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1996 J. Phys. A: Math. Gen. 29 6253

(http://iopscience.iop.org/0305-4470/29/19/011)

J. Phys. A: Math. Gen. **29** (1996) 6253–6264. Printed in the UK

Adsorption and collapse of self-avoiding walks and polygons in three dimensions

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Received 20 March 1996, in final form 30 May 1996

Abstract. We consider self-avoiding walks and polygons on the simple cubic lattice, confined to the half-space $z \geqslant 0$ and interacting with the plane $z = 0$. In addition there is a short-range vertex–vertex interaction in the walk or polygon which can lead to a collapse transition. We explore the interaction between collapse and adsorption in these systems, and discuss the form of the phase diagram. Key results include a proof of the existence of an adsorption transition for polygons for every value of the vertex–vertex interaction, a corresponding proof for walks when the vertex–vertex interaction term is repulsive, and a proof that if polygons exhibit a collapse transition, then the phase boundary between the expanded and desorbed phase and the collapsed and desorbed phase must be a straight line.

1. Introduction

Self-avoiding walks on a regular lattice are a good model of the equilibrium properties of linear polymer molecules in dilute solution in a good solvent, and lattice polygons are a correspondingly good model of ring polymers. If near-neighbour interactions are suitably weighted, the (infinite) walk is thought to undergo a transition which models the internal transition in a polymer brought about by the dominance of attractive forces between monomers at low temperatures. This transition has been studied theoretically for many years (see e.g. Mazur and McCrackin 1968, Finsy *et al* 1975, Ishinabe 1985, Saleur 1986, Privman 1986, Meirovitch and Lim 1989, Tesi *et al* 1996a and many other papers), although there is still no proof of the *existence* of the transition in this model. A transition has been proved to exist in a directed version of this model in two dimensions (Brak *et al* 1992).

Self-avoiding walks are also useful as a model of polymer adsorption. In this case one considers a self-avoiding walk on (say) the simple cubic lattice Z^3, with the first vertex of the walk at the origin and all other vertices having non-negative z-coordinate. That is, the walk is confined to the half-space $z \geqslant 0$. Each vertex in the plane $z = 0$ contributes an additional energy term and, if this energy is attractive, the walk can be adsorbed onto the plane $z = 0$. In fact the desorbed phase is characterized by the mean fraction of vertices in this plane going to zero as the number of vertices in the walk goes to infinity. For this problem one can prove that a phase transition (the adsorption transition) exists (Hammersley *et al* 1982), and derive bounds on the location of the transition. For a review of work on this problem see De'Bell and Lookman (1993).

One can also consider the system in which the self-avoiding walk has an internal (vertex–vertex) interaction term and also a vertex–plane interaction term, so that the system can exhibit both a collapse transition and an adsorption transition. Rather less is known about this problem although Monte Carlo work on adsorption at the Θ-point has appeared (Chang and Meirovitch 1993), and there is an exact enumeration study in two dimensions which investigates the form of the phase diagram (Foster *et al* 1992). In addition, the directed version of this model (in two dimensions) has been extensively studied (Foster 1990, Foster and Yeomans 1991, and references therein).

We shall be concerned with the three-dimensional version of this model. In section 2 we define the free energy for walks and polygons with both vertex–vertex and vertex–plane interactions, and prove some results about the existence of the limiting free energy, using methods related to those of Hammersley *et al* (1982). For all values of the interaction parameters for polygons, and for certain ranges of values for walks, we prove that the free energy is doubly convex and therefore continuous. In section 3 we investigate the form of the phase diagram. We prove that there is an adsorption transition for polygons, for any value of the vertex–vertex interaction, and we prove some partial results along these lines for walks. In addition we discuss the form of the phase boundary between the desorbed–expanded and desorbed–collapsed phases. We show, under certain mild assumptions, that this phase boundary is a straight line, as found for directed models in two dimensions (Foster 1990, Foster and Yeomans 1991) and in an exact enumeration study of self-avoiding walks in two dimensions (Foster *et al* 1992). This is in contrast to the work of Cattarinussi and Jug (1991), who argued that this phase boundary would curve so that a collapse transition could be induced by adsorption.

2. Convexity and continuity of the free energy

We begin by defining some notations. Let c_n be the number of n-step self-avoiding walks (or, for short, walks) on Z^3, and let p_n be the number of (self-avoiding) polygons with n vertices, where in each case two walks or polygons are considered to be distinct if they cannot be superimposed by translation. It is known that (Hammersley 1961)

$$\lim_{n\to\infty} n^{-1}\log p_n = \lim_{n\to\infty} n^{-1}\log c_n \equiv \kappa_3 \tag{2.1}$$

where κ_3 is called the *connective constant* of the lattice Z^3.

