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‘Smart’ self-avoiding trails and the θ collapse of chain polymers in three dimensions

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Abstract. Recently, it was shown that certain ‘smart’ self-avoiding trails have end-to-end distances $R_N^2 \sim N$ in three dimensions. Also, the corrections to scaling of R_N^2/N and the specific heat are qualitatively very similar to those for polymers exactly at the θ point. The question was thus posed whether they are in the same universality class as linear polymers at the θ temperature. We show that this is not the case since these trails show a first-order transition, instead of the second-order transition at the usual θ point. We argue that this is due to the fact that the ‘smartness’ of these trails implies that the renormalized n -body interactions vanish identically for any finite $n \gg 3$. We conjecture that the qualitative similarity with recent simulations of θ polymers indicates that for n -body interactions the renormalized three-body interaction is small in real polymers.

1. Introduction

Chain polymers continue to be an interesting object of study, both because of their importance in biochemistry and because of the challenges they offer to theoretical descriptions. In particular, the θ collapse from an open coil to a closely packed globule has been a source of controversy and a subject of numerous studies.

In the present paper we shall deal only with the θ collapse in three dimensions, though we should stress that some of our arguments hold for two dimensions as well. Since the θ collapse is a tricritical phenomenon with the upper critical dimension $d_c = 3$, we should expect mean-field behaviour with logarithmic corrections. These corrections have been computed to leading order [1], and it has even been claimed that they were seen in experiments which confirmed these predictions [2, 3].

The present work was triggered by two independent recent papers. One was a Monte Carlo study of fairly long chains (mostly $N = 5000$, but some much longer) with very high statistics [4], where we showed that most detailed renormalization-group (RG) predictions of corrections to the mean-field behaviour are not verified for lattice polymers. Indeed, they are typically violated by orders of magnitude, and even one critical exponent (that which describes the T dependence of the density inside a large globule) seems to be different from its mean-field value. Some of our findings, such as the fact that the specific heat at the θ point diverges much faster with N (the chain length) than the RG prediction $c \sim (\ln N)^{3/11}$ were found already in previous studies [5], but it was only our study in [4] which showed that there is a definite problem.

The other paper which motivated the present work is due to Prellberg and Owczarek [6]. They observed that some kinetically grown self-avoiding trails as well as the ‘tricolour walk’ of [7] show obvious similarity with self-avoiding chains *exactly* at the θ point. They

show that the end-to-end distance scales as $R_N^2 \sim N$ asymptotically, but there seem to be corrections of the form

$$\frac{R_N^2}{N} = A - \frac{B}{\sqrt{N}} + \dots \quad (1)$$

with $B > 0$. Comparison with the simulations of [4] shows that indeed those data are also very well fitted by equation (1) with B having the same order of magnitude. In contrast, the RG prediction [1]

$$\frac{R_N^2}{N} = A \left(1 - \frac{37}{363 \ln N} + \dots \right) \quad (2)$$

describes neither of these data, since the correction term is too small by about one order of magnitude.

Similarly, the authors of [6] show that the specific heat (per monomer) scales roughly as

$$c \sim [\ln N]^\zeta \quad (3)$$

with $\zeta \approx 1-2.5$ for the various models, but not with $\zeta = \frac{3}{11}$ as predicted by the RG. In our simulations in [4], we had found $\zeta \approx 1$.

The main interest in these kinetically grown walks is twofold: first, one knows their θ point *exactly*, and secondly, they are extremely easy to simulate, much easier than self-avoiding walks with nearest-neighbour attraction. To understand this, we have first to recall how a self-avoiding walk (SAW) is generated on a computer. The most naive way would be to choose a starting point, and add monomer by monomer in a random way. In order to take into account the self-avoidance without introducing a bias, one should *throw away* all configurations where this leads to a self-crossing. This leads to a roughly constant chance that the entire chain has to be discarded when adding the next monomer, and thus to an exponential *attrition*.

