

The pressure exerted by adsorbing directed lattice paths and staircase polygons

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Abstract

A directed path in the vicinity of a hard wall exerts pressure on the wall because of loss of entropy. The pressure at a particular point may be estimated by estimating the loss of entropy if the point is excluded from the path. In this paper we determine asymptotic expressions for the pressure on the X -axis in models of adsorbing directed paths in the first quadrant. Our models show that the pressure vanishes in the limit of long paths in the desorbed phase, but there is a non-zero pressure in the adsorbed phase. We determine asymptotic approximations of the pressure for finite length Dyck paths and directed paths, as well as for a model of adsorbing staircase polygons with both ends grafted to the X -axis.

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

1. Introduction

A linear polymer attached to a hard wall by an endpoint loses entropy due to the presence of the wall. The loss of entropy induces a repulsive force on the wall. Such forces have been measured experimentally [1, 3, 4] and decay with distance from the point where the polymer is attached.

A simple model of the above is a directed path from the origin in the first quadrant of the square lattice. More precisely, let d_n^+ be the number of directed paths from the origin given North–East and South–East steps in the half square lattice $\mathbb{Z}_+^2 = \{(n, m) \in \mathbb{Z}^2 | m \geq 0\}$. Since the path loses entropy due to the boundary of \mathbb{Z}_+^2 (the X -axis) there is a net pressure on the X -axis (which we shall also call a *hard wall*).

The entropy of the paths is given by $S_n^+ = k_B \log d_n^+$, where k_B is Boltzmann's constant. The pressure at a point $x = (N, 0)$ in the hard wall may be computed by calculating the reduction in entropy if paths passing through this point are excluded from the ensemble.

Let the number of paths avoiding the point x be denoted by $d_n^+(x)$. Then the loss of entropy is given by

$$\Delta S_n^+(x) = k_B \log d_n^+(x) - k_B \log d_n^+. \tag{1}$$

In this case the change in free energy of the model is also given by $\Delta \mathcal{F}_n(T) = -T \Delta S_n^+(x)$ at temperature T . Hence the pressure of the path on the wall can be estimated by computing the change in extensive free energy if the point x is excluded and thereby changing the volume by ΔV_x .

That is, the pressure on the point x is given by the discrete derivative of $\mathcal{F}_n(T)$ to the volume element containing x :

$$P_n(x) = -\frac{\Delta \mathcal{F}_n(T)}{\Delta V_x} = \frac{k_B T \Delta S_n^+(x)}{\Delta V_x}. \tag{2}$$

In two dimensions, ΔV_x will be an area element containing the point x .

Adopt units $k_B T = 1$ and $\Delta V_x = 1$ to see that the pressure at the point x in this model is given by

$$P_n(x) = \log d_n^+(x) - \log d_n^+. \tag{3}$$

In other words, the pressure at x is the discrete derivative of the extensive free energy with respect to a unit change in volume at the point x in reduced units.

Observe that we use the convention that $P_n(x)$ is negative.

More generally, the paths may be interacting with the hard wall by adsorbing in it, or may be interacting in some other way. In this case the above is a directed model of a polymer adsorbing in the hard wall, and $P_n(x)$ is the pressure due to presence of the hard wall.

If $k_B T = 1$ as above, then the interaction strength of the path with the wall is given by an activity z , and the partition function $Z_n^+(z)$ of the model gives the extensive free energy $\mathcal{F}_n(z) = \log Z_n^+(z)$. The pressure at a point x in the hard wall is then obtained as above, and is given by

$$P_n(x) = \log Z_n^+(z; x) - \log Z_n^+(z) \tag{4}$$

where $Z_n^+(z; x)$ is the partition function of the ensemble of paths which avoids the point x is excluded from the ensemble.

The above approach was used for a square lattice self-avoiding walk model of linear polymers grafted to a hard wall [7]. In this exact enumeration study the data show that pressure decreases with distance from the origin.

In this paper our intension is to add to these self-avoiding walk results by examining a directed version of this model. We shall in particular look at the asymptotic behaviour of the pressure as function of the length of the directed walk and the location of pressure point x . We shall also extend our results to include adsorbing directed paths, as well as a model of an adsorbing staircase polygon.

1.1. The pressure due to directed paths

The number of directed paths of n steps from the origin in the square lattice \mathbb{Z}^2 is $P_n = 2^n$. If the path is restricted to the half lattice \mathbb{Z}_+^2 , then it is a *positive path*, and if it is further constrained by having to end in the X -axis (which is the hard wall), then it is a *Dyck path* [8]. Examples are illustrated in figures 1(a) and (b).

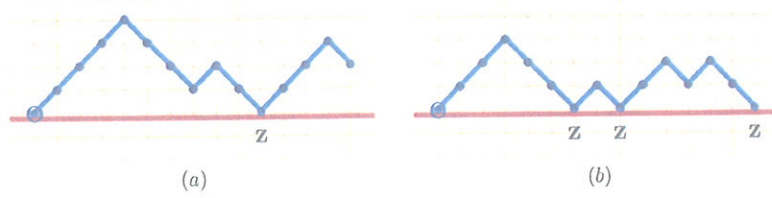


Figure 1. Two models of an adsorbing polymer grafted to a hard wall. (a) A directed path from the origin in \mathbb{Z}_+^2 . The path interacts with the X -axis with an activity $z > 0$. If $z > 1$ then the path is attracted to the X -axis, if $z < 1$ it is repelled. The path exerts a force on vertices of the X -axis. (b) This model is similar to (a), but both endpoints of the path are constrained to lie in the X -axis. This is a model of adsorbing Dyck paths. Observe that we use the convention that the vertex at the origin is not weighted by z .

The number of positive paths of length n is given by

$$T_{2n} = \binom{2n}{n} \quad \text{and} \quad T_{2n+1} = \binom{2n+1}{n+1}, \tag{5}$$

and the number of Dyck paths of length $2n$ is given by

$$D_{2n} = \frac{1}{n+1} \binom{2n}{n}. \tag{6}$$

From these expressions one may determine that the number of Dyck paths passing through the point x with coordinates $x = (2N, 0)$. This is given by

$$D_{2N} \cdot D_{2n-2N} = \frac{1}{(N+1)(n-N+1)} \binom{2N}{N} \binom{2(n-N)}{n-N}. \tag{7}$$

Thence, one may determine the pressure on the hard wall at the point x from equation (3) to be

$$P_{2n}^D(2N) = \log(D_{2n} - D_{2N} \cdot D_{2n-2N}) - \log D_{2n} = \log \left(1 - \frac{D_{2N} \cdot D_{2n-2N}}{D_{2n}} \right). \tag{8}$$

Putting $N = \lfloor an \rfloor$ for some $a \in (0, 1)$ and expanding asymptotically in n gives

$$P_{2n}^D(2 \lfloor an \rfloor) = -\frac{1}{\sqrt{\pi n^3 a^3 (1-a)^3}} + O(n^{-5/2}). \tag{9}$$

Observe that $P_{2n}^D(2 \lfloor an \rfloor) = O(n^{-3/2})$ and that if pressure is rescaled by $n^{3/2}$, then one obtains

$$p^D(a) = \lim_{n \rightarrow \infty} (n^{3/2} P_{2n}^D(2 \lfloor an \rfloor)) = -\frac{1}{\sqrt{\pi a^3 (1-a)^3}}, \tag{10}$$

as a residual rescaled pressure in the scaling limit.

A similar calculation may be done with positive paths. In this case the pressure on the point $(2N, 0)$ is given by

$$P_{2n}^T(2N) = \log(T_{2n} - D_{2N} \cdot T_{2n-2N}) - \log T_{2n} = \log \left(1 - \frac{D_{2N} \cdot T_{2n-2N}}{T_{2n}} \right). \tag{11}$$

Expanding asymptotically, and keeping the leading order term gives

$$P_{2n}^T(2an) = -\frac{1}{\sqrt{\pi n^3 a^3 (1-a)^3}} + O(n^{-5/2}) \tag{12}$$

for pressure of positive paths of length $2n$ at a distance $2N = 2 \lfloor an \rfloor$ from the origin.

Observe that $P_{2n}^T(2\lfloor an \rfloor) = O(n^{-3/2})$ (as was seen for Dyck paths) and again rescaling the pressure by $n^{3/2}$ one obtains

$$p^T(a) = \lim_{n \rightarrow \infty} (n^{3/2} P_{2n}^T(2\lfloor an \rfloor)) = -\frac{1}{\sqrt{\pi a^3(1-a)}}, \tag{13}$$

as the residual rescaled pressure in the scaling limit.