A self-avoiding walk which starts at the origin, and has no vertices with negative z-coordinate, is called a *positive walk* (Hammersley *et al* 1982) or a *tail* (Silberberg 1967, Cosgrove *et al* 1984). Let the number of n-step tails having $v+1$ vertices in the plane $z=0$ be $c_n^+(v)$. We say that such a tail *visits* the plane $z=0$ $v+1$ times, or has $v+1$ *visits*. A *contact* is an edge of the lattice which is not an edge of the walk or polygon but which is incident on two vertices of the walk or polygon. Let the numbers of n-step walks and polygons with k contacts be $c_n(k)$ and $p_n(k)$, respectively. Let the number of n-step tails with $v+1$ visits and k contacts be $c_n^+(v,k)$.

Define the generating functions $Z_n(\beta)=\sum_k c_n(k)\mathrm{e}^{\beta k}$, $Z_n^0(\beta)=\sum_k p_n(k)\mathrm{e}^{\beta k}$, $Z_n^+(\alpha)=\sum_v c_n^+(v)\mathrm{e}^{\alpha v}$ and

$$Z_n^+(\alpha,\beta)=\sum_{v,k} c_n^+(v,k)\mathrm{e}^{\alpha v+\beta k}. \tag{2.2}$$

Clearly $Z_n^+(\alpha)=Z_n^+(\alpha,0)$.

We are interested in the properties of the corresponding limiting free energies, and we next recall some results from the literature.

Theorem 2.1 (Hammersley et al 1982). The limiting free energy

$$\kappa^+(\alpha)=\lim_{n\to\infty} n^{-1}\log Z_n^+(\alpha) \tag{2.3}$$

exists for all $\alpha < \infty$ and is a convex, monotone non-decreasing function of α. Moreover,

$$\kappa^+(\alpha) = \kappa^+(0) = \kappa_3 \qquad \forall \alpha \leqslant 0 \tag{2.4}$$

and

$$\max[\kappa_3, \kappa_2 + \alpha] \leqslant \kappa^+(\alpha) \leqslant \kappa_3 + \alpha \qquad \forall \alpha \geqslant 0 \tag{2.5}$$

where κ_3 is the connective constant of Z^3 and κ_2 is the connective constant of Z^2.

This theorem implies that there is an adsorption transition (i.e. $\kappa^+(\alpha)$ is non-analytic) at some value of α in the range $0 \leqslant \alpha \leqslant \kappa_3 - \kappa_2$. In fact Hammersley *et al* (1982) prove that the transition is neither at $\alpha = 0$ nor at $\alpha = \kappa_3 - \kappa_2$.

For interacting walks and polygons (i.e. with $\beta \neq 0$) there are results about the existence of the limiting free energy.

Theorem 2.2 (Tesi et al 1996b). The limiting free energy

$$\kappa^0(\beta) = \lim_{n\to\infty} n^{-1} \log Z_n^0(\beta) \tag{2.6}$$

exists for all $\beta < \infty$ and is a convex, monotone non-decreasing function of β. Moreover, the limiting free energy $\lim_{n\to\infty} n^{-1} \log Z_n(\beta)$ exists for $\beta \leqslant 0$ and is equal to $\kappa^0(\beta)$ for these values of β.

There is no proof of the existence of a collapse transition, although the numerical evidence for a transition seems compelling.

We next consider the set of polygons with n edges, with at least one edge in the plane $z = 0$ and with no vertex having negative z-coordinate. We call such polygons *positive polygons*. (Note that every polygon is a translation of a positive polygon.) Let the number of n-edge positive polygons with $v+2$ vertices in the plane $z = 0$ and k contacts be $p_n(v, k)$, with the corresponding generating function

$$Z_n^0(\alpha, \beta) = \sum_{v,k} p_n(v, k) \mathrm{e}^{\alpha v + \beta k}. \tag{2.7}$$

We first prove that the corresponding free energy exists.

Theorem 2.3. The limiting free energy

$$\kappa^0(\alpha, \beta) = \lim_{n\to\infty} n^{-1} \log Z_n^0(\alpha, \beta) \tag{2.8}$$

exists for all $\alpha < \infty$ and $\beta < \infty$.

Proof. For a polygon with n edges the maximum value of v is $n - 2$, and the maximum value of k is less than $2n$. Hence

$$n^{-1} \log Z_n^0(\alpha, \beta) \leqslant \max[\log 6, \log 6 + \alpha, \log 6 + 2\beta, \log 6 + \alpha + 2\beta] \tag{2.9}$$

