Location of the adsorption transition for lattice polymers

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Abstract

We consider various lattice models of polymers: lattice trees, lattice animals, and self-avoiding walks. The polymer interacts with a surface (hyperplane), receiving an energy reward of $\beta$ for each site in the surface. It is known that there is an adsorption transition at a critical value of $\beta$. We present a new proof of the result of Hammersley et al. (1982 J. Phys. A: Math. Gen. 15 539–71) that the transition occurs at a strictly positive value of $\beta$ when the surface is impenetrable, i.e. when the polymer is restricted to a half-space. In contrast, for a penetrable surface, it is an open problem to prove that the transition occurs at $\beta = 0$. We reduce this problem to proving that the fraction of $N$-site polymers whose span is less than $N \log^2 N / N$ is not too small.

Keywords: lattice tree, lattice animal, self-avoiding walk, adsorption transition

(Some figures may appear in colour only in the online journal)

1. Introduction

We shall consider polymer models in the $d$-dimensional hypercubic lattice $\mathbb{L}^d$ ($d \geq 2$), with sites $x = (x_1, \ldots, x_d) \in \mathbb{Z}^d$ and edges connecting nearest neighbours. Let $\mathbb{L}_d^+\mathbb{L}$ be the part of $\mathbb{L}^d$ in the half-space $x_1 \geq 0$.

Here is our ‘big picture’ of adsorption for lattice polymer models. We have a surface in our space $\mathbb{L}^d$ (in our case, the hyperplane $x_1 = 0$). For each $N \geq 1$, we have a finite set $P_N$ of possible configurations of a polymer molecule of size $N$ attached to a fixed site in the surface (the origin). In this paper, $P_N$ will be the set of lattice trees or lattice animals (representing branched polymers) or self-avoiding walks (representing linear polymers) with $N$ sites (representing monomers). These are classical lattice models of polymer configurations (see for example de Gennes (1979) and Vanderzande (1998)). Each polymer $\rho$ in $P_N$ is rewarded
according to the number of sites of \( \rho \) that lie in the surface, which we denote \( \sigma(\rho) \). For real \( \beta \), we define the partition function

\[
Z_N(\beta) := \sum_{\rho \in \mathcal{P}_N} \exp(\beta \sigma(\rho)).
\]

The number \( \beta \) is a dimensionless parameter corresponding to \(-\epsilon / kT\), where \( \epsilon \) is the adsorption energy per monomer, \( T \) is absolute temperature, and \( k \) is Boltzmann’s constant. The sign of \( \beta \) is positive for an attractive surface, and negative for a repulsive one. In our cases, there exists a limiting free energy

\[
\mathcal{F}(\beta) := \lim_{N \to \infty} \frac{1}{N} \log Z_N(\beta).
\]

The limit \( \mathcal{F}(\beta) \) is a finite non-decreasing function of \( \beta \) that is automatically convex (e.g. lemma 4.1.2 of Madras and Slade (1993)) and hence continuous.

In particular, we have \( \lim_{N \to \infty} |\mathcal{P}_N|^{1/N} = \exp(\mathcal{F}(0)) \) (where the cardinality of a set \( A \) is denoted \( |A| \)). In our models, we also find that \( \mathcal{F}(\beta) = \mathcal{F}(0) \) for every negative \( \beta \), which says that in the repulsive regime, the energy imparted by surface interaction is negligible—i.e. the polymer desorbs and most of it does not lie in the surface. We say that \( \beta \) is the adsorption transition at the critical point \( \beta_c \), which is the right endpoint of the desorbed regime. We know that \( \beta_c \) is finite (Hammersley et al 1982b).

In the context of polymer modelling, the surface could either be impenetrable (e.g. the wall of a container) or penetrable (e.g. an interfacial layer between two fluids). We shall always represent the surface by the hyperplane \( x_1 = 0 \). In the impenetrable case, the polymer configurations will be restricted to the half-space \( \mathbb{R}_+^{d-1} \). We shall write \( \beta^* \) and \( \beta^p \) to denote the adsorption critical points for the impenetrable and penetrable models respectively.

A basic qualitative question about the adsorption transition is whether \( \beta_c \) is zero or nonzero. It turns out that when the surface is impenetrable, then \( \beta^* > 0 \)—that is, for a given attractive surface, the adsorption transition occurs at a finite temperature. This had been proven by other authors (Hammersley et al 1982b), for self-avoiding walks; Janse van Rensburg (1998), for lattice trees), but we present a new and shorter proof. In the case of a penetrable surface, with the polymers not restricted to a half-space, it is generally believed that \( \beta^p = 0 \)—that is, the transition occurs when the surface interaction changes from repulsive to attractive, through vanishingly small surface-monomer interaction energy. It is an open problem to prove this rigorously. We do not fully solve this problem, but we show that it is a rigorous consequence of a weak assertion about the diameter of polymers which seems to be beyond reasonable doubt. Specifically, let the span of the polymer \( \rho \) be the maximum value of \( |u_i - v_i| \) where \( u \) and \( v \) range over all sites of \( \rho \). Let \( f_N \) be the fraction of polymers in \( \mathcal{P}_N \) whose span is at most \( N/\log^2 N \). We prove that if \( f_N \) is bounded below by \( N^{-\delta} \) for some fixed \( \delta \), then \( \beta^p \) must be zero. This condition seems to be very weak. Indeed, a standard scaling assumption about polymers is that the average span of members of \( \mathcal{P}_N \) scales as \( N^\nu \) for a critical exponent \( \nu \) that is strictly less than 1. If it were proven, this scaling assumption would imply that the fraction \( f_N \) converges to 1, and hence that \( \beta^p \) is 0.