We shall generalize the results in equations (9) and (12) to models of adsorbing Dyck paths, adsorbing directed paths, and a model of adsorbing staircase polygons grafted to the X -axis. While we extract the infinite n behaviour in each model, we will mostly be concerned with finite n behaviour, which we shall approximate by asymptotic expressions.

1.2. Adsorbing paths and staircase polygons

A directed path with steps $(1, -1)$ and $(1, 1)$ from the origin in the half lattice \mathbb{Z}_+^2 is illustrated in figure 1(a). Vertices of the path in the *adsorbing line* $Y = 0$ are called *visits*, and they are weighted with the generating variable z (which is related to temperature by $z = e^{1/k_B T}$ in lattice units). By convention, the origin, although itself a visit, is not weighted. A directed path with weighted visits is an *adsorbing directed path*.

If the directed path is constrained to end in the adsorbing line, then it is a Dyck path (see figure 1(b)). A Dyck path with weighted visits is an *adsorbing Dyck path* [2, 10].

The model in figure 1(b) is that of an adsorbing Dyck path [2]. If the partition function of this model is denoted by $D_n(z)$, then the generating function of the model may be evaluated:

$$g(t, z) = \sum_{n=0}^{\infty} D_n(z) t^n = \frac{2}{2 - z(1 - \sqrt{1 - 4t^2})}, \tag{14}$$

where the generating variable t is conjugate the length n (the number of steps in the path). The *intensive* limiting free energy of the model is defined by

$$\mathcal{F}_D(z) = \lim_{n \rightarrow \infty} \frac{1}{n} \log D_n(z) \tag{15}$$

and by comparison to $g(t, z)$ it follows that $\mathcal{F}_D(z) = -\log t_c(z)$, where $t_c(z)$ is the radius of convergence of $g(t, z)$. One may explicitly compute this from the above:

$$\mathcal{F}_D(z) = \begin{cases} \log 2, & \text{if } z \leq 2; \\ \log z - \frac{1}{2} \log(z - 1), & \text{if } z > 2. \end{cases} \tag{16}$$

In other words, $\mathcal{F}_D(z)$ is non-analytic at $z_c^+ = 2$. For $z < 2$ the density of visits (given by $\mathcal{E}(z) = z \frac{d}{dz} \mathcal{F}_D(z)$) is zero—this is the *desorbed phase*. For $z > 2$ this is $\mathcal{E}(z) = \frac{z-2}{2(z-1)} > 0$ and the model is said to be in an *adsorbed phase* since the density of visits to the hard wall is positive.

Similar calculations can be done for the model in figure 1(a), and the critical point is also at $z_c^+ = 2$ with a desorbed phase for $z < 2$ and an adsorbed phase for $z > 2$.

The partition functions of adsorbing directed and Dyck paths are known to be given by

$$T_n(z) = \sum_{m=0}^{\lfloor n/2 \rfloor} \binom{n}{\lfloor n/2 \rfloor + m} (z - 1)^m \tag{17}$$

for adsorbing directed paths, and

$$D_n(z) = \sum_{m=0}^{\lfloor n/2 \rfloor} \frac{4m + 2}{n + 2(m + 1)} \binom{n}{\lfloor n/2 \rfloor + m} (z - 1)^m \tag{18}$$

for Dyck paths, see for example [2, 6].

The *extensive* free energies of these models are defined by

$$\mathcal{F}_n^T(z) = \log T_n(z), \quad \text{and} \quad \mathcal{F}_n^D(z) = \log D_n(z). \quad (19)$$

If $(q, 0)$ is a vertex in the adsorbing line $Y = 0$, then define, similar to the above, the free energies of paths which avoids $(q, 0)$, and denote these by $\mathcal{F}_n^T(z; q)$ and $\mathcal{F}_n^D(z; q)$.

By equation (3) the pressure on the vertex $(q, 0)$ is given by the free energy differences

$$P_n^T(z; q) = \mathcal{F}_n^T(z; q) - \mathcal{F}_n^T(z) \quad \text{and} \quad P_n^D(z; q) = \mathcal{F}_n^D(z; q) - \mathcal{F}_n^D(z) \quad (20)$$

in each model. Observe that $P_n^T(z; q) = P_n^D(z; q) = 0$ if q is odd, so that a non-zero force can be obtained only for even values of q .

For both models we shall show that for $a \in (0, 1)$,

$$\lim_{n \rightarrow \infty} P_n^T(z; 2\lfloor an/2 \rfloor) = \lim_{n \rightarrow \infty} P_n^D(z; 2\lfloor an/2 \rfloor) = \begin{cases} 0, & \text{if } z \leq 2; \\ -\log(z-1), & \text{if } z > 2. \end{cases} \quad (21)$$

For finite values of n , we determine asymptotic approximations for $P_n^T(z; 2\lfloor an/2 \rfloor)$ and $P_n^D(z; 2\lfloor an/2 \rfloor)$ (for n even). These are given by

$$P_n^T(z; 2\lfloor an/2 \rfloor) \simeq \begin{cases} \frac{8}{\sqrt{2\pi n^3 a^3 (1-a)} \log^2(z-1)}, & \text{if } z < 2; \\ \frac{\sqrt{2}}{\sqrt{\pi n a}}, & \text{if } z = 2; \\ -\log(z-1) - \frac{A_T}{12na(1-a)(z-1)(z-2)}, & \text{if } z > 2; \end{cases} \quad (22)$$

where

$$A_T = (a^2 - a + 1)(z^4 + 8z^3 + 30z^2 - 32z + 16) - 6a^2 z^2,$$

for the model of directed paths. In the case of adsorbing Dyck paths,

$$P_n^D(z; 2\lfloor an/2 \rfloor) \simeq \begin{cases} \frac{8}{\sqrt{2\pi n^3 a^3 (1-a)^3} \log^2(z-1)}, & \text{if } z < 2; \\ \frac{\sqrt{2}}{\sqrt{\pi n a (1-a)}}, & \text{if } z = 2; \\ -\log(z-1) - \frac{A_D}{12na(1-a)(z-1)(z-2)}, & \text{if } z > 2; \end{cases} \quad (23)$$

for even values of n , where

$$A_D = (a^2 - a + 1)(z^4 + 8z^3 + 30z^2 - 32z + 16).$$

From these results one can easily extract the residual rescaled pressures similar to equations (10) and (13). However, notice the different scaling in n in the different regimes: In the desorbed phase the pressure is of order $O(n^{-3/2})$, at the critical adsorption point $O(n^{-1/2})$ and in the adsorbed phase $-\log(z-1) + O(n^{-1})$.

In the case of a model of adsorbing staircase polygons with both endpoints grafted to the adsorbing line (figure 7(a)), a similar asymptotic analysis gives the following expressions for the pressure:

$$P_n^S(z; 2\lfloor an/2 \rfloor) \simeq \begin{cases} \frac{5z}{2n^{3/2} (2-z)^2 \sqrt{\pi a^3 (1-a)^3}}, & \text{if } z < 2; \\ \frac{2\sqrt{\pi n a (1-a)}}{3(4z^2 - 29z + 16)} \left(1 + \frac{9z}{8n(z-2)^2} \right), & \text{if } z = 2; \\ \frac{-\log(z-1) - \frac{3z^2}{8n(z-2)}}{2\sqrt{\pi n^3 a^3 (1-a)^3 (z-1)^2 (z-2)} |\log(z-1)|}, & \text{if } z > 2. \end{cases} \quad (24)$$

From these expressions one similarly obtains that there are different scalings in the different regimes: In the desorbed phase the pressure is of order $O(n^{-3/2})$, at the critical adsorption point $O(n^{-1/2})$ and in the adsorbed phase $-\log(z-1) + O(n^{-1})$.

2. The forces exerted by adsorbing directed paths in a half-space

The partition function of adsorbing directed paths which pass through the vertex $(q, 0)$ is given by $D_q(z) T_{n-q}(z)$ (by equations (17) and (18)). Thus the partition function of paths avoiding the vertex $(q, 0)$ is $T_n(q) - D_q(z) T_{n-q}(z)$. Substitution into equation (20) and simplifying gives

$$P_n^T(z; q) = \log \left(1 - \frac{D_q(z) T_{n-q}(z)}{T_n(z)} \right). \tag{25}$$

Observe that $P_n^T(z; q)$ is negative, since the pressure is directed onto the vertex $(q, 0)$ from above (and in the negative direction).

A similar argument shows that

$$P_n^D(z; q) = \log \left(1 - \frac{D_q(z) D_{n-q}(z)}{D_n(z)} \right) \tag{26}$$

in the case of adsorbing Dyck paths.