which is finite for $\alpha, \beta < \infty$. Define the *right (left) plane* of a polygon to be the plane containing vertices with the largest (smallest) x-coordinate. Let Y_r (Y_l) be the set of vertices in the right (left) plane, having the largest y-coordinate, and call the vertex in Y_r (Y_l) having the largest z-coordinate the *right (left) vertex* of the polygon. Write (x_r, y_r, z_r) for the coordinates of the right vertex (v_r), and (x_l, y_l, z_l) for the coordinates of the left vertex (v_l). The right vertex must be incident on either one or two edges which are in the right plane, and these edges must be incident on one or both of the vertices with coordinates $(x_r, y_r - 1, z_r)$ and $(x_r, y_r, z_r - 1)$. Similarly the left vertex must be incident on either one or two edges in the left plane, and these edges must be incident on one or both of the vertices with coordinates $(x_l, y_l - 1, z_l)$ and $(x_l, y_l, z_l - 1)$. If the polygon contains the edge $(x_r, y_r - 1, z_r) - (x_r, y_r, z_r)$, then that edge is the *right edge* of the polygon, and we say that the right edge is of *type 1*. Otherwise the edge joining $(x_r, y_r, z_r - 1)$ to v_r is the right edge, and the right edge is of *type 2*. We define the *left edge* as the edge joining v_l to $(x_l, y_l - 1, z_l)$, if that edge is in the polygon (and the edge is then of type 1). Otherwise it is the edge joining v_l to $(x_l, y_l, z_l - 1)$, and the edge is of type 2. Polygons can be subdivided into classes according to the values of z_r, a_r, z_l, a_l, where a_r and a_l are equal to 1 or 2 according to whether the right and left edges are of type 1 or 2. Each polygon can be assigned two indices i and j according to the values of z_l, a_l and z_r, a_r, and we say that such a polygon is *of type* (i, j). Let the number of polygons of type (i, j) with n edges, $v + 2$ visits and k contacts be $p_n(v, k, i, j)$. By symmetry $p_n(v, k, i, j) = p_n(v, k, j, i)$. A polygon of type (i, j) with n edges, $v_1 + 2$ visits and k_1 contacts can be concatenated with a polygon of type (j, i) with n edges, $v_2 + 2$ visits and k_2 contacts by translating in the (x, y)-plane so that the right edge of the first polygon is parallel to the left edge of the second polygon, and these two edges are two lattice spaces apart. Deleting the right edge of the first polygon and the left edge of the second polygon, and adding four edges to form a new polygon, gives a polygon of type (i, i) with $2n + 2$ edges, $k_1 + k_2 + 3$ contacts, and $v_1 + v_2 + l$ visits where $l = 2, 3$ or 4, depending on how many of the added vertices are in the plane $z = 0$. Hence

$$\sum_{v_1,k_1} p_n(v_1, k_1, i, j)p_n(v - v_1, k - k_1, j, i) \leqslant p_{2n+2}(v + l, k + 3, i, i) \qquad (2.10)$$

where $l = l(j) \in \{2, 3, 4\}$. If we set $j = i$ (2.10) becomes

$$\sum_{v_1,k_1} p_n(v_1, k_1, i, i)p_n(v - v_1, k - k_1, i, i) \leqslant p_{2n+2}(v + l, k + 3, i, i) \qquad (2.11)$$

with $l = l(i) \in \{2, 3, 4\}$, depending again on the number of vertices of the left and right edges which are in the plane $z = 0$. This inequality, together with the fact that the partition function is exponentially bounded above, is sufficient (Wilker and Whittington 1979) to establish the existence of the limit

$$\lim_{n\to\infty} n^{-1} \log Z_n^0(\alpha, \beta, i, i) = \kappa^0(\alpha, \beta, i, i) \qquad (2.12)$$

where

$$Z_n^0(\alpha, \beta, i, i) = \sum_{v,k} p_n(v, k, i, i)\mathrm{e}^{\alpha v+\beta k}. \qquad (2.13)$$

For α, β fixed, let i_0, j_0 be the lexicographically first values of i, j such that the set of polygons with these indices makes a contribution to $Z_n^0(\alpha, \beta)$ at least as large as any other class of polygons. We call this the *most popular class* and the corresponding set of indices the *most popular index set*. Clearly, for the most popular index set,

$$Z_n^0(\alpha, \beta, i_0, j_0) = \sum_{v,k} p_n(v, k, i_0, j_0)\mathrm{e}^{\alpha v+\beta k} \geqslant Z_n^0(\alpha, \beta)/M \qquad (2.14)$$

where $M = M(n) = \mathrm{O}(n^2)$ is the number of possible pairs of values (i, j). We can now rewrite (2.10) for the most popular class as

$$\sum_{v\geqslant 0}\sum_{k\geqslant 0} p_{2n+2}(v + l, k + 3, i_0, i_0)\mathrm{e}^{\alpha v+\beta k} \geqslant [Z_n^0(\alpha, \beta, i_0, j_0)]^2 \qquad (2.15)$$

where $l = l(j_0) \in \{2, 3, 4\}$. Hence

$$\begin{aligned}\kappa^0(\alpha, \beta, i_0, i_0) &\geqslant \limsup_{n\to\infty} n^{-1} \log Z_n^0(\alpha, \beta, i_0, j_0) \\ &\geqslant \limsup_{n\to\infty} n^{-1} \log[Z_n^0(\alpha, \beta)/M(n)] \\ &= \limsup_{n\to\infty} n^{-1} \log Z_n^0(\alpha, \beta). \end{aligned} \qquad (2.16)$$

But clearly

$$Z_n^0(\alpha, \beta) \geqslant Z_n^0(\alpha, \beta, i_0, i_0) \tag{2.17}$$

so that

$$\liminf_{n\to\infty} n^{-1} \log Z_n^0(\alpha, \beta) \geqslant \kappa^0(\alpha, \beta, i_0, i_0). \tag{2.18}$$

The theorem follows from (2.16) and (2.18) with $\kappa^0(\alpha, \beta) = \kappa^0(\alpha, \beta, i_0, i_0)$. □

Theorem 2.4. $\kappa^0(\alpha, \beta)$ is a doubly convex and continuous function of α and β.

