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Interacting self-avoiding walks and polygons in three dimensions

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Abstract. Self-interacting walks and polygons on the simple cubic lattice undergo a collapse transition at the θ-point. We consider self-avoiding walks and polygons with an additional interaction between pairs of vertices which are unit distance apart but not joined by an edge of the walk or polygon. We prove that these walks and polygons have the same limiting free energy if the interactions between nearest-neighbour vertices are repulsive. The attractive interaction regime is investigated using Monte Carlo methods, and we find evidence that the limiting free energies are also equal here. In particular, this means that these models have the same θ-point, in the asymptotic limit. The dimensions and shapes of walks and polygons are also examined as a function of the interaction strength.

1. Introduction

Linear polymers in dilute solution appear to undergo a sudden collapse from an expanded coil form to a compact ball when the temperature is decreased. This has been detected by light scattering measurements of the radius of gyration [1, 2] and by viscosity measurements [3].

A model which has become standard for investigating this phenomenon is a self-avoiding walk on a regular lattice with an additional interaction between pairs of vertices of the walk which are unit distance apart but not joined by an edge of the walk. In two dimensions this model has been investigated by transfer matrices [4], exact enumeration [5–8], Monte Carlo methods [9, 10], and by a combination of techniques [11]. The corresponding model in three dimensions has been studied by exact enumeration [12, 13] and by Monte Carlo methods [14–18].

An interesting extension of this problem is to ask if the topology of the polymer has an effect on the collapse behaviour. The simplest case to investigate is a ring polymer, which can be modelled as a (self-avoiding) polygon on a lattice. This model has been investigated by Maes and Vanderzande [19] using exact enumeration and series analysis for the square lattice, who found that rings and walks collapse at about the same temperature. See also [20].

In this paper we investigate the corresponding problem on the three-dimensional simple cubic lattice. In three dimensions there are additional interesting effects since polygons can be knotted [21]. Here we concentrate on comparing the behaviour of walks with the behaviour of the set of all polygons, without regard to knot type. The plan of the paper is as follows. In section 2 we prove that polygons have a limiting free energy

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(i.e. the thermodynamic limit exists) at all temperatures for both attractive and repulsive interactions. When the interaction is repulsive we prove that the limiting free energy for polygons is identical to that of walks, at all temperatures. This proof does not extend to attractive interactions and we study that regime, in section 3, using Monte Carlo methods. We present results consistent with the limiting free energies of walks and polygons being equal at all temperatures for attractive interactions. In section 3 we also present results about the dimensions and shapes of walks and polygons in the attractive regime. Section 4 contains a summary and discussion of our results.

2. Rigorous results on free energies

Let Z^3 be the simple cubic lattice whose vertices are the integer points in R^3, and with edges between vertices which are unit distance apart. An *n-step self-avoiding walk* is an ordered sequence of $n + 1$ vertices such that the first vertex is the origin, neighbouring pairs of vertices in the sequence are unit distance apart and all vertices are distinct. We often use *walk* to mean self-avoiding walk. A walk and any translation of the walk form an equivalence class and we also use walk as a shorthand for *equivalence class of self-avoiding walks* when it is not likely to cause confusion.

An n-step self-avoiding circuit (n-SAC) is an $(n-1)$-step self-avoiding walk whose first and last vertices are unit distance apart, and the additional edge between these two vertices. Any cyclic permutation of an n-SAC is also an n-SAC, and so is the reverse permutation and all cyclic permutations of the reverse permutation. The resulting set of $2n$ n-SACs which originate from a given n-SAC can be regarded as a single geometrical object, which we call an n-step (self-avoiding) polygon. Two n-step polygons are equivalent if one is a translation of the other. We also use the word polygon for an equivalence class of polygons, when no confusion is likely to arise.

A *contact* is a pair of vertices of the walk or polygon which are unit distance apart, but which are not incident on a common edge of the walk or polygon. We write $c_n(m)$ and $p_n(m)$ for the numbers of self-avoiding walks and polygons with n edges and m contacts. We shall be interested in the partition functions

$$Z_n(\beta) = \sum_m c_n(m)\, \mathrm{e}^{\beta m} \tag{2.1}$$

and

$$Z_n^o(\beta) = \sum_m p_n(m)\, \mathrm{e}^{\beta m}\,. \tag{2.2}$$

$\beta = 0$ corresponds to the pure walk and pure polygon problems (i.e. the infinite temperature limit), $\beta < 0$ corresponds to repulsive interactions between pairs of vertices, and $\beta > 0$ to attractive interactions. We expect a phase transition from a coil to a ball form for some positive value of β.

Theorem 2.1. The limit

$$\lim_{n\to\infty} n^{-1} \log Z_n^o(\beta) \equiv \mathcal{F}^o(\beta) \tag{2.3}$$

exists for all $\beta < \infty$.