For overcoming this attrition, we mention just two methods. One is *enrichment* [8]: after each successful attempt of adding one or a group of monomers, we store one or more copies of the (partially constructed) chain and try to prolong *each* copy. Carefully controlling the copying rate, one can compensate exactly for the attrition and obtain very long chains. Essentially a randomized and recursive implementation of this idea was used in [4], and we shall also use it in the present paper. We shall not say more about this algorithm, but refer to [4, 9, 10] where it is described in detail. We just point out that it allows us to obtain (among others) grand canonical distributions where the chain length fluctuates, its average being controlled by a constant fugacity.

The other method is the Rosenbluth–Rosenbluth (RR) method [11]. Here, one chooses a different direction for the newly added step if the first choice would lead to a self-crossing. Of course, this is not always possible: the walk might have run into a ‘cage’ where *all* neighbours are already occupied. Thus this method, in general, only reduces attrition (often very substantially!) without being able to eliminate it completely. It would also lead to a bias, if all generated chains were given the same weight. Let us consider a lattice with coordination number \mathcal{N} . One of the \mathcal{N} neighbours of a site is occupied by its predecessor (unless it is the start of the chain). If k other neighbours are also occupied, each of the allowed continuations gets a weight $1/(\mathcal{N} - k - 1)$ instead of the correct weight $1/(\mathcal{N} - 1)$. To compensate for this bias, each successful chain has to be weighted by a factor $\prod_{i=1}^N (\mathcal{N} - k_i - 1)$ which gives a larger weight to stretched configurations than to denser ones. If this factor is *not* included, this would essentially simulate an attractive potential between neighbouring monomers.

Let us now discuss how this applies to self-avoiding trails ('dsATS'; we shall not consider the tricolour walk further since it is somewhat more complicated without presenting essentially new physics). A SAT is a lattice walk where each *bond* can be traversed only once, while sites can be visited arbitrarily often. Actually, of course, each site can be visited at most $\mathcal{N}/2$ times, since afterwards all connecting bonds have been traversed. A model for the θ collapse is obtained if we give a Boltzmann factor $q = e^{\beta\epsilon} > 1$ to each pair of monomers at the same site, i.e. a factor $q^{(m-1)m/2}$ for each site which is visited m times.

Now consider the RR method for lattices where $\mathcal{N}/2$ is even. For any such lattice, we can never run into a 'cage', since one bond will always be free to continue the chain. The only exception is the starting point, and thus the only way to terminate such a chain is by forming a loop which encompasses the entire chain. Since the probability for this to happen (on an infinite 3D lattice) is less than one, we have a finite probability (actually very close to one for most lattices [6]) that a random chain will never form a loop and can thus be continued arbitrarily far. Following [12], we shall call such walks 'smart', as they 'know' how to avoid traps.

Finally, let us give the same weight to all generated chains. As we said above, this corresponds essentially to adding an attractive potential, without using an *explicit* Boltzmann factor. If $\mathcal{N} = 4$, each site can be occupied by at most one pair, and this gives exactly the same ensemble as if we generated chains without an RR bias, and with the Boltzmann factor [6]

$$q = \mathcal{N} - 1 = 3 \tag{4}$$

i.e. this method simulates SATs at $\beta\epsilon = \ln 3$. For $\mathcal{N} > 4$ this is no longer exactly true, since the RR weights are no longer exponential functions of the number of pairs [6].

The observation of [6] was that this algorithm seems to generate chains with statistics of polymers at the θ point. Thus, this locates the θ point for a SAT on any lattice with $\mathcal{N} = 4$ at $T_\theta = \epsilon/(k_B \ln 3)$.

In three dimensions, this applies, in particular, to the diamond lattice which we shall study exclusively in the following. But we should point out that we have also checked our results for the simple cubic lattice where the above RR method leads to a different model than the standard SAT model studied for example in [13, 4].

To see whether the kinetic chains defined by these models are in the same universality class as the usual θ collapse, we have to study them either in a finite volume or off the (tri-)critical point. This will be done in the next section. We shall see that they are not. Instead, they show a first-order critical point. The reason for this will be given in section 3, and our conclusions are presented in section 4.