Proof. $Z_n^0(\alpha, \beta)$ is monotone non-decreasing in both α and β and, since it is a polynomial in e^α and e^β, it is continuous and bounded in any closed interval. To prove that $\log Z_n^0(\alpha, \beta)$ is doubly convex in α and β it is sufficient to show that

$$\frac{\log Z_n^0(\alpha_1, \beta_1) + \log Z_n^0(\alpha_2, \beta_2)}{2} \geqslant \log Z_n^0\left(\frac{\alpha_1+\alpha_2}{2}, \frac{\beta_1+\beta_2}{2}\right). \tag{2.19}$$

Using Cauchy's inequality we have

$$\begin{aligned} Z_n^0(\alpha_1, \beta_1) Z_n^0(\alpha_2, \beta_2) &= \sum_{v_1,k_1} p_n(v_1, k_1) e^{\alpha_1 v_1 + \beta_1 k_1} \sum_{v_2,k_2} p_n(v_2, k_2) e^{\alpha_2 v_2 + \beta_2 k_2} \\ &\geqslant \left[\sum_{v,k} p_n(v, k) \exp\left(\frac{\alpha_1+\alpha_2}{2} v + \frac{\beta_1+\beta_2}{2} k\right)\right]^2 \\ &= \left[Z_n^0\left(\frac{\alpha_1+\alpha_2}{2}, \frac{\beta_1+\beta_2}{2}\right)\right]^2 \end{aligned} \tag{2.20}$$

and, after taking logarithms, this establishes (2.19). Since $\kappa^0(\alpha, \beta)$ is therefore the limit of a sequence of convex functions, it must be convex, and therefore continuous (Hardy *et al* 1952). □

We next turn to some corresponding results for tails. In particular we are interested in the existence of the limit $\lim_{n\to\infty} n^{-1} \log Z_n^+(\alpha, \beta)$. In fact we shall prove that the limit exists for all α and for all $\beta \leqslant 0$.

Lemma 2.5. The generating function $Z_n^+(\alpha, \beta)$ satisfies the bound

$$Z_n^+(\alpha, \beta) \geqslant e^{\alpha+\beta} Z_{n+1}^0(\alpha, \beta) \tag{2.21}$$

so that

$$\liminf_{n\to\infty} n^{-1} \log Z_n^+(\alpha, \beta) \geqslant \kappa^0(\alpha, \beta) \tag{2.22}$$

for all $\alpha, \beta < \infty$.

Proof. Let $(x_b, y_b, 0)$ be the coordinates of the vertex of the polygon in the plane $z = 0$ with lexicographically smallest (x, y)-coordinates. This vertex must be incident on at least one edge and at most two edges in the plane $z = 0$. If there is one such edge we call it the *bottom edge* of the polygon. If there are two such edges, they will each be incident on a second vertex, one of which has lexicographically smaller coordinates. We call the corresponding edge the bottom edge. Each positive polygon can be converted to a tail by deleting the bottom edge of the polygon. This construction decreases the number of edges by unity, increases the number of contacts by unity, and leaves unchanged the number of vertices in the plane $z = 0$. Hence

$$c_n^+(v, k) \geqslant p_{n+1}(v - 1, k - 1). \tag{2.23}$$

Multiplying both sides by $e^{\alpha v + \beta k}$ and summing over v and k gives (2.21). Taking logarithms, dividing by n and letting n go to infinity, gives (2.22). □

It will be convenient to work with x-unfolded tails, and loops, which we now define. A tail with n edges is an x-*unfolded* tail if, in addition to having $z_0 = 0$ and $z_i \geqslant 0$ for all $i \leqslant n$, it satisfies the following conditions:

(i) $x_0 = 0$, and

(ii) $x_0 < x_i < x_n$ for all $i \neq 0, n$.

Note that this implies that the first and last edges are in the x-direction so, in particular, $z_1 = 0$. An x-unfolded tail with n edges is a *loop* if it satisfies the additional condition that $z_n = 0$. Note that, because the first and last edges are in the x-direction, this means that $z_1 = z_{n-1} = 0$. Let $c_n^{\ddagger}(v, k)$ and $l_n(v, k)$ be the numbers of x-unfolded tails and loops (respectively) with n edges, k contacts and $v + 1$ vertices in the plane $z = 0$. We define the generating functions

$$Z_n^{\ddagger}(\alpha, \beta) = \sum_{v,k} c_n^{\ddagger}(v, k)\mathrm{e}^{\alpha v+\beta k} \tag{2.24}$$

and

$$Z_n^{l}(\alpha, \beta) = \sum_{v,k} l_n(v, k)\mathrm{e}^{\alpha v+\beta k}. \tag{2.25}$$

We first prove that the thermodynamic limit exists for loops.