It is worth remarking that the methods of Hammersley et al (1982b) and Janse van Rensburg (1998) yield explicit positive lower bounds on \( \beta^* - \beta^p \); the strict positivity of \( \beta^* \) is then a corollary of such a bound and the relatively easy observation that \( \beta^p \geq 0 \). In contrast, the method of the present paper provides an explicit positive lower bound on \( \beta^* \) but does not give a direct proof that \( \beta^* > \beta^p \).
Beaton et al (2014) considered the important special case of self-avoiding walks on the hexagonal lattice, and proved that $\beta^+_c = \ln(1 + \sqrt{2})$, thus verifying a prediction of Batchelor and Yung (1995). This result depends on special properties of the hexagonal lattice, and seems difficult to generalize.

We note that when $\mathcal{P}_N$ is the set of $N$-step nearest-neighbour random walk paths (not self-avoiding), then a relatively straightforward application of generating functions shows that $c_\beta$ is 0 in the penetrable case and is strictly positive in the impenetrable case, where in fact it equals $\frac{\ln(2d(2d-1))}{2d}$ (Rubin 1965, Hammersley 1982a). The book of Giacomin (2007) deals extensively with related random walk models.

Our proofs are simplest in the case of lattice trees and lattice animals. The same methods work for self-avoiding walks, but some technical modifications are necessary.

Here is the organization of the rest of the paper. The results are stated formally in section 2. After section 2.1 sets up the basic framework and some terminology, sections 2.2 and 2.3 present the results for lattice trees (and lattice animals) and for self-avoiding walks respectively. Section 2.4 outlines the essential ideas behind the proofs of the main results. Section 3 presents the proofs for lattice trees, as well as the minor modifications needed for lattice animals. Section 4 presents the proofs for self-avoiding walks. Section 5 is a concluding discussion.

2. Results

2.1. Basic background and notation

We denote the standard basis of $\mathbb{R}^d$ by $u^{(1)}, \ldots, u^{(d)}$, that is, $u^{(i)}$ is the unit vector in the $+x_i$ direction.

We write $\mathbb{Z}^d$ for the set of points $(x_1, \ldots, x_d)$ in $\mathbb{R}^d$ whose coordinates $x_i$ are all integers. The $d$-dimensional hypercubic lattice $\mathbb{L}^d$ is the infinite graph embedded in $\mathbb{R}^d$, whose sites are the points of $\mathbb{Z}^d$ and whose edges join each pair of sites that are distance 1 apart. Let $\mathbb{L}^d_+$ be the part of $\mathbb{L}^d$ that lies in the half-space $\{ x : x_1 \geq 0 \}$.

If $A \subset \mathbb{R}^d$ (or if $A$ is a subgraph of $\mathbb{L}^d$) and $x \in \mathbb{Z}^d$, then the translation of $A$ by the vector $x$ is denoted $A + x$.

For a subgraph $\rho$ of $\mathbb{L}^d$, let $\mathcal{H}(\rho)$ be the set of sites $x$ of $\rho$ such that $x_1 = 0$. Thus, referring to equation (1), the quantity $\sigma(\rho)$ equals $|\mathcal{H}(\rho)|$, the cardinality of $\mathcal{H}(\rho)$.

We shall frequently use superscripts $+$ and $P$ to denote impenetrable and penetrable surfaces respectively. Also, we shall use $T$, $A$, and $W$ superscripts to denote trees, animals, and (self-avoiding) walks.

2.2. Branched polymers: trees and animals

A lattice animal is a finite connected subgraph of $\mathbb{L}^d$, and a lattice tree is a lattice animal with no cycles. Each corresponds to a standard discrete model of the configuration of a branched polymer. Let $\mathcal{T}_N$ be the set of all $N$-site lattice trees that contain the origin. Let $\hat{T}_N$ be the set of $N$-site lattice trees whose lexicographically smallest site is the origin (The elements of $\hat{T}_N$ correspond to equivalence classes of all $N$-site lattice trees up to translation.). Then $|\mathcal{T}_N| = N |\hat{T}_N|$.

Let $t_N = |\hat{T}_N|$. It is well known (Klarner 1967, Klein 1981) that $t_{NM} \leq t_{N+M}$ for all $N, M \geq 1$, and that $t_N^N$ has a finite limit $\lambda_d$ with the property that

\[ t_N \leq \lambda_d^N \quad \text{for every } N. \]
The notation and results for lattice animals are exactly analogous: $A_N, \mathcal{A}_N, a_N = |\mathcal{A}_N| = |A_N|/N$, $\lambda_{d,A} := \lim_{n \to \infty} d_N^{[\lambda_{d,A}]^N}$, and $a_N \subseteq \lambda_{d,A}^N$ (by analogy, we should write $\lambda_{d,T}$ instead of $\lambda_d$ for the tree model, but dropping the $T$ makes the notation simpler, and we shall mainly discuss trees.)

Let $T_N^+$ be the set of all trees $\tau \in T_N$ such that $\tau \subset \mathbb{L}^d$. Then for every site $x$ of every tree $\tau$ in $T_N^+$, we have $x_i \geq 0$. Observe that $T_N^+ \subset T_N^+ \subset T_N$.

We now consider the ensemble of lattice trees in the half-space $\mathbb{L}_+^d$ in which each site in the boundary hyperplane $x_1 = 0$ receives reward $\beta$, for real $\beta$. Define the partition function

$$Z_N^T(\beta) := \sum_{\tau \in T_N^+} \exp(\beta |\mathcal{H}(\tau)|).$$ (4)

As shown in theorem 6.23 of Janse van Rensburg (2000), a concatenation argument can be used to prove that the limiting free energy

$$\mathcal{F}^{T+}(\beta) := \lim_{N \to \infty} \frac{1}{N} \log Z_N^T(\beta)$$ (5)

exists and is finite for every real $\beta$.

