Interacting lattice polygons

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1 Introduction

A polymer is a long chain molecule of repeated chemical units, monomers. A *ring polymer* is simply a polymer whose ends have been joined so that topologically the molecule forms a circle. Lattice polygons are useful models of the configurational properties of flexible ring polymers in dilute solution in so-called "good" solvents. Good solvents are those where any attractive interactions between parts of the polymer have been effectively screened by the solvent molecules, leaving only entropic repulsion. The model of ring polymers as lattice polygons then can be modified by adding interactions to mimic phenomena such as ring polymer *adsorption* and *collapse.* Lattice polygons play the same role for ring polymers as self-avoiding walks do for linear polymers.

Polymers in dilute solution interacting with an impenetrable surface to which the monomers are attracted can undergo a phase transition, known as the adsorption transition. At high temperatures the polymer is repelled entropically from the wall and has very few monomers in contact with the wall: this is known as the desorbed phase. There is a phase transition at some particular temperature and at low temperatures the system behaves differently: in this adsorbed phase there is a positive density of monomers in contact with the wall. See Figure 1. The lattice polygon model of ring polymer adsorption will be discussed in Section 2.

When a polymer is in dilute solution in a good solvent the polymer forms an open random coil and its root-mean-square radius of gyration scales like n^ν where n is the degree of polymerization and ν is about 0.588 (in three dimensions). In so-called "poor" solvent conditions the monomer-solvent contacts are energetically unfavourable and the polymer collapses to a compact ball to favour monomer-monomer contacts rather than monomer-solvent contacts. See Figure 2. This collapse phenomenon has been observed for linear polymers by light scattering measurements. A useful model of the collapse transition for ring polymers is a lattice polygon with an additional vertex-vertex interaction which can be varied to favour or disfavour the collapse. In a sense this

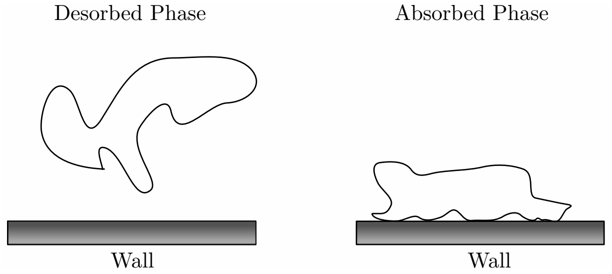

Fig. 1. A schematic picture of a ring polymer in the desorbed (left-hand side) and adsorbed phases (right-hand side).

vertex-vertex interaction can be thought of as a potential of mean force which takes account of solvent-monomer interactions. The model will be discussed in Section 3.

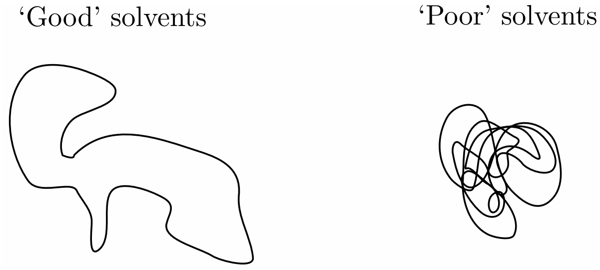

Fig. 2. A schematic picture of a ring polymer in a good solvent as an open coil (left-hand side) and in a poor solvent as a compact globule (right-hand side).

In principle the phenomena of adsorption and collapse can both occur and the situation then results in a rich phase diagram which is discussed in Section 4.

An interesting question which occurs in each of these three cases is whether the free energies of the walk and polygon models are identical in the infinite size limit. This will be a particular focus of this chapter and we shall say something both about what is known rigorously and about some numerical studies of this question.

2 The adsorption transition

Polymer molecules in dilute solution in a good solvent can adsorb at an impenetrable surface. This phenomenon plays an important role in such phenomena as steric stabilization of dispersions [11]. At high temperatures the polymer will be desorbed and will have only a vanishingly small fraction of its monomers near the wall while at low temperatures it will adsorb and have a positive density of its monomers near the wall.