A result in [2] shows that for $z > 0$ the partition function $D_n(z)$ may be expressed in as

$$D_{2n}(z) = \frac{z-2}{z-1} \left(\frac{z^2}{z-1} \right)^n \theta(z-2) + \frac{1}{z} \sum_{s=n}^{\infty} C_s \left(\frac{z-1}{z^2} \right)^{s-n} \tag{27}$$

where the $C_s = \frac{1}{s+1} \binom{2s}{s}$ are Catalan numbers and θ is the Heaviside step function. The summation can be bound as follows: $C_s \leq 4^s$ and thus

$$\sum_{s=n}^{\infty} C_s \left(\frac{z-1}{z^2} \right)^{s-n} \leq 4^n \sum_{s=n}^{\infty} 4^{s-n} \left(\frac{z-1}{z^2} \right)^{s-n} = \frac{4^n z^2}{(z-2)^2}. \tag{28}$$

This shows that for $z \geq 2$

$$\frac{z-2}{z-1} \left(\frac{z^2}{z-1} \right)^n \leq D_{2n}(z) \leq \frac{z-2}{z-1} \left(\frac{z^2}{z-1} \right)^n \left(1 + \frac{z(z-1)}{(z-2)^3} \left(\frac{4(z-1)}{z^2} \right)^n \right). \tag{29}$$

Since $4 < z^2/(z-1)$ if $z > 2$, the above proves that

$$D_n(z) = \frac{z-2}{z-1} \left(\frac{z}{\sqrt{z-1}} \right)^n (1 + o(1)), \quad \text{if } z > 2. \tag{30}$$

The result in equation (30) can be substituted into equation (26) to give the following lemma:

Lemma 1. *The limiting force on the adsorbing line by a Dyck path if $z > 2$ is*

$$\lim_{n \rightarrow \infty} P_n^D(z; 2 \lfloor an/2 \rfloor) = -\log(z-1),$$

for any $a \in (0, 1)$, where the limit is taken through even values of n .

A similar argument may be made for directed paths, using the following representation for the partition function

$$T_{2n}(z) = \left(\frac{z^2}{z-1} \right)^n \theta(z-2) + \frac{1}{z^2} \sum_{s=n}^{\infty} C_s (1-s(z-2)) \left(\frac{z-1}{z^2} \right)^{s-n} \tag{31}$$

from [2]. This shows that

$$T_n(z) = \left(\frac{z}{\sqrt{z-1}} \right)^n (1 + o(1)), \quad \text{if } z > 2. \tag{32}$$

Substitution of equations (30) and (32) into equation (25) shows that

Lemma 2. The limiting force on the adsorbing line by a directed path if $z > 2$ is

$$\lim_{n \rightarrow \infty} P_n^D(z; 2 \lfloor an/2 \rfloor) = -\log(z - 1),$$

for any $a \in (0, 1)$.

Lemmas 1 and 2 show that the limiting force in the regime $z > 2$ is $-\log(z - 1)$ in both models. Observe that this force approaches zero as $z \rightarrow 2^+$. By equation (20) the force cannot be positive, and thence $\lim_{n \rightarrow \infty} P_n^D(z; 2 \lfloor an/2 \rfloor) = \lim_{n \rightarrow \infty} P_n^I(z; 2 \lfloor an/2 \rfloor) = 0$ if $z \in (0, 2]$.

2.1. Approximating the pressure

The partition functions $T_n(z)$ and $D_n(z)$ will be approximated by using the Stirling approximation for the factorial

$$n! = \sqrt{2\pi} n^{n+1/2} e^{-n} \left(1 + \frac{1}{12n} + O\left(\frac{1}{n^2}\right) \right) \quad (33)$$

to approximate the binomial coefficients. The summations will be approximated by an integral which itself will be estimated using a saddle point method.

Substitute the Stirling approximation in the summands of equations (17) and (18), take logarithms and simplify the results. This gives

$$1 + \log \left(\frac{(z-1)^m 2^{n+1} \sqrt{2} n^m \sqrt{n} (n-2m)^{m-1/2} (2m+1)}{\sqrt{\pi} (n+2m+2)^{m+3/2+1/2n} \sqrt{n-2m}} \right). \quad (34)$$

Fixing n , there is an $m = \lfloor \delta n \rfloor$ which maximizes the above (for $\delta \in [0, 1/2]$). The parameter δ is determined by an asymptotic expansion in $1/n$: Put $n = 1/\epsilon$, $m = \delta/\epsilon$ in the summand, expand the result in ϵ to leading order and simplify. This gives

$$\log \left(\frac{2}{\epsilon} \left(\frac{1-2\delta}{\epsilon} \right)^{(2\delta-1)/2} \left(\frac{1+2\delta}{\epsilon} \right)^{-(2\delta+1)/2} (z-1)^\delta \right). \quad (35)$$

Take the derivative with respect to δ and solve for δ to find the saddle point at

$$\delta = \max \left\{ \frac{z-2}{2z}, 0 \right\}, \quad (36)$$

where we note that δ cannot be negative.

A similar approach in the case of $T_n(z)$ gives exactly the same result for the location of the saddle point, as expected.

2.2. Case 1: $1 < z < 2$

The general approach is to approximate the summations in equation (17) and (18) by integrals

$$T_n(z) \simeq \int_0^{\lfloor n/2 \rfloor} \binom{n}{\lfloor n/2 \rfloor + m} (z-1)^m dm \quad (37)$$

for adsorbing directed paths, and

$$D_n(z) \simeq \int_{m=0}^{\lfloor n/2 \rfloor} \frac{4m+2}{n+2(m+1)} \binom{n}{\lfloor n/2 \rfloor + m} (z-1)^m dm \quad (38)$$

for adsorbing Dyck paths (and where the binomial coefficients are generalized to continuous values of m by replacing factorials by Gamma functions).

For asymptotic values of n , the integrals above are dominated by values of m close to the saddle points which are located close to $m = 0$ by equation (36) and which have a spread of \sqrt{n} above $m = 0$.

The approximation of $T_n(z)$ and $D_n(z)$ are achieved by substituting $n = 1/\epsilon^2$ and $m = \alpha/\epsilon = \alpha\sqrt{n}$ in the summands above. Expand the results in ϵ , and simplify.

In the case of $T_n(z)$, the above prescription results in

$$T_n(z) \simeq \frac{2^{3+1/\epsilon^2} \epsilon}{\sqrt{2\pi}} \int_0^\infty (z-1)^{\alpha/\epsilon} e^{-2\alpha^2} \alpha \, d\alpha. \tag{39}$$

Evaluating the integral gives

$$T_n(z) \simeq 2^{n-1} e^{(n \log^2(z-1))/8} (1 + \operatorname{erf}(\sqrt{2n} |\log(z-1)|/4)). \tag{40}$$

An asymptotic expansion of this in n and keeping only leading order terms gives

$$T_n(z) \simeq \frac{2^{n+1}}{\sqrt{\pi n} |\log(z-1)|}. \tag{41}$$

The same procedure may be applied to $D_n(z)$: this shows that

$$D_n(z) \simeq \frac{2^{1+1/\epsilon^2}}{\sqrt{2\pi}} \int_0^\infty (z-1)^{\alpha/\epsilon} e^{-2\alpha^2} \, d\alpha. \tag{42}$$

Evaluating the integral produces

$$D_n(z) \simeq 2^{n+1/2} \left(\frac{1}{\sqrt{\pi n}} + |\log(z-1)| e^{n \log^2(z-1)/8} (1 + \operatorname{erf}(\sqrt{2n} |\log(z-1)|/4)) \right).$$

Expanding this asymptotic in n and simplifying gives

$$D_n(z) \simeq \frac{2^{n+3}}{\sqrt{2\pi n^3} \log^2(z-1)}. \tag{43}$$

The above results produces the following approximations for the pressures:

$$P_n^T(z; 2 \lfloor an/2 \rfloor) \simeq \log \left(1 - \frac{8}{\sqrt{2\pi n^3} a^3 (1-a) \log^2(z-1)} \right) \tag{44}$$

for directed paths, and

$$P_n^D(z; 2 \lfloor an/2 \rfloor) \simeq \log \left(1 - \frac{8}{\sqrt{2\pi n^3} a^3 (1-a)^3 \log^2(z-1)} \right) \tag{45}$$

for Dyck paths. For large values of n the logarithms may be expanded, and the results should be compared to equations (9) and (12) for $z = 1$.

In figure 2 the approximation for $P_n^T(z; 2 \lfloor an/2 \rfloor)$ (solid curve) is compared with the exact values (dotted curve) for $n = 128$ and $z = 3/2$. Observe that as $n \rightarrow \infty$, then $P_n^T(z; 2 \lfloor an/2 \rfloor)$ approaches zero.

Expanding the expression for the pressures asymptotically in n gives the expressions for $z < 2$ in equations (22) and (23).