Proof. For a given polygon define the *top vertex* to be the vertex with lexicographically largest coordinates and the *bottom vertex* to be the vertex with lexicographically smallest coordinates. Let (x_t, y_t, z_t) be the coordinates of the top vertex, and (x_b, y_b, z_b) the coordinates of the bottom vertex. The top vertex has two edges incident on it, which are also

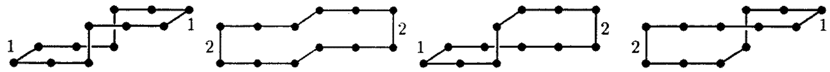

Figure 1. Polygons used in the concatenation construction.

incident on vertices at two of the three points $(x_t - 1, y_t, z_t)$, $(x_t, y_t - 1, z_t)$, $(x_t, y_t, z_t - 1)$. If the edge $(x_t, y_t, z_t) - (x_t, y_t - 1, z_t)$ is an edge of the polygon we call this the *top edge*, and say that the polygon has a top edge of type 1. Otherwise we call the edge $(x_t, y_t, z_t) - (x_t, y_{rmt}, z_t - 1)$ the top edge of the polygon, and say that the polygon has a top edge of type 2. Similarly the edge $(x_b, y_b, z_b) - (x_b, y_b + 1, z_b)$, if it exists, is the *bottom edge* and the polygon has a bottom edge of type 1, otherwise $(x_b, y_b, z_b) - (x_b, y_b, z_b + 1)$ is the bottom edge of the polygon, and the polygon has a bottom edge of type 2. We can concatenate a polygon whose top edge is of type a $(a = 1, 2)$ and a polygon whose bottom edge is of type b $(b = 1, 2)$, through one of the four polygons shown in figure 1. In each case we delete four edges and add twelve edges, so that the net increase is eight edges. In addition we create six new contacts. This gives the inequality

$$p_{n+8}(m + 6) \geqslant \sum_{m_1} p_{n_1}(m_1) p_{n-n_1}(m - m_1) . \tag{2.4}$$

Since the number of polygons is exponentially bounded, it follows immediately [22] from (2.4) that the limit

$$\lim_{n\to\infty} n^{-1} \log Z_n^o = \mathcal{F}^o \tag{2.5}$$

exists. □

Theorem 2.2. For all $\beta < \infty$ the limiting free energy $\mathcal{F}^o(\beta)$ is a convex and continuous function of β, with non-decreasing left and right derivatives.

Proof. $Z_n^o(\beta)$ is monotonically increasing in β and, since it is a polynomial in e^β, it is continuous and bounded in any closed interval in β. Therefore to prove that $\log Z_n^o(\beta)$ is a convex function of β it is sufficient [23] to show that

$$\frac{\log Z_n^o(\beta_1) + \log Z_n^o(\beta_2)}{2} \geqslant \log Z_n^o((\beta_1 + \beta_2)/2) . \tag{2.6}$$

Using Cauchy's inequality we have

$$\begin{aligned} Z_n^o(\beta_1) Z_n^o(\beta_2) &= \sum_{m_1} p_n(m_1)\, e^{\beta_1 m_1} \sum_{m_2} p_n(m_2)\, e^{\beta_2 m_2} \\ &\geqslant \left(\sum_m p_n(m)\, e^{(\beta_1+\beta_2)m/2} \right)^2 \\ &= \left[Z_n^o((\beta_1 + \beta_2)/2) \right]^2 \end{aligned} \tag{2.7}$$

and, after taking logarithms, this establishes (2.6). Since the limit (when it exists) of a sequence of convex functions is itself convex, this establishes that $\mathcal{F}^o(\beta)$ is convex (and bounded above for finite β). It is therefore continuous and has left and right derivatives at every $\beta < \infty$. Moreover, both derivatives are non-decreasing functions of β [23]. □

In order to prove results about the limiting free energy of self-avoiding walks we need some subsidiary lemmas about unfolded walks. We write (x_i, y_i, z_i), $i = 0, \ldots, n$ for the coordinates of vertex i in an n-step self-avoiding walk. A self-avoiding walk is x-*unfolded* if $x_0 < x_i, \forall i > 0$ and $x_i < x_n, \forall i < n$. Similarly, we define a walk (with $n \geqslant 2$) to be

(x, z)-*unfolded* if $x_0 \leqslant x_i$ and $z_0 < z_i, \forall i > 0$ and $x_n > x_i$ and $z_n \geqslant z_i, \forall i < n$. We write $c_n^\dagger(m)$ ($c_n^\ddagger(m)$) for the number of x-unfolded ((x, z)-unfolded) n-step walks with m contacts, and define the partition function

$$Z_n^\dagger(\beta) = \sum_m c_n^\dagger(m)\, \mathrm{e}^{\beta m} \tag{2.8}$$

with a similar definition of $Z_n^\ddagger(\beta)$.

We have the following lemmas about the free energies of unfolded walks.

Lemma 2.3. The limiting free energies

$$\mathcal{F}^\dagger(\beta) = \lim_{n\to\infty} n^{-1} \log Z_n^\dagger(\beta) \tag{2.9}$$

and

$$\mathcal{F}^\ddagger(\beta) = \lim_{n\to\infty} n^{-1} \log Z_n^\ddagger(\beta) \tag{2.10}$$

exist for all $\beta < \infty$.