A natural model of this phenomenon is a self-avoiding walk (for linear polymers) or a lattice polygon (for ring polymers) with an interaction with the wall. We shall describe both models. Consider the simple cubic lattice $\mathbb{Z}^3$, though most things go through to $\mathbb{Z}^d$, $d > 3$, with no real difficulty. The $d = 2$ case turns out to have some special features and we consider this case separately. Attach a coordinate system (x, y, z) to the vertices so that x, y and z are integers. Suppose that the impenetrable adsorbing surface is the plane $z = 0$ and that the solvent corresponds to the half-space $z > 0$. Suppose that $c_n^+(v)$ is the number of self-avoiding walks with n edges, starting at the origin, having no vertices with negative z-coordinate and having $v + 1$ vertices in the plane $z = 0$. We say that such a walk *visits* the plane $z = 0$ v times or that it has v *visits*. Similarly let $p_n(v)$ be the number of lattice polygons with n edges, having no vertices with negative z-coordinate and having $v \geq 2$ vertices in $z = 0$. See Figure 3. We shall be interested in the partition functions

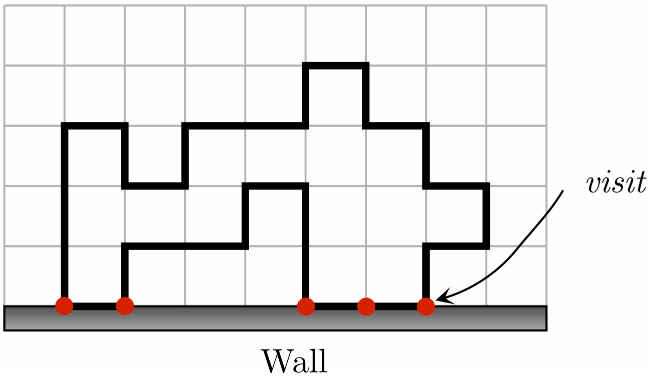

Fig. 3. A polygon on the square latttice with $v = 5$ *visits* to the surface (wall).

$$C_n(\alpha) = \sum_{v=0}^{n} c_n(v) e^{\alpha v} \tag{1}$$

and

$$P_n(\alpha) = \sum_{v=2}^{n} p_n(v) e^{\alpha v}. \tag{2}$$

We can define corresponding (reduced, intensive) free energies

$$\kappa_n(\alpha) = n^{-1} \log C_n(\alpha) \tag{3}$$

and

$$\kappa_n^0(\alpha) = n^{-1} \log P_n(\alpha) \tag{4}$$

and we shall be interested in quantities such as

$$\rho_n(\alpha) = \frac{\partial \kappa_n(\alpha)}{\partial \alpha} = \frac{1}{n} \frac{\sum_v v c_n(v) e^{\alpha v}}{\sum_v c_n(v) e^{\alpha v}} \tag{5}$$

and

$$\rho_n^0(\alpha) = \frac{\partial \kappa_n^0(\alpha)}{\partial \alpha} = \frac{1}{n} \frac{\sum_v v p_n(v) e^{\alpha v}}{\sum_v p_n(v) e^{\alpha v}}. \tag{6}$$

These are the mean fractions of visits for the two models and we expect that these will be small (in fact zero in the infinite n limit) when the polymer is desorbed. For the infinite n case we expect behaviour similar to that sketched in Figure 4.

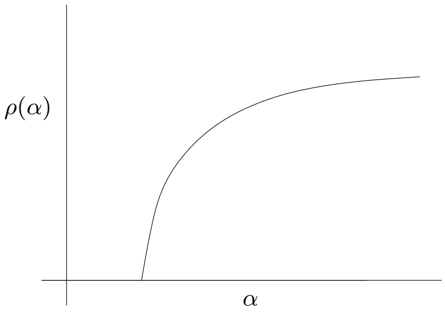

Fig. 4. The expected dependence of the mean fraction of visits on α.

Rigorous results are available [5, 16] about the existence of the limits in (3) and (4). It is known rigorously that these two free energies are equal for $d \geq 3$ for all α [16] and that they are non-analytic functions of α. This means that the two models have a phase transition (corresponding to adsorption) and that this transition is at the same place for the two models. Bounds are available on the location of the transition [5, 7] but these are weak and one must turn to numerical methods for estimates of the location of the transition [3, 6, 8]. Similarly the order of the transition is not known rigorously but numerical results are available, though there is some disagreement [3, 6, 8] about the value of the crossover exponent ϕ, defined below, see eqn. (14).

Other interesting properties include the n-dependence of the mean span of the polygon or walk in the z-direction and in the x- (or y-) direction as a function of α. Equivalently one could look at the various components of the radius of gyration. All of these can act as signals that the walk or polygon is desorbed or adsorbed. These quantities can be estimated by Monte Carlo methods [6, 8] or by exact enumeration techniques.