It is not hard to see that the number of trees $\tau$ in $T_N^+$ with $|\mathcal{H}(\tau)| = 1$ is exactly $|T_{N-1}^+|$ for every $N$, and hence

$$\tau_{N-1} \leq Z_N^T(\beta).$$ (6)

For $\beta \leq 0$, we also have $Z_N^T(\beta) \leq |T_N^+| \leq N_0$, and combining this with equation (6) shows that

$$\mathcal{F}^{T+}(\beta) = \log \lambda_d$$ for every $\beta \leq 0$. (7)

This says that the polymer desorbs from the surface whenever $\beta$ is nonpositive—that is, we have $\beta_c^+ \geq 0$. The following result tells us that, in fact, the polymer desorbs whenever $\beta \leq \lambda_d^{-1}$.

**Theorem 2.1.** For lattice trees, we have $\mathcal{F}^{T+}(\beta) = \log \lambda_d$ for every $\beta \leq \lambda_d^{-1}$.

Theorem 2.1 says that for adsorption of lattice trees to an impenetrable surface, the critical point satisfies $\beta_c^+ \geq \lambda_d^{-1}$. This result is somewhat better than the bound $\beta_c^+ \geq \beta_T^+ - \beta_{cP}^+ \geq \frac{1}{2} \log(1 + \lambda_d^{-1})$ that follows from theorem 4.7 of Janse van Rensburg (1998) (which however applies to a larger class of tree models). However, the main contribution of our theorem 2.1 is the new method of proof, rather than the improved numerical value of the bound.

We now consider adsorption at a penetrable surface, and the relevant ensemble $T_N$ of all $N$-site trees that contain the origin. The corresponding partition function is

$$Z_N^{TP}(\beta) := \sum_{\tau \in T_N} \exp(\beta |\mathcal{H}(\tau)|).$$ (8)

As in the impenetrable case, a concatenation argument (see theorem 6.23 of Janse van Rensburg (2000)) shows that the limit

$$\mathcal{F}^{TP}(\beta) := \lim_{N \to \infty} \frac{1}{N} \log Z_N^{TP}(\beta)$$ (9)

exists and is finite for every real $\beta$. As was the case for $\mathcal{F}^{T+}$,

$$\mathcal{F}^{TP}(\beta) = \log \lambda_d$$ for every $\beta \leq 0$. (10)

It is not hard to show that $0 \leq \beta_{cP}^+ \leq \beta_c^+ \leq \ln(\lambda_d/\lambda_{d-1})$ (see Hammersley et al (1982b), or Janse van Rensburg (1998)). However, in marked contrast to the situation for $\mathcal{F}^{T+}$, it is
generally believed that $\mathcal{F}_{\text{TP}}(\beta) > \log \lambda_d$ for every $\beta > 0$—i.e. that $\beta_{\text{TP}}^* = 0$. Proving this is a challenging open problem. We shall show that it is a consequence of a different property that has not been proven rigorously but is widely believed to be true.

In the following, we let $\Pr_A$ denote the uniform probability distribution on the set $A$. Define the $x_1$-span of a tree $\tau$ to be the number of integers $j$ such that $\tau$ contains a site $v$ with $v_1 = j$. We write $\text{Span}(\tau)$ to denote the $x_1$-span of $\tau$. Since trees are connected, we have

$$\text{Span}(\tau) := 1 + \max\{|u_i - v_i| : u, v \in \tau\}.$$

**Theorem 2.2.** Assume there exists $\delta \in (0, \infty)$ such that

$$\Pr_{\mathcal{T}_d}\left\{ \tau : \text{Span}(\tau) \leq \frac{N}{\log^2 N} \right\} \geq \frac{1}{N^\delta}$$

for all sufficiently large $N$. Then $\mathcal{F}_{\text{TP}}(\beta) > \log \lambda_d$ for every $\beta > 0$ (that is, $\beta_{\text{TP}}^* = 0$).

**Remark 2.3.**

(i) It is generally believed that the expected value of $\text{Span}(\tau)$ over $\mathcal{T}_N$ scales as $N^\nu$ for some (dimension-dependent) critical exponent $\nu < 1$ (see for example section 9.2 of Vanderzande (1998)). This would imply the truth of equation (11); indeed, it would imply that the left-hand side of (11) converges to 1 as $N$ tends to $\infty$.

(ii) It will be seen from the proof that the statement of theorem 2.2 can be strengthened slightly, e.g. by replacing the square (of the logarithm) by a power greater than 1.

(iii) The direct analogues of theorems 2.1 and 2.2 also hold for lattice animals (see remarks 3.1 and 3.2).

(iv) There are other ways to define the span of a tree, but the choice will not substantially affect the statement of the theorem. Our choice, using the $x_1$ coordinate, is for convenience.

### 2.3. Linear polymers: self-avoiding walks

An $N$-step self-avoiding walk (SAW) in $\mathbb{L}^d$ is a sequence $\omega = (\omega(0), \omega(1), \ldots, \omega(N))$ of $N + 1$ distinct points of $\mathbb{Z}^d$ such that $\omega(i)$ is a nearest neighbour of $\omega(i - 1)$ for $i = 1, \ldots, N$. We write $\omega_i(i)$ to denote the $i$th coordinate of the $i$th point of $\omega$. The self-avoiding walk is a classical model of the configuration of a linear polymer.

Let $S_N$ be the set of all $N$-step self-avoiding walks in $\mathbb{L}^d$ that start at the origin, and let $c_N = |S_N|$. Then the limit $\mu_d = \lim_{N \to \infty} c_N^{1/N}$ exists (Hammersley and Morton (1954); or see section 1.2 of Madras and Slade (1993)).