Proof. Clearly $Z_n^\dagger(\beta) \leqslant 6^n \mathrm{e}^{2\beta n}$ so $n^{-1} \log Z_n^\dagger(\beta)$ is bounded above for all $\beta < \infty$. Two unfolded walks can be concatenated by identifying the first vertex of one walk with the last vertex of the other walk. This gives the inequality

$$c_n^\dagger(m) \geqslant \sum_{m_1} c_{n_1}^\dagger(m_1) c_{n-n_1}^\dagger(m - m_1) \tag{2.11}$$

since no new contacts are formed in the concatenation, and not all unfolded walks can be obtained by this construction. Now multiply both sides by $\mathrm{e}^{\beta m}$, take logarithms and divide by n, and let $n \to \infty$. The existence of the limiting free energy $\mathcal{F}^\dagger(\beta)$ follows immediately. The argument for the existence of the limit in (2.10) is essentially the same. □

We next prove that the limiting free energy for walks exists for $\beta \leqslant 0$.

Theorem 2.4. For all $\beta \leqslant 0$, the limit $\lim_{n\to\infty} n^{-1} \log Z_n(\beta) \equiv \mathcal{F}(\beta)$ exists and $\mathcal{F}(\beta) = \mathcal{F}^\dagger(\beta) = \mathcal{F}^\ddagger(\beta)$.

Proof. Let C_n be the set of n-step self-avoiding walks, and let $C_n^\dagger$ be the set of n-step x-unfolded walks. Unfolding defines a surjection from C_n to $C_n^\dagger$. However, at most $\mathrm{e}^{O(\sqrt{n})}$ members of C_n map to the same member of $C_n^\dagger$ [24]. Number the members of C_n $i = 1, 2, \ldots, c_n$, and the members of $C_n^\dagger$ $l = 1, 2, \ldots, c_n^\dagger$. Suppose that unfolding maps the ith member of C_n to the $l(i)$th member of $C_n^\dagger$. Let $m(i)$ be the number of contacts in the ith walk in C_n, and let $m(l(i))$ be the number of contacts in the $l(i)$th member of $C_n^\dagger$. Clearly

$$m(l(i)) \leqslant m(i) \tag{2.12}$$

so that

$$\mathrm{e}^{\beta m(i)} \leqslant \mathrm{e}^{\beta m(l(i))} \tag{2.13}$$

for any $\beta \leqslant 0$.

Since any unfolded walk is a walk

$$Z_n^\dagger(\beta) \leqslant Z_n(\beta)\,. \tag{2.14}$$

Moreover,

$$
\begin{aligned}
Z_n(\beta) = \sum_m c_n(m)\,\mathrm{e}^{\beta m} &= \sum_{i=1}^{c_n} \mathrm{e}^{\beta m(i)} \\
&\leqslant \sum_{i=1}^{c_n} \mathrm{e}^{\beta m(l(i))} \leqslant \mathrm{e}^{\mathrm{O}(\sqrt{n})} \sum_{l=1}^{c_n^\dagger} \mathrm{e}^{\beta m(l)} \\
&= \mathrm{e}^{\mathrm{O}(\sqrt{n})} Z_n^\dagger(\beta)
\end{aligned}
\tag{2.15}
$$

for any $\beta \leqslant 0$. After taking logarithms, dividing by n and letting n tend to infinity, this (together with (2.14)) implies that $\mathcal{F}(\beta) = \mathcal{F}^\dagger(\beta)$. Using a similar argument we can show that

$$
\mathcal{F}^\ddagger(\beta) = \mathcal{F}^\dagger(\beta) \tag{2.16}
$$

for all $\beta \leqslant 0$, and this is a key ingredient in the proof of the following lemma. □

Lemma 2.5. The limiting free energies of polygons and (x, z)-unfolded walks are related by the inequality $\mathcal{F}^o(\beta) \geqslant \mathcal{F}^\ddagger(\beta)$ for $\beta \leqslant 0$.

Proof. The set of n-step (x, z)-unfolded walks can be divided into subsets according to the value of the *height* $h = z_n - z_0$ of the walk. There are no more than n such subsets, which we call $C_n^\ddagger(h), h = 1, \ldots, n$, where h is the height of the members of the subset. Let the number of members of $C_n^\ddagger(h)$, which have m contacts, be $c_n^\ddagger(m, h)$ and define the partition function $Z_n^\ddagger(\beta, h) = \sum_m c_n^\ddagger(m, h)\,\mathrm{e}^{\beta m}$.

For a given value of β, let $h_o = h_o(\beta)$ be the smallest integer such that $Z_n^\ddagger(\beta, h_o) \geqslant Z_n^\ddagger(\beta, h)$ for all h. We define an *n-loop* as an n-step self-avoiding walk such that $x_0 \leqslant x_i \leqslant x_n, \forall i$ and $z_0 = z_n < z_i, \forall i \neq 0, n$. Let the number of n-loops with m contacts be $l_n(m)$, with corresponding partition function $Z_n^l(\beta) = \sum_m l_n(m)\,\mathrm{e}^{\beta m}$. Concatenating a member of $C_n^\ddagger(h_o)$, with a second (not necessarily different) member, reflected in the plane $x = x_n$, gives a loop with $2n$ edges, so that

$$
l_{2n}(m) \geqslant \sum_{m_1} c_n^\ddagger(m_1, h_o) c_n^\ddagger(m - m_1, h_o)\,. \tag{2.17}
$$

Hence

$$
Z_{2n}^l(\beta) \geqslant Z_n^\ddagger(\beta, h_o)^2 \geqslant \left(\frac{Z_n^\ddagger(\beta)}{n}\right)^2. \tag{2.18}
$$

In a similar way one can split loops into classes and concatenate in pairs to form polygons, giving the inequality

$$
Z_{2n}^o(\beta) \geqslant \left(\frac{Z_n^l(\beta)}{n^2}\right)^2\,. \tag{2.19}
$$

Therefore

$$
\mathcal{F}^o(\beta) \geqslant \mathcal{F}^\ddagger(\beta) \tag{2.20}
$$

which completes the proof. □

Next we give an inequality between walks and polygons.