2.1 Rigorous results

We focus on the results for polygons though the theorems were originally proved for self-avoiding walks [5]. At first we confine ourselves to $d = 3$ though the results go over in a straightforward way to $d > 3$. Concatenation arguments can be used to prove the existence of the limit

$$\lim_{n\to\infty} \kappa_n^0(\alpha) \equiv \kappa^0(\alpha) \tag{7}$$

for all $\alpha < \infty$. Similarly it is possible to prove that $\kappa^0(\alpha)$ is a convex function of α and is therefore continuous. Moreover $\kappa^0(\alpha)$ is differentiable almost everywhere.

For $\alpha \geq 0$ it is easy to see that $P_n(\alpha) \leq p_n e^{\alpha n}$ where $p_n = \sum_v p_n(v)$ is the number of n-edge polygons on $\mathbb{Z}^3$. Writing $\lim_{n\to\infty} n^{-1} \log p_n = \kappa_3$ we have

$$\kappa^0(\alpha) \leq \kappa_3 + \alpha, \quad \alpha \geq 0. \tag{8}$$

By picking out a particular term we have

$$P_n(\alpha) \geq p_n(n) e^{\alpha n} \tag{9}$$

and, by monotonicity in α, $P_n(\alpha) \geq P_n(0) = p_n$. Note that $p_n(n)$ counts polygons on $\mathbb{Z}^2$. If we write $\lim_{n\to\infty} n^{-1} \log p_n(n) = \kappa_2$ we then obtain

$$\kappa^0(\alpha) \geq \max[\kappa_3, \kappa_2 + \alpha], \quad \alpha \geq 0. \tag{10}$$

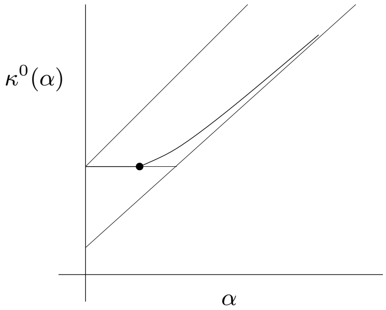

Fig. 5. The dependence of the reduced limiting free energy, $\kappa^0(\alpha)$ on α. The straight lines are bounds and the filled circle shows the location of the adsorption transition.

For $\alpha \leq 0$ we have $P_n(\alpha) \leq P_n(0) = p_n$ by monotonicity and hence $\kappa^0(\alpha) \leq \kappa_3$. Again we can pick out a particular term to give

$$P_n(\alpha) \geq p_n(2) e^{2\alpha} \tag{11}$$

and, since $p_n(2) \geq p_{n-2}$, we have $\kappa^0(\alpha) \geq \kappa_3$. This means that the free energy is equal to κ_3, independent of α, for $\alpha \leq 0$ but strictly greater than κ_3 for

$\alpha > \kappa_3 - \kappa_2$. Hence $\kappa^0(\alpha)$ has a singular point at $\alpha = \alpha_0$ with $0 \leq \alpha_0 \leq \kappa_3 - \kappa_2$. With a little more work these two inequalities can be made strict [5, 7]. In addition it can be shown that $\kappa^0(\alpha)$ is asymptotic to the line $\kappa_2 + \alpha$ as $\alpha \to \infty$. The behaviour is sketched in Figure 5.

Soteros [16] showed that $\kappa(\alpha) = \kappa^0(\alpha)$ so the two limiting free energies are equal and, in particular, the adsorption points are the same for the two models.

If we are interested in the mean fraction of visits in the infinite n limit we need to look at

$$\rho^0(\alpha) = \lim_{n\to\infty} \rho_n^0(\alpha) = \lim_{n\to\infty} \frac{\partial \kappa_n^0(\alpha)}{\partial \alpha}. \tag{12}$$

$\kappa_n^0(\alpha)$ is a convex function of α so the order of the limit and derivative can be interchanged so that

$$\rho^0(\alpha) = \frac{\partial \kappa^0(\alpha)}{\partial \alpha} \tag{13}$$

and hence $\rho^0(\alpha)$ is zero for $\alpha < \alpha_0$. This is the desorbed phase where the mean fraction of visits vanishes in the infinite n limit. When $\alpha > \alpha_0$ $\rho^0(\alpha) > 0$ and we are in the adsorbed phase. It is not known rigorously whether or not $\rho^0(\alpha)$ is continuous at $\alpha = \alpha_0$.