Lemma 2.6. The limit $\lim_{n\to\infty} n^{-1} \log Z_n^l(\alpha, \beta) = \kappa^l(\alpha, \beta)$ exists for all $\alpha, \beta < \infty$.

Proof. Two loops can be concatenated by translating so that the last vertex of the first loop is coincident with the first vertex of the second loop. The number of edges is additive under this operation and no new contacts are formed. Not all loops can be constructed in this way, so we have the inequality

$$l_n(v, k) \geqslant \sum_{v_1} \sum_{k_1} l_{n_1}(v_1, k_1) l_{n-n_1}(v - v_1, k - k_1). \tag{2.26}$$

Multiplying both sides by $\mathrm{e}^{\alpha v+\beta k}$ and summing over v and k gives the super-multiplicative inequality

$$Z_n^l(\alpha, \beta) \geqslant Z_{n_1}^l(\alpha, \beta) Z_{n-n_1}^l(\alpha, \beta). \tag{2.27}$$

This, together with the exponential upper bound

$$Z_n^l(\alpha, \beta) \leqslant \max[6^n, 6^n\mathrm{e}^{\alpha n}, 6^n\mathrm{e}^{\beta(2n+1)}, 6^n\mathrm{e}^{\alpha n+\beta(2n+1)}] \tag{2.28}$$

immediately gives the existence of the limit for all $\alpha, \beta < \infty$ (Hille 1948). □

Next we relate the behaviour of x-unfolded tails and loops.

Lemma 2.7. The generating functions of x-unfolded tails and loops have the same exponential behaviour, in that

$$\lim_{n\to\infty} n^{-1} \log Z_n^{\ddagger}(\alpha, \beta) = \lim_{n\to\infty} n^{-1} \log Z_n^l(\alpha, \beta) \tag{2.29}$$

for all $\alpha, \beta < \infty$.

Proof. Since every loop is an x-unfolded tail, we have the inequality

$$Z_n^l(\alpha, \beta) \leqslant Z_n^{\ddagger}(\alpha, \beta). \tag{2.30}$$

At fixed n the x-unfolded tails can be classified according to their *height*, h, which we define as the z-coordinate of their last vertex. Let $c_n^{\ddagger}(v, k, h)$ be the number of x-unfolded tails with n edges, $v + 1$ visits, k contacts and height h. An x-unfolded tail with n edges, $v_1 + 1$ visits, k_1 contacts and height h can be concatenated with an x-unfolded tail with n

edges, $v - v_1 + 1$ visits, $k - k_1$ contacts and height h, by reflecting the second tail in the plane $x = x_n$ (where x_n is the x-coordinate of the last vertex in the tail), and identifying the last vertices of the two tails. The resulting object is a loop with $2n$ edges, $v + 1$ visits if $h = 0$, $v + 2$ visits if $h > 0$, and k contacts. Summing over h we have

$$\sum_{q=0}^{1} \ell_{2n}(v + q, k) \geqslant \sum_{h} \sum_{v_1} \sum_{k_1} c_n^{\ddagger}(v_1, k_1, h) c_n^{\ddagger}(v - v_1, k - k_1, h). \tag{2.31}$$

Multiplying both sides by $e^{\alpha v + \beta k}$ and summing over v and k gives

$$(1 + e^{-\alpha}) Z_{2n}^{l}(\alpha, \beta) \geqslant [Z_n^{\ddagger}(\alpha, \beta)]^2. \tag{2.32}$$

Taking logarithms in (2.30) and (2.32), dividing by n and letting n go to infinity, gives (2.29). □

The next lemma gives an inequality between the free energies of loops and polygons.

Lemma 2.8. For all $\alpha < \infty$ and $\beta \leqslant 0$ the limiting free energies of polygons and loops are related by the inequality

$$\lim_{n\to\infty} n^{-1} \log Z_n^{l}(\alpha, \beta) \leqslant \kappa^0(\alpha, \beta). \tag{2.33}$$

Proof. We say that a loop is a *y-unfolded loop* if the y-coordinates of the vertices of the loop obey the inequalities $y_0 \leqslant y_i \leqslant y_n$ for all i such that $0 < i < n$. We can convert a loop to a y-unfolded loop by successive reflections in the planes $y = y_{\min}$ and $y = y_{\max}$, as in Hammersley and Welsh (1962). The number of visits is unchanged by these reflections but the number of contacts can decrease. If we write L_n for the set of loops with n edges and $L_n^{\ddagger}$ for the corresponding set of y-unfolded loops, then unfolding defines a surjection from L_n to $L_n^{\ddagger}$ but at most $e^{O(\sqrt{n})}$ members of L_n map to the same member of $L_n^{\ddagger}$ (Hammersley and Welsh 1962). Let $l_n^{\ddagger}(v, k)$ be the number of y-unfolded loops with $v + 1$ visits and k contacts, with the corresponding partition function

$$Z_n^{l\ddagger}(\alpha, \beta) = \sum_{v,k} l_n^{\ddagger}(v, k) e^{\alpha v + \beta k}. \tag{2.34}$$