2. 'Smart' growing walks on the diamond lattice

Let us denote by $C_{N,m}$ the number of distinct N -step chains on the diamond lattice which start at the origin, traverse each bond at most once, and have m doubly visited sites. The energy of such a site is assumed to be q^m with $q > 1$. Using a fugacity p , the grand (in the sense of fluctuating number of monomers) canonical partition sum is

$$Z(p, q) = \sum_{N,m} p^N q^m C_{N,m}. \tag{5}$$

The phase diagram for this system is sketched in figure 1. To the left of a curve $p = p_c(q)$ we have only chains of finite length. The average chain length diverges as $p \rightarrow p_c(q)$. For $p > p_c(q)$, it would be infinite on an infinite lattice, and to render the theory finite we have to use a large but *finite* lattice.

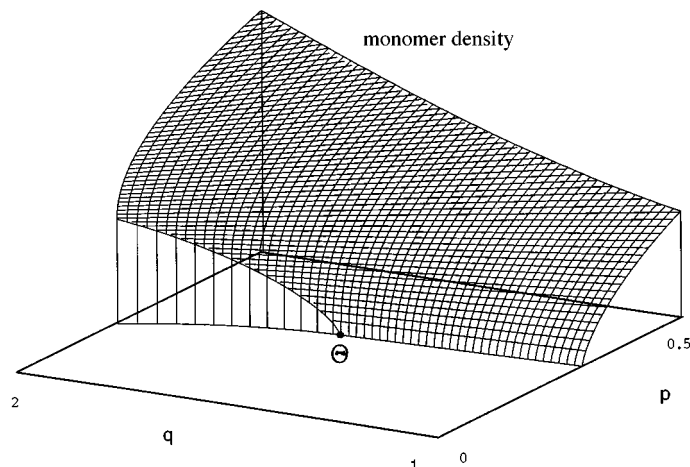


Figure 1. Schematic drawing of the monomer density in a finite volume filled by a single polymer in the grand canonical ensemble governed by fugacity p and Boltzmann factor q .

Athermal polymers SATs correspond to $q = 1$. They should be in the same universality class as athermal SAW. Indeed, we expect that the behaviour along the entire critical curve is in the SAW universality class, up to the θ point $\Theta = (p_\theta, q_\theta)$. This implies, in particular, that the monomer density in a finite but large lattice scales for $p = p_c(q) + 0$ as [14]

$$\rho \sim (p - p_c)^{3\nu-1} \sim (p - p_c)^{0.76} \quad (6)$$

as was checked for athermal SAWs in [15].

The standard assumption that the θ point is tricritical with mean-field exponents in $d = 3$ implies that the monomer density increases as

$$\rho \sim \sqrt{q - q_\theta} \quad (7)$$

if we pass through Θ transversely to the critical line $p = p_c(q)$. The typical behaviour of $\rho(p, q)$ is sketched in figure 1. Simulations in [15] verified the global behaviour, showing, in particular, that $\rho \rightarrow 0$ for $(p = p_c(q), q \rightarrow q_\theta + 0)$ and for $(q = q_\theta, p \rightarrow p_\theta + 0)$.

We now want to show that the latter is not true for the smart kinetic trails studied in [6]. As shown there and discussed in the last section, the point (p_θ, q_θ) for these trails corresponds just to ensembles generated by the RR method with unit weights for all generated chains. In figure 2 we show the chain length distribution $P(n) = \text{prob}(N > n)$ for chains grown on lattices of size L^3 with periodic boundary conditions (actually, for efficient coding we used helical BC, but this should not make an essential difference). The chains stopped only when forming loops. We see that this distribution scales as

$$P(n) = f(n/L^3) \quad (8)$$

showing, in particular, that the average monomer density $\langle N \rangle / L^3$ is *finite* and positive for $L \rightarrow \infty$. This is indeed not at all surprising, since we should expect that loops are formed typically only after a finite fraction of the sites have been visited. Thus we see that (6) cannot be correct for smart kinetic trails. Instead, the density makes a discontinuous jump when passing through (p_θ, q_θ) along lines $q = q_\theta = \text{constant}$.