The behaviour of the free energy near $\alpha = \alpha_0$ is governed by the crossover exponent, ϕ. Formally this is defined as

$$\frac{1}{\phi} = \lim_{\alpha\to\alpha_0+} \frac{\kappa^0(\alpha) - \kappa^0(\alpha_0)}{\alpha - \alpha_0}. \tag{14}$$

It is not known rigorously that the limit exists but, if it does, the above result of Soteros [16] means that the crossover exponent has the same value for the walk and polygon models, for $d \geq 3$.

When we turn to examine the situation for $d = 2$ there are some important differences. One can prove that the limiting free energies $\kappa^0(\alpha)$ and $\kappa(\alpha)$ exist and both functions are convex in α. For the walk problem we have

$$\max[\kappa_2, \alpha] \leq \kappa(\alpha) \leq \kappa_2 + \alpha, \quad \alpha \geq 0 \tag{15}$$

and

$$\kappa(\alpha) = \kappa_2, \quad \alpha \leq 0 \tag{16}$$

which is analogous to the results for $d \geq 3$ for walks. For polygons in $\mathbb{Z}^2$ we have $\kappa^0(\alpha) = \kappa_2$ for $\alpha \leq 0$. However, for $\alpha \geq 0$ the maximum number of vertices of the polygon which can be in the line $y = 0$ is $n/2$. Hence

$$\max[\kappa_2, \alpha/2] \leq \kappa^0(\alpha) \leq \kappa_2 + \alpha/2, \quad \alpha \geq 0. \tag{17}$$

This means that $\kappa^0(\alpha)$ has an asymptote with slope $1/2$ as $\alpha \to \infty$ (*cf* walks which have an asymptote with unit slope). Therefore $\kappa(\alpha) > \kappa^0(\alpha)$ for large enough values of α and the two free energies are not identical. Both $\kappa(\alpha)$ and $\kappa^0(\alpha)$ have singular points (at α_w and α_0 respectively) and $\alpha_0 \geq \alpha_w$. Whether these are distinct is not known.

2.2 Numerical results

The two primary numerical methods which have been used to investigate this problem are exact enumeration coupled with series analysis and Monte Carlo methods. In addition there are some transfer matrix calculations in two dimensions. The main quantities of interest are

1. The temperature dependence of the free energy.
2. The location of the phase transition.
3. The shape of the free energy curve close to the phase transition, in the low temperature (adsorbed) phase, characterized by the crossover exponent ϕ, and hence the value of ϕ.
4. Various metric quantities such as the mean-square radius of gyration or the mean distance of a vertex from the surface, as a function of temperature.

It isn't too difficult to use exact enumeration methods to calculate the values of $\kappa_n(\alpha)$ and $\kappa_n^0(\alpha)$, defined by (3) and (4), for modest values of n. Series analysis techniques, discussed in Chapter 8, such as ratio methods, can then be used to estimate $\kappa(\alpha)$ and $\kappa^0(\alpha)$, which we know to be identical in three and higher dimensions. The difficulty is to extract a reliable estimate of the critical value of α since one is asking where a function stops being constant. It is easy enough to get a reasonable upper bound on α_0 (or on α_w in two dimensions where α_0 and α_w may be different) but it is extraordinarily difficult to estimate a reliable lower bound. One might hope to examine the corresponding fluctuation quantity $\partial^2\kappa_n(\alpha)/\partial\alpha^2$ but this doesn't behave well for small n and is difficult to extrapolate. As a result the most reliable estimates of α_0 (and α_w) come from Monte Carlo calculations.

We are not aware of any Monte Carlo calculations for adsorption of ring polymers (*ie* polygons) but there are many studies of the adsorption of linear polymers (*ie* self-avoiding walks) both in two and in three dimensions. In three dimensions we know, *vide supra*, that polygons and walks have the same limiting free energies so calculations for walks give useful information for polygons, in the thermodynamic limit. We shall not attempt to give a systematic survey of the literature on Monte Carlo studies for walks but we content ourselves with mentioning some recent papers and pointing to an interesting open question.

Hegger and Grassberger [6] carried out a very thorough Monte Carlo study of adsorption of self-avoiding walks in three dimensions (on the simple cubic lattice), obtaining data for values of n up to about 2000. At the time of their work the value of α_0 was not known very precisely but the balance of evidence suggested a value around 0.285. Hegger and Grassberger examined a variety of different properties and concluded that α_0 was probably between 0.2857 and 0.2861, with a preferred value of about 0.2859. They also noticed strong corrections to scaling which make it difficult to extrapolate from data for short walks. There were several previous attempts to estimate the value of ϕ in three dimensions and they estimated

$$\phi = 0.496 \pm 0.004 \tag{18}$$

which was somewhat smaller than previous estimates.