Since the number of contacts cannot increase on unfolding we have the inequalities

$$Z_n^{l\ddagger}(\alpha, \beta) \leqslant Z_n^{l}(\alpha, \beta) \leqslant e^{O(\sqrt{n})} Z_n^{l\ddagger}(\alpha, \beta) \tag{2.35}$$

for $\alpha < \infty$ and $\beta \leqslant 0$. For each y-unfolded loop we define its *width* as $w = y_n - y_0$, and these y-unfolded loops can be partitioned into classes according to their width. We write $l_n^{\ddagger}(v, k, w)$ for the number of n-edge y-unfolded loops, with $v + 1$ visits, k contacts and width w. Each such loop can be concatenated with a loop having the same width, reflected in the plane $x = x_n$ and suitably translated. If the first loop has n edges, $v_1 + 1$ visits and k_1 contacts, and the second has n edges, $v_2 + 1$ visits and k_2 contacts, then the loop resulting from this construction has $2n$ edges, $v_1 + v_2 + 1$ visits and $k_1 + k_2$ contacts. In addition its first vertex is at the origin, its last vertex is on the x-axis, and no vertex has negative y-coordinate. These objects can be modified by deleting their first and last edges, and adding edges $(1, 0, 0) - (1, -1, 0)$ and $(x_{2n-1}, 0, 0) - (x_{2n-1}, -1, 0)$. These modified loops can be partitioned into classes according to the value of $w' = x_{2n-1} - 1$, and concatenated with a member of the same class reflected in the plane $y = -1$. The resulting object is a polygon. If, in both stages of the construction, we only concatenate members from the most popular class (i.e. with the values of w and w' which make the largest contribution to the partition function at a fixed value of α and β) then we obtain the following inequality:

$$p_n(v,k) \geqslant \frac{1}{4n^2}\sum\left[\frac{l_n^{\ddagger}(v_2,k_2)}{n}\frac{l_n^{\ddagger}(v_1-v_2,k_1-k_2)}{n}\right] \times\left[\frac{l_n^{\ddagger}(v_3,k_3)}{n}\frac{l_n^{\ddagger}(v-v_1-v_3,k-k_1-k_3)}{n}\right] \tag{2.36}$$

where the sum is over all values of $v_1, k_1, v_2, k_2, v_3, k_3$. Multiplying both sides of (2.36) by $\mathrm{e}^{\alpha v+\beta k}$, summing over v and k, taking logarithms, dividing by n and letting n go to infinity gives (2.33). □

Next we obtain an inequality for tails and x-unfolded tails.

Lemma 2.9. For all $\alpha < \infty$ and $\beta \leqslant 0$

$$\limsup_{n\to\infty} n^{-1}\log Z_n^{+}(\alpha,\beta) \leqslant \kappa^{\ddagger}(\alpha,\beta). \tag{2.37}$$

Proof. Every tail can be unfolded by successive reflections in the planes $x = x_{\min}$ and $x = x_{\max}$, in a manner similar to that described in Hammersley and Welsh (1962). At most $\mathrm{e}^{\mathrm{O}(\sqrt{n})}$ different tails with n-edges map to the same x-unfolded tail by this construction (Hammersley and Welsh 1962). The number of visits is not changed by the unfolding operation but the number of contacts can decrease. Hence, for any $\beta \leqslant 0$ we have the inequality

$$Z_n^{+}(\alpha,\beta) \leqslant \mathrm{e}^{\mathrm{O}(\sqrt{n})} Z_n^{\ddagger}(\alpha,\beta) \tag{2.38}$$

and the theorem follows after taking logarithms, dividing by n and letting n go to infinity. □

Finally, these lemmas allow us to prove the following theorem:

Theorem 2.10. The limiting free energies of tails and polygons are equal for all finite values of α for all $\beta \leqslant 0$.

Proof. This comes from a combination of the above lemmas, which imply that

$$\liminf_{n\to\infty} n^{-1}\log Z_n^{+}(\alpha,\beta) \geqslant \kappa^0 \geqslant \kappa^l = \kappa^{\ddagger} \geqslant \limsup_{n\to\infty} n^{-1}\log Z_n^{+}(\alpha,\beta) \tag{2.39}$$

for all finite α and all non-positive β, so that $\lim_{n\to\infty} n^{-1}\log Z_n^{+}(\alpha,\beta)$ exists for these values of α and β, and is equal to $\kappa^0(\alpha,\beta)$. □

This result extends a theorem due to Soteros (1992) which established this result for all finite α at $\beta = 0$, for $d > 2$. Note that this result is not true in two dimensions (Whittington and Soteros 1991, Soteros 1992).

In view of theorem 2.10, one might expect that the limiting free energies of tails and polygons will be equal for all finite values of α and β. The analogous question for interacting walks and interacting polygons (without the presence of a surface) is still unresolved, but Tesi *et al* (1996b) showed that if the mean number of contacts for an interacting polygon is at least as large as for an interacting self-avoiding walk (for all $\beta > 0$ and all sufficiently large even values of n) then the thermodynamic limit exists for the walk problem, and the limiting free energies are identical for walks and polygons. In order to state the corresponding theorem for tails and polygons, we need some additional notation.

