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Free energy of self-interacting uniform stars

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Abstract. We consider uniform star polymers on a variety of lattices, with an additional contact interaction between pairs of vertices which are unit distance apart and are not joined by an edge of the star. We present some rigorous results and other evidence which indicate that these systems have the same limiting free energy as self-interacting self-avoiding walks. We discuss the extension of these results to other homeomorphism types and to systems with an additional surface interaction term.

Light scattering (Sun *et al* 1980, Park *et al* 1992) and viscosity (Sun 1990) measurements on long linear polymers in dilute solution suggest that such systems undergo a sudden collapse transition from an expanded coil to a compact ball as the temperature is decreased. This collapse has been the subject of a great deal of theoretical work. In particular, it has been studied using transfer matrices (Saleur 1986), exact enumeration data (Privman 1986, Ishinabe 1987, Bennett-Wood *et al* 1994) and Monte Carlo methods (Mazur and McCrackin 1968, Webman *et al* 1981, Meirovitch and Lim 1990, Tesi *et al* 1996a).

It is interesting to enquire whether the nature and location of the collapse transition are affected by the architecture of the polymer. It seems that for randomly branched polymers (modelled by lattice animals or trees) the location and crossover exponent ϕ depend on the details of the model (Derrida and Herrmann 1983, Flesia and Gaunt 1992) and are different from the corresponding values for self-avoiding walks (Duplantier and Saleur 1987, Bennett-Wood *et al* 1994, Seno *et al* 1988). On the other hand, there is good evidence (Maes and Vanderzande 1990, Bennett-Wood *et al* 1995) that the location of the transition is the same for walks and polygons. Indeed, there is evidence that the dependence of the limiting free energy on the value of the interaction parameter is the same for walks and polygons, at least in three dimensions (Tesi *et al* 1996b). In this paper, we present evidence using a variety of techniques that the limiting free energy (per edge) of uniform stars is the same as for walks for all values of the interaction parameter.

An f-star is a connected subgraph of the lattice with one vertex of degree f and f vertices of degree one. A branch is the sequence of edges connecting the vertex of degree f to a vertex of degree one. A star is uniform if each of the f branches has the same number of edges. Let the number of uniform f-stars on a d-dimensional simple hypercubic lattice with n edges in each branch and with k contacts be $s_n(k; f)$. Clearly, $s_n(k; 1) \equiv c_n(k)$, the number of self-avoiding walks with n edges and k contacts. Define the corresponding partition functions as

$$Z_n(\beta; f) = \sum_k s_n(k; f)\mathrm{e}^{\beta k} \tag{1}$$

and

$$Z_n(\beta) = \sum_k c_n(k) e^{\beta k}. \tag{2}$$

We want to show that the limiting free energy for stars exists for all $\beta \leqslant 0$ and is equal to the free energy of interacting self-avoiding walks but, before proving this theorem, we need some definitions and lemmas.

Lemma 1. The limiting free energy

$$\kappa(\beta) = \lim_{n\to\infty} n^{-1} \log Z_n(\beta) \tag{3}$$

exists for all $\beta \leqslant 0$.

Proof. This was proved by Tesi *et al* (1996b) for $d = 3$ and the proof can be easily extended to general d. □

We write $(x_1, x_2, \ldots, x_d)$ for the coordinates of a point in $\mathbb{Z}^d$ and define a θ-wedge to be the set of points in $\mathbb{Z}^d$ such that $x_1 \geqslant 0$, $0 \leqslant x_i \leqslant ax_1$, for $i \geqslant 2$, where $a = \tan\theta > 0$. Let $c_n(k;\theta)$ be the number of n-step self-avoiding walks which start at the origin and lie in a θ-wedge, with k contacts.