Janse van Rensburg and Rechnitzer [8] attacked the problem somewhat differently by producing very high quality Monte Carlo data on shorter walks (with n values up to 120) and then doing a careful statistical analysis in which they attempted to incorporate correction to scaling terms. They estimated $\alpha_0 = 0.288 \pm 0.020$ for the simple cubic lattice and

$$\phi = 0.5005 \pm 0.0036. \tag{19}$$

The two approaches give values of α_0 which are in reasonable agreement and both studies are consistent with a value of $\phi = 1/2$. Since there is good evidence that $\phi = 1/2$ also in two dimensions this would imply a super-universality for ϕ in dimensions 2 to 4 [6]. However, Grassberger [3] returned to the problem using a somewhat different algorithm and obtained data for walks with n up to 8000. He gave the very precise estimate

$$\alpha_0 = 0.28567 \pm 0.00008 \tag{20}$$

but gave a lower estimate for ϕ, namely

$$\phi = 0.484 \pm 0.002. \tag{21}$$

If this value is correct then ϕ is not super-universal.

In two dimensions we know that walks and polygons do not have the same limiting free energy and we do not know of any Monte Carlo calculations for polygons in two dimensions.

3 The collapse transition

In dilute solution in a good solvent polymers are typically expanded coils. In these conditions the monomer-solvent contacts are favourable and monomers tend to be surrounded by solvent. In a poor solvent monomer-solvent contacts become less favourable and the polymer collapses to a compact ball producing monomer-monomer contacts at the expense of monomer-solvent contacts. Typically the solvent becomes worse as the temperature decreases and there is a temperature, the θ-temperature, at which the polymer collapses.

This situation for a ring polymer can be modelled by considering polygons with n edges where we keep track of the number of pairs of vertices which are unit distance apart but are not joined by an edge of the polygon. We call these *contacts*. See Figure 6 for an example on the square lattice. We can weight polygons according to the number of contacts. Suppose that $p_n(k)$ is the number of n-edge polygons with k contacts. For example, on the square lattice $p_8(2) = 6$ and $p_8(0) = 1$.

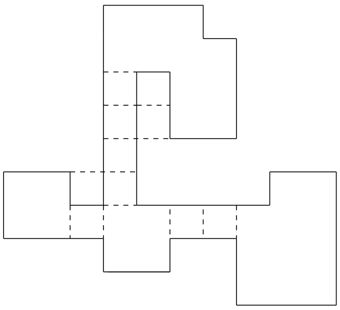

Fig. 6. A polygon with 13 contacts. The contacts are indicated by dashed lines.

Define the partition function

$$Z_n^0(\beta) = \sum_k p_n(k) e^{\beta k} \tag{22}$$

and the corresponding free energy

$$F_n^0(\beta) = n^{-1} \log Z_n^0(\beta). \tag{23}$$

We expect that the limit $F^0(\beta) = \lim_{n\to\infty} F_n^0(\beta)$ will exist and that $F^0(\beta)$ will have a singularity at $\beta = \beta_c^0$ corresponding to the θ-point.

One can define a similar model for self-avoiding walks. Let $c_n(k)$ be the number of n-edge self-avoiding walks with k contacts. Define the partition function

$$Z_n(\beta) = \sum_k c_n(k) e^{\beta k} \tag{24}$$

and the corresponding free energy

$$F_n(\beta) = n^{-1} \log Z_n(\beta). \tag{25}$$

Again we expect that the limit $F(\beta) = \lim_{n\to\infty} F_n(\beta)$ will exist and that $F(\beta)$ will be singular at some $\beta = \beta_c$. Some natural questions which arise are whether $F^0(\beta) = F(\beta)$. If not is β_c^0 different from β_c?

If we write $S_n(\beta)$ and $S_n^0(\beta)$ for the mean-square radius of gyration of n-edge walks and polygons at parameter β, it is natural to expect that $S_n(\beta) \sim An^\nu$ for $\beta < \beta_c$, where ν is the exponent corresponding to a good solvent. For $\beta > \beta_c$ (*ie* at low temperatures) $S_n(\beta) \sim Bn^{1/d}$, with similar expressions for the polygon problem. That is, the transition is associated with a change in the radius of gyration exponent.