Theorem 2.6.

$$
\liminf_{n\to\infty} n^{-1} \log Z_n(\beta) \geqslant \mathcal{F}^o(\beta) \tag{2.21}
$$

for all values of β. In particular, for $\beta \leqslant 0$, $\mathcal{F}^o(\beta) \leqslant \mathcal{F}(\beta)$.

Proof. Each polygon can be converted to a walk by deleting the bottom edge, and assigning a direction. This reduces the number of edges by one, and increases the number of contacts by one, so that

$$c_{n-1}(m+1) \geqslant p_n(m) \tag{2.22}$$

and the result follows after multiplying both sides by $e^{\beta m}$, summing over m, taking logarithms, dividing by n, and letting n go to infinity. □

Corollary 2.7. The limiting free energies of walks and polygons are equal for all $\beta \leqslant 0$.

Proof. This follows immediately from lemma 2.5 and theorems 2.4 and 2.6. □

We next explore the consequences of an additional hypothesis, whose validity we shall test numerically in the next section. If we assume that the mean number of contacts in a (large) polygon is at least as large as the mean number of contacts in a walk, then we can prove that the limiting free energy for walks exists, and that it is equal to $\mathcal{F}^o$. This hypothesis seems to be a very reasonable one since polygons are expected to have a smaller radius of gyration than walks, and so are expected to be more 'compact', and therefore to have more contacts. The condition is easily checked numerically, and this theorem will play an important role in our interpretation of the numerical evidence presented in the following section.

In order to state the theorem we need some additional notation. Let $\langle m \rangle_n$ be the mean number of contacts for an n-step walk (where we suppress the β dependence), and let $\langle m \rangle_n^o$ be the corresponding quantity for polygons. Clearly

$$\langle m \rangle_n = \frac{\partial \log Z_n(\beta)}{\partial \beta} \tag{2.23}$$

with a similar relation for $\langle m \rangle_n^o$. Let $F_n = n^{-1} \log Z_n(\beta)$ and $F_n^o = n^{-1} \log Z_n^o(\beta)$.

Theorem 2.8. If $\langle m \rangle_n^o \geqslant \langle m \rangle_n$ for all sufficiently large even n and for all $\beta > 0$, then $\lim_{n\to\infty} F_n \equiv \mathcal{F}$ exists and $\mathcal{F} = \mathcal{F}^o$ for all β.

Proof. Since $\langle m \rangle_n^o \geqslant \langle m \rangle_n$ then $F_n(\beta) - F_n^o(\beta)$ is a non-increasing function of β. Hence, for any $\beta \geqslant 0$,

$$F_n(0) - F_n^o(0) \geqslant F_n(\beta) - F_n^o(\beta)\,. \tag{2.24}$$

Let $n \to \infty$, giving

$$\mathcal{F}(0) - \mathcal{F}^o(0) \geqslant \limsup_{n\to\infty} F_n(\beta) - \mathcal{F}^o(\beta) \tag{2.25}$$

where we have made use of theorem 2.1. But by corollary 2.1, we know that $\mathcal{F}(0) = \mathcal{F}^o(0)$, so

$$\limsup_{n\to\infty} F_n(\beta) \leqslant \mathcal{F}^o(\beta)\,. \tag{2.26}$$

This, together with theorem 2.6, implies the existence of the limit $\lim_{n\to\infty} F_n(\beta)$, and that it is equal to $\mathcal{F}^o(\beta)$. □

3. Monte Carlo simulation of walks and polygons

3.1. Numerical methods

In this section we describe the numerical techniques which we use to estimate thermodynamic and metric properties of walks and polygons for positive β. The numerical simulation of interacting walks by a Monte Carlo algorithm was discussed in [18], and we use similar methods for polygons. In particular, two novel implementations of the Metropolis algorithm were used for walks, namely *umbrella sampling* and *multiple Markov chain sampling*. These algorithms were implemented on an underlying Markov chain realized by a hybrid algorithm acting on the state space of walks or polygons. The hybrid algorithm was composed of a pivot algorithm for walks or polygons [25, 26] and a Verdier–Stockmayer algorithm [27] enriched by crankshaft moves. The pivot algorithm operates well in the expanded phase, but we found that the local algorithm is essential in shortening autocorrelations in the strongly interacting regime [18].

