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Collapsing and adsorbing polygons

E J Janse van Rensburg
Mathematics and Statistics, York University, Toronto, Ontario, M3J 1P3, Canada

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Abstract. The adsorption transition in the phase diagram of a self-interacting lattice polygon is examined. The polygon has a nearest-neighbour contact fugacity and the interaction between the polygon and an impenetrable wall is modelled by a visit fugacity which is conjugate to the number of vertices of the polygon incident with the wall. The partition function of this model is $Z_n^+(y,z) = \sum_{v,c} p_n^+(v,c) y^v z^c$, where $p_n^+(v,c)$ is the number of polygons with c nearest-neighbour contacts, v visits to the wall, and n edges (and counted up to translations parallel to the wall). The limiting free energy of this model is $\mathcal{F}^+(y,z) = \lim_{n\to\infty} \frac{1}{n} \log Z_n^+(y,z)$, and it is known to be a non-analytic function of y for each $z < \infty$. The non-analyticity is at $y = y_c^+(z)$, and this corresponds to an adsorption transition of the polygon on the wall. In this paper it is proved that $y_c(z) > 1$ for all $z \in (0, \infty)$.

1. Introduction

Linear polymers in dilute solution in a good solvent undergo a θ-transition if the quality of the solvent (which may be a function of temperature, or of other factors) deteriorates beyond a critical value. This transition is brought about by an internal rearrangement of monomers, which occurs when the effective attractive forces between monomers overcomes the entropic repulsions due to excluded volume. The result is a collapse to a phase of compact conformations. The collapse transition and the θ-point have been studied at least since the 1960s, and remain the focus of much attention, see for example Mazur and McCrackin (1968), Finsy *et al* (1975), Saleur (1985), Privman (1986), Meirovitch and Lim (1989) and Tesi *et al* (1996). Linear polymers can also be adsorbed onto a wall. This adsorption occurs when the entropic repulsive force between the polymer and the wall is overcome by an attractive interaction between the monomers in the polymer, and molecules in the wall. The result is a phase transition which occurs at a critical value of the interaction of the polymer with the wall. The scaling theory of the adsorption transition has been reviewed by De'Bell and Lookman (1993).

The self-avoiding walk is a good model of a linear polymer in dilute solution (Flory 1949). This model was used as a model for an adsorbing and collapsing polymer by Vrbová and Whittington (1996) (see also Whittington 1998). An unfortunate problem in this model is that it is not known that the limiting free energy exists for attractive interactions between monomers (Tesi *et al* 1996, Vrbová and Whittington 1996). This is rather unsatisfactory, and I will confine the discussion in this paper to polygons (closed, self-avoiding cycles in the lattice which may be used as a model of ring polymers), where it is known that there is a limiting free energy (Tesi *et al* 1996a). I aim to extend some of the results obtained by Vrbová and Whittington (1996) in this paper. In particular, I shall show that the adsorption of a self-interacting polygon occurs at a strictly positive value of the attractive interaction between the self-interacting polygon and the wall.

I will work in the d-dimensional hypercubic lattice with coordinates $\{x, y, \ldots, z\}$, where the z-coordinate will always correspond to the dth coordinate. The adsorption will be modelled by an interaction between the polygon and the hyperplane $z = 0$ (it is still possible for the polygon to penetrate this hyperplane). Since the model demands that the polygon is in the vicinity of the hyperplane, I shall only consider conformations of polygons which have at least one vertex with a z-coordinate equal to zero. Such polygons are called *attached polygons*†. Two attached polygons are equivalent if we can translate one onto the other by a translation which leaves all z-coordinates unchanged (we say that the translation is parallel to the $z = 0$ hyperplane).

A vertex in a polygon with z-coordinate equal to zero is a *visit*, and two vertices in a polygon which are adjacent in the lattice, but not in the polygon, form a *contact*. Contacts may also occur between two visits, or between a visit and any other vertex in the polygon. Let $p_n(v, c)$ be the number of distinct attached polygons with v visits and c contacts. The partition function in this model is given by

$$Z_n(y, z) = \sum_{v,c} p_n(v, c) y^v z^c \tag{1.1}$$

where y is the *visit fugacity* and z is the *contact fugacity*. It is known that there is a limiting free energy

$$\mathcal{F}(y, z) = \lim_{n\to\infty} \frac{1}{n} \log Z_n(y, z) \tag{1.2}$$

for all values $0 \leqslant y < \infty$ and $0 \leqslant z < \infty$ (Vrbová and Whittington 1998b). Since the polygon can penetrate the plane $z = 0$, this is a model of a self-interacting ring polymer which adsorbs onto an interface between two solvents. We call the hyperplane $z = 0$ a *defect plane*. A related model makes the hyperplane $z = 0$ impenetrable to the polygon. A *positive polygon* is a polygon with vertices with all z-coordinates non-negative. We indicate the number of positive attached polygons with v visits and c contacts by $p_n^+(v, c)$. The partition function in this model is

$$Z_n^+(y, z) = \sum_{v,c} p_n^+(v, c) y^v z^c \tag{1.3}$$

and the limiting free energy

$$\mathcal{F}^+(y, z) = \lim_{n\to\infty} \frac{1}{n} \log Z_n^+(y, z) \tag{1.4}$$

is also known to exist for all values $0 \leqslant y < \infty$ and $0 \leqslant z < \infty$ (Vrbová and Whittington 1996). The hyperplane $z = 0$ is called a *wall* in this model. We will be primarily interested in the model of positive polygons. However, the relation between these models is the key to proving that the adsorption of positive polygons occurs at a positive value of the visit-fugacity y, for any value of $z \in (0, \infty)$.