Our notation for SAWs is very similar to our notation for trees. Let $S_N^+$ be the set of all SAWs in $S_N$ that are contained in $\mathbb{L}_+^d$. Then $|S_N^+|^{1/N}$ also converges to $\mu_d$ (e.g. by corollary 3.1.6 of Madras and Slade (1993)). The partition function for adsorption at an impenetrable surface is defined to be

$$Z_N^W(\beta) := \sum_{\omega \in S_N^+} \exp(\beta \mathcal{H}(\omega)).$$

Hammersley et al (1982b) proved the existence of the limit

$$\mathcal{F}_W^*(\beta) := \lim_{N \to \infty} \frac{1}{N} \log Z_N^W(\beta)$$
for every real $\beta$. The following result is the analogue of theorem 2.1 for SAWs, proving that $\beta_{\text{SAW}}^+ \geq \frac{1}{2} \mu_d^{-2}$.

**Theorem 2.4.** We have $\mathcal{F}^W(\beta) = \log \mu_d$ for every $\beta \leq \frac{1}{2} \mu_d^{-2}$.

For the case of a penetrable surface, let

$$Z_N^{WP}(\beta) := \sum_{\tau \in \mathcal{S}_N} \exp(\beta |\mathcal{H}(\tau)|).$$

(14)

Hammersley *et al.* (1982b) proved that the limit

$$\mathcal{F}^{WP}(\beta) := \lim_{N \to \infty} \frac{1}{N} \log Z_N^{WP}(\beta)$$

exists and is finite for every real $\beta$, and equals $\log \mu_d$ whenever $0 \leq \beta \leq 1$.

We define the $x_1$-span of a SAW exactly as for trees:

$$\text{Span}(\omega) := 1 + \max \{ |\omega(i) - \omega(j)| : 0 \leq i, j \leq N \}.$$ We define an $N$-step bridge to be an $N$-step self-avoiding walk with the property that $\omega_d(i) < \omega_d(j) \leq \omega_d(N)$ for $i = 1, \ldots, N$.

Let $S_N^B$ be the set of all bridges in $\mathcal{S}_N$, and let $b_N = |S_N^B|$. The following result provides a sufficient condition for $\beta^{WP}$ to be zero, analogously to theorem 2.2.

**Theorem 2.5.** Assume there exists $\delta \in (0, \infty)$ such that

$$\text{Pr}_{S_N^B} \left( \left\{ \omega : \text{Span}(\omega) \leq \frac{N}{\log^2 N} \right\} \right) \geq \frac{1}{N^\delta}$$

(16)

for all sufficiently large $N$. Then $\mathcal{F}^{WP}(\beta) > \log \mu_d$ for every $\beta > 0$.

Similarly to remark 2.3(i), it is generally believed that the left side of equation (16) converges to 1 as $N$ tends to infinity.

2.4. Ideas behind the proofs

In this section, we sketch the main ideas behind the proofs of theorems 2.1 and 2.2. We restrict our attention here to lattice trees, since the same ideas apply to all of our models.

First we consider trees at an impenetrable boundary with $\beta > 0$. Consider a tree $\tau \in T_N$ with $k$ sites in the hyperplane $x_1 = 0$. The contribution of this tree to the partition function $Z_N^{T}(\beta)$ of equation (4) is

$$e^{\beta k} = \sum_{j=0}^{\infty} \frac{\beta^j k^j}{j!}.$$ We show that there are at least $k/j!$ ways to extend $\tau$ to a tree $\hat{\tau}$ with $N + j$ sites such that the restriction of $\hat{\tau}$ to the half-space $\mathbb{Z}_d^+$ is precisely $\tau$. In fact, these $\hat{\tau}$’s are obtained by appending line segments parallel to the $x$-axis to the sites of $\mathcal{H}(\tau)$ (i.e. to the sites of $\tau$ in the boundary hyperplane; see figure 2). Since all the trees $\hat{\tau}$ are distinct, we obtain

$$Z_N^{T}(\beta) = \sum_{\tau \in T_N} e^{\beta |\mathcal{H}(\tau)|} \leq \sum_{j=0}^{\infty} \sum_{\tau \in T_{N+j}} \beta^j \leq \sum_{j=0}^{\infty} |T_{N+j}| \beta^j \approx \sum_{j=0}^{\infty} \chi_d \lambda_d^{N+j} \beta^j.$$
For $0 < \beta < \lambda_d^{-1}$, the final expression is a convergent geometric series, and hence $Z_N(\beta)$ cannot grow (exponentially) faster than $\lambda_N$. This, together with equation (7) and the monotonicity of $F^T(\beta)$, implies theorem 2.1.

Next, we consider trees at a penetrable boundary, with a small positive value of $\beta$. Consider a fixed value of $n$ (that will depend on $\beta$ in a way to be specified later). If $s_n$ is the typical value of Span($\tau$) for trees $\tau$ in $T_n$, then it is not unusual for a tree of size $n$ to have about $n/s_n$ sites in the hyperplane $x_1 = 0$. For each positive integer $k$, we can concatenate $k$ typical members of $T_n$ in a suitable way to get a tree of size $kn$ having at least about $kn/s_n$ sites on the surface $x_1 = 0$. Therefore

$$Z_T^P(\beta) \geq (t_n)^k e^{\beta kn/s_n}.$$ 

If we know that $t_n \geq \lambda_n n^{-A}$ for some constant $A$, then we would get

$$Z_T^P(\beta) \geq \lambda_n^{nk} n^{-Ak} e^{\beta kn/s_n} = \left[ \lambda_d \exp \left( -A \frac{\ln n}{n} + \frac{\beta}{s_n} \right) \right]^{nk}.$$ 

Now, if $s_n < n/\ln n$, then we can choose $n$ to make the argument of the rightmost exponential strictly positive. Then, letting $k \rightarrow \infty$, we see that the limit of $(Z_T^P(\beta))^{1/nk}$ must be strictly bigger than $\lambda_d$. It follows that $F^T(\beta) > \log \lambda_d$. This is the basic idea behind the proof of theorem 2.2. The vagueness of the word ‘typical’ in the above argument is offset in the actual proof by factors that decrease slowly in $n$, and as such are relatively harmless. The inequality $t_n \geq \lambda_n n^{-A}$ is not known rigorously in general (although this is believed to be the actual scaling form of $t_n$); fortunately, a mean-field bound proves the inequality rigorously for infinitely many values of $n$, which is sufficient for our needs.