2.3. Case 2: $z = 2$

The partition functions evaluate exactly in terms of factorials and Gamma functions if $z = 2$:

$$T_n(2) = 2^{n-1} \left(\frac{\Gamma(\frac{n+1}{2})}{\sqrt{\pi} \Gamma(\frac{n+2}{2})} + 1 \right), \quad \text{and} \quad D_n(2) = \frac{n!}{(n/2)!(n/2)!}. \tag{46}$$

Substituting these expressions into equations (25) and (26) gives exact expressions for the pressure, which we do not reproduce here. Observe that as $n \rightarrow \infty$, then it follows from the above that $\lim_{n \rightarrow \infty} P_n^D(2; 2 \lfloor an/2 \rfloor) = \lim_{n \rightarrow \infty} P_n^T(2; 2 \lfloor an/2 \rfloor) = 0$. The exact pressure $P_n^T(2; 2 \lfloor an/2 \rfloor)$ is plotted for $n = 128$ in figure 4.

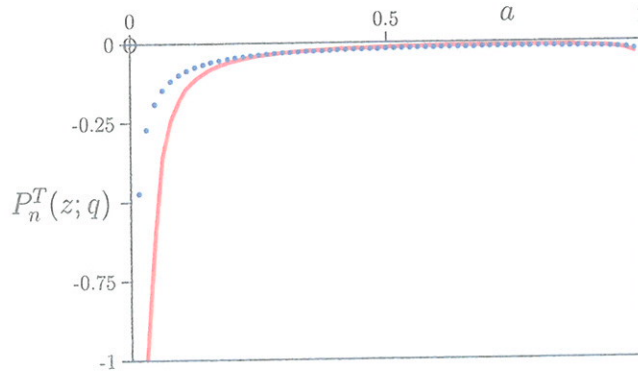


Figure 2. The pressure $P_n^T(z; q)$ for directed paths in \mathbb{Z}_+^2 for $n = 128$, $z = 3/2$ and $q = 2 \lfloor an/2 \rfloor$, plotted as a function of a . The magnitude of the pressure is large close to the origin and decays with increasing a towards the free endpoint of the path. The curve is the asymptotic expression for $P_n^T(z; q)$ as in equation (44). The dotted curve is the exact computed pressure, as determined from the partition functions in equations (17) and (18).

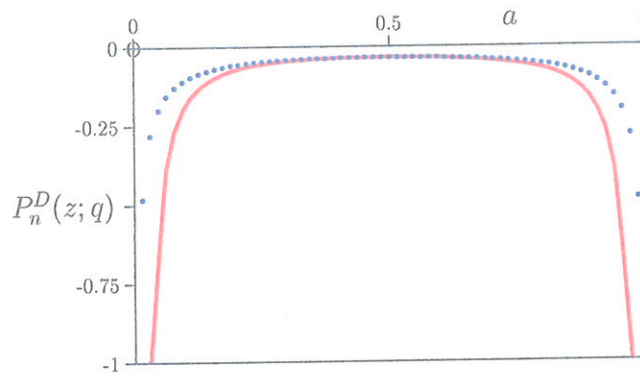


Figure 3. The pressure $P_n^D(z; q)$ for Dyck paths for $n = 128$, $z = 3/2$ and $q = 2 \lfloor an/2 \rfloor$, plotted as a function of a . The magnitude of the pressure is large close to the endpoints of the path, but is smaller for values of a towards the middle region of the path. The curve is the asymptotic expression for $P_n^D(z; q)$ as in equation (45). The dotted curve is the exact computed pressure, as determined from the partition functions in equation (18).

Asymptotic expressions for the pressure can be determined by using Stirling's approximation in equations (46). Substitution and simplification gives

$$P_n^T(2; 2 \lfloor an/2 \rfloor) = \log \left(1 - \frac{2}{\sqrt{2\pi na}} + \frac{2(1-a-\sqrt{1-a})}{\pi n \sqrt{a}(1-a)} + O(n^{-3/2}) \right), \quad (47)$$

$$P_n^D(2; 2 \lfloor an/2 \rfloor) = \log \left(1 - \frac{2}{\sqrt{2\pi na(1-a)}} + O(n^{-3/2}) \right) \quad (48)$$

for the pressure in these models. Expanding the pressures asymptotically in n gives the results for $z = 2$ in equations (22) and (23).

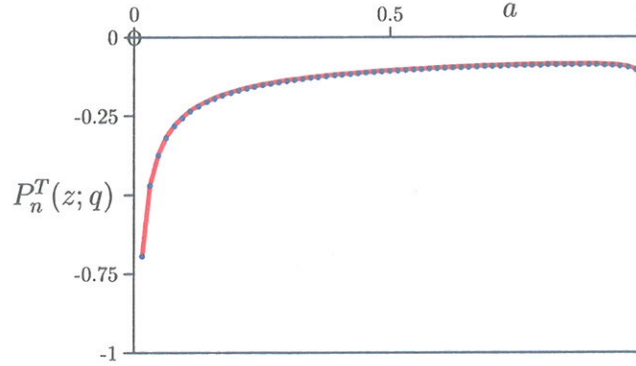


Figure 4. The pressure $P_n^T(z; q)$ for directed paths in \mathbb{Z}_+^2 for $n = 128$, $z = 2$ and $q = 2\lfloor an/2 \rfloor$, plotted as a function of a . The pressure is large close to the origin and decays with increasing a towards the free endpoint of the path. The curve and dotted points are determined from the exact expressions for the pressure, which is obtained from equations (17) and (18) on the one hand, and equation (46) on the other hand.

2.4. Case 3: $z > 2$

Asymptotic expressions in this regime are obtained by exploring the saddle point in the summands of $D_n(z)$ and $T_n(z)$. This saddle point is located at δn in the asymptotic regime (where δ is given by $(z - 2)/2z$ in equation (36)).

The width of the saddle is proportional to \sqrt{n} . Hence, use the Stirling approximation in the summands, put $m = \left(\frac{z-2}{2z}\right)n + \alpha\sqrt{n}$ and $n = 1/\epsilon^2$, expand in ϵ to $O(1)$, and simplify. This gives the saddle point approximations

$$T_n(z) \simeq \frac{\epsilon\sqrt{n}}{\sqrt{2\pi}} \left(\frac{z}{\sqrt{z-1}}\right)^{\frac{\epsilon^2+1}{\epsilon^2}} \int_{-\infty}^{\infty} e^{-\frac{\alpha^2 z}{2(z-1)}} d\alpha \tag{49}$$

and

$$D_n(z) \simeq \frac{\epsilon\sqrt{n}}{\sqrt{2\pi}} \left(\frac{z-2}{z-1}\right) \left(\frac{z}{\sqrt{z-1}}\right)^{\frac{\epsilon^2+1}{\epsilon^2}} \int_{-\infty}^{\infty} e^{-\frac{\alpha^2 z}{2(z-1)}} d\alpha. \tag{50}$$

Integrating α over $(-\infty, \infty)$ gives the saddle point approximations

$$T_n(z) \simeq \left(\frac{z}{\sqrt{z-1}}\right)^n, \quad \text{and} \quad D_n(z) \simeq \frac{z-2}{z-1} \left(\frac{z}{\sqrt{z-1}}\right)^n. \tag{51}$$

These results are not unexpected, since substitution and simplification into equations (25) and (26) give the results in lemmas 1 and 2.

This also shows that the expansion to $O(1)$ in ϵ does not produce expressions which give corrections for finite n effects.

Finite n corrections to the pressures are obtained by improving the saddle point approximations above. Expanding to $O(\epsilon)$ instead gives the approximations

$$T_n(z) \simeq \frac{\epsilon\sqrt{n}}{\sqrt{2\pi}} \left(\frac{z}{\sqrt{z-1}}\right)^{\frac{\epsilon^2+1}{\epsilon^2}} \int_{-\infty}^{\infty} e^{-\frac{\alpha^2 z}{2(z-1)} - A_T \epsilon} d\alpha \tag{52}$$

where

$$A_T = \frac{(\alpha^2 z^4 - (4\alpha^2 - 3)z^3 + (4\alpha^2 + 9)z^2 - 18z + 12) \alpha z}{6(z-1)^2(z-2)}$$