Let $\langle k\rangle^0$ and $\langle k\rangle^+$ be the mean number of contacts in a polygon and tail, respectively, at some fixed n, α and β. Clearly

$$\langle k\rangle^0 = \frac{\partial \log Z_n^0(\alpha,\beta)}{\partial\beta} \tag{2.40}$$

and

$$\langle k\rangle^+ = \frac{\partial \log Z_n^+(\alpha,\beta)}{\partial\beta}. \tag{2.41}$$

Theorem 2.11. If $\langle k\rangle^0 \geqslant \langle k\rangle^+$ for all $\beta > 0$, for all sufficiently large even n, then the limit $\lim_{n\to\infty} n^{-1}\log Z_n^+(\alpha,\beta)$ exists for all finite α and β, and the value of the limit is $\kappa^0(\alpha,\beta)$.

Proof. The proof is an easy extension of the proof of theorem 2.8 in Tesi *et al* (1996b).

3. The form of the phase diagram

In this section we shall be concerned with some general features of the phase diagram in the (α,β)-plane for both walks and polygons. We begin by showing that polygons exhibit an adsorption transition for every value of $\beta < \infty$.

Lemma 3.1. For every value of $\beta < \infty$, the limiting free energy $\kappa^0(\alpha,\beta)$ is independent of α for all $\alpha \leqslant 0$.

Proof. Consider a positive n-gon. Suppose that the bottom edge is incident on the vertices with coordinates $(x_b, y_b, 0)$ and $(x_{b'}, y_{b'}, 0)$. If we delete the bottom edge, translate the polygon through unit distance in the positive z-direction, and add the three edges $(x_b, y_b, 0) - (x_b, y_b, 1)$, $(x_{b'}, y_{b'}, 0) - (x_{b'}, y_{b'}, 1)$ and $(x_b, y_b, 0) - (x_{b'}, y_{b'}, 0)$, we obtain a positive $(n+2)$-gon with exactly two vertices in the plane $z = 0$. Moreover, the number of contacts has increased by unity, so that

$$\sum_v p_n(v,k) \leqslant p_{n+2}(0,k+1). \tag{3.1}$$

Starting with a polygon with $n+2$ edges and exactly two vertices in $z = 0$ and reversing the construction, at most n polygons with n edges can have the same pre-image. Hence

$$p_{n+2}(0,k+1) \leqslant n\sum_v p_n(v,k). \tag{3.2}$$

For every $\beta < \infty$ and for every $\alpha \leqslant 0$

$$\sum_k p_n(0,k)\mathrm{e}^{\beta k} \leqslant Z_n^0(\alpha,\beta) \leqslant Z_n^0(0,\beta) = \sum_v\sum_k p_n(v,k)\mathrm{e}^{\beta k}. \tag{3.3}$$

Taking logarithms, dividing by n and letting $n\to\infty$, and using (3.1), implies that

$$\kappa^0(\alpha,\beta) = \kappa^0(\beta) \tag{3.4}$$

for all $\alpha \leqslant 0$ and for all $\beta < \infty$. □

The next lemma concerns bounds on the free energy for $\alpha > 0$ for all values of β.

Lemma 3.2. For $\alpha > 0$

$$\max[\kappa^0(0,\beta), \kappa_2(\beta)+\alpha] \leqslant \kappa^0(\alpha,\beta) \leqslant \kappa^0(0,\beta)+\alpha \tag{3.5}$$

where $\kappa_2(\beta)$ is the free energy of interacting polygons in the square lattice Z^2.

Proof. The monotonicity of $Z_n^0(\alpha, \beta)$ implies that $\kappa^0(0, \beta) \leqslant \kappa^0(\alpha, \beta)$, for all β and all positive α. By picking out one term in the sum we have

$$\sum_k p_n(n-2, k)\mathrm{e}^{\alpha(n-2)+\beta k} \leqslant Z_n^0(\alpha, \beta) \tag{3.6}$$

so that

$$\kappa^0(\alpha, \beta) \geqslant \lim_{n\to\infty} n^{-1} \log \sum_k p_n^{(2)}(k)\mathrm{e}^{\beta k} + \alpha = \kappa_2(\beta) + \alpha \tag{3.7}$$

where $p_n^{(2)}(k)$ is the number of n-gons in Z^2 with k contacts. The existence of the limit $\kappa_2(\beta)$ follows by an argument similar to that given in theorem 2.1 of Tesi *et al* (1996b). This completes the proof of the lower bound. To obtain the upper bound we note that

$$Z_n^0(\alpha, \beta) \leqslant \mathrm{e}^{\alpha v_{\max}} \sum_{v,k} p_n(v, k)\mathrm{e}^{\beta k} \tag{3.8}$$

where $v_{\max} = n - 2$. The bound follows on taking logarithms, dividing by n and letting $n \to \infty$. □

Theorem 3.3. The limiting free energy $\kappa^0(\alpha, \beta)$ is a non-analytic function of α for every value of $\beta < \infty$, and the phase boundary $\alpha_c(\beta)$ is bounded by $0 \leqslant \alpha_c(\beta) \leqslant \kappa_3 - \kappa_2 + 2\beta$ for $\beta \geqslant 0$.