Write $(x_1^j, x_2^j, \ldots, x_d^j)$ for the coordinates of the jth vertex of a self-avoiding walk, $j = 0, 1, 2, \ldots, n$. A *loop* is a self-avoiding walk with the additional restrictions that $0 = x_1^0 < x_1^i < x_1^n$, $\forall 0 < i < n$ and $x_j^0 = x_j^n = 0$, $\forall j > 1$, $x_j^i \geqslant 0$, $\forall i$ and $\forall j > 1$. This means that the first and last edges of a loop are along the x_1-axis. Let $l_n(k)$ be the number of loops with n edges and k contacts, and define $Z_n^l(\beta) = \sum_k l_n(k) e^{\beta k}$. We say that a self-avoiding walk is *multiply unfolded* if $x_1^0 < x_1^i < x_1^n$, $\forall 0 < i < n$, and $x_j^0 \leqslant x_j^i \leqslant x_j^n$, $\forall j > 1$ and $\forall i$. Let the number of multiply unfolded walks with n edges and k contacts be $w_n(k)$ with partition function $W_n(\beta) = \sum_k w_n(k) e^{\beta k}$.

Lemma 2. The limit $\lim_{n\to\infty} n^{-1} \log Z_n^l(\beta) \equiv \kappa_l(\beta)$ exists for all $\beta < \infty$.

Proof. Two loops can be concatenated to form a third loop by translating so that the first vertex of the second loop is coincident with the last vertex of the first loop. This operation produces no new contacts. Hence

$$\sum_{k_1} l_{n_1}(k_1) l_{n-n_1}(k - k_1) \leqslant l_n(k) \tag{4}$$

so that

$$Z_{n_1}^l(\beta) Z_{n-n_1}^l(\beta) \leqslant Z_n^l(\beta). \tag{5}$$

The result follows from this supermultiplicative inequality and the upper bound $Z_n^l(\beta) \leqslant \max[(2d)^n, (2d)^n e^{\beta(d-1)n}]$. □

Lemma 3. The limiting free energy for loops is identical to that of self-avoiding walks for all values of $\beta \leqslant 0$.

Proof. We first note that the limiting free energy for multiply unfolded walks exists and is equal to $\kappa(\beta)$ for $\beta \leqslant 0$. This can be proved by successive unfoldings in the d coordinate directions. Each unfolding is a surjection but is at most $e^{O(\sqrt{n})}$ to 1. Unfolding can delete contacts but cannot create them. We omit the details, which are similar to those in the proof of theorem 2.4 in Tesi *et al* (1996b).

To construct a lower bound on $Z_n^l(\beta)$ we concatenate pairs of multiply unfolded walks as follows. Fix $\beta \leqslant 0$. The set of n-edge multiply unfolded walks can be divided into subsets according to the coordinates of the nth vertex. For fixed n there are less than

$(n+1)^d$ such subsets. We label these subsets with the coordinates $(x_2, x_3, \ldots, x_d)$ of the nth vertex. Define the *most popular set* to be the first subset (in lexicographic order) which contributes at least as much as any other subset to the partition function $W_n(\beta)$. Clearly the most popular set depends on both n and β. This set will have a partition function at least as large as $W_n(\beta)/(n+1)^d$. Concatenate a multiply unfolded walk from the most popular set with another (or possibly the same) walk from this set, reflected in the plane $x_1 = 0$ and suitably translated. The resulting object will be a loop, with no contacts between the two parts coming from the two multiply unfolded walks. Therefore

$$Z^l_{2n}(\beta) \geqslant \left(\frac{W_n(\beta)}{(n+1)^d}\right)^2. \tag{6}$$

Taking logarithms, dividing by $2n$ and letting n go to infinity gives

$$\liminf_{n\to\infty} n^{-1} \log Z^l_n(\beta) \geqslant \lim_{n\to\infty} n^{-1} \log W_n(\beta) = \kappa(\beta). \tag{7}$$

Together with the obvious upper bound $Z^l_n(\beta) \leqslant Z_n(\beta)$ (since every loop is a walk) this inequality completes the proof. □

Lemma 4. For all $\beta \leqslant 0$, and for any $\theta > 0$,

$$\lim_{n\to\infty} n^{-1} \log \sum_k c_n(k;\theta)\mathrm{e}^{\beta k} = \kappa(\beta). \tag{8}$$

Proof. The proof is based on an idea which appears in Hammersley and Whittington (1985). Fix $\beta \leqslant 0$ and $\theta > 0$. We first note that $\sum_k c_n(k;\theta)\mathrm{e}^{\beta k} \leqslant Z_n(\beta)$ for any value of θ, so that

$$\limsup_{n\to\infty} n^{-1} \log \sum_k c_n(k;\theta)\mathrm{e}^{\beta k} \leqslant \kappa(\beta). \tag{9}$$