Umbrella sampling is achieved by sampling from an *umbrella distribution*, which we choose to cover the Boltzmann distribution(s) from which we are interested in sampling [28]. The only parameter in the partition function (2.1) is the interaction strength β, which can also be thought of as an inverse temperature. Our aim is to estimate ensemble averages at fixed temperatures. The umbrella distribution is chosen not only to cover the Boltzmann distribution of interest, but also to extend to higher temperatures where the mobility of the Markov chain is increased, so that we avoid 'quasi-ergodicity' problems [29] in our simulation. In addition, we can compute ensemble averages at any temperature covered by the umbrella distribution. In order to define the umbrella distribution, we define the following distributions by the generic functional

$$\pi_k = \sum_j w(\beta_j)\, \mathrm{e}^{\beta_j m(k)} \tag{3.1}$$

where $w(\beta)$ is a weighting factor which we must choose to define the umbrella, and where $m(k)$ is the number of contacts in the polygon (or walk) labelled by k. In terms of π_k we define our umbrella distribution as $\Pi = \sum_k \pi_k$. The set $\{\beta_j\}$ is chosen to cover the range we wish to cover in a single run. The elements of this set cannot be too far apart if we want to have adequate sampling, and not too close either, since the exponentials are expensive in computer time. The main advantage of this form for the umbrella distribution is that the weights can be estimated from excess free energies estimated in some other way. Loosely speaking, we wish to sample equally from every distribution in Π. We can achieve this by adjusting the weighting factors such that $w(\beta_j) \sum_k \mathrm{e}^{\beta_j m(k)}$ is independent of β_j, and we can conveniently put it equal to $Z_n^o(0)$, the partition function at infinite temperature (or zero interaction strength). Now since $\sum_k \mathrm{e}^{\beta_j m(k)} = Z_n^o(\beta_j) = \mathrm{e}^{n F_n^o(\beta_j)}$, where $F_n^o(\beta)$ is the free energy of a polygon with n vertices, we can solve for the weighting factors to find

$$w(\beta_j) = \mathrm{e}^{-n(F_n^o(\beta_j) - F_n^o(0))}\,. \tag{3.2}$$

The umbrella distribution can be implemented Metropolis-style on the underlying (symmetric) hybrid algorithm by assigning a weight π_k to each conformation. Note that the weighting factors are exponentials of relative free energies of the walks or polygons; hence, we need to have good preliminary estimates of these in order to find a suitable umbrella. On the other hand, if a suitable umbrella is used, then one can compute improved weighting factors, and thus more accurate relative free energies.

The multiple Markov chain algorithm [30] is similarly implemented on the hybrid algorithm above. In this case, we sample Metropolis-style for a Boltzmann distribution at some fixed temperature. A number of these Markov chains are realized in parallel at a sequence of β-values $\beta_1 < \beta_2 < \cdots < \beta_m$, and we allow the chains to interact (by possibly exchanging conformations) as follows. Select two chains at (say) β_j and β_{j+1} with uniform probability. A trial move is an attempt to swap the two current conformations of these chains. If $\rho_k(\beta)$ is the probability of the state k in the chain at β, and S_j and S_{j+1} are the current states in the jth and $(j+1)$th chain, then we accept the trial move (and swap S_j and S_{j+1}) with probability

$$r(S_j, S_{j+1}) = \min\left(1, \frac{\rho_{S_{j+1}}(\beta_j)\rho_{S_j}(\beta_{j+1})}{\rho_{S_j}(\beta_j)\rho_{S_{j+1}}(\beta_{j+1})}\right). \tag{3.3}$$

The whole process is itself a Markov chain, which we call the *composite Markov chain*. Since the underlying Markov chains are ergodic, so is the composite Markov chain, and the composite chain is in detailed balance since the 'swap' move as well as the moves in the underlying chain are in detailed balance [18, 30]. Consequently, the invariant limit distribution is the product distribution of separate Markov chains at $\beta_1 < \beta_2 < \cdots < \beta_m$.

3.2. Numerical results: thermodynamic properties

In this section we report our numerical estimates of a variety of properties of both polygons and walks, and we include results both from umbrella sampling and from multiple Markov chains. In obtaining results by umbrella sampling we made use of preliminary estimates of the free energies by multiple Markov chain sampling [18], in order to form preliminary estimates of the weighting factors, and the weighting factors were then improved iteratively.

Table 1. Peak positions of the heat capacity estimated by multiple Markov chains and by umbrella sampling, for both walks and polygons. The error bars are one standard deviation.

n	mmc walk	umbrella walk	mmc poly	umbrella poly
300	0.400 ± 0.020	0.397 ± 0.010	0.375 ± 0.030	0.400 ± 0.015
400	0.380 ± 0.010	0.383 ± 0.012	0.367 ± 0.022	0.373 ± 0.015
500	0.370 ± 0.010	0.375 ± 0.012	0.358 ± 0.011	0.363 ± 0.020
600	0.370 ± 0.010	0.366 ± 0.011	0.355 ± 0.025	0.358 ± 0.015
800	0.356 ± 0.015	0.350 ± 0.010	0.350 ± 0.025	
1200	0.340 ± 0.010	0.334 ± 0.010	0.338 ± 0.020	
1600	0.329 ± 0.010		0.330 ± 0.010	

In order to compare the results from umbrella sampling and from multiple Markov chains, we report in table 1 our estimates of the peak positions in the heat capacity as a function of n, for both walks and polygons. Typically the umbrellas used were made up from 100 Boltzmann contributions, and we used between 10 and 20 parallel Markov chains in the multiple Markov chain sampling. For polygons, the agreement between the results using the two methods is excellent up to $n = 600$ but, for larger values of n, we were unable to construct adequate umbrella distributions, and the corresponding estimates were less reliable. Hence, for values of n greater than 600 we rely on multiple Markov chain estimates for properties of polygons. For walks, we were able to construct good umbrella distributions for $n \leqslant 1200$ but not for larger values of n. For $n = 1600$ we rely on estimates from multiple Markov chains. The estimates given here for walks are in some cases improvements over the values reported in [18].