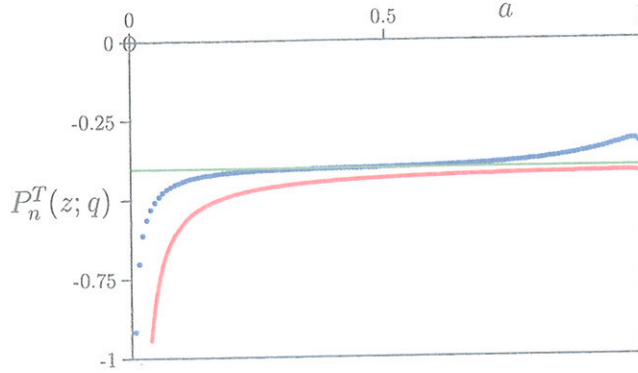


Figure 5. The pressure $P_n^T(z; q)$ for directed paths in \mathbb{Z}_+^2 for $n = 256$, $z = 5/2$ and $q = 2 \lfloor an/2 \rfloor$, plotted as a function of a . The pressure is large close to the origin and decays with increasing a towards the free endpoint of the path. The curve is determined using the asymptotic expressions in equations (54) and (55). The dotted curve is the exact pressure (determined from equations (17) and (18)).

and

$$D_n(z) \simeq \frac{\epsilon \sqrt{n}}{\sqrt{2\pi}} \left(\frac{z-2}{z-1} \right) \left(\frac{z}{\sqrt{z-1}} \right)^{\frac{z^2+1}{\epsilon^2}} \int_{-\infty}^{\infty} e^{-\frac{\alpha^2 z^2}{2(z-1)} - A_D \epsilon} d\alpha \quad (53)$$

where

$$A_D = \frac{(\alpha^2 z^3 - (2\alpha^2 + 3)z^2 + 9z - 6) \alpha z}{6(z-1)^2}.$$

Expanding $e^{-A_T \epsilon} = 1 - A_T \epsilon + \frac{1}{2} A_T^2 \epsilon^2 + O(\epsilon^3)$ and $e^{-A_D \epsilon} = 1 - A_D \epsilon + \frac{1}{2} A_D^2 \epsilon^2 + O(\epsilon^3)$ in the above and integrating to α should give improved asymptotic expressions for $T_n(z)$ and $D_n(z)$ if z is not too large. Simplification gives

$$T_n(z) \simeq \frac{z^2 + 4(3n-1)z - 4(3n-1)}{12n(z-1)} \left(\frac{z}{\sqrt{z-1}} \right)^n, \quad (54)$$

and

$$D_n(z) \simeq \frac{z^4 + 4(3n-2)z^3 - 30(2n-1)z^2 + 16(2z-1)(3n-1)}{12n(z-1)^2(z-2)} \left(\frac{z}{\sqrt{z-1}} \right)^n. \quad (55)$$

Substitution of the above in equations (20) and (25) and taking $n \rightarrow \infty$ again gives $-\log(z-1)$, the expected limiting pressure.

For finite values of n these results show a correction. In figure 5 a plot of $P_n^T(z, 2 \lfloor an/2 \rfloor)$ against a is shown for $n = 256$ and $z = 5/2$. Similarly, in figure 6 a plot of the Dyck path case is shown by plotting $P_n^D(z, 2 \lfloor an/2 \rfloor)$ as a function of a for $n = 256$ and for $z = 5/2$.

3. The forces exerted by adsorbing staircase polygons

A staircase polygon adsorbing in the upper half plane is illustrated in figure 7(a). If the left-most and right-most vertex in the staircase polygon is deleted, then it becomes a pair of directed paths in the upper half plane, one path below the other, and avoiding each other.

The bottom path is assumed to start in the origin, and by geometry the top path starts in the vertex with coordinates $(0, 2)$. In this situation we say that the staircase polygon is attached

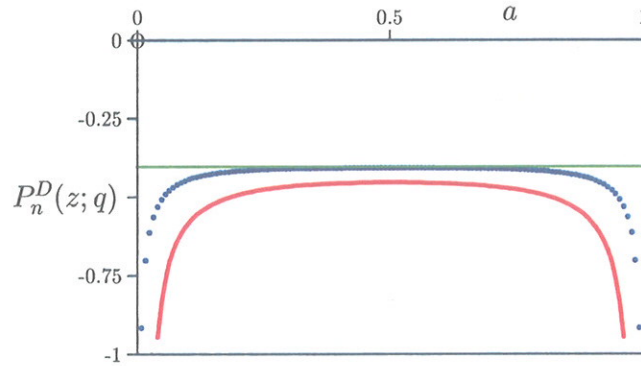


Figure 6. The pressure $P_n^D(z; q)$ for Dyck paths in \mathbb{Z}_+^2 for $n = 256$, $z = 5/2$ and $q = 2 \lfloor an/2 \rfloor$, plotted as a function of a . The pressure is large close to the endpoints of the path, and smaller towards the centre. The curve is the asymptotic approximation of the pressure, obtained by using equation (55). The dotted curve is the exact pressure (determined from equation (17) and (18)).

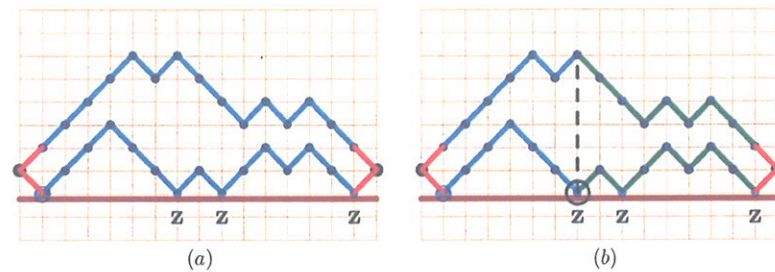


Figure 7. A model of staircase polygons. (a) A staircase polygon with its left-most and right-most endpoints grafted to the adsorbing line. If the first two and last two edges are deleted, then a pair of osculating directed paths are obtained. These paths avoid one another, and the bottom path interacts with the adsorbing line via the activity z . (b) A staircase polygon can be cut in a vertical line through one of the visits of the bottom path to the adsorbing line into a left and a right pair of paths. If the first two and last two edges of the polygon is removed, then each pair of paths consists of a Dyck path below a directed path.

to the X -axis. Observe that if the final vertex in the bottom path has coordinates (X, Y) , then the final vertex in the top path necessarily has coordinates $(X, Y + 2)$.

The bottom path may visit the X -axis, and these *visits* are weighted by z . By convention, the visit at the origin is not weighted.

In this model we assume that the bottom path always ends in the X -axis in a point with coordinates $(2n, 0)$ —these are *grafted* staircase polygons.

Since we have reduced the model to two directed paths, we relax the conditions above and assume that the top path ends in a point with coordinates $(2n, 2j + 2)$. In this case the partition function of the model is known [2]. This generalization will be useful, since it will enable use to compute the partition function of staircase polygons passing through a point x in the adsorbing line (or hard wall).

Hence, consider two directed paths in the square lattice, avoiding one another, and with steps $(1, 1)$ and $(1, -1)$. Suppose the first path is a Dyck path starting at the origin and

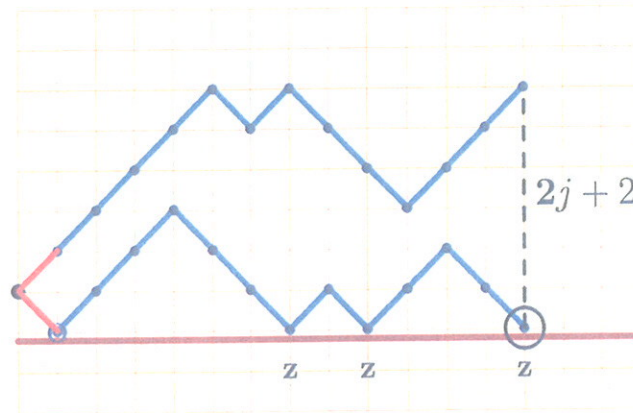


Figure 8. A Dyck path below a direct path. By deleting the first two edges of this pair of paths, two directed paths which avoids one another are obtained. The bottom path is constrained to end in the adsorbing line; it is a Dyck path, and it adsorbs via the activity z in the adsorbing line. The top path is a directed path, and its endpoint has height $2j + 2$ above the adsorbing line.

terminating in the vertex with coordinates $(2n, 0)$. Suppose furthermore that visits of the first path to the X -axis are weighted by z .

Let the second path start in the vertex with coordinates $(0, 2)$ and terminate in the vertex with coordinates $(2n, 2j + 2)$, as illustrated in figure 8.

Then the partition function of the pair of paths is

$$C_n(z; j) = \sum_{m_1=0}^n \sum_{m_2=0}^j K(m_1, m_2, j, n) \times \binom{2n+3}{n+m_2+2} \binom{2n+3}{n+m_1+j+3} (z-1)^{m_1+m_2} \tag{56}$$

where

$$K(m_1, m_2, j, n) = \frac{(2m_2 + 1)(2m_1 + 2j + 3)(m_1 + m_2 + j + 2)(m_1 - m_2 + j + 1)}{(2n + 1)(2n + 2)(2n + 3)^2}$$

One may check that $C_0(z; 0) = 1$, $C_1(z; 0) = z$, $C_1(z; 1) = z$ and $C_2(z; 0) = z + 2z^2$. For a derivation of this result, see for example [2, 9, 6] but note the misprint in those expressions when compared to the above. Observe that the length of each path is $2n$ so that n is the half-length of each path. Similarly, the distance between the endpoints is $2j + 2$, so that $j + 1$ is the half-distance between the endpoints.