3.1 Rigorous results

Remarkably little is known rigorously about this problem, either for the polygon model or for the self-avoiding walk model. Concatenation arguments [17] can be used to prove the existence of the limit

$$F^0(\beta) = \lim_{n\to\infty} n^{-1} \log Z_n^0(\beta). \tag{26}$$

In addition it can be shown that $F^0(\beta)$ is a convex function of β and hence is continuous. Tesi *et al* [17] also showed that, if $\beta \le 0$, the limiting free energy $F(\beta) = \lim_{n\to\infty} F_n(\beta)$ exists and that $F(\beta) = F^0(\beta)$. So the polygon and walk models have the same free energy for $\beta \le 0$, *ie* for repulsive interactions. To get a bound in one direction one deletes an edge from a polygon giving

$$c_{n-1}(k+1) \ge p_n(k) \tag{27}$$

since the edge deletion creates a contact. This immediately gives

$$\liminf_{n\to\infty} F_n(\beta) \ge F^0(\beta) \tag{28}$$

and this bound works for all β. The idea behind the bound in the other direction is to relate polygons and walks to *unfolded walks* and to use a theorem about unfolded walks due to Hammersley and Welsh [4]. This does not work for $\beta > 0$ because unfolding can destroy contacts. The existence of the thermodynamic limit for the walk model is an open question.

Tesi *et al* proved another potentially useful lemma [17]. Suppose that $K_n(\beta)$ is the mean number of contacts for n-edge self-avoiding walks at parameter β, *ie*

$$K_n(\beta) = \frac{\sum_k k c_n(k) e^{\beta k}}{\sum_k c_n(k) e^{\beta k}} \tag{29}$$

and that $K_n^0(\beta)$ is the corresponding quantity for the polygon model. Tesi *et al* showed that if $K_n^0(\beta) \ge K_n(\beta)$ for all sufficiently large even n and for all $\beta > 0$ then $\lim_{n\to\infty} F_n(\beta)$ exists and $F(\beta) = F^0(\beta)$ for all β.

3.2 Numerical results

The question of whether or not the limiting free energies of walks and polygons are equal for $\beta > 0$ has been addressed numerically [2, 17]. Tesi *et al* [17] used Monte Carlo methods (in fact umbrella sampling and multiple Markov chain methods, as described in Chapter 9) to study self-interacting polygons on the simple cubic lattice. They estimated the heat capacity $\partial^2 F_n^0(\beta)/\partial\beta^2$ as a function of n and β and observed peaks in the heat capacity (as a function of β) which increase in height as n increases, consistent with a second order phase transition at a critical value of β which they estimated to be 0.2782 ± 0.0070. The corresponding estimate for the walk problem is 0.2779 ± 0.0041, so the results are consistent with walks and polygons collapsing at the same temperature.

Tesi *et al* [17] also estimated the free energy difference

$$\Delta F_n(\beta) = [F_n^0(\beta) - F_n^0(0)] - [F_n(\beta) - F_n(0)] \tag{30}$$

(recall that $F(0) = F^0(0)$). They observed that $\Delta F_n(\beta)$ is positive for $\beta > 0$ but decreases as n increases, again consistent with the free energies being equal in the infinite n limit.

To test this further they estimated the ratio $K_n^0(\beta)/K_n(\beta)$ as a function of n and β. The ratio is greater than unity for the range of β and n values studied, going through a maximum at fixed n and decreasing towards unity as β increases. The height of the maximum decreases as n increases. Using the result discussed in Section 3.1, this is strong evidence that the two models have the same limiting free energy for all values of β. Incidently, this implies that they have the same value for the crossover exponent, ϕ.

For the square lattice in two dimensions the critical value of β has been estimated for the walk and polygon problems and the results are consistent with a common value $\beta_c = 0.663 \pm 0.016$. The evidence is reviewed briefly in [2].

Bennett-Wood *et al* [2] derived exact enumeration data for the square lattice for $n \leq 29$ for the walk model and for $n \leq 42$ for the polygon model, enabling them to calculate $Z_n(\beta)$ and $Z_n^0(\beta)$ for these values of n. They computed $K_n(\beta)$ and $K_n^0(\beta)$. For $\beta < 0.6$ (*ie* at high temperature) they observed that $K_n^0(\beta) > K_n(\beta)$ at the largest values of n considered, and gave evidence that $K_n^0(\beta) - K_n(\beta) \to 0$ as $n \to \infty$, for $\beta < 0.663$. For larger values of β (beyond the collapse transition) $K_n(\beta) > K_n^0(\beta)$ for the values of n considered so the Lemma of Tesi *et al* [17] does not apply.