To see that (7) also does not hold for smart kinetic trails, we have to study them off the θ point.

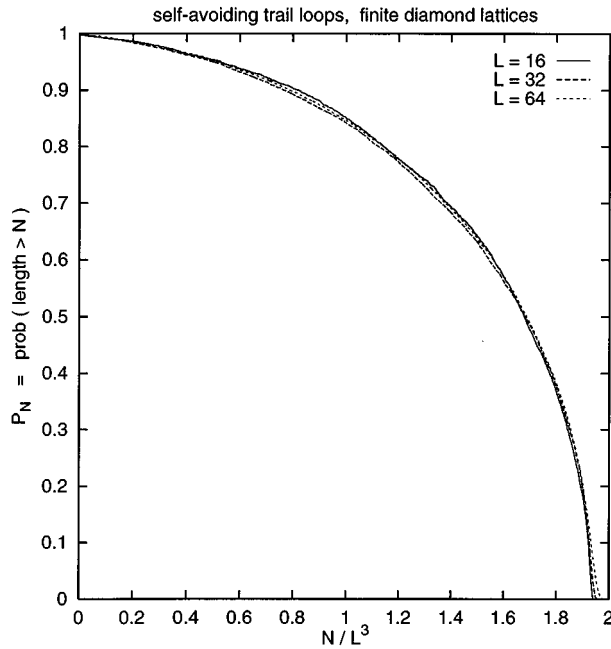


Figure 2. Chain length (\cong monomer density) distribution for SAT loops generated by the RR method on diamond lattices of size L^3 . Notice that each site can be visited at most two times, whence the distribution must stop at density ≤ 2 .

In order to achieve $p > p_\theta$, we use the enrichment method. In order to simulate at $q \neq q_\theta$, we could just re-weight the chains generated by the standard RR method, but we prefer to use enrichment factors which depend on the occupation number of the next selected site. More precisely, if we call P_{m_x} the average number of continuations towards a site x with occupation number m_x ($= 0, 1$ for the diamond lattice), then we should take

$$P_0 = \frac{p}{p_\theta} \quad P_1 = \frac{pq}{p_\theta q_\theta} \tag{9}$$

(as discussed in [4], we should deviate from the grand canonical ensemble if we want to simulate at $q \gg q_\theta$, by making P_m depend on N ; this was not necessary for the present study).

Instead of using a finite lattice and running the algorithm until all chains close to form loops, we now introduce a finite cut-off N_{\max} , and we show in figures 3 and 4 the canonical distributions at three different chain lengths and at different temperatures.

In figure 3 we show the distributions at $T = \infty$, i.e. the numbers $C_{N,m}$, in a semi-logarithmic plot. The chain lengths are $N = 1250, 5000$ and $20\,000$. Each curve combines data from three different runs at $q = q_\theta, q > q_\theta$ and $q < q_\theta$, each of which involved between 10^6 – 10^7 chains. The curves are shifted arbitrarily so that all three maxima coincide. On the horizontal axis we plot m/\sqrt{N} , so that mean-field theory (which gives constant specific heat per monomer) would imply that the widths of the curves are independent of N . We see the broadening with N which underlies the increase of the specific heat observed in [6]. But if we look carefully, we see that the curves for $N = 5000$ and $20\,000$ seem not to be convex.

