimension are described in [5,6]. The major conclusion is that the finite-size character of the coil-globule transition in four dimensions is first-order despite the thermodynamic limit being probably adequately described by mean-field tricritical behaviour. We propose to call this a *pseudo-first-order transition.* One consequence is the breakdown of conventional tri-critical scaling; the single-variable scaling form needs to be replaced by more complex scaling forms.

When 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 $N = 2048$. To quantify this observation, we turn to the scaling predictions of LGK theory. An important parameter in the theory is the quotient a^d/v, where a is the mean-square distance between two subsequent monomers (repeated unit element of the polymer: equivalent to occupied sites of the lattice model) along a chain and v is the effective excluded volume of a monomer, defined via the vanishing of the second virial coefficient at the θ-temperature. For instance, the shift of the transition temperature is given by

$$\frac{\omega_{c,N} - \omega_\theta}{\omega_\theta} \sim \left(\frac{\tilde{s}a^4}{Nv}\right)^{1/3} \tag{1}$$

where $\tilde{s}$ is a constant proportional to the quotient of the third virial coeffficient and the excluded volume squared. We estimate that $N^{1/3}(\omega_{c,N} - \omega_\theta)$ asymptotes to 3.4(1) for trails, and for walks we estimate for the same quantity the value 0.92(3). Identifying a with the lattice constant, which in both models is set equal to one, we can get a rough estimate for the relative size of the effective excluded volume v in both models. We obtain

$$\frac{v_{SAT}}{v_{SAW}} \approx 0.03\frac{\tilde{s}_{SAT}}{\tilde{s}_{SAW}} \tag{2}$$

and thereby quantify the intuitive notion that the excluded volume effect is numerically "weaker" in trails than in walks, though of the same basic type.

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