The peak positions decrease to smaller values of β as n increases both for walks and for polygons, as shown in figure 2. The rate of change is controlled by the cross-over exponent

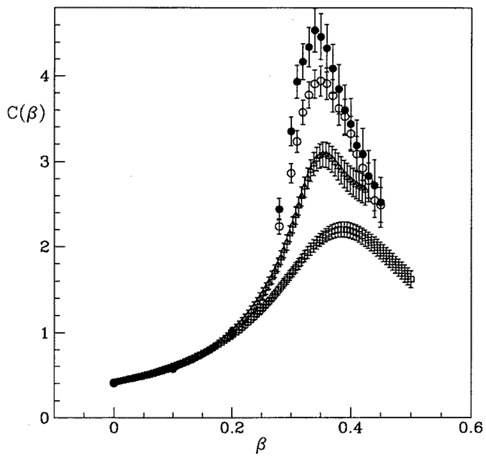

Figure 2. The heat capacity of polygons as a function of the interaction parameter β, for $n = 200$ (□), 400 (△), 800 (○), 1200 (•).

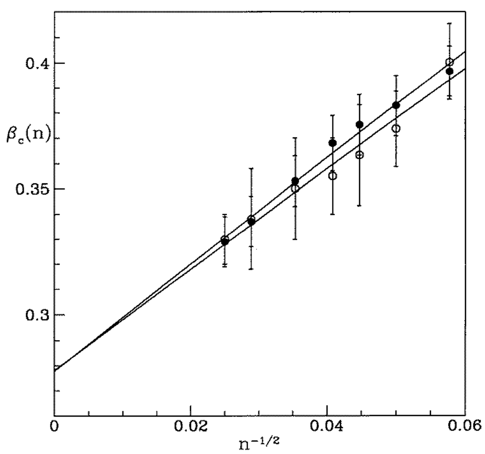

Figure 3. The locations of the heat capacity peaks for walks (•) and polygons (○) extrapolated against $1/\sqrt{n}$.

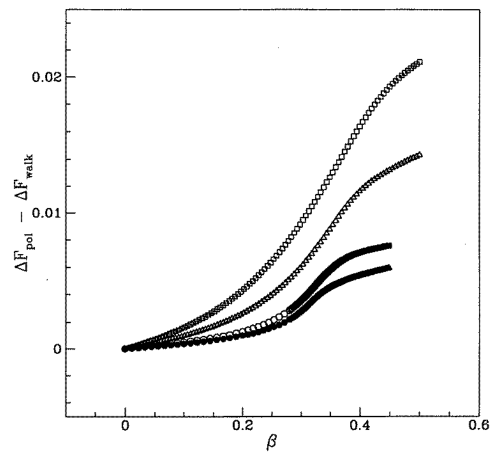

Figure 4. The difference in the relative free energies of polygons and walks, $[F_n^o(\beta) - F_n^o(0)] - [F_n(\beta) - F_n(0)]$, as a function of β, for $n = 200$ (□), 400 (△), 800 (○), 1200 (•).

ϕ which we believe has mean-field value $\frac{1}{2}$ [31, 32] in three dimensions for both walks and polygons. Assuming this value, and ignoring a possible log correction, we can extrapolate the peak positions to infinite n, as shown in figure 3, obtaining

$$\beta_\Theta = \begin{cases} 0.2779 \pm 0.0041 & \text{for walks} \\ 0.2782 \pm 0.0070 & \text{for polygons}. \end{cases} \tag{3.4}$$

These values are consistent with walks and polygons collapsing at the same value of β. Results in two dimensions [19, 33] are also consistent with this transition occurring at the same value of the interaction parameter for walks and polygons.

We next examine directly the difference between the free energies for walks and polygons as a function of β. In figure 4 we plot $[F_n^o(\beta) - F_n^o(0)] - [F_n(\beta) - F_n(0)]$ against β for several values of n. The difference in the relative free energies decreases as n increases, consistent with the limiting free energies being equal for all values of β. To test this idea further we make use of theorem 2.8, proved in the previous section. There we

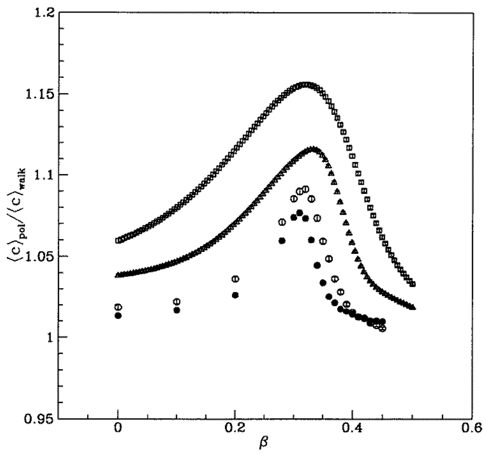

Figure 5. The ratio of the mean number of contacts for polygons and walks as a function of β, for $n =$ 200 ($\square$), 400 ($\triangle$), 800 ($\circ$), 1200 ($\bullet$).