The phase diagram of positive polygons was investigated by Vrbová and Whittington (1996), and its generally accepted appearance is presented in figure 1. In three dimensions we expect that there will be four phases. At small values of the fugacities y and z we should have desorbed–expanded (DE) polygons. Increasing y should lead to an adsorbed–expanded phase (AE), while increasing z instead is expected to lead to a desorbed–collapsed (DC) phase. Increasing both y and z will presumably give an adsorbed–collapsed (AC) phase, although it seems that such a phase is absent in two dimensions (Foster 1990, Foster and Yeomans 1991, Foster *et al* 1992). The phase boundary separating the desorbed and

† These definitions are slightly different from those in Vrbová and Whittington (1996). However, it is not difficult to see that only minor modifications of the methods in that paper will lead to identical results.

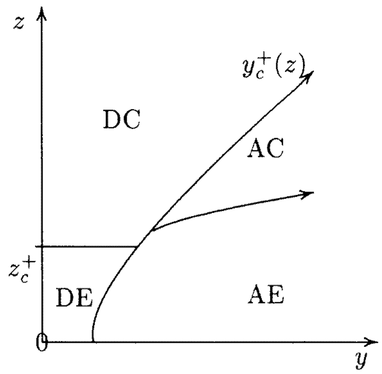

Figure 1. The phase diagram for adsorbing and collapsing attached positive polygons in more than two dimensions.

adsorbed phases of positive polygons will be indicated by $y_c^+(z)$, and will enjoy some attention in this paper. In the next section I shall review some of the known results about this phase diagram. My aim is to add to these; I shall prove that the phase boundary between the desorbed and adsorbed phases is strictly bigger than 1 for all values of the contact-fugacity $z \in (0, \infty)$: $y_c^+(z) > 1$ if $z \in (0, \infty)$. The proof of this result is not simple, and relies on the ideas developed in the study of adsorbing walks by Hammersley *et al* (1982).

2. Collapsing and adsorbing polygons

The existence of limiting free energies in the models of self-interacting positive polygons interacting with a wall, and of self-interacting polygons interacting with a defect plane was shown by Vrbová and Whittington (1996). These free energies are convex in both their arguments, and are continuous for $0 < y < \infty$ and $0 < z < \infty$, and monotonic non-decreasing in both arguments. From the convexity it also follows that they are differentiable almost everywhere. It is also known that

$$\mathcal{F}(y, z) = \mathcal{F}^+(y, z) = \mathcal{F}^+(1, z) \qquad \forall\ 0 \leqslant y \leqslant 1,\ \forall\ z < \infty. \tag{2.1}$$

Thus, $\mathcal{F}(y, z)$ and $\mathcal{F}^+(y, z)$ are constant functions of y if $0 \leqslant y \leqslant 1$. Evidently,

$$\mathcal{F}(1, z) = \mathcal{F}^+(1, z) = \mathcal{F}(z) \tag{2.2}$$

is the limiting free energy of a model of self-interacting polygons which has a critical θ-point at $z = z_c$. If both of the fugacities are equal to 1, then we obtain the free energy of uniformly sampled polygons, which equals the logarithm of the growth constant (this is also called the *connective constant* of the lattice):

$$\mathcal{F}(1, 1) = \mathcal{F}^+(1, 1) = \log \mu_d \tag{2.3}$$

where μ_d is the growth constant of polygons in the d-dimensional hypercubic lattice (the presence of the wall for positive polygons does not change the value of μ_d)†.

The adsorption transition manifests itself as non-analyticities in $\mathcal{F}(y, z)$ and $\mathcal{F}^+(y, z)$. These free energies are non-analytic functions of y for each finite value of z (Vrbová and Whittington 1996, 1998b). As proposed in figure 1, one would expect there to be a critical curve $y_c^+(z)$ of non-analyticities in the phase diagram, such that $\mathcal{F}^+(y, z)$ is a constant

† Note that $p_n^+ \leqslant p_n$. Moreover, by translating a polygon so that it becomes a positive attached polygon, note that $p_n \leqslant n p_n^+$. Thus, $\lim_{n\to\infty} \frac{1}{n} \log p_n^+ = \lim_{n\to\infty} \frac{1}{n} \log p_n = \log \mu_d$.

function of y if $y < y_c^+(z)$, and that $\mathcal{F}^+(y,z)$ is not constant if $y > y_c^+(z)$. We define this critical value by

$$y_c^+(z) = \sup_y \{y | \mathcal{F}^+(y,z) = \mathcal{F}(z)\}. \tag{2.4}$$

The critical curve $y_c(z)$ in the model of a polygon adsorbing on a defect plane is similarly defined. An important result is that both $y_c(z)$ and $y_c^+(z)$ are finite for each finite value of z. The following bound was shown by Vrbová and Whittington (1996):

$$1 \leqslant y_c(z) \leqslant y_c^+(z) \leqslant z^{d-1} \frac{\mu_d}{\mu_{d-1}} \qquad \text{if } z \geqslant 1. \tag{2.5}$$

The same techniques also show that

$$1 \leqslant y_c(z) \leqslant y_c^+(z) \leqslant \frac{\mu_d}{\sqrt{\mu_{d-1}}} \qquad \text{if } z < 1. \tag{2.6}$$

These bounds justify the hypothetical shape given to the desorbed–adsorbed phase boundary in figure 1.