The pressure on a vertex with coordinates $(q, 0)$ in the X -axis can be computed by determining the partition function of pairs of paths which avoids this vertex. This, in turn, can be done if one first determines the partition function of pairs of paths which passes through the vertex with coordinates $(q, 0)$. This situation is illustrated in figure 7(b), where the bottom path is constrained to pass through the marked visit. By cutting the polygon into two parts in the vertical line which passes through the visit, the pair of paths are divided into two sets of two paths each (one pair stepping from the left, and the other from the right), and each pair with endpoints a distance $2j + 2$ apart as illustrated in figure 8. (Reflect the paths on the right-hand side of the cut to get it in the same orientation.)

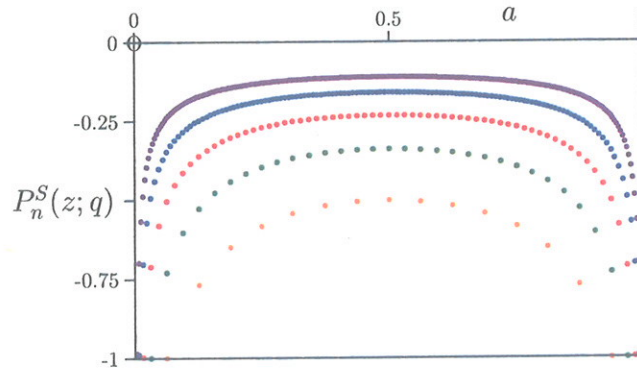


Figure 9. Exact pressures for adsorbing staircase polygons with $z = 2$, $q = 2 \lfloor an/2 \rfloor$ and for $n \in \{16, 32, 64, 128, 256\}$. The pressure is zero in the limit that $n \rightarrow \infty$. These points were computed by using equation (64), which is the exact expression for $P_n^S(2; q)$.

In other words, the partition function of the model in figure 7(b) is given by

$$Z_n^*(z; q) = \sum_{j=0}^n C_q(z; j) C_{n-q}(z; j). \tag{57}$$

The partition function of staircase polygons avoiding the visit $(q, 0)$ is given by

$$Z_n^*(z; q) = C_n(z; 0) - Z_n^*(z; q). \tag{58}$$

These give an expression for the net pressure on the vertex with coordinates $(q, 0)$:

$$P_n^S(z; q) = \log(C_n(z; 0)) - \log(Z_n^*(z; q)) = \log\left(1 - \frac{Z_n^*(z; q)}{C_n(z; 0)}\right). \tag{59}$$

In other words, to determine the force, one must compute both $C_n(z; 0)$ and $Z_n^*(z; q)$.

In principle, $P_n^S(z; q)$ can be determined exactly from the results above, but these expressions are complicated and not very informative. Hence, we shall approximate them to both estimate the pressure at finite values of n , and in the case that $n \rightarrow \infty$. As in the case of directed walks, there will be different results for $z > 2$ (the adsorbed phase) and $z \leq 2$.

3.1. $z = 2$:

In the case that $z = 2$ and $j = 0$, equation (56) simplifies to

$$C_n(2; 0) = \left[\frac{2(2n+1)}{n+2} \right] C_n^2 \tag{60}$$

where $C_n = \frac{1}{n+1} \binom{2n}{n}$ is Catalan's number.

Summing $j = 0$ to n instead in equation (56) gives

$$\sum_{j=0}^n C_n(z; j) = \frac{\Gamma(n + \frac{1}{2}) 16^n}{\sqrt{\pi} \Gamma(n+2)}. \tag{61}$$

More generally, for fixed j , $C_n(2; j)$ simplifies to

$$C_n(2; j) = \left[\frac{2(2n+1)(j+1)^2 C_n}{(n+j+1)(n+j+2)} \right] \binom{2n}{n+j}. \tag{62}$$

These results can be used to obtain exact expressions for the force $P_n^S(2; q)$ in equation (59).

In particular, one may evaluate $Z_n^S(2; q)$ in equation (57) exactly to

$$Z_n^S(2; q) = \frac{2(n(3q+2) - 3q^2 + 1)\Gamma(n + \frac{1}{2})\Gamma(q + \frac{1}{2})\Gamma(n - q + \frac{1}{2})16^n}{\sqrt{\pi^3}\Gamma(q+2)\Gamma(n+3)\Gamma(n-q+2)}. \quad (63)$$

Dividing by $C_n(2; 0)$ and computing $P_n^S(2; q)$ in equation (59) gives

$$P_n^S(2; q) = \log \left(1 - \frac{(n(3q+2) - 3q^2 + 1)\Gamma(q + \frac{1}{2})\Gamma(n - q + \frac{1}{2})\Gamma(n+2)}{2\sqrt{\pi}\Gamma(q+2)\Gamma(n-q+2)\Gamma(n + \frac{3}{2})} \right). \quad (64)$$

If one put $q = 2 \lfloor an/2 \rfloor$ where $0 < a < 1$ and take the limit $n \rightarrow \infty$, then a symbolic computations program [5] shows that $\lim_{n \rightarrow \infty} P_n^S(2; 2 \lfloor an/2 \rfloor) = 0$. This shows that the pressure is zero in the limit as $n \rightarrow \infty$ and $z = 2$.

3.2. Asymptotics

By putting $m_1 + m_2 = k$ and summing over m_1 , equation (56) can be cast in the form

$$C_n(z; j) = \sum_{k=0}^n \frac{(j+k+2)}{(n+1)^2} \binom{2n}{n} \binom{2n+2}{n+j+k+3} (z-1)^k - \sum_{k=0}^n \left(\frac{(j+k+2)(n-2j(k+1)-2k-1)}{2(n+1)^2(2n+1)} \right) \times \binom{2n+2}{n+k+2} \binom{2n+2}{n+j+2} (z-1)^k. \quad (65)$$

This form presents a single summand over k which one may consider for approximation.

Isolate the summands of $C_n(z; j)$ above and cast them in terms of Gamma functions. This gives

$$C_1 = \frac{8(j+k+2)\Gamma^2(n + \frac{3}{2})(z-1)^k 16^n}{\pi(n+1)(2n+1)\Gamma(n+j+k+4)\Gamma(n-j-k)}, \quad (66)$$

$$C_2 = \frac{2(j+k+2)(2j(k+1)-n+2k+1)\Gamma^2(2n+2)(z-1)^k}{(2n+1)\Gamma(n+j+3)\Gamma(n-j+1)\Gamma(n+k+3)\Gamma(n-k+1)}, \quad (67)$$

where C_1 is the summand of the first summation in equation (65) and C_2 is the summand of the second summation.

Numerical evaluations of C_1 and C_2 for given n indicate that the summands are large for small $k \ll j$ (and j is also small) for $z < 2$, at both k and j small for $z = 2$ and at $k \gg j$ for $z > 2$ (and both k and j are large). In addition, both sums in the above make a substantial contribution of opposite signs, and so both must be examined to determine suitable asymptotics.

Proceed by determining the dominant terms in the summands of equation (65). The binomial coefficients will be approximated by using the Stirling approximation for factorials (see equation (33)). Take logarithms of the first summand, substituting $n = 1/\epsilon$, $j = \delta/\epsilon$ and $k = \alpha/\epsilon$ and expand the resulting expression in ϵ . The leading term is

$$\log \left(\frac{16(1-\delta-\alpha)^{\delta+\alpha-1}}{(\delta+\alpha+1)^{\delta+\alpha+1}} (z-1)^\alpha \right). \quad (68)$$

Taking the derivative and solving for α gives

$$\alpha_m = \max \left\{ \frac{z-2}{z} - \delta, 0 \right\} \quad (69)$$

since α_m cannot be negative.

A similar treatment of the summand in the second sum in equation (65) gives the leading term in an expansion in ϵ :

$$\log \left(\frac{16(1-\delta)^{\delta-1}(1-\alpha)^{\alpha-1}}{(1+\alpha)^{\alpha+1}(1+\delta)^{\delta+1}} (z-1)^\alpha \right). \tag{70}$$

Taking the derivative and solving for α gives

$$\alpha_M = \max \left\{ \frac{z-2}{z}, 0 \right\} \tag{71}$$

since α_m cannot be negative.

