Models of pulled and compressed polymers

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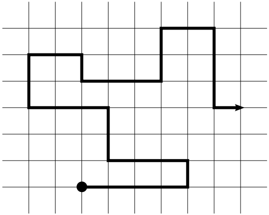
Outline

Self-avoiding walks

A self-avoiding walk (SAW) is a walk on a lattice which cannot revisit vertices.



For a given lattice, c_n is the number of n-step SAWs (up to translation).
eg. square lattice:

$$
\begin{aligned}
c_0 &= 1\\
c_1 &= 4\\
c_2 &= 12\\
c_3 &= 36\\
c_4 &= 100, \ldots
\end{aligned}
$$

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Any SAW of length $m+n$ can be split into two smaller SAWs, of lengths m and n. So

$$c_{m+n} \leq c_m c_n.$$

So $\{c_n\}$ is a sub-multiplicative sequence. Then

$$\log c_{m+n} \leq \log c_m + \log c_m,$$

so $\{\log c_n\}$ is a sub-additive sequence. It follows that the limit

$$\log \mu = \lim_{n\to\infty} \frac{1}{n} \log c_n$$

exists. $\log \mu$ is called the connective constant of the lattice. Then

$$c_n = \theta(n)\mu^n,$$

where μ is called the growth constant (sometimes connective constant) and $\theta(n) = e^{o(n)}$. By submultiplicativity, we know that $\theta(n) \geq 1$.

In general, μ is not known exactly. Honeycomb lattice is special:

Theorem (Duminil-Copin and Smirnov 2012)

On the honeycomb (hexagonal) lattice, $\mu = \sqrt{2+\sqrt{2}}$.

For other lattices, have numerical estimates based on series data (eg. 70 terms for square lattice)

$$\mu_{\text{square}} \approx 2.63815853031 \qquad \mu_{\text{triangular}} \approx 4.150797226$$

Subexponential factors unproven, but

Conjecture (Nienhuis 1982)

$$c_n \sim A n^{\gamma-1} \mu^n$$

for A, μ, γ *constant.* A *and* μ *are lattice-dependent,* γ *depends only on dimension. In two dimensions,* $\gamma = 43/32$.

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In high dimensions, can do a bit better:

Theorem (Hara and Slade 1992)

On the hypercubic lattice in five or more dimensions,

$$c_n \sim A \mu^n.$$

Also interested in the size and shape of SAWs. eg. let $\langle R_e^2 \rangle_n$ be the mean-squared end-to-end distance of SAWs of length n.

Conjecture (Nienhuis 1982; Lawler, Schramm and Werner 2004)

$$\langle R_e^2 \rangle_n \sim C n^{2\nu}$$

with C lattice-dependent and ν dimension-dependent. In two dimensions, $\nu = 3/4$.

The exponents γ and ν are also connected to the scaling limit of SAWs:

Conjecture (Lawler, Schramm and Werner 2004)

Self-avoiding walks have a conformally invariant scaling limit, namely $SLE_{8/3}$.

Generating functions

The (ordinary) generating function for $\{c_n\}$ is

$$C(z) = \sum_{n\geq 0} c_n z^n$$

Then $z_c = 1/\mu$ is the radius of convergence of $C(z)$. In general, expect the behaviour near z_c to be

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Because $c_n \geq \mu^n$,

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Expect that $C(z)$ is non-D-finite, ie. does not satisfy a linear ODE with polynomial coefficients.

Polymer models

SAWs are an important model in statistical mechanics of linear polymers in a solvent: chains of monomers, connected by bonds of fixed length and at fixed angles.

Unlike random walks (another, simpler model), SAWs encapsulate the excluded volume principle: two different monomers can't occupy the same point in space.

Monomers in a polymer can interact with each other, other polymers, surfaces (both penetrable and impenetrable) or with other external agents. Usually, these interactions are either attractive or repulsive.

Can also model forces applied to the polymer at various points/directions.

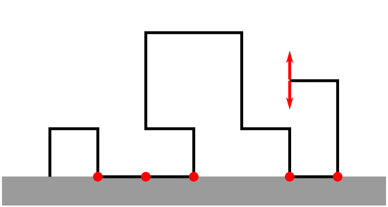
Pulling and pushing

We can model an external agent which is pulling the polymer away from the surface or pushing it onto the surface.

If one end of the polymer is tied to the surface, there are two natural places the force could be applied:

at the endpoint

at the highest point(s)



Force applied at the endpoint

Let $u_n^e(h)$ be the number of n-step SAWs in the upper half-plane which end at height h above the surface. Then define the partition function

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When y is small, walks whose endpoint is close to the surface dominate. When y is large, walks whose endpoint is far away from the surface dominate. So we can interpret $y = e^f$, where f is force: $f > 0$ if pulling up, $f < 0$ if pushing down.

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For $y > 0$, $\lambda^e(y)$ is

- convex in $\log y$ ($\Rightarrow$ continuous)
- non-decreasing

$U_n^e(1)$ just counts walks in the upper half-plane. $U_n^e(0)$ counts walks in the upper half-plane which start and end on the surface. Both of these have the same growth rate as full-plane walks, i.e. μ. (Easy to show.)