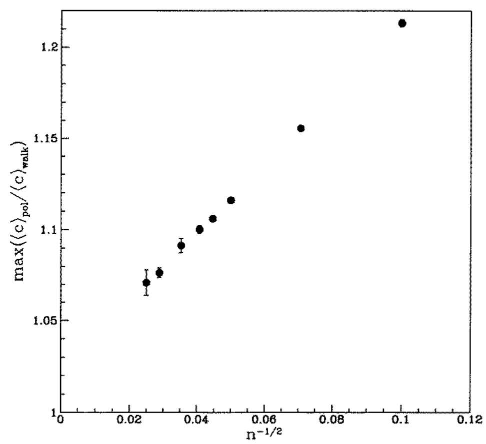

Figure 6. The maximum value of the ratio of the mean number of contacts for polygons and walks, extrapolated against $1/\sqrt{n}$.

showed that if the mean number of contacts for polygons is at least as large as the mean number of contacts for walks, at all $\beta > 0$, for n sufficiently large, then the limiting free energies are equal. We test this condition numerically by plotting $\langle m\rangle_n^o/\langle m\rangle_n$ against β for several values of n, in figure 5. These results clearly support the validity of the hypothesis, and therefore the equality of the limiting free energies.

If the limiting free energies are equal, then the ratio $\langle m\rangle_n^o/\langle m\rangle_n$ must approach unity as n increases, for all β. In figure 6 we extrapolate the maximum value of $\langle m\rangle_n^o/\langle m\rangle_n$ over all positive β against $1/\sqrt{n}$. The intercept is about 1.02 and supports the scenario described above.

3.3. *Numerical results: metric properties*

We now turn to a consideration of the radii of gyration of polygons and walks as a function of n and β. We have computed the mean-square radii of gyration, $\langle S_n(\beta)^2\rangle$ and $\langle S_n^o(\beta)^2\rangle$, for walks and polygons, respectively, using both multiple Markov chain and umbrella sampling for $n \leqslant 600$. The agreement between the two sets of estimates is excellent. For larger values of n we rely largely on estimates from multiple Markov chain sampling.

In figure 7 we show the β dependence of $\langle S_n(\beta)^2\rangle$ and $\langle S_n^o(\beta)^2\rangle$ for $n = 800$. We note the strong dependence on β consistent with collapse of both walks and polygons for large positive β, and the fact that the radii of gyration of walks and polygons become almost equal for β sufficiently large.

We expect that

$$\frac{\langle S_n^o(\beta)^2\rangle}{\langle S_n(\beta)^2\rangle} = \frac{A^o(\beta)}{A(\beta)}\left(1 + \frac{B^o(\beta) - B(\beta)}{n^\Delta} + \cdots\right) \tag{3.5}$$

for $\beta < \beta_\Theta$. We have estimated the amplitude ratio $A^o(0)/A(0)$ at $\beta = 0$, and our estimate is 0.538 ± 0.006, in good agreement with previous series estimates [34, 35], and with a first-order ϵ calculation [36].

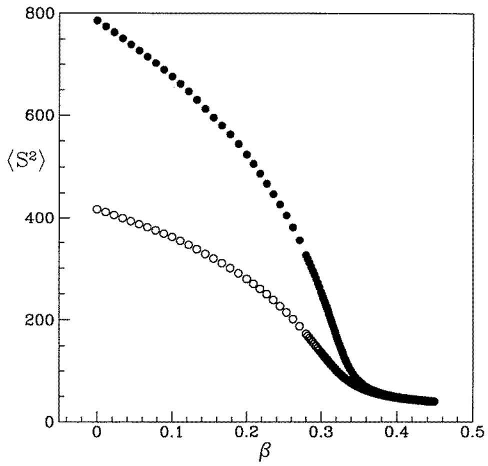

Figure 7. The radii of gyration of walks (upper curve) and polygons (lower curve) for $n = 1200$.

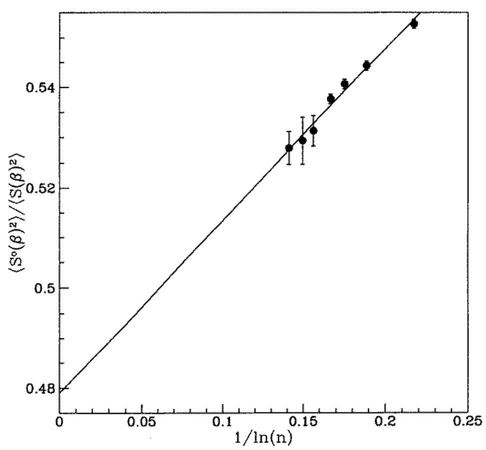

Figure 8. Extrapolation of the ratio of mean-square radii of gyration against $1/\ln n$ at $\beta = 0.28$.