3.2.J. $z < 2$. Proceed by approximating the summands C_1 and C_2 above. Take logarithms of C_1 and C_2 , substitute the Stirling approximation for factorials (see equation (33)) and simplify the results. Since the summands are dominated by $k \ll j$, and j small, substitute $j = \delta/\epsilon$ and $n = 1/\epsilon^2$ and expand to $O(\epsilon)$. Summing over k and replacing $\epsilon = 1/\sqrt{n}$ and $\delta = j/\sqrt{n}$ show that to leading order C_1 and C_2 cancel.

This shows that higher order terms must be determined in this case. Expanding to $O(\epsilon^{12})$, summing over k and combining the contributions of C_1 and C_2 and then extracting the leading order terms give

$$\sum_k (C_1 + C_2) \simeq \frac{4(j+1)(2j^2(2-z) + j(8-z) + 6) e^{-j^2/n} z 16^n}{\pi n^5 (z-2)^4}. \tag{72}$$

One may extract the asymptotic behaviour for $j = 0$ and $j = O(\sqrt{n})$. The above can be simplified taking only the fastest growing terms in each factor. This shows that

$$C_n(z; j) = \sum_k (C_1 + C_2) \simeq \begin{cases} \frac{24 z 16^n}{\pi n^5 (2-z)^4}, & \text{if } j = 0; \\ \frac{8z j^3 e^{-j^2/n} 16^n}{\pi n^5 (2-z)^3}, & \text{if } j = O(\sqrt{n}). \end{cases} \tag{73}$$

The partition function in equation (57) can be approximated from these last expressions, and similarly, one may approximate $C_n(z; 0)$ in equation (56). This finally gives an approximation for $P_n^S(z; q)$ in equation (59).

In particular, one obtains that

$$\sum_{j=0}^n C_q(z; j) C_{n-q}(z; j) \simeq \int_0^\infty \left(\frac{8z j^3 e^{-j^2/q} 16^q}{\pi q^5 (2-z)^3} \cdot \frac{8z j^3 e^{-j^2/(n-q)} 16^{n-q}}{\pi (n-q)^5 (2-z)^3} \right) dj. \tag{74}$$

The integral can be readily done, and after division by the asymptotic expression for $C_n(z; 0)$ one is left with the following approximation for the force:

$$P_n^S(z; q) \simeq \log \left(1 - \frac{5z n^{3/2}}{2\sqrt{\pi} (q(n-q))^{3/2} (2-z)^2} \right). \tag{75}$$

Replacing q by $2 \lfloor an/2 \rfloor$ and simplifying then gives

$$P_n^S(z; 2 \lfloor an/2 \rfloor) \simeq \log \left(1 - \frac{5z}{2n^{3/2} \sqrt{\pi a^3 (1-a)^3} (2-z)^2} \right). \tag{76}$$

Hence, for $a \in (0, 1)$ $P_n^S(z; 2 \lfloor an/2 \rfloor) \rightarrow 0$ as $n \rightarrow \infty$. By expanding the logarithm, the case that $z < 2$ in equation (24) is obtained.

In figure 10 the pressure $P_n^S(z; 2 \lfloor an/2 \rfloor)$ is plotted for $a \in (0, 1)$, $z = 3/2$ and $n = 256$ comparing the approximate expression in equation (76) against the exact calculated pressure.

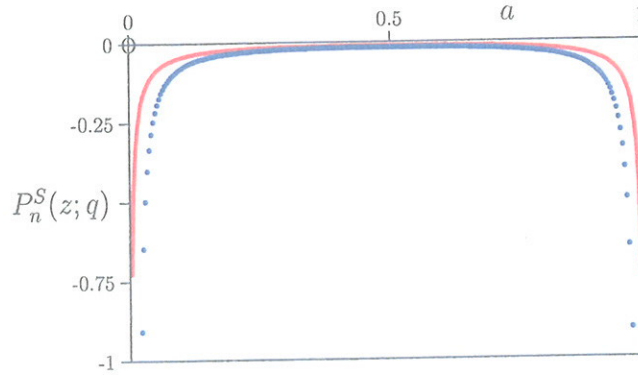


Figure 10. The pressure $P_n^S(z; q)$ for staircase polygons in \mathbb{Z}_+^2 for $n = 256$, $z = \frac{3}{2}$ and $q = 2 \lfloor an/2 \rfloor$, plotted as a function of a . The pressure is large close to the endpoints of the polygons. The curve is the approximate pressure (equation (76)) while the dotted curve are the exact values of the pressure.

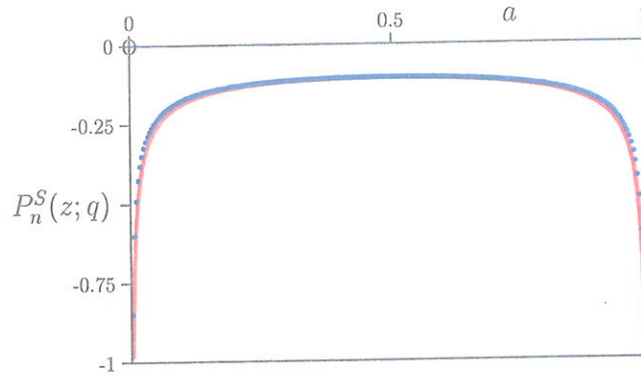


Figure 11. The pressure $P_n^S(z; q)$ for staircase polygons in \mathbb{Z}_+^2 for $n = 256$, $z = 2$ and $q = 2 \lfloor an/2 \rfloor$, plotted as a function of a . The pressure is large close to the endpoints of the polygons. The curve was determined from equation (64) and the points along the dotted curve are the exact values computed from the partition function in equation (65).

3.2.2. $z = 2$. The case $z = 2$ has been solved explicitly, as seen in equations (63) and (64). The expression for $P_n^S(2; q)$ in equation (64) is in terms of Gamma functions, and these can be approximated when $q = 2 \lfloor an/2 \rfloor$ for large n using Stirling's approximation. This shows that

$$P_n^S(2; 2 \lfloor an/2 \rfloor) = \log \left(1 - \frac{3}{2\sqrt{n\pi a(1-a)}} + O(n^{-3/2}) \right). \tag{77}$$

By expanding the logarithm, the case that $z = 2$ in equation (24) is obtained. In figure 11 a plot of the approximation and exactly calculated values of the pressure is presented.

3.2.3. $z > 2$. The summands C_1 and C_2 in equations (66) and (67) provide the starting point. Numerical experimentation shows that C_1 is dominated by terms with $k = O(n)$ and $j = O(\sqrt{n})$ while $j + k = O(n)$ with a spread of the peak proportional to \sqrt{n} . This is in

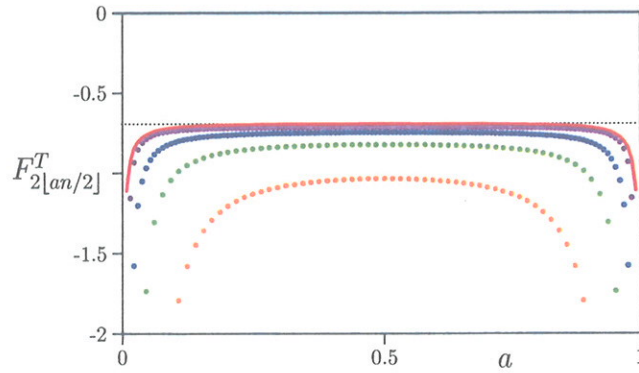


Figure 12. The pressure $P_n^S(z; q)$ for staircase polygons in \mathbb{Z}_+^2 for $n \in \{32, 64, 128, 256\}$, $z = 3$ and $q = 2 \lfloor an/2 \rfloor$, plotted as a function of a . The pressure is large close to the endpoints of the polygons. The solid curve is the exact pressure at $n = 256$ (determined from equation (65)) while the set of dotted curves are the asymptotic results (equation (81)) for n doubling from 32 to 256.

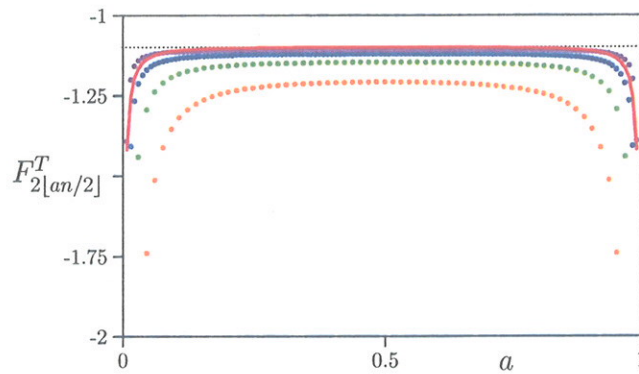


Figure 13. The pressure $P_n^S(z; q)$ for staircase polygons in \mathbb{Z}_+^2 for $n \in \{32, 64, 128, 256\}$, $z = 4$ and $q = 2 \lfloor an/2 \rfloor$, plotted as a function of a . The pressure is large close to the endpoints of the polygons. The solid curve is the exact pressure at $n = 256$ (determined from equation (65)) while the set of dotted curves are the asymptotic results (equation (81)) for n doubling from 32 to 256.

particular confirmed by the result in equation (69) which indicates that the dominant values of j and k in equation (66) are at $k = ((z - 2)/z)n - j$ and $j = O(\sqrt{n})$.