In order to see this more clearly, we computed from these data the canonical distributions $C_{N,m}q^m$ at roughly the temperatures where the specific heat is maximal (figure 4). We see

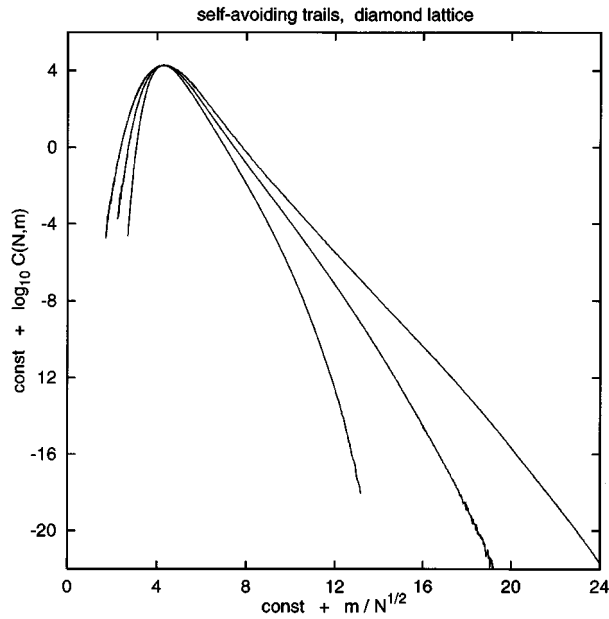


Figure 3. Same data as in figure 3, but weighted with Boltzmann factors q^m . The values of q are different for each curve and chosen such that both maxima have the same height (respectively, so that the top part of the curve is horizontal). They are $1.132q_\theta$ ($N = 1250$), $1.053q_\theta$ ($N = 5000$), $1.021q_\theta$ ($N = 20000$).

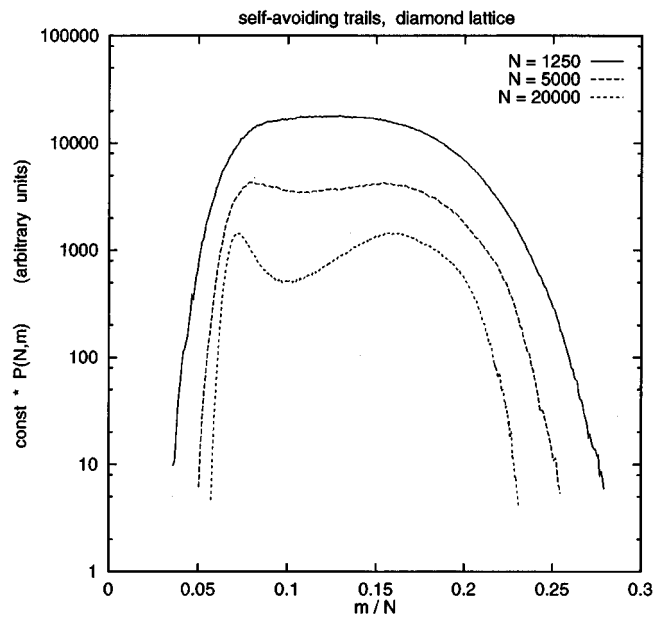


Figure 4. Distribution of the number of doubly visited sites for fixed chain length N ($N = 20000, 5000, 1250$ from top to bottom) on a semi-logarithmic plot. The horizontal axis shows m/\sqrt{N} since that is the scaling variable for free chains. The curves are arbitrarily shifted so that their maxima coincide.

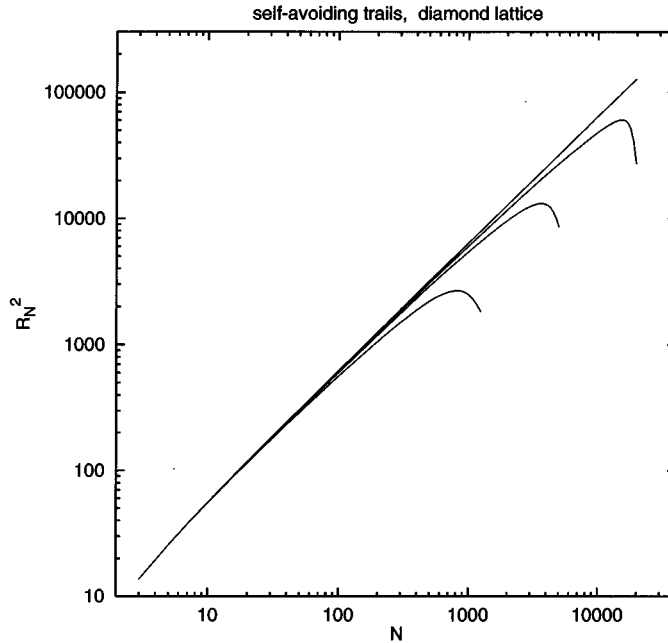


Figure 5. Average squared end-to-end distances versus N for the same three temperatures shown in figure 4.