We construct a lower bound on the partition function for walks in a wedge by concatenating loops in such a way that new contacts are not formed by the concatenation. For any $\epsilon > 0$, lemmas 2 and 3 show that there is a value of $N = N(\epsilon, \beta)$ such that

$$\kappa(\beta) - \epsilon \leqslant N^{-1} \log Z^l_N(\beta). \tag{10}$$

Let $q_0 = \lceil N \cot\theta \rceil$. For a given n write $n = Np + q_0 + q_1$ where $0 \leqslant q_1 < N$. Concatenate p loops each with N edges with the left-most vertex at $(q_0 + q_1, 0, 0, \ldots, 0)$. The resulting object is a loop which fits inside the θ-wedge. By adding $q_0 + q_1$ edges to join $(q_0 + q_1, 0, 0, \ldots, 0)$ to the origin we obtain a walk with n edges within the θ-wedge. Since the separate loops can be chosen independently, and since the contacts can be distributed over the p loops and there are no contacts between loops, we have

$$\sum_k c_n(k,\theta)\mathrm{e}^{\beta k} \geqslant Z^l_N(\beta)^p. \tag{11}$$

Taking logarithms, dividing by n and letting n go to infinity gives

$$\liminf_{n\to\infty} n^{-1} \log \sum_k c_n(k,\theta)\mathrm{e}^{\beta k} \geqslant N^{-1} \log Z^l_N(\beta) \geqslant \kappa(\beta) - \epsilon. \tag{12}$$

Since ϵ is arbitrary we can let $\epsilon \to 0^+$. This, together with (9), gives the required result. □

We are now in a position to prove the main theorem of this paper.

Theorem 1. The limiting free energy

$$\lim_{n\to\infty} \frac{1}{nf} \log Z_n(\beta; f) \equiv \kappa_f(\beta) \tag{13}$$

exists for all $\beta \leqslant 0$ and $\kappa_f(\beta) = \kappa(\beta)$, independent of f, where $\kappa(\beta)$ is the limiting free energy for self-avoiding walks.

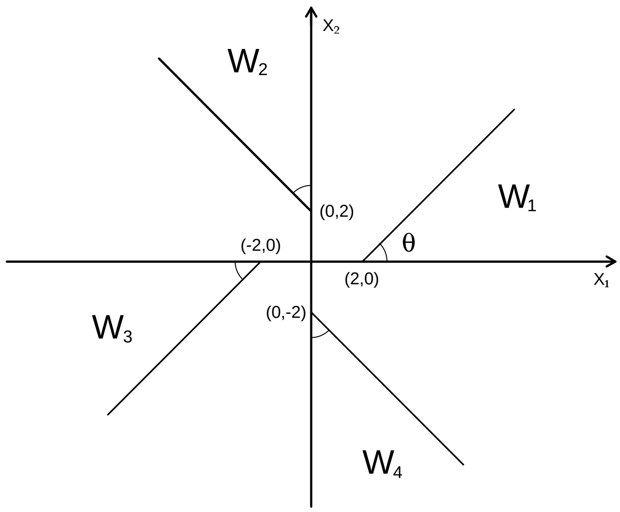

Figure 1. A suitable arrangement of wedges in $d = 2$.

Proof. To obtain a lower bound on $Z_n(\beta; f)$ we construct a set of f disjoint wedges which are θ-wedges or rotations or translations of θ-wedges with the additional condition that vertices in disjoint wedges are not unit distance apart. Figure 1 gives a suitable arrangement in two dimensions. By adding pairs of edges to join the apices of the wedges to the origin, along coordinate axes, and embedding walks with $n-2$ edges independently in f wedges, we have

$$\sum_k s_n(k; f)\mathrm{e}^{\beta k} \geqslant \sum_k \prod_{i=1}^{f} \sum_{k_i} c_{n-2}(k_i; \theta)\mathrm{e}^{\beta k_i} \tag{14}$$

with $\sum_{i=1}^{f} k_i = k$.