3. Branched polymers: proofs

3.1. Branched polymers at an impenetrable boundary

Remark 3.1. Everything in this section holds if lattice trees are replaced by lattice animals.

For $\tau \in T_N^+$, we think of the set of sites $H(\tau)$ as the ‘left side of’ $\tau$. The set $H(\tau)$ is not empty because $\tau$ contains the origin. For $1 \leq k \leq N$, let

$$\text{left}_N(k) = \{ \tau \in T_N^+ : |H(\tau)| = k \}.$$ 

Then we can write (recalling equation (4))

$$|T_N^+| = \sum_{k=1}^{N} \text{left}_N(k) \quad \text{and} \quad Z_N^T(\beta) = \sum_{k=1}^{N} \text{left}_N(k) e^{\beta k}.$$ 

(17)

Proof of theorem 2.1. Fix $\beta$ such that $0 < \beta < \lambda_d^{-1}$. From equation (17) we have

$$Z_N^T(\beta) = \sum_{k=1}^{N} \sum_{j=0}^{\infty} \frac{\beta^j k^j}{j!} \text{left}_N(k).$$ 

(18)

For any $j \geq 0$ and $k \geq 1$, we have

$$\frac{k^j}{j!} \leq \binom{k+j-1}{j}.$$ 

(19)
The right hand side of inequality (19) is the number of ways to put $j$ identical balls into $k$ distinct boxes. More formally, it is the number of $k$-tuples $w_1, \ldots, w_k$ of nonnegative integers such that $w_1 + \cdots + w_k = j$.

We shall define a marked tree (with $N$ sites) to be a tree $\tau$ in $T_N^+$ that has a nonnegative integer $w(\tau; v)$ assigned to each site $v$ of $\mathcal{H}(\tau)$. (We think of $w(\tau; v)$ as the number of ‘marks’ on the site $v$ of $\tau$.) Let $T_N^{(j)}$ be the set of all marked trees $\tau$ with $N$ sites such that the total number of marks on the sites of $\tau$ is $j$ (that is, $\sum_{v \in \mathcal{H}(\tau)} w(\tau; v) = j$). See figure 1. Then

$$|T_N^{(j)}| = \sum_{k=1}^{N} \binom{k+j-1}{j} \left\lfloor \left( \frac{k}{j} \right) \right\rfloor_{\text{left}}(k). \quad (20)$$

Combining equations (18)–(20) shows that

$$Z^T_N(\beta) \leq \sum_{j=0}^{\infty} \beta^j |T_N^{(j)}|. \quad (21)$$

Now, consider an arbitrary marked tree $\tau \in T_N^{(j)}$. For every site $v$ in $\mathcal{H}(\tau)$, enlarge the tree by attaching a segment of length $w(\tau; v)$ from $v$ to $v - w(\tau; v)u(1)$. The result is a tree $f(\tau)$ in $T_{N+j}$ (with no marks). See figure 2.

The mapping $f : T_N^{(j)} \to T_{N+j}$ is clearly one-to-one (since $\tau = f(\tau) \cap \mathbb{L}^d$ and the marks are easily recovered from the segments of $f(\tau)$ outside of $\mathbb{L}^d$), and hence $|T_N^{(j)}| \leq |T_{N+j}| = (N+j)_{i=0}^N$. Combining this with equations (21) and (3) gives

$$Z^T_N(\beta) \leq \sum_{j=0}^{\infty} (N+j)_{i=0}^j \beta^j \lambda_d^{N+j} = \frac{N \lambda_d^N}{1 - \beta \lambda_d} + \frac{\lambda_d^N (\beta \lambda_d)}{(1 - \beta \lambda_d)^2} \leq \frac{N \lambda_d^N}{1 - \beta \lambda_d^2} \quad (22)$$

(the above series converge because $0 < \beta < \lambda_d^{-1}$). Equations (22) and (6) imply that $F^T(\beta) = \log \lambda_d$.

This proves that equation (7) extends to every $\beta < \lambda_d^{-1}$. The extension to $\beta = \lambda_d^{-1}$ holds by continuity of $F^T$ (see equation (2) and the comments below it).
3.2. Branched polymers at a penetrable boundary

**Proof of theorem 2.2.** A mean-field bound due to Bovier et al (1986) (see section 7.2 of Slade (2006) for a more detailed proof) says that there exists a constant $A$ such that

$$1 + \sum_{N=1}^{\infty} N^2 t_N e^N \geq \frac{A}{\sqrt{1 - \lambda_d^z}} \quad \text{for all } z \in [0, \lambda_d^{-1}).$$

(23)

In particular, the power series on the left diverges at $z = 1/\lambda_d$. It follows that

$$t_n \geq n^{-4} \lambda_d^N \quad \text{for infinitely many values of } n.$$  

(24)