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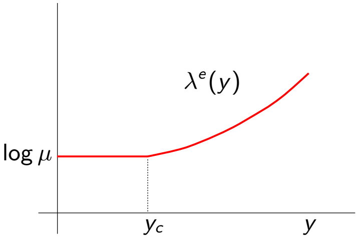
So $\lambda^e(y)$ must be non-analytic at some point $y = y_c^e \geq 1$. This is the critical point, where walks change from free to ballistic.



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Put a Boltzmann distribution on the walks of length n by setting

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Then the mean (endpoint) height per unit length for walks of length n is

$$\delta_n(y) = \frac{1}{n}\frac{\sum_h h u_n^e(h) y^h}{U_n^e(y)} = \frac{y}{n}\frac{\partial \log U_n^e(y)}{\partial y}.$$

As $n \to \infty$, this becomes

$$\delta_n(y) \to y\frac{\partial \lambda^e(y)}{\partial y} \begin{cases} = 0 & \text{if } y < y_c \\ > 0 & \text{if } y > y_c. \end{cases}$$

So in the free phase, the average height of the endpoint is $o(n)$, and walks "drift" away from the surface slowly. In the ballistic phase, the endpoint is at distance $\Theta(n)$ from the surface.

(In the free phase, would expect the average height to grow like $n^\nu = n^{3/4}$.)

Including a surface interaction

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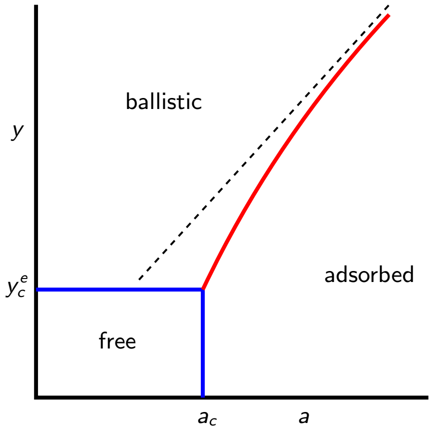
Bivariate free energy $\kappa^e(a, y)$, which has critical points along several lines in the $a - y$ plane.



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(It may also follow from some very technical probabilistic results of Ioffe and Velenik, but this remains unpublished.)

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Let $\mu_u^e(y) = \exp(\lambda^e(y))$ be the growth rate of the partition functions $U_n^e(y)$, and

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So we need to show that the radius of convergence $z_u^e(y)$ of $U^e(z, y)$ is strictly decreasing for $y > 1$.

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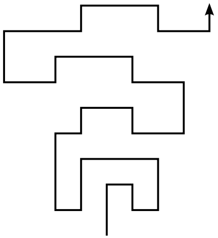
3. Show that this can only happen when the generating function of irreducible bridges is equal to 1.
4. Show that the value of z solving this must decrease as y increases.

Self-avoiding bridges

A self-avoiding bridge is a SAW $\gamma = (\gamma_0, \gamma_1, \ldots, \gamma_n)$, where $\gamma_i = (x_i^{(1)}, x_i^{(2)}, \ldots, x_i^{(d)})$, such that

$$x_0^{(d)} < x_i^{(d)} \leq x_n^{(d)} \text{ for } i = 1, \ldots, n.$$

In 2 dimensions, a bridge is a SAW whose starting point has strictly minimal y-coordinate and whose end point has maximal y-coordinate:



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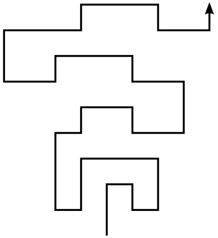
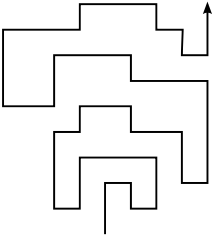


Bridges are useful because they can be freely concatenated without intersecting.

Irreducible bridges

A bridge which cannot be split into a concatenation of two or more smaller bridges is irreducible:



Growth constants etc. are well-defined for bridges and irreducible bridges, and are the same as full-plane and half-plane walks, ie. μ.

Decompositions

We already have the generating function $U^e(z, y)$ for upper half-plane walks, with z tracking length and y tracking endpoint height.

Define $B(z, y)$ and $I(z, y)$ for bridges and irreducible bridges. (Endpoint and uppermost point are the same thing.)

Finally, introduce $C^e(z, y)$ for full-plane SAWs. Because the endpoint can be lower than the starting point, the coefficient of z^n is a Laurent polynomial in y.

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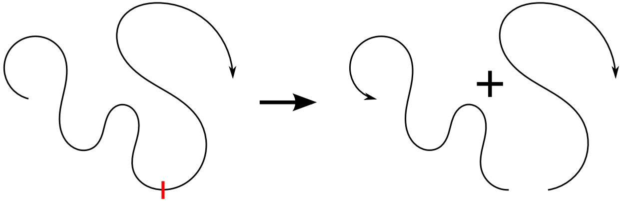