There are also (in a limited sense) some results on the expanded–collapse phase boundary of θ-transitions. It is not known that $\mathcal{F}^+(y,z)$ or $\mathcal{F}(y,z)$ are non-analytic functions of z for fixed values of y. On the other hand, if we assume that there is a phase boundary of θ-transitions separating the DE-phase from the DC-phase at $z = z_c^+(y)$, then $z_c^+(y) = z_c^+$ is a constant function of y, for all $y < y_c^+(z_c^+)$ (provided that $y_c^+(z)$ is continuous at $z = z_c$); this follows from equations (2.1) and (2.2). Therefore, if there is a collapse transition in the model, then the phase boundary separating the DE-phase from the DC-phase is a straight line (as in figure 1). Little is known about the collapse of adsorbed polygons; the phase boundary in figure 1 is conjecture (and there is strong evidence that it is not present in the two-dimensional version of this problem (see Foster *et al* 1992)). The presence of the phase boundary in three dimensions is strongly supported by numerical simulations of collapsing walks interacting with a wall (Vrbová and Whittington 1998a, b).

In this paper we will focus on the use of density functions to prove more results about figure 1. These are the Legendre transforms of the free energies defined in equations (1.2) and (1.4). In the case of positive polygons the density functions of visits is defined by

$$\log \mathcal{P}^+(\epsilon; z) = \inf_{0<y<\infty} \{\mathcal{F}^+(y,z) - \epsilon \log y\} \tag{2.7}$$

$$\mathcal{F}^+(y,z) = \sup_{0<\epsilon<1} \{\log \mathcal{P}^+(\epsilon; z) + \epsilon \log y\}. \tag{2.8}$$

It can be shown that

$$\mathcal{P}^+(\epsilon; z) = \lim_{n\to\infty} \left[\sum_c p_n^+(\lfloor \epsilon n \rfloor, c) z^c \right]^{1/n} \tag{2.9}$$

see for example Hammersley *et al* (1982), Ellis (1985), Madras *et al* (1988), Vanderzande (1995). Moreover, since each polygon may have at most n visits, $\epsilon \in [0,1]$, and $\log \mathcal{P}^+(\epsilon; z)$ is concave in ϵ. On the other hand, the concatenation of polygons (Vrbová and Whittington 1996) interacting with a surface shows that $\mathcal{P}^+(\epsilon; z)$ is convex in z. Therefore, $\mathcal{P}^+(\epsilon; z)$ is a continuous function for $z \in (0,\infty)$ and for $\epsilon \in (0,1)$. The density function may have discontinuities on the boundary of this interval; but such discontinuities do not play a role in the thermodynamic properties of the model, except at zero or infinite values of the fugacities (this follows from equation (2.4)). We do not know if there are any such discontinuities, but we remove any which may exist by redefining the value of the density function there by the right limit

$$\mathcal{P}^+(0; z) = \lim_{\epsilon \searrow 0} \mathcal{P}^+(\epsilon; z). \tag{2.10}$$

By concavity, $\mathcal{P}^+(\epsilon; z)$ has a right derivative everywhere in $(0, 1)$, and by defining the value of the density function at $\epsilon = 0$ as in equation (2.10), there is also a right derivative at $\epsilon = 0$. The density function of attached polygons interacting with a defect plane, $\mathcal{P}(\epsilon; z)$, is defined similarly to $\mathcal{P}^+(\epsilon; z)$, and it has the same properties. There is an important connection between this right derivative and the critical curve $y_c^+(z)$.

Lemma 2.1. For every $z \in (0, \infty)$,

$$\log y_c^+(z) = -\left[\frac{\mathrm{d}^+}{\mathrm{d}\epsilon} \log \mathcal{P}^+(\epsilon; z)\right]_{\epsilon=0}$$

where $\frac{\mathrm{d}^+}{\mathrm{d}\epsilon}$ indicates the right derivative to ϵ, and where we evaluate this derivative at $\epsilon = 0$.

Proof. Let $Q(\epsilon) = \log \mathcal{P}^+(\epsilon; z) + \epsilon \log y$. By equation (2.4), $\mathcal{F}^+(y, z) = \sup_\epsilon Q(\epsilon)$. Moreover, $Q(\epsilon)$ is concave, and its right derivative at $\epsilon = 0$ is

$$\left[\frac{\mathrm{d}^+}{\mathrm{d}\epsilon} Q(\epsilon)\right]_{\epsilon=0} = \left[\frac{\mathrm{d}^+}{\mathrm{d}\epsilon} \log \mathcal{P}^+(\epsilon; z)\right]_{\epsilon=0} + \log y.$$

If $\log y < -[\frac{\mathrm{d}^+}{\mathrm{d}\epsilon} \log \mathcal{P}^+(\epsilon; z)]_{\epsilon=0}$, then $Q(\epsilon)$ has a negative right derivative at $\epsilon = 0$, and is strictly decreasing in $[0, 1]$ since it is concave. Thus, the supremum in equation (2.4) is found when $\epsilon = 0$, in which case $\mathcal{F}^+(y, z) = \log \mathcal{P}^+(0; z) = \mathcal{F}(z)$ by equations (2.2) and (2.9). If, on the other hand, $\log y > -[\frac{\mathrm{d}^+}{\mathrm{d}\epsilon} \log \mathcal{P}^+(\epsilon; z)]_{\epsilon=0}$, then the right derivative is greater than zero at $\epsilon = 0$. Since this derivative exists as a limit, there is an $\epsilon_c > 0$ such that $Q(\epsilon) > Q(0)$ for all $\epsilon \in [0, \epsilon_c)$. Thus, the supremum in $Q(\epsilon)$ is at some $\epsilon_1 > 0$, in which case $\mathcal{F}^+(y, z) = \log \mathcal{P}^+(\epsilon_1; z) + \epsilon_1 \log y > \log \mathcal{P}^+(0; z) = \mathcal{F}(z)$. Since we can choose $\log y$ arbitrarily close to $-[\frac{\mathrm{d}^+}{\mathrm{d}\epsilon} \log \mathcal{P}^+(\epsilon; z)]_{\epsilon=0}$, this shows that there is a non-analyticity in $\mathcal{F}^+(y, z)$ at $-[\frac{\mathrm{d}^+}{\mathrm{d}\epsilon} \log \mathcal{P}^+(\epsilon; z)]_{\epsilon=0}$.