Let $B_N$ be the set of trees in $T_N$ whose $x_1$-span is at most $N\log^2 N$. Observe that the left-hand side of equation (11) does not change if we replace $\Pr_{T_N}$ by $\Pr_{T_N}$. Thus equation (11) says that $|B_N| \geq t_n/N^k$. By equation (24), we obtain

$$|B_n| \geq n^{-(4+k)} \lambda_d^N \quad \text{for infinitely many values of } n.$$  

(25)

For every $N > 1$, let

$$T_N^* := \{ \tau \in T_N : 0 \text{ is the lexicographically smallest site of } \mathcal{H}(\tau) \}$$

(so that $T_N \subset T_N^*$), and

$$D_N := \{ \tau \in T_N^* : |h(\tau)| \geq \log^2 N \}.$$  

Observe that every tree in $T_N$ can be uniquely expressed as the translation of a tree in $T_N^*$ by a vector in the hyperplane $x_1 = 0$. Now, consider an arbitrary $\tau$ in $B_N$. There must be some integer $j \in [0, (N/\log^2 N) - 1]$ such that $\tau$ has at least $\log^2 N$ sites $x$ satisfying $x_1 = j$. Let $\tilde{x}$ be the lexicographically smallest site in $\{x \in \tau : x_1 = j\}$, and let $\tilde{\tau}$ be the translation of $\tau$ by the vector $-\tilde{x}$. Then $\tilde{\tau} \in D_N$. Observe that each $\tilde{\tau}$ uniquely determines $\tau$, since $B_N \subset T_N$ and no two trees in $T_N$ can be translations of one another. Therefore

$$|D_N| \geq |B_N|.$$  

(26)

Now fix $\beta > 0$. By equation (25), there exists an integer $n$ for which

$$|B_n| \exp(\beta \log^2 n) > \lambda_d^N.$$  

(27)
Fix this $n$ for the rest of the proof.

We can concatenate members of $D_n$ by translating them along vectors in the hyperplane $x_1 = 0$. Details are given in section 3.3 below. For any integer $k \geq 2$, we can concatenate any $k$ members of $D_n$ in this way to produce a member $\tau$ of $T_{kn}$ with $\mathcal{H}(\tau) \geq k \log^2 n$. Moreover, this map $(D_n)^k \to T_{kn}$ is injective (see section 3.3). Therefore, using equation (26), we have

$$
Z_{kn}^{TP}(\beta) \geq |D_n|^k \exp(\beta k \log^2 n) \\
\geq |B_n|^k \exp(\beta k \log^2 n) \quad (k = 1, 2, \ldots).
$$

(28)

Take the $(kn)$th root of equation (28) and let $k \to \infty$. Since the limit of the left-hand side exists, we obtain

$$
\exp(\mathcal{F}^{TP}(\beta)) \geq (|B_n| \exp(\beta \log^2 n))^{1/n},
$$

and the right hand side is strictly greater than $\lambda_d$ by equation (27). This proves that $\mathcal{F}^{TP}(\beta) > \log \lambda_d$. \hfill \Box

**Remark 3.2.** The analogue of equation (23) for lattice animals appears in section 1.3 of Hara and Slade (1990). Everything else in this section extends immediately to lattice animals.

### 3.3. Concatenation of lattice branched polymers

This section describes a concatenation procedure that preserves the number of sites in the surface $x_1 = 0$. We shall discuss trees, but the argument for animals is essentially the same.

Let $N$ and $M$ be positive integers. We shall describe an operation $\oplus$ such that, for every pair of trees $\tau \in \mathcal{T}_N$ and $\psi \in \mathcal{T}_M$, we obtain a tree $\tau \oplus \psi \in \mathcal{T}_{N+M}$ such that $|\mathcal{H}(\tau \oplus \psi)| = |\mathcal{H}(\tau)| + |\mathcal{H}(\psi)|$. Moreover, the operation $\oplus : \mathcal{T}_N \times \mathcal{T}_M \to \mathcal{T}_{N+M}$ is one-to-one.

Let $\tau \in \mathcal{T}_N$ and $\psi \in \mathcal{T}_M$. Let

$$
K = \max\{k \in \mathbb{Z} : (\psi + ku^{(2)}) \cap \tau \neq \emptyset\}.
$$

Since $\psi \cap \tau$ contains the origin, we see that $K \geq 0$. Let $v$ be a site in $(\psi + ku^{(2)}) \cap \tau$, and let $b$ be the edge from $v$ to $v + u^{(2)}$. Observe that $\psi + (K + 1)u^{(2)}$ contains $v + u^{(2)}$ but contains no point of $\tau$. Therefore $(\psi + (K + 1)u^{(2)}) \cup \tau \cup b$ is a tree, which we shall call $\theta$. We define $\tau \oplus \psi$ to be $\theta$. We shall now check that $\theta$ has the claimed properties of $\oplus$.

First observe that the construction ensures that we have

**Property 1.** $\mathcal{H}(\theta)$ is the disjoint union of $\mathcal{H}(\psi) + (K + 1)u^{(2)}$ and $\mathcal{H}(\tau)$.

It is clear that $\theta \in \mathcal{T}_{N+M}$. To show that $\theta \in \mathcal{T}_{N+M}$, we must show that 0 is the lexicographically smallest site of $\mathcal{H}(\theta)$. But this follows from property 1, the fact that 0 is the lexicographically smallest site of $\mathcal{H}(\tau)$ and of $\mathcal{H}(\psi)$, and our earlier observation that $K \geq 0$. The relation $|\mathcal{H}(\tau \oplus \psi)| = |\mathcal{H}(\tau)| + |\mathcal{H}(\psi)|$ also follows from property 1.