Proof. From lemmas 3.1 and 3.2, there must be a non-analytic point $\alpha_c(\beta)$ characterized by

$$\alpha_c(\beta) = \max[\alpha | \kappa^0(\alpha, \beta) = \kappa^0(\beta)]. \tag{3.9}$$

Note that $\kappa^0(0, \beta) = \kappa^0(\beta)$. The above lemmas imply that $0 \leqslant \alpha_c(\beta) \leqslant \kappa^0(\beta) - \kappa_2(\beta)$. But, for positive β,

$$Z_n^0(\beta) \leqslant \sum_k p_n(k)\mathrm{e}^{2n\beta} \tag{3.10}$$

which implies that $\kappa^0(\beta) \leqslant \kappa_3 + 2\beta$. By monotonicity, $\kappa_2(\beta) \geqslant \kappa_2$, so we have the bound

$$\alpha_c(\beta) \leqslant \kappa_3 - \kappa_2 + 2\beta. \tag{3.11}$$

In particular, the phase boundary $\alpha_c(\beta)$ cannot have a vertical asymptote, i.e. there is a singularity for every value of β. □

We next turn to the shape of the phase boundary between the two desorbed phases.

Theorem 3.4. If $\kappa^0(\beta)$ is singular at $\beta = \beta_0$ and if the phase boundary $\alpha_c(\beta)$ is continuous at $\beta = \beta_0$ then $\kappa^0(\alpha, \beta)$ is also singular at $\beta = \beta_0$ for every $\alpha < \alpha_c(\beta_0)$.

Proof. Fix $\epsilon > 0$. Choose α such that

$$\alpha < \min[\alpha_c(\beta) | \beta \in [\beta_0 - \epsilon, \beta_0 + \epsilon]]. \tag{3.12}$$

For each such α, $\kappa^0(\alpha, \beta) = \kappa^0(\beta)$ for $\beta \in [\beta_0 - \epsilon, \beta_0 + \epsilon]$. Therefore $\kappa^0(\alpha, \beta)$ is singular at β_0. Furthermore, if the phase boundary is continuous at $\beta = \beta_0$ then ϵ can be made arbitrarily small so α can be taken to be arbitarily close to $\alpha_c(\beta_0)$. □

4. Discussion

We have proved a number of results about the form of the free energy for polygons which have both a vertex–plane interaction and a vertex–vertex interaction. We have shown that tails and polygons have the same free energy, for all values of the vertex–plane interaction, when the vertex–vertex interaction is repulsive. The corresponding question when the vertex–vertex interaction is attractive is still open, even in the absence of a surface (Tesi *et al* 1996b).

We have also established two important qualitative features of the phase diagram in this two-variable model. We have shown that there is an adsorption transition for polygons for all values of the vertex–vertex interaction parameter, and have deduced a bound on the form of this phase boundary. We have also shown that, if polygons exhibit a collapse transition (see Tesi *et al* 1996b), then the phase boundary between the desorbed–expanded and desorbed–collapsed phases is a straight line.

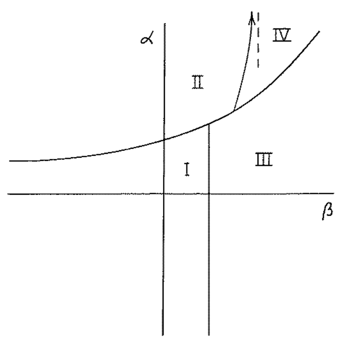

Figure 1. Hypothetical phase diagram for adsorption and collapse in three dimensions. The boundary between the desorbed–expanded phase (I) and the desorbed–collapsed phase (III) is known to be a vertical line, and there is known to be an adsorption transition for all values of β. The shape of the phase boundary between the adsorbed–expanded phase (II) and the adsorbed–compact phase (IV) is not well understood.

In figure 1 we show a sketch of the phase diagram in the (α, β)-plane which reflects the information which we have deduced here, but contains other interesting features which we have not addressed. The four phases shown are (I) desorbed–expanded, (II) adsorbed–expanded, (III) desorbed–compact, and (IV) adsorbed–compact. There are several interesting open questions. For instance, is there a phase transition in the adsorbed regime between an expanded phase (II) and a collapsed phase (IV) and, if so, what is the shape of this phase boundary? Where does this phase boundary meet the phase boundary corresponding to adsorption? Can anything be said about the order of the various phase transitions? We are currently addressing some of these questions using Monte Carlo methods.

Acknowledgments

We would like to thank Christine Soteros, Carla Tesi, Enzo Orlandini and John Valleau for valuable discussions, and NSERC of Canada for financial support.

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