Notice that ϵ is the density of visits in the class of polygons which determines the free energy, and is therefore also the expected value of the density of visits. If $y < y_c^+(z)$, then the supremum is realized at $\epsilon = 0$, and the expected density of visits is zero. If $y > y_c^+(z)$, then the supremum is found at a positive value of ϵ, so that the free energy is determined by a class of polygons which has a positive expected density of visits. □

This lemma has an important corollary.

Corollary 2.2. For every $z \in (0, \infty)$,

$$\log y_c^+(z) - \log y_c(z) = \mathrm{e}^{-\mathcal{F}(z)} \lim_{\epsilon \searrow 0} \frac{1}{\epsilon} (\mathcal{P}(\epsilon; z) - \mathcal{P}^+(\epsilon; z)).$$

Proof. Lemma 2.1 is also true if we consider $y_c(z)$ and $\mathcal{P}(\epsilon; z)$. The result now follows immediately from lemma 2.1, equation (2.2) and the definition of the right derivative. □

This relation between the locations of the critical curves and the density functions in these models will be exploited in the next section to prove that $y_c^+(z) > 1$ for all $z \in (0, \infty)$.

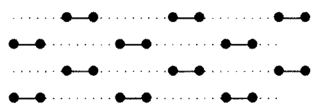

Figure 2. A grid of non-adjacent edges in two dimensions. All of these edges point in the same direction, and if the intersection of a family of parallel edges is taken with a translate of this pattern, then there is an intersection which will contain at least a quarter of all the edges in the family. In one dimension the pattern reduces to every fourth edge along a line. In d dimensions the pattern is found by recursively stacking copies (translated by two steps horizontally) of the pattern in $(d-1)$ dimensions.

3. The location of $y_c^+(z)$

In this section I prove that $y_c^+(z) > 1$ for all $0 < z < \infty$. This will be done by examining the relation between the critical curves and the density functions in corollary 2.2: since $\mathcal{F}(z)$ is finite, we only have to show that $\lim_{\epsilon\searrow 0}(\mathcal{P}(\epsilon; z) - \mathcal{P}^+(\epsilon; z))/\epsilon > 0$.

Consider any positive polygon with n edges, v visits and c contacts, and with a visit a to the hyperplane $z = 0$. Since a is incident with two edges in the polygon, and there is only one direction out of the hyperplane, a is incident with an edge with both endpoints in the hyperplane $z = 0$. In other words, for every two visits, there is at least one edge of the polygon in the hyperplane $z = 0$. Thus, any polygon counted by $p_n^+(v, c)$ must have at least $\lfloor v/2\rfloor$ edges in the hyperplane $z = 0$. Let $\mathcal{V}$ be the set of edges in the polygon which are also in the hyperplane $z = 0$. Then $|\mathcal{V}| \geqslant \lfloor v/2\rfloor$. Each edge in $\mathcal{V}$ points in one of $(d-1)$ possible directions (since the hyperplane $z = 0$ is a $(d-1)$-dimensional space), and so there must be at least one direction which contains at least $|\mathcal{V}|/(d-1)$ edges. Without loss of generality let this be the x-direction, and let this set of edges be $\mathcal{W}$. Then $|\mathcal{W}| \geqslant \lfloor\lfloor v/2\rfloor/(d-1)\rfloor$.

The aim is to select a subset of non-adjacent edges from those in $\mathcal{W}$. If the hyperplane $z = 0$ is one dimensional, then it can be done as follows. Let R_0 be the (infinite) set of edges $\{\ldots, (-4, -3), (0, 1), (4, 5), \ldots\}$ in one dimension. Define R_i by adding i to each coordinate in R_0. Then the R_i are disjoint if $i = 0, 1, 2, 3$ and $R_0 \cup R_1 \cup R_2 \cup R_3$ contains all the edges in the hyperplane $z = 0$. Thus, there is an i such that $\mathcal{W} \cap R_i$ contains at least one out of every four edges in $\mathcal{W}$. These edges are non-adjacent, and we have selected at least $\lfloor\lfloor\lfloor v/2\rfloor/(d-1)\rfloor/4\rfloor$ of them.

In higher dimensions we define the R_i recursively. Suppose that we have defined them in $(d-1)$ dimensions. Let $R_i^{(z)}$ be a copy of R_i inserted in the first $(d-1)$ coordinates in a d-dimensional space, and with the last coordinate put equal to z. Then we define $R_0(d) = \ldots, R_0^{(-2)} \cup R_2^{(-1)} \cup R_0^{(0)} \cup R_2^{(1)} \cup R_0^{(2)} \cup \ldots$. In other words, we stack copies of R_0 and R_2 in an alternating fashion in the z-direction (all edges point in the x-direction) to find R_0 in d dimensions. The outcome in two dimensions is illustrated in figure 2. R_i is again defined by adding i to all x-coordinates in R_0. Then $R_0 \cup R_1 \cup R_2 \cup R_3$ contains all edges in the x-direction in the hyperplane $z = 0$, and so there is an i such that R_i contains at least one quarter of the edges in $\mathcal{W}$. In other words, we can pick a set of at least $\lfloor\lfloor\lfloor v/2\rfloor/(d-1)\rfloor/4\rfloor$ non-adjacent edges in the hyperplane $z = 0$.