To investigate the situation at low temperatures ($\beta > 0.663$) Bennett-Wood *et al* [2] defined

$$Q_n = \frac{\sqrt{Z_{n+1}^0 Z_{n-1}^0}}{Z_n} \tag{31}$$

for n odd and $Q_n = Z_n^0/Z_n$ for n even. They used series analysis techniques to estimate $\lim_{n\to\infty} Q_n^{1/n}$ for various values of β. For $0 < \beta < 1.5$ (so well into the collapsed phase) they estimated that $\lim_{n\to\infty} Q_n^{1/n}$ is unity within the estimated error bars. This is consistent with the equality of the limiting free energies for the walk and polygon models for all values of β which were considered.

4 Adsorption and collapse

One can also consider the situation where a polymer can adsorb at a surface and collapse into a compact ball. This involves having two different energy terms, one corresponding to the attraction of a monomer to the surface at which adsorption can occur, and another corresponding to the monomer-monomer attraction which can lead to collapse.

Consider the simple cubic lattice and the half-space $z \geq 0$. Suppose that $p_n(v, k)$ is the number of n-edge polygons with v vertices in the plane $z = 0$ ($v \geq 2$) and with k contacts. The appropriate partition function is now

$$Z_n^0(\alpha,\beta) = \sum_{v,k} p_n(v,k) e^{\alpha v + \beta k} \tag{32}$$

and the corresponding (intensive) free energy is

$$F_n^0(\alpha,\beta) = n^{-1} \log Z_n^0(\alpha,\beta). \tag{33}$$

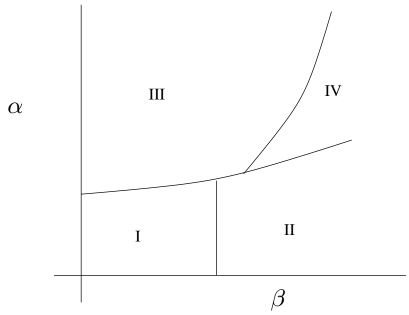

Fig. 7. The phase diagram for polygons which can both adsorb at a surface and collapse. The four phases are I: desorbed and expanded, II: desorbed and collapsed, III: adsorbed and expanded, and IV: adsorbed and collapsed.

One might expect four different phases in the (α,β)-plane. At small α and small β the polymer should be desorbed and expanded. As α increases at small fixed β the polymer should adsorb to give a phase where the polymer is adsorbed and expanded. Increasing β at fixed small α should give a desorbed and collapsed phase. From the interior of the adsorbed and expanded phase increasing β should lead to collapse in the adsorbed phase, to give a collapsed phase at the surface. See Figure 7 for a sketch of a possible phase diagram.

4.1 Rigorous results

A few rigorous results for this model have been obtained by Vrbovà and Whittington [19]. They used concatenation arguments to prove the existence of the limit

$$\lim_{n\to\infty} F_n^0(\alpha,\beta) \equiv F^0(\alpha,\beta) \tag{34}$$

for all $\alpha < \infty$ and $\beta < \infty$. They also showed that $F^0(\alpha,\beta)$ is doubly convex (*ie* convex as a surface, which is a stronger statement than being convex in both arguments), and hence a continuous function of α and β.

The arguments of Section 2.1 can be extended to show that polygons exhibit an adsorption transition at some critical value of $\alpha = \alpha_c(\beta)$ for all $\beta < \infty$. This establishes the existence of the phase boundary between the desorbed phases (I and II) and the adsorbed phases (III and IV) in Figure 7. It is not known if the phase boundary $\alpha = \alpha_c(\beta)$ is a continuous function of

β. It is also not known rigorously that there is a collapse transition at some $\beta = \beta_o$ when $\alpha = 0$. However, if these two conditions are met then the phase boundary between the desorbed and expanded phase (I) and the desorbed and collapsed phase (II) is a straight line and the critical value of β is independent of α.

4.2 Numerical results

The polygon problem does not seem to have been studied numerically but one would expect the same phase diagram for walks and for polygons so we discuss some numerical results for the corresponding walk problem. Vrbovà and Whittington [20] used Monte Carlo methods to investigate this problem for a self-avoiding walk model on the simple cubic lattice. They found clear evidence for four phases: desorbed-expanded, desorbed-collapsed, adsorbed-expanded and adsorbed-collapsed, with a phase diagram qualitatively similar to that shown in Figure 7. In particular they found evidence for two triple points and a phase boundary between the adsorbed-expanded and desorbed-collapsed phases. Vrbovà and Procházka [18] found evidence from Monte Carlo data that the phase boundary between the desorbed-expanded and adsorbed-expanded phases is a horizontal line in Figure 7. That is, the adsorption critical point doesn't depend on β until the collapse point is reached.