It remains to show that $\oplus$ is one-to-one, i.e. that we can recover $\tau$ and $\psi$ knowing $\theta$ (for given $N$ and $M$). To do this, we first observe that for the edge $b$ in our construction, the following property holds with $e = b$:

**Property 2.** Deleting the edge $e$ from $\theta$ creates two components, and the component containing the origin has exactly $N$ sites.
In general, there may be two or more edges $e$ of $\theta$ that satisfy property 2, so we need to decide which of them is $b$. Let $J = \max\{j \in \mathbb{Z} : j\mu^{(2)} \in \theta\}$. Since $(K + 1)\mu^{(2)} \in \theta$, we see that $J \geq K + 1$. Thus, whatever $\tau$ and $\psi$ are, we know that $0 \in \tau$ and $J\mu^{(2)} \not\in \tau$ (by the definition of $K$ and the fact that $J\mu^{(2)} \in \psi + J\mu^{(2)}$). Therefore the edge $b$ belongs to $\pi$, where $\pi$ is any path in $\theta$ from 0 to $Ju^{(2)}$. (When $\theta$ is a tree, there is only one such path.) Furthermore, it is not hard to see that at most one edge of $\pi$ can satisfy property 2. Therefore the edge $b$ is determined from $\theta$, and hence $\tau$ and $\psi$ are determined. This proves that $\oplus$ is one-to-one.

4. Linear polymers

4.1. Self-avoiding walks at an impenetrable boundary

Proof of theorem 2.4. Hammersley et al (1982b) proved that $F^{\beta}(W) = \log \mu_d$ for every $\beta \leq 0$, so we shall only consider positive $\beta$. The general idea of the proof is the same as for trees (theorem 2.1), but there is a technical difficulty when it comes to proving the analogue of $|T_N^{(1)}| \leq |T_{N+1}|$. To get around this, we introduce a slightly different model of adsorption, in which we weight a walk according the number of edges in the surface. For $\omega \in S_N$, define $H(\omega)$ to be the set of edges of $\omega$ that have both endpoints in $x_1 = 0$, and define $Z_N^{WW}(\beta) := \sum_{\omega \in S_N^w} \exp(\beta|H(\omega)|)$.

Then $|H(\omega)| \leq 2|H(\omega)|$ for every $\omega \in S_N$, and hence for every $\beta \geq 0$ we have

$$Z_N^{WW}(\beta) \leq Z_N^{WW}(2\beta).$$

(29)

We define a marked walk (with $N$ sites) to be a SAW $\omega$ in $S_N$ that has a nonnegative integer $m(\omega; b)$ assigned to each edge $b$ of $H(\omega)$. Let $S_N^{[j]}$ be the set of all marked walks $\omega$ with $N$ sites such that $\sum_{b \in H(\omega)} m(\omega; b) = j$. Then the same argument as in the proof of theorem 2.1 shows that

$$Z_N^{WW}(2\beta) \leq \sum_{j=0}^{\infty} (2\beta)^j |S_N^{[j]}|.$$

(30)

Now, fix a positive $\beta < \frac{1}{2}\mu_d^{-2}$. Choose $\epsilon > 0$ small enough so that $2\beta(\mu_d + \epsilon)^2 < 1$. Then there exists a constant $A$ such that

$$\sum_{n=0}^{M} \epsilon^n \leq A(\mu_d + \epsilon)^M \text{ for all } M \geq 0.$$

(31)

Consider an arbitrary marked walk $\omega$ in $S_N^{[j]}$. Let $E_1$ be the set of edges of $\omega$ that are not in $H(\omega)$. Let $E_2$ be the set of edges in $H(\omega)$ after each edge is translated in the $-x_1$ direction by a distance equal to the number of marks on that edge:

$$E_2 = \{b - m(\omega; b)\mu^{(1)} : b \in H(\omega)\}.$$

Let $f(\omega)$ be the shortest SAW starting at the origin that contains all edges of $E_1 \cup E_2$ and all of whose remaining edges are parallel to $\pm u^{(1)}$. Observe that $f(\omega)$ is obtained by adding at most
edges to $E_1 \cup E_2$. It is not hard to see that the function $f : S_N^{(i)} \to \bigcup_{n=N}^{N+2} S_N$ is one-to-one, so by equation (31)

$$|S_N^{(i)}| \leq A(\mu_d + \epsilon)^{N+2}.$$ 

From this and equation (30), and our choice of $\epsilon$, we obtain

$$Z_N^{W^+}(2,\beta) \leq \frac{A(\mu_d + \epsilon)^N}{1 - 2\beta(\mu_d + \epsilon)^2}.$$ 

Combining this with equation (29) proves that $\mathcal{F}^W(\beta) \leq \log(\mu_d + \epsilon)$. Since $\epsilon$ can be made arbitrarily small, and since $\mathcal{F}^W(\beta) \geq \mathcal{F}^W(0) = \log \mu_2$, we are done. \hfill \Box

4.2. Self-avoiding walks at a penetrable boundary

Proof of theorem 2.5. First observe that if $\omega \in S_N^B$, then $\omega(1) = (0, \ldots, 0, 1)$ and $|\omega_j(N)| \leq N - 1$.