indeed very clearly that this distributions has two peaks for $N \geq 5000$. The precise values of the temperature were chosen such that both peaks have the same height. We see very clearly that the corresponding values of q tend towards q_θ (roughly like $q/q_\theta \sim 1 + \text{constant}/N^{0.65}$). Notice that now we have plotted m/N on the horizontal axis. The fact that the peak positions seem to be independent of N shows that the maximum c_{\max} of the specific heat per monomer increases proportionally to N . It also shows that the density inside a large globule makes a discontinuous jump at the effective transition temperature. Notice that our finding of $c_{\max} \sim N$ is not in conflict with the finding $c_{T=T_\theta} \sim (\ln N)^\zeta$ of [6] since the maximum occurs for finite N at a temperature $< T_\theta$.

As a final indication that the transition is of first order we show in figure 5 the average end-to-end distance at the temperatures corresponding to the three curves shown in figure 4. We see that R_N^2 makes a very sharp drop at the effective transition temperature, indicating a true collapse which should become discontinuous in the limit $N \rightarrow \infty$. This is reminiscent of the results of [4], but much more extreme.

3. Theoretical considerations

We want to show now that the smartness of the chains implies that the renormalized n -body forces vanish for all finite n . Thus there is no interaction which stops the collapse before a finite density is reached, which immediately explains the results found in the last section.

Renormalization means that we look at the chain not microscopically but coarse-grained. At the θ point, we have microscopically both attractive and repulsive interactions. In a coarse-grained picture this means that one also has these interactions, but they are *random* since the exact positions of the monomers are no longer controlled. Thus we can replace

the Edwards Hamiltonian by a Hamiltonian which contains random two-body interactions,

$$H = \frac{1}{2} \int dl \left(\frac{d\mathbf{x}}{dl} \right)^2 + \frac{1}{2} \iint dl dl' g(l, l') \delta(\mathbf{x}(l) - \mathbf{x}(l')) \quad (10)$$

where g is a Gaussian random variable with

$$\begin{aligned} \langle g(l, l') \rangle &= g_2 \\ \langle g(l, l') g(m, m') \rangle &= g_2^2 + g_3 [\delta(l - m) + \delta(l' - m') + \delta(l - m') + \delta(l' - m)]. \end{aligned} \quad (11)$$

Performing the average over g ,

$$\begin{aligned} e^{H_{\text{ren}}} &= \int \mathcal{D}g e^H = \exp \left\{ \frac{1}{2} \int dl \left(\frac{d\mathbf{x}}{dl} \right)^2 + \frac{1}{2} g_2 \iint dl dl' \delta(\mathbf{x}(l) - \mathbf{x}(l')) \right. \\ &\quad \left. + g_3 \iiint dl dl' dl'' \delta(\mathbf{x}(l) - \mathbf{x}(l')) \delta(\mathbf{x}(l) - \mathbf{x}(l'')) \right\} \end{aligned} \quad (12)$$

we obtain then the usual Hamiltonian with two-body interaction g_2 and three-body interaction g_3 .

The important message of this derivation is that the renormalized three-body interaction results from *fluctuations* of the basic (microscopic) two-body interaction. But we have to be a bit more careful: actually, not only the (inner) *energy* can fluctuate but also the entropy. What determines the renormalized three-body interaction should then be fluctuations of the *free energy* $F = E - TS$.