Select m of the $\lfloor\lfloor\lfloor v/2\rfloor/(d-1)\rfloor/4\rfloor$ non-adjacent edges in the hyperplane $z = 0$. These edges will be changed to turn the positive polygon into an attached polygon; this will relate the density functions in corollary 2.2 to one another. Translate each of the m edges one step in the negative z-direction, and add two edges at their endpoints each to reconnect the polygon. The removal of each edge creates one more contact, but no other contacts are

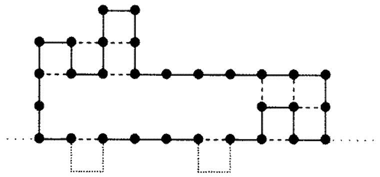

Figure 3. We change the positive attached polygon into an attached polygon by translating edges in the adsorbing plane in the $-z$-direction. This creates a new contact for each edge translated, but the number of visits remains unchanged.

formed since none of the m edges are adjacent to one another. The outcome is an attached polygon with $n+2m$ edges, and $c+m$ contacts (this is illustrated in figure 3). This shows that

$$\binom{\lfloor\lfloor\lfloor v/2\rfloor/(d-1)\rfloor/4\rfloor}{m} p_n^+(v,c) \leqslant p_{n+2m}(v,c+m) \tag{3.1}$$

since, for each choice of the positive polygon, and for each choice of m edges, we will obtain a different attached polygon as the outcome. Multiply equation (3.1) by z^c and sum over c, and note that $\sum_c p_{n+2m}(v,c+m)z^c \leqslant z^{-m}\sum_c p_{n+2m}(v,c)z^c$. This changes the inequality to a relation between the partition functions in equations (1.1) and (1.3):

$$\binom{\lfloor\lfloor\lfloor v/2\rfloor/(d-1)\rfloor/4\rfloor}{m} Z_n^+(v;z) \leqslant z^{-m} Z_{n+2m}(v;z). \tag{3.2}$$

A consequence of this relation is the following theorem.

Theorem 3.1. For all $0<z<\infty$

$$(1+z\mathrm{e}^{-2\mathcal{F}(z)})^{\epsilon/(8d-8)}\ \mathcal{P}^+(\epsilon;z) \leqslant \mathcal{P}\left(\frac{\epsilon}{1+2\delta};z\right)$$

where $\delta = z\mathrm{e}^{-2\mathcal{F}(z)}\epsilon/((8d-8)(1+z\mathrm{e}^{-2\mathcal{F}(z)}))$.

Proof. Let $v=\lfloor\epsilon n\rfloor$ in equation (3.2), and let $m=\lfloor\delta n\rfloor$, where $\delta<\epsilon/(8d-8)$. Take the $(1/n)$th power of the equation, and let $n\to\infty$. Then by equation (2.9)

$$\frac{(\epsilon/(8d-8))^{\epsilon/(8d-8)}}{\delta^\delta(\epsilon/(8d-8)-\delta)^{\epsilon/(8d-8)-\delta}}\mathcal{P}^+(\epsilon;z) \leqslant z^{-\delta}\left[\mathcal{P}\left(\frac{\epsilon}{1+2\delta};z\right)\right]^{1+2\delta}. \tag{A}$$

Let $Z_n(v;z)$ be the partition function of a model of attached polygons with v visits, and contact fugacity z. Then $Z_n(z) = \sum_v Z_n(v,z)$ is the partition function of a model of polygons with contact fugacity z, and it has a limiting free energy given by $\mathcal{F}(z)=\lim_{n\to\infty}\frac{1}{n}\log\sum_v Z_n(v;z)$. On the other hand, let v_* be that least value of v which maximizes $Z_n(v;z)$. Define $\epsilon_*=\liminf_{n\to\infty}(v_*/n)$, then the inequalities

$$Z_n(v_*;z)\leqslant\sum_v Z_n(v;z)\leqslant nZ_n(v_*;z)$$

gives $\mathcal{P}(\epsilon_*;z)=\mathrm{e}^{\mathcal{F}(z)}$. But $\mathcal{P}(\epsilon_*;z)=\sup_\epsilon\mathcal{P}(\epsilon;z)$, so that

$$\mathcal{P}(\epsilon;z)\leqslant\mathrm{e}^{\mathcal{F}(z)}. \tag{B}$$

Substitution of this, and rearrangements of the factors in equation (A) gives

$$\left[\frac{(\epsilon/(8d-8))^{\epsilon/(8d-8)}z^\delta\mathrm{e}^{-2\delta\mathcal{F}(z)}}{\delta^\delta(\epsilon/(8d-8)-\delta)^{\epsilon/(8d-8)-\delta}}\right]\mathcal{P}^+(\epsilon;z)\leqslant\mathcal{P}\left(\frac{\epsilon}{1+2\delta};z\right).$$

The factor in square brackets is maximum when

$$\delta = \frac{z\mathrm{e}^{-2\mathcal{F}(z)}\epsilon}{(8d-8)(1+z\mathrm{e}^{-2\mathcal{F}(z)})}$$

in which case we obtain

$$(1+z\mathrm{e}^{-2\mathcal{F}(z)})^{\epsilon/(8d-8)}\mathcal{P}^+(\epsilon;z) \leqslant \mathcal{P}\left(\frac{\epsilon}{1+2\delta};z\right)$$

with δ as given above. □

If we combine theorem 3.1 with corollary 2.2, we find corollary 3.2.