It is known that the series $\sum_{n=1}^{\infty} b_n z^n$ diverges at $z = \mu_d^{-1}$ (Kesten (1963); or corollary 3.1.8 of Madras and Slade (1993)). Therefore we have

$$b_n \geq n^{-2} \mu_d^n \quad \text{for infinitely many values of } n. \quad (32)$$

For every $N > 1$, let

$$D_N := \{ \omega \in S_N^B : \text{Span}(\omega) \leq N/\log^2 N \}.$$ 

By the assumption (16), $|D_N|/b_N \geq N^{-3}$ for sufficiently large $N$. Therefore by (32),

$$|D_n| \geq n^{-(2+\delta)} \mu_d^n \quad \text{for infinitely many values of } n. \quad (33)$$

Fix $\beta > 0$. Fix a positive integer $n$ such that $\frac{\beta}{2} \log^2 n > \log(4n^{4+\delta})$ and the inequality of (33) holds. For integers $j$ and $m$ let

$$D_{n,j,m} := \{ \omega \in D_n : |i : \omega(i) = j| \geq \log^2 n, \omega(n) = m \}.$$ 

Since

$$D_n = \bigcup_{j=-\infty}^{n-1} \bigcup_{m=-\infty}^{n-1} D_{n,j,m}$$

and by symmetry, there exist integers $J \geq 0$ and $M$ such that $|D_{n,j,M}| \geq |D_n|/(2n - 1)^2$. By this and (33),

$$|D_{n,j,M}| \geq \frac{\mu_d^j}{4n^{2+\delta}}. \quad (34)$$

For two SAWs $\omega = (\omega(0), \ldots, \omega(N))$ and $\psi = (\psi(0), \ldots, \psi(M))$, we define the concatenation $\omega \oplus \psi$ to be the $(N + M)$-step walk $\theta$ defined by
\[ \theta(i) = \omega(i) \quad \text{for } i = 0, \ldots, N, \text{ and} \]
\[ \theta(N + j) = \omega(N) + \psi(j) - \psi(0) \quad \text{for } j = 1, \ldots, M. \]

In general, \( \theta \) need not be self-avoiding. However, if \( \omega \) and \( \psi \) are both bridges, then \( \theta \) is self-avoiding—indeed, \( \theta \) is a bridge. Thus \( \oplus \) defines a one-to-one map from \( S_N^B \times S_M^B \) into \( S_{N+M}^B \).

Suppose now that \( \omega \in D_{n,J,M} \) and \( \psi \in D_{n,-J,-M} \), and let \( \theta = \omega \oplus \psi \). Then \( \theta \) is a \((2n)\)-step bridge such that \( \theta((2n) = 0 \) and \( |\{i : \theta(i) = J\}| \geq \log^2 n \) (the inequality is due only to sites in the first half of \( \theta \)). We shall use these observations in the construction that follows.

For any positive integer \( k \), let \( \omega^{[1]} \ldots, \omega^{[k]} \) be bridges in \( D_{n,J,M} \) and let \( \psi^{[1]} \ldots, \psi^{[k]} \) be bridges in \( D_{n,-J,-M} \). Consider the bridge \( \pi \) obtained by repeated concatenation of these bridges:
\[ \pi := \omega^{[1]} \oplus \omega^{[2]} \oplus \cdots \oplus \omega^{[k]} \oplus \psi^{[1]} \oplus \psi^{[2]} \oplus \cdots \oplus \psi^{[k]}. \]

Then \( |\{i : \pi(i) = J\}| \geq k \log^2 n \). Next, let \( \xi \) be the \((J+1)\)-step bridge with \( \xi(0) = 0 \) and \( \xi(J+1) = \{-J, 0, \ldots, 0, 1\} \). For \( \zeta := \xi \oplus \pi \), we have \( \zeta \in S_{J+1+2kn}^B \) and \( |\mathcal{H}(\zeta)| \geq k \log^2 n \). Since \( \zeta \) unambiguously determines the \( \omega^{[i]} \)'s and \( \psi^{[i]} \)'s, it follows that
\[ |\{ \zeta \in S_{J+1+2kn}^B : |\mathcal{H}(\zeta)| \geq k \log^2 n \}| \geq (|D_{n,J,M}| \cdot |D_{n,-J,-M}|)^k = |D_{n,J,M}|^{2k} \quad \text{(by symmetry)}. \]

Using this and equation (34), we see that
\[ Z_{J+1+2kn}^{WP}(\beta) \geq \exp(\beta k \log^2 n) \frac{\mu_d^{2kn}}{(4n^{a+\beta})^{2k}}. \]

Therefore
\[ \log Z_{J+1+2kn}^{WP}(\beta) \geq \frac{\beta k \log^2 n - 2k \log(4n^{a+\beta}) + 2kn \log \mu_d}{J + 1 + 2kn}. \]

Now let \( k \to \infty \), and we obtain
\[ Z^{WP}(\beta) \geq \frac{1}{n} \left( \frac{\beta \log^2 n}{2} + \log \mu_d \right) + \log \mu_d \]
where the strict inequality follows from our choice of \( n \). This proves the result. \( \square \)

5. Discussion

We have considered polymer adsorption at both an impenetrable and a penetrable surface, using the standard lattice models of trees, animals, and self-avoiding walks.

In the impenetrable case, we presented a new proof that the adsorption transition occurs at a strictly positive value of the interaction parameter \( \beta \). In contrast to the known proofs of this result, our method does not rely on showing that the critical values for the impenetrable and the penetrable cases are different. Our method, based on the power series expansion of the exponential, is also considerably shorter.
In the penetrable case, the longstanding conjecture that the critical value of $\beta$ is 0 remains open, but we do prove that it would be a rigorous consequence of knowing that the fraction of $N$-site polymers whose span is less than $N/\log^2 N$ is at least $N^{-1000}$. It is widely believed, but not proven, that the average span of an $N$-site polymer scales as $N^\nu$, where $\nu$ is a critical exponent less than 1 (indeed, $\nu$ should be the same critical exponent as for radius of gyration). If this could be rigorously proved, then the condition in our theorem would follow immediately.

So we still have a gap in our knowledge, but it now seems to be beyond reasonable doubt that the critical value is 0 in the penetrable case. Although we don’t yet know how to prove the condition in our theorem rigorously, the fact that it is so much weaker than knowing the actual scaling behaviour creates the hope that a proof could soon be found.

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