The crucial observation now is that the free energy does not fluctuate for smart growing walks. They are constructed precisely such that the fluctuations of the entropy (due to the prohibition of double-bond occupancy) are *exactly* cancelled by the fluctuations of the energy corresponding to the RR factors. Actually, this is true only at the θ point, and in the limit $N \rightarrow \infty$. For finite N , there are additional contributions to the entropy from the probability that loops are formed, but this probability tends towards a constant for $N \rightarrow \infty$ [6]. For SATs with RR weights on the diamond lattice, e.g., we have $F = \text{constant} + N \ln 3$, and only the additive constant fluctuates with the microscopic degrees of freedom. Thus we should expect that the renormalized three-body interaction vanished exactly. Renormalized n -body interactions with $n > 3$ would be obtained either if the fluctuations of g are not Gaussian or if there exists a fluctuating $(n-1)$ -body interaction which is to be renormalized. Since neither exist for smart growing walks, we also expect that all n -body interactions with finite n are absent.

Notice that similar arguments should, in principle, also apply to smart SATs in two dimensions. But for reasons which we have not yet understood, the situation there is less clear. As shown in [16], the θ transition of self-avoiding trails on the square lattice is not in the universality class of interacting SAWs. The latter was shown in [17] to follow the predictions of [18]. On the other hand, the collapse of self-avoiding trails on the two-choice square (where the walker has to make a 90° turn at each step), *is* in the latter universality class [19]. Thus, it is not that all trails are in one universality class and all SAWs in the other. Since 2D SAWs and trails on the two-choice square lattice cannot cross themselves while trails on the ordinary square lattice can, it was speculated in [16] that it might be this which determines the universality class. If this is true, the Domb–Joyce model [20] with attractive interactions between nearest neighbours should show a θ collapse which is not in the universality class of interacting SAWs, but which follows the behaviour seen in [16]. To verify this, we have simulated the Domb–Joyce model with $5 \leq -\epsilon_0/\epsilon_{\text{nn}} \leq 8$, where $\epsilon_0 (> 0)$ is the energy of a monomer pair at the same site, while $\epsilon_{\text{nn}} (< 0)$ is the energy of a pair at neighbouring sites. Unfortunately, because of extremely large corrections to

scaling we were unable to draw any definite conclusion from the runs with $-\epsilon_0/\epsilon_{nn} < 6$, though we simulated chains of length up to 10^4 with very high statistics. For $-\epsilon_0/\epsilon_{nn} \geq 6$ the data seemed to agree with the standard [18] θ transition, but we are not sure that this is not a cross-over effect since this behaviour must hold at $-\epsilon_0/\epsilon_{nn} = \infty$. We might add that we did not see any hint of a first-order θ transition in any of the 2D models we looked at.

4. Conclusions

We have shown that the three-dimensional ‘smart’ self-avoiding trails studied in [6] have a θ collapse which is *not* in the universality class of the ordinary θ collapse. The latter is believed to govern the collapse of real chain polymers, and is a tricritical point in the $O(n)$ model with $n = 0$. Instead, the collapse in these models is a first-order transition. We have argued that this is due to a vanishing renormalized three-body interaction.

On the other hand, we have pointed out that *qualitatively* many features of the collapse of smart self-avoiding trails are surprisingly similar to properties of the θ collapse of lattice polymers. The latter were in flagrant contradiction of field-theoretic predictions based on the assumption that corrections to mean-field theory are dominated by (renormalized) three-body interactions.

The present findings suggest strongly that in these lattice polymers the three-body interactions are relatively weak at presently reachable chain lengths, and that n -body interactions with $n > 3$ play a substantial role. We conjecture that this is also true for real polymers, though analyses based on the assumption that all deviations from mean-field behaviour are due to three-body forces have not found any inconsistencies. We propose that these analyses should be redone, and that new experiments are needed.

Finally, we might wonder whether the first-order transition is confined to chain collapses where the renormalized three-body interaction vanishes exactly, or whether it can also arise if the three-body interaction is non-zero but sufficiently small. The latter should also lead to non-convex canonical distributions for finite N like those observed in the present work. This might suggest that indeed a first-order transition cannot be excluded even if the three-body interaction is not zero, but more work is needed to settle this question.

Acknowledgments

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