Corollary 3.2.

$$\log y_c^+(z) - \log y_c(z) \geqslant \frac{1}{8d-8}\log(1+z\mathrm{e}^{-2\mathcal{F}(z)}).$$

Proof. From corollary 2.2 and theorem 3.1 we obtain

$$\begin{aligned}\log y_c^+(z) - \log y_c(z) &= \mathrm{e}^{\mathcal{F}(z)}\lim_{\epsilon\searrow 0}\frac{1}{\epsilon}(\mathcal{P}(\epsilon;z)-\mathcal{P}^+(\epsilon;z))\\ &\geqslant \lim_{\epsilon\searrow 0}\frac{1}{\epsilon}\left(1-\frac{\mathcal{P}(\frac{\epsilon}{1+2\delta};z)}{\mathcal{P}(\epsilon;z)}(1+z\mathrm{e}^{-2\mathcal{F}(z)})^{-\epsilon/(8d-8)}\right).\end{aligned} \tag{C}$$

Suppose that $\mathcal{P}'(0;z) < 0$. If ϵ is close to zero, then

$$\mathcal{P}(0;z) + \epsilon(1-\eta)\mathcal{P}'(0;z) \geqslant \mathcal{P}(\epsilon;z) \geqslant \mathcal{P}(0;z) + \epsilon(1+\eta)\mathcal{P}'(0;z)$$

where $\eta > 0$ can be made arbitrarily small if $\epsilon = 0$. Let $\epsilon < -\mathcal{P}(0;z)/(2(1+\eta)\mathcal{P}'(0;z))$, then these inequalities can be used to show that

$$\frac{\mathcal{P}(\frac{\epsilon}{1+2\delta};z)}{\mathcal{P}(\epsilon;z)} \leqslant 1 - \epsilon\left(\frac{2\delta}{1+2\delta}+2\eta\right)\frac{\mathcal{P}'(0;z)}{\mathcal{P}(0;z)} + \eta_1\epsilon^2$$

where

$$\eta_1 = (1+2(1+\eta)^2)\left(\frac{\mathcal{P}'(0;z)}{\mathcal{P}(0;z)}\right)^2$$

is a finite and fixed positive number. It is now important to note that $\delta \leqslant z\mathrm{e}^{-2\mathcal{F}(z)}\epsilon$ for fixed values of z. By using this bound on δ, the above simplifies to

$$\frac{\mathcal{P}(\frac{\epsilon}{1+2\delta};z)}{\mathcal{P}(\epsilon;z)} \leqslant 1 - 2\eta\epsilon\frac{\mathcal{P}'(0;z)}{\mathcal{P}(0;z)} + \eta_2\epsilon^2$$

where $\eta_2 = \eta_1 - 2z\mathrm{e}^{-2\mathcal{F}(z)}\mathcal{P}'(0;z)/\mathcal{P}(0;z)$. Substitition of this bound into equation (C) gives

$$\log y_c^+(z) - \log y_c(z) \geqslant \frac{1}{8d-8}\log(1+z\mathrm{e}^{-2\mathcal{F}(z)}) + 2\eta\frac{\mathcal{P}'(0;z)}{\mathcal{P}(0;z)}$$

and since $\epsilon = 0$, we can take η arbitrarily small. If $\mathcal{P}'(0,z) = 0$ then use $\mathcal{P}(0,z) - \epsilon\eta \leqslant \mathcal{P}(\epsilon,z) \leqslant \mathcal{P}(0,z) + \epsilon\eta$ instead. □

Notice that $Z_n(z) = \sum_c p_n(c)z^c \leqslant dnp_n z^{dn}$ if $z \geqslant 1$. Thus $\mathcal{F}(z) \leqslant \log\mu_d + d\log z$ if $z \geqslant 1$. Otherwise, if $z < 1$, then $Z_n(z) \leqslant dnp_n$ and $\mathcal{F}(z) \leqslant \log\mu_d$. Therefore, $\mathrm{e}^{-2\mathcal{F}(z)} \geqslant \mu_d^{-2}\phi(z)$, where $\phi(z) = \min\{1, z^{-2d}\}$. This gives the bound

$$\log y_c^+(z) - \log y_c(z) \geqslant \frac{1}{8d-8}\log(1+z\mu_d^{-2}\phi(z)). \tag{3.3}$$

In three dimensions, and if $z = 1$, this gives the approximate lower bound $\log y_c^+(z) \geqslant \frac{1}{8d-8}\log(1+\mu_d^{-2}) \approx 0.0028$.

4. Excursions in polygons with a density of visits

A subwalk with its first and last vertex in the hyperplane $z = 0$, and with all its internal vertices disjoint with this hyperplane, is an *excursion*. Maximal subwalks in a polygon which are contained in the hyperplane $z = 0$ are called *incursions*. An attached polygon is an alternating sequence of incursions and excursion. If the polygon is completely adsorbed in the wall (defect plane), then it has no excursions.

In this section we use a construction on excursions in adsorbing walks to produce an alternative proof that $y_c^+(z) > 0$. The density of visits $\langle v\rangle_n/n$ is given by the first derivative of the free energy with respect to the visit-fugacity; in the desorbed phase we can calculate directly that

$$\lim_{n\to\infty}\frac{\langle v\rangle_n}{n} = \frac{\mathrm{d}}{\mathrm{d}y}\mathcal{F}^+(y,z) = 0 \qquad \text{if } y < y_c^+(z) \tag{4.1}$$

and since the number of excursions is at most equal to the number of visits, the density of excursions is also zero. We can also see this by noting that the density function $\mathcal{P}^+(\epsilon; z) + \epsilon\log y$ attains its supremum at $\epsilon = 0$ if $y < y_c^+(z)$ (see the proof of lemma 2.1), so that the density of visits is zero in the infinite n limit. On the other hand, if $y > y_c^+(z)$, then there is a non-zero density of visits, and perhaps a non-zero density of excursions. We will examine this in the following paragraphs.