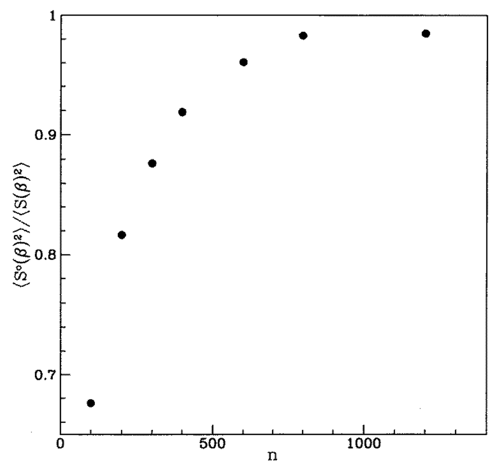

Figure 9. The n dependence of the ratio of mean-square radii of gyration at $\beta = 0.45$.

At the critical point $\beta = \beta_\Theta$ we expect [32] that

$$\frac{\langle S_n^o(\beta)^2\rangle}{\langle S_n(\beta)^2\rangle} = \frac{A_\Theta^o}{A_\Theta}\left(1 + \frac{B_\Theta^o - B_\Theta}{\ln n} + \cdots\right). \tag{3.6}$$

In figure 8 we plot $\langle S_n^o(\beta)^2\rangle/\langle S_n(\beta)^2\rangle$ evaluated at $\beta = 0.28$ against $1/\ln n$. The behaviour is quite linear, supporting the logarithmic behaviour of the correction term, and we estimate the amplitude ratio to be 0.479 ± 0.003.

In the collapsed regime the way in which the limiting behaviour is approached is not so clear and we simply plot the ratio of the radii of gyration, at $\beta = 0.45$, against n in figure 9. It seems likely that the ratio is going to unity and, certainly, the limiting value is greater than about 0.98.

We have also computed the radii of gyration tensors, and their eigenvalues, $\lambda_1 \geqslant \lambda_2 \geqslant \lambda_3$, and we show in figure 10 the ratio $\langle\lambda_3\rangle/\langle\lambda_1\rangle$ for both walks and polygons, as a function of β for $n = 600$. At small β the walks are more aspherical than the polygons, as expected. This asphericity decreases as β increases, and the asphericities approach one another at

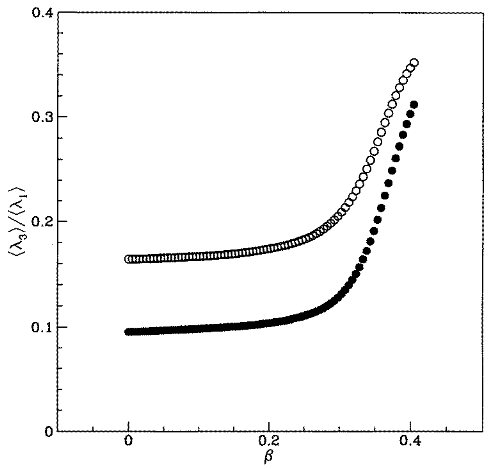

Figure 10. The β dependence of $\langle\lambda_3\rangle/\langle\lambda_1\rangle$ for walks (lower curve) and polygons (upper curve) for $n = 600$.

larger values of β.

4. Summary and discussion

In this paper we have considered the thermodynamic and metric properties of interacting self-avoiding walks, and interacting polygons on the simple cubic lattice, Z^3. In section 2 we showed that the limiting free energy of polygons exists, for all $\beta < \infty$, and is a continuous and convex function of β. For walks we have shown that the corresponding limiting free energy exists for $\beta \leqslant 0$ and is equal to that of polygons. In addition, we showed that if the mean number of contacts for polygons is at least as large as the mean number of contacts for walks (for all positive β and n sufficiently large), then the limiting free energy for walks exists for positive β and is equal to that of polygons. In particular, this would imply that if walks and polygons collapse, they do so at the same temperature. Although we are unable to establish the validity of this additional hypothesis, we regard it as being likely to be true, since it seems closely related to the fact that polygons have a smaller radius of gyration than walks.

In section 3 we briefly described the two sampling techniques used in our Monte Carlo study of this problem. We presented evidence that the hypothesis described above is satisfied, providing strong evidence that the limiting free energies are equal. The behaviour of the heat capacities strongly supports the existence of a collapse transition, and we have estimated its location. We also examined the behaviour of the radii of gyration as a function of n and β, and of the shape ratio $\langle\lambda_3\rangle/\langle\lambda_1\rangle$. We estimated the ratio of amplitudes for the radii of gyration for polygons and walks and our estimate is in good agreement with previous work at $\beta = 0$. At the critical point we see evidence of a logarithmic approach to the limiting behaviour, and form an estimate of the corresponding amplitude ratio. Similarly, in the collapsed phase, we present evidence that the amplitude ratio is close to unity, and examine the rate of approach as n increases.

It would be very interesting and useful to establish rigorously the validity of the auxiliary hypothesis used in section 2.

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