Singh and coworkers [12, 14] studied the same problem in three dimensions, using exact enumeration techniques. Although there was some initial disagreement as to whether the phase diagram had two triple points or a quadruple point (where four phases coexist) there now seems to be general agreement that there are two triple points, as sketched in Figure 7. Vrbovà and Whittington [21] also studied a similar model with adsorption at a penetrable surface and found a similar phase diagram.

Krawczyk *et al* [9] have investigated the problem in three dimensions also with a Monte Carlo technique known as FlatPERM, which allowed the consideration of a large part of the phase space at once. Walks attached to the surface up to length 256 were considered. While unusual features appear at low temperatures for finite lengths they find a phase diagram in agreement with that in Figure 7 from Vrbovà and Whittington [20].

Singh *et al* [13] (see also [10]) suggested the existence of an additional *surface attached globule phase* though it seems [9] that this doesn't correspond to a bulk phase transition. That is, its phase boundary does not correspond to singularities in the limiting free energy defined in (34) but to singularities in a suitably defined surface free energy.

Bachmann and Janke [1] have simulated a variant of the problem where the walk is not attached to the attractive surface. As a consequence they need to place a second wall some distance from the first. Walks of length 100 were simulated and the pseudo phase diagram suggests extra phases. It will be interesting for future work to delineate the exact difference between the tethered and non-tethered cases.

References

1. M. Bachmann and W. Janke: Phys. Rev. Lett. **95**, 058102 (2005)
2. D. Bennett-Wood, I. G. Enting, D. S. Gaunt, A. J. Guttmann, J. L. Leask, A. L. Owczarek and S. G. Whittington: J. Phys. A: Math. Gen. **31**, 4725 (1998)
3. P. Grassberger: J. Phys. A: Math. Gen. **38**, 323 (2005)
4. J. M.Hammersley and D. J. A. Welsh: Quart. J. Math. Oxford **18**, 108 (1962)
5. J. M. Hammersley, G. M. Torrie and S. G. Whittington: J. Phys. A: Math. Gen. **15**, 539 (1982)
6. R. Hegger and P. Grassberger: J. Phys. A: Math. Gen. **27**, 4069 (1994)
7. E. J. Janse van Rensburg: J. Phys. A: Math. Gen, **31**, 8295 (1998)
8. E. J. Janse van Rensburg and A. Rechnitzer: J. Phys. A: Math. Gen. **37**, 6875 (2004)
9. J. Krawczyk, A. L. Owczarek, T. Prellberg and A. Rechnitzer: Europhysics Lett., **70**, 726 (2005)
10. P. Mishra, D. Giri, S. Kumar and Y. Singh: Physica A **318**, 171 (2003)
11. D. Napper, *Polymeric Stabilisation of Colloidal Dispersions*, Academic Press, London, 1983.
12. R. Rajesh, D. Dhar, D. Giri, S. Kumar and Y. Singh: Phys. Rev. E **65**, 056124 (2002)
13. Y. Singh, D. Giri and S. Kumar: J. Phys. A: Math. Gen. **34**, L67 (2001)
14. Y. Singh, S. Kumar and D. Giri: J. Phys. A: Math. Gen. **32**, L407 (1999)
15. C. E. Soteros and S. G. Whittington: J. Phys. A: Math. Gen. **21**, L857 (1988)
16. C. E. Soteros: J. Phys. A: Math. Gen. **25**, 3153 (1992)
17. M. C. Tesi, E. J. Janse van Rensburg, E. Orlandini and S. G. Whittington: J. Phys. A: Math. Gen. **29**, 2451 (1996)
18. T. Vrbovà and K. Procházka: J. Phys. A: Math. Gen. **32**, 5469 (1999)
19. T. Vrbovà and S. G. Whittington: J. Phys. A: Math. Gen. **29**, 6253 (1996)
20. T. Vrbovà and S. G. Whittington: J. Phys. A: Math. Gen. **31**, 3989 (1998)
21. T. Vrbovà and S. G. Whittington: J. Phys. A: Math. Gen. **31**, 7031 (1998)