Let $p_n^+(v, c, k)$ be the number of attached, positive polygons with n edges, v visits, c contacts and k excursions. We can define the partition function of a model of positive polygons with $\lfloor\epsilon n\rfloor$ visits and $\lfloor\delta n\rfloor$ excursions by

$$Z_n^+(\lfloor\epsilon n\rfloor; z; \lfloor\delta n\rfloor) = \sum_c p_n^+(\lfloor\epsilon n\rfloor, c, \lfloor\delta n\rfloor)z^c. \tag{4.2}$$

The density function of visits and excursions of this model is defined by

$$\mathcal{P}^+(\epsilon; z; \delta) = \limsup_{n\to\infty}[Z_n^+(\lfloor\epsilon n\rfloor; z; \lfloor\delta n\rfloor)]^{1/n} \tag{4.3}$$

we only define this as a lim sup, but note that the existence of the limit can be shown. Since $p_n^+(v, c) = \sum_k p_n^+(v, c, k)$, we necessarily have that

$$\mathcal{P}^+(\epsilon; z) = \sup_\delta \mathcal{P}^+(\epsilon; z; \delta). \tag{4.4}$$

It can be checked that the domain of (ϵ, δ) is as follows

$$\begin{aligned} &\epsilon \in [0, \tfrac{1}{2}] \qquad 0 \leqslant \delta \leqslant \min\{\epsilon/2, \tfrac{1}{2} - \epsilon\} \qquad \text{in } d = 2 \\ &\epsilon \in [0, 1] \qquad 0 \leqslant \delta \leqslant \min\{\epsilon/2, (1-\epsilon)/2\} \qquad \text{in } d \geqslant 3. \end{aligned} \tag{4.5}$$

Let ρ be a polygon counted by $p_n^+(v, c, k)$. Since there are v visits and k excursions in ρ, there are also $v - k$ edges of ρ in the plane $z = 0$. Choose m non-adjacent edges from this set; this can be done in at least $\binom{\lfloor(v-k)/2\rfloor}{m}$ different ways. Fix these edges in the $z = 0$ hyperplane, and translate the rest of the polygon one step in the z-direction to obtain the polygon ρ'. This is illustrated in figure 4.

No contacts are broken by this construction, but each of the m chosen edges produces a contact, and each new vertex may have as many as d new contacts; thus, ρ' may have at least c, and at most $c + (2d + 1)m$ contacts. In addition, there are $2m$ visits and m excursions in ρ'. Thus

$$\binom{\lfloor(v-k)/2\rfloor}{m} p_n^+(v, c, k) \leqslant \sum_{i=0}^{(2d+1)m} p_{n+2m}^+(2m, c + i, m). \tag{4.6}$$

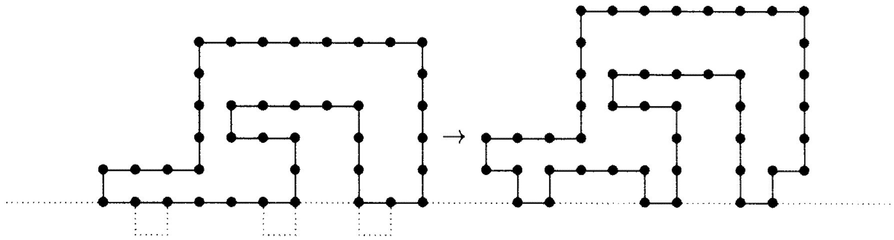

Figure 4. By fixing edges in the $z = 0$ hyperplane and translating the rest of the polygon in the z-direction, we can create excursions.

Multiply this equation by z^c and sum over c. This gives a relation between partition functions:

$$\binom{\lfloor (v-k)/2 \rfloor}{m} Z_n^+(v; z; k) \leqslant \left[\sum_{i=0}^{(2d+1)m} z^{-i} \right] Z_{n+2m}^+(2m; z; m). \tag{4.7}$$

Equation (4.7) has the following consequence.

Theorem 4.1. For every ϵ in the interval $(0, 1]$ there exists a $\delta_* > 0$ such that

$$(1 + [\phi(z)\mathrm{e}^{2\mathcal{F}(z)}]^{-1})^{(\epsilon-\gamma)/2} \mathcal{P}^+(\epsilon; z; \gamma) \leqslant \mathcal{P}^+(2\delta_*; z; \delta_*)$$

where $0 < z < \infty$, $2\delta_* < \epsilon - \gamma$, and $\phi(z) = \max\{1, z^{-(2d+1)}\}$.

Proof. Put $v = \lfloor \epsilon n \rfloor$, $k = \lfloor \gamma n \rfloor$, $m = \lfloor \delta n \rfloor$ in equation (4.7). Take the $(1/n)$th power, and take the lim sup as $n \to \infty$ of the left-hand side of the equation. This gives

$$\frac{((\epsilon-\gamma)/2)^{(\epsilon-\gamma)/2}}{\delta^\delta ((\epsilon-\gamma)/2 - \delta)^{(\epsilon-\gamma)/2-\delta}} \mathcal{P}^+(\epsilon; z; \gamma) \leqslant [\phi(z)]^\delta \left[\mathcal{P}^+ \left(\frac{2\delta}{1+2\delta}; z; \frac{\delta}{1+2\delta} \right) \right]^{1+2\delta}$$

where $\phi(z) = 1$ if $z \geqslant 1$ and $\phi(z) = z^{-(2d+1)}$ if $z < 1$. By equation (4.4) and theorem (3.1), equation (B), we note that $\mathcal{P}^+(2\delta; z; \delta) \leqslant \mathcal{P}^+(2\delta; z) \leqslant \mathrm{e}^{\mathcal{F}(z)}$. Thus

$$\frac{((\epsilon-\gamma)/2)^{(\epsilon-\gamma)/2}}{\delta^\delta ((\epsilon-\gamma)/2 - \delta)^{(\epsilon-\gamma)/2-\delta}} [\phi(z)\mathrm{e}^{2\mathcal{F}(z)}]^{-\delta} \mathcal{P}^+(\epsilon; z; \gamma) \leqslant \mathcal{P}^+ \left(\frac{2\delta}{1+2\delta}; z; \frac{\delta}{1+2\delta} \right).$$