We next construct an upper bound on $Z_n(\beta; f)$. If we embed f n-step self-avoiding walks independently, but with a common origin, then

$$s_n(k; f) \leqslant \sum_{\{k_i\}} \prod_{i=1}^{f} c_n(k_i) \tag{15}$$

where the sum is over all sets of k_i such that $k_i \geqslant 0$ $\forall i$ and $\sum_{i=1}^{f} k_i \leqslant k$. Note that $k - \sum_{i=1}^{f} k_i \equiv k_0$ is the number of contacts *between* branches of the star. Multiplying both sides of equation (15) by $\mathrm{e}^{\beta k}$ and summing over k gives

$$Z_n(\beta; f) \leqslant [(d-1)nf + d] \times [Z_n(\beta)]^f. \tag{16}$$

Equation (13) then follows from (14) and (16), using lemma 4. □

Tesi *et al* (1996b) proved that the limiting free energies for walks and polygons are identical for $\beta \leqslant 0$ in $d = 3$ and similar arguments should work for general d. The corresponding result for $\beta > 0$ has not been established rigorously for walks and polygons and we have been unable to construct a proof for $\beta > 0$ for walks and stars. We now address this problem numerically.

For small values of n, we have derived exact enumeration data for $s_n(k; f)$ for all values of f on the simple cubic, square and triangular lattices. We have formed the corresponding

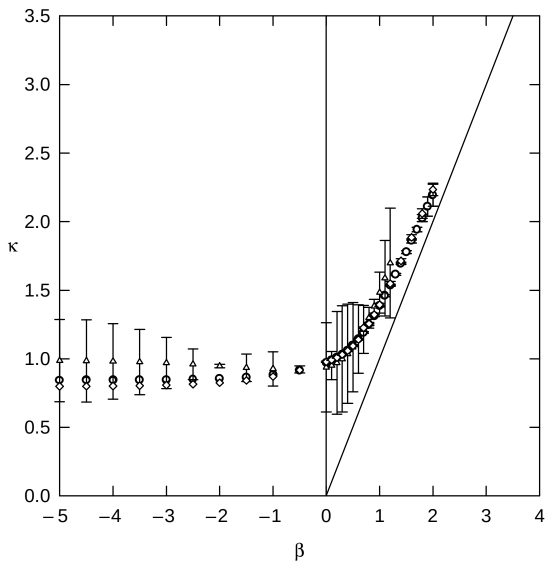

Figure 2. Estimates of the limiting free energy as a function of β for the square lattice. The symbol ● denotes self-avoiding walks, ○ denotes 3-stars, △ denotes 4-stars and ◇ denotes polygons. Where uncertainties are not shown, they are comparable with the size of the symbols. The straight line shown is parallel to the conjectured asymptote for large β (see for instance Madras *et al* 1990), $\kappa = \beta + c_2$, where c_2 is a positive constant.

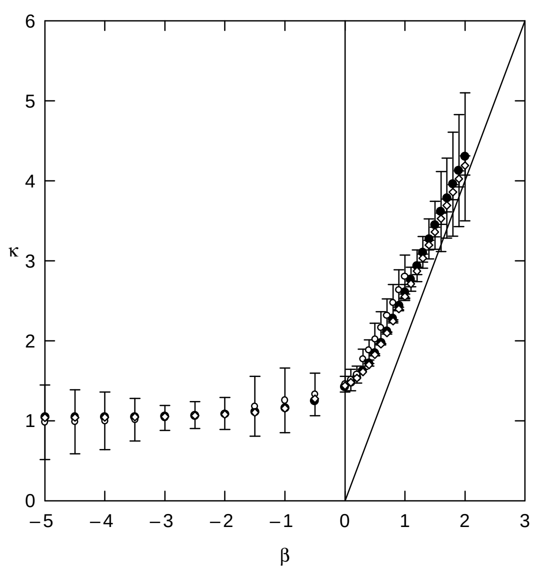

Figure 3. Estimates of the limiting free energy as a function of β for the triangular lattice. The symbol ● denotes self-avoiding walks, ○ denotes 3-stars and ◇ denotes polygons. Where uncertainties are not shown, they are comparable with the size of the symbols. The straight line shown is parallel to the conjectured asymptote for large β (see for instance Madras *et al* 1990), $\kappa = 2\beta + c_{\triangle}$, where $c_{\triangle}$ is a positive constant.