Hence, put $n = 1/\epsilon^2$, $k = (z - 2)/(z\epsilon^2) - \delta/\epsilon + \alpha/\epsilon$ and $j = \delta/\epsilon$ in equation (66). Take logarithms and expand in ϵ to $O(1)$. Exponentiating and integrating the resulting expression gives the asymptotic expression

$$C_1(n, j) = \frac{(z - 2)4^n z^{2n+1}}{\sqrt{\pi}(z - 1)^{n+j+3} n^{3/2}} \left(1 - \frac{9}{8n}(1 + o(1)) \right) \tag{78}$$

where the substitution $\delta = j/\sqrt{n}$ was made. Expanding to higher order in ϵ before integrating gives subleading corrections, and does not alter this leading term correction.

A similar approach should give an approximation to C_2 . However, some care is needed in this case. Determining only leading term behaviour leads to incorrect results, and it is necessary to include higher order corrections. The arguments leading to equation (71) show

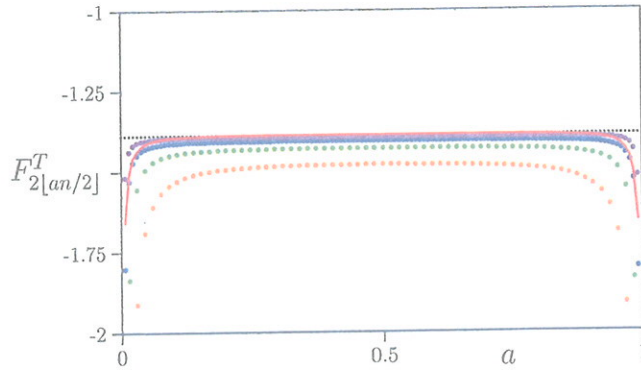


Figure 14. The pressure $P_n^S(z; q)$ for staircase polygons in \mathbb{Z}_+^2 for $n \in \{32, 64, 128, 256\}$, $z = 5$ and $q = 2 \lfloor an/2 \rfloor$, plotted as a function of a . The pressure is large close to the endpoints of the polygons. The solid curve is the exact pressure at $n = 256$ (determined from equation (65)) while the set of dotted curves are the asymptotic results (equation (81)) for n doubling from 32 to 256.

that the appropriate choices for j and k is $n = 1/\epsilon^2$ and $k = (z - 2)/(z\epsilon^2) + \alpha/\epsilon$ and $j = \delta/\epsilon$. Substitute this into equation (67), and as before, take the logarithm, expand to $O(\epsilon)$ (rather than just $O(1)$). Exponentiate the result and expand in ϵ to $O(\epsilon^2)$. Integrating $\alpha \in (-\infty, \infty)$ for small ϵ then gives the asymptotic expression

$$C_2(n, j) = \frac{z - 2}{(z - 1)^2} \left(\frac{z^2}{z - 1} \right)^n \frac{4^n e^{-j^2/n}}{\sqrt{\pi n^3}} \times \left(z(2j + 1) - 4(j + 1) - \frac{2(z - 2)j^2}{n} + o(1/n) \right) \quad (79)$$

for the summand C_2 .

The approximation for C_1 peaks sharply at $j = 0$ while that for C_2 dominates the contribution from C_1 when $j > 0$ and peaks at a value of $j > 0$. At $j = 0$ both terms make a contribution. Hence, approximate the pressure at the point $(q, 0)$ by

$$\log \left(1 - \int_{-\infty}^{\infty} \left[\frac{(C_1(q, j) + C_2(q, j))(C_1(n - q, j) + C_2(n - q, j))}{C_1(n, 0) + C_2(n, 0)} \right] dj \right). \quad (80)$$

Put $q = 2 \lfloor an/2 \rfloor$ and expand the integrand above and integrate term by term. Expand the results asymptotically in n and keep terms to $O(n^{-2})$. This finally gives the result

$$P_n^S(z; 2 \lfloor an/2 \rfloor) \simeq \log \left(\frac{1}{z - 1} - \frac{3}{8} \frac{4z^2 - 29z + 64}{n(z - 1)(z - 2)} \left(1 + \frac{9z}{8n(z - 2)^2} \right) - \frac{3z^2}{2\sqrt{\pi n^3} a^3 (1 - a)^3 (z - 2)(z - 1)^3 \log(z - 1)} \right). \quad (81)$$

Taking $n \rightarrow \infty$ shows that $P_n^S(z; 2 \lfloor an/2 \rfloor) \rightarrow -\log(z - 1)$, consistent with the result for adsorbing Dyck paths in the $z > 2$ regime (see lemma 2). By factoring $(z - 1)$ from the argument of the logarithm in equation (81) and expanding the logarithm asymptotically, the case $z > 2$ in equation (24) is obtained.

4. Conclusions

In this paper we have investigated the pressure exerted by a directed path in a half-space on the X -axes. This is a directed model of the forces exerted by a two dimensional polymer grafted to a hard wall. Our first model is of a directed path, in which we considered two cases, namely an adsorbing Dyck path model with both endpoints grafted to the adsorbing line, and a directed path with only one endpoint grafted to the adsorbing line.

The pressure curve for the Dyck path is both a function of the length of the path (n), and the adsorption activity (z). Asymptotic expressions were obtained for the pressure at $(q, 0) = (2 \lfloor an/2 \rfloor, 0)$ for $a \in (0, 1)$. The pressure curve is symmetric about $a = 1/2$ and is asymptotically given by equation (45) for $z < 2$, equation (48) for $z = 2$ and equation (55) for $z > 2$. The pressure is zero as $n \rightarrow \infty$ and $z \leq 2$, but there is a net constant limiting pressure of magnitude $\log(z - 1)$ for $z > 2$. In this regime the adsorbed paths are close to the hard wall, and the result is a non-vanishing pressure.

Similar observations can be made for the pressure due to an adsorbing directed path. In this model, asymptotic expressions for the pressure were determined and is given in equation (45) for $z < 2$, and by substituting equation (47) into equation (26) for $z = 2$, and equation (54) for $z > 2$. The pressure profiles for finite length paths are not symmetric in this model, but the limiting pressure is equal to the limiting pressure of Dyck paths.

We have also determined the pressure due to adsorbing staircase polygons which were grafted to the adsorbing line at both ends. Determining the limiting pressure involved more careful analysis, but the results are given by expressions which are similar to the Dyck path results. The pressures are given asymptotically by equation (76) for $z < 2$, equation (77) for $z = 2$ and equation (81) for $z > 2$.

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References

- [1] Bijsterbosch H D, de Haan V O, de Graaf A W, Mellema M, Lcernakers F A M, Stuart Cohen M A and van Well A A 1995 Tethered adsorbing chains: neutron reflectivity and surface pressure of spread diblock copolymer monolayers *Langmuir* **11** 4467–73
- [2] Brak R, Essam J W and Owczarek A L 1998 New results for directed vesicles and chains near an attractive wall *J. Stat. Phys.* **93** 155–92
- [3] Carignano M A and Szleifer I 1995 On the structure and pressure of tethered polymer layers in good solvent *Macromolecules* **28** 3197–204
- [4] Currie E P K, Norde W and Cohen Stuart M A 2003 Tethered polymer chains: surface chemistry and their impact on colloidal and surface properties *Adv. Colloid Interface Sci.* **100–102** 205–65
- [5] Waterloo Maple Inc. 2008 *Maple 12*
- [6] Janse van Rensburg E J 2000 *The Statistical Mechanics of Interacting Walks, Polygons, Animals and Vesicles* vol 18 (Oxford: Oxford University Press)
- [7] Jensen I, Dantas W G, Marques C M and Stilck J F 2013 Pressure exerted by a grafted polymer on the limiting line of a semi-infinite square lattice *J. Phys. A: Math. Theor.* **46** 115004
- [8] Stanley R P 1999 *Enumerative Combinatorics (Cambridge Studies in Advanced Mathematics* vol 62) vol 2 (Cambridge: Cambridge University Press)
- [9] van Rensburg B 1999 Adsorbing staircase walks and staircase polygons *Ann. Comb.* **3** 451–73
- [10] Whittington S G 1998 A directed-walk model of copolymer adsorption *J. Phys. A: Math. Gen.* **31** 8797–804