The left-hand side is a maximum if

$$\delta_* = \frac{\epsilon - \gamma}{2(1 + \phi(z)\mathrm{e}^{2\mathcal{F}(z)})}$$

in which case we have

$$(1 + [\phi(z)\mathrm{e}^{2\mathcal{F}(z)}]^{-1})^{(\epsilon-\gamma)/2} \mathcal{P}^+(\epsilon; z; \gamma) \leqslant \mathcal{P}^+(2\delta_*; z; \delta_*)$$

where $\delta_* = \delta/(1 + 2\delta)$ and where δ is given above. This completes the proof. □

Notice that $\delta_* \leqslant \epsilon/2$ in the proof above, so that the optimal value of δ in theorem 4.1 is in the interval specified by equation (4.5). The implication of theorem 4.1 is that any set of polygons with $\lfloor \epsilon n \rfloor$ visits and no excursions is exponentially rare in comparison with a set of polygons with $\lfloor 2\delta_* n \rfloor$ visits and $\lfloor \delta_* n \rfloor$ excursions (and where $2\delta_* = \epsilon/(1 + \phi(z)\mathrm{e}^{2\mathcal{F}(z)})$).

From equation (2.4) we see that the free energy is defined by

$$\mathcal{F}^+(y, z) = \sup_{\epsilon,\delta} \log(\mathcal{P}^+(\epsilon; z; \delta) y^\epsilon) = \log(\mathcal{P}^+(\epsilon^*; z; \delta^*) y^{\epsilon^*}). \tag{4.8}$$

If $y < y_c^+(z)$, then we know from the proof of lemma 2.1 that $\epsilon^* = \delta^* = 0$ in equation (4.8). We now use theorem 4.1 to give an alternative proof that $y_c^+(z) > 1$: Suppose that $y > y_c^+(z)$ so that $\epsilon^* > 0$ in equation (4.8). Then by theorem 4.1 we note

$$\mathcal{F}^+(y,z) = \log(\mathcal{P}^+(\epsilon^*; z; \delta^*) y^{\epsilon^*}) \leqslant \log\left(\mathcal{P}^+(2\delta^\dagger; z; \delta^\dagger) y^{2\delta^\dagger} \left[\frac{y^{\epsilon^* - 2\delta^\dagger}}{\Delta}\right]\right) \tag{4.9}$$

where we used theorem 4.1 and where $2\delta^\dagger = (\epsilon^* - \delta^*)/\Delta < \epsilon^* - \delta^*$; and where $\Delta = (1 + [\phi(z)\mathrm{e}^{2\mathcal{F}(z)}]^{-1})^{(\epsilon^*-\delta^*)/2}$ by theorem 4.1. This is a contradiction if

$$\log y < \frac{\log \Delta}{\epsilon^* - 2\delta^*} \tag{4.10}$$

and if we suppose that $\delta^* = \alpha\epsilon^*$, where $0 \leqslant \alpha \leqslant \frac{1}{2}$, then simplification of equation (4.10) gives

$$\log y < \frac{(1-\alpha)(1+\phi(z)\mathrm{e}^{\mathcal{F}(z)}) \log(1 + [\phi(z)\mathrm{e}^{\mathcal{F}(z)}]^{-1})}{\alpha + 2\phi(z)\mathrm{e}^{\mathcal{F}(z)}}. \tag{4.11}$$

This bound is positive for any value of α in $[0, \frac{1}{2}]$. In other words, if y satisfies the bound in equation (4.11), then equation (4.9) is a contradiction (by the definition of $\mathcal{F}^+(y,z)$), *unless* $\epsilon^* = 0$. Thus, if y satisfies the bound in equation (4.11), then we must be in the desorbed phase, and so $y_c^+(z) > 1$.

5. Conclusions

In this paper I revisited a model of adsorbing and collapsing polygons introduced by Vrbová and Whittington (1996). This model is a generalized version of the model in Hammersley *et al* (1982). In this paper it has been shown that the adsorption transition of positive attached polygons can only occur when there is a strictly attractive interaction between the polygons and the wall (that is, if the visit-fugacity y is in $[1, y_c^+(z))$, then we are in the desorbed phase, and $y_c^+(z) > 1$ for all $0 < z < \infty$). A construction for adsorbing polygons (without a contact-fugacity) in the paper by Hammersley *et al* (1982) shows that there is a density of excursions in the adsorbed phase. In our phase diagram this corresponds to a density of excursions for $y > y_c^+(1)$ and $z = 1$. The construction in that paper will not generalize to the model of interacting polygons in this paper (too many nearest-neighbour contacts are lost)†. Thus, it remains to show that there is a density of excursions in the adsorbed phases for values of $z \neq 1$. In addition, an easy extension of the construction will show that a density of the excursions will be tight knots (Janse van Rensburg *et al* 1992); this result was also shown by Vanderzande (1995).

Monte Carlo simulations by Vrbová and Whittington (1998a, b) support the hypothetical phase diagram in figure 1. There are also some outstanding issues. Most importantly, what can be said about the AC-phase? Is it present in the two-dimensional version of this model? Numerical work suggests that it is present in three dimensions; but this raises a second issue: are there two triple points in the phase diagram (figure 1), or is there only one quadruple point?

† This construction will work for related models, such as for example a model of polygons with a curvature fugacity.

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