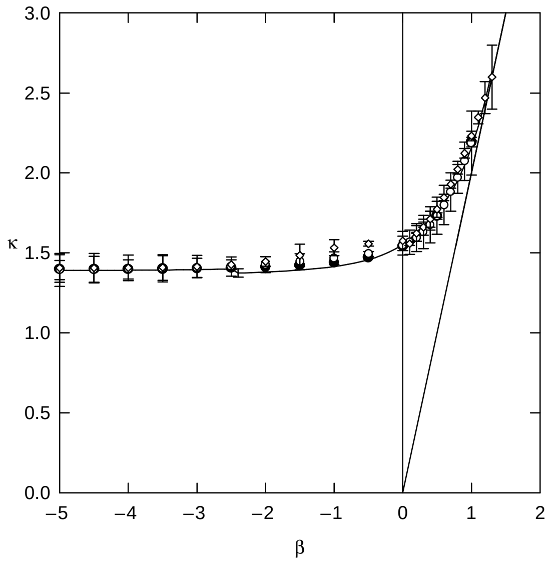

Figure 4. Estimates of the limiting free energy as a function of β for the simple cubic lattice. The symbol ● denotes self-avoiding walks, ○ denotes 3-stars and ◊ denotes polygons. Where uncertainties are not shown, they are comparable with the size of the symbols. The straight line shown is parallel to the conjectured asymptote for large β (see for instance Madras *et al* 1990), $\kappa = 2\beta + c_3$, where c_3 is a positive constant. The full curve is obtained by truncating the $1/d$-expansion.

partition functions (1), and used ratio methods to estimate the limiting free energy $\kappa_f(\beta)$ as a function of f and β, on the assumption that the limit in (13) exists also for $\beta > 0$. In figure 2, we show our estimates of $\kappa_f(\beta)$ for $f = 3$ and 4 on the square lattice. For comparison, we show our corresponding numerical estimates for self-avoiding walks and polygons. Figures 3 and 4 give corresponding results for the triangular and simple cubic lattices, respectively. For $\beta \leqslant 0$, these estimates are consistent with our theorem 1 and with corollary 2.7 of Tesi *et al* (1996b). For $\beta > 0$, no such theorems have been proved but the numerical results strongly suggest that the limiting free energies of f-stars, walks and polygons are identical at *all* values of β. In particular, this implies that the location of the collapse transition, and the value of the crossover exponent ϕ, are the same for all of these polymer architectures.

We have obtained further support for the equality of the free energies $\kappa_f(\beta)$ and $\kappa(\beta)$ by investigating their $1/d$-expansions (Fisher and Gaunt 1964). The $1/d$-expansion for the free energy, $\kappa(\beta)$, of walks has been obtained by Nemirovsky *et al* (1992). We have derived the corresponding expansion for the free energy of f-stars, $\kappa_f(\beta)$, for general f to order $1/d$, and for $f = 3$ to order $1/d^2$. The terms in the expansion are independent of f and agree term-by-term with the results for walks.

The fact that walks, polygons and f-stars all appear to have the same limiting free energy for all values of β raises the interesting question of whether this is also true for uniform embeddings of graphs of every fixed homeomorphism type. For the special case $\beta = 0$, uniform combs and uniform brushes were investigated by Gaunt *et al* (1986) and Soteros and Whittington (1989), and more general architectures by Soteros (1992). For the case $\beta \leqslant 0$, we have extended theorem 1 to apply to uniform combs and uniform brushes, the proof will appear elsewhere. It would be interesting to investigate the case $\beta > 0$ numerically.

Another interesting extension is to the case where the self-interacting polymer also interacts with a surface. For the case $\beta = 0$, Soteros (1992) has shown that the dependence of the free energy on the strength α of the interaction with the surface is independent of homeomorphism type for $d \geqslant 3$ but depends on homeomorphism type when $d = 2$. Recently, Vrbová and Whittington (1996) have shown that walks and polygons in $d = 3$ have the same limiting free energy for all values of α when $\beta \leqslant 0$. We have proved the corresponding result for uniform stars, combs and brushes, details will be published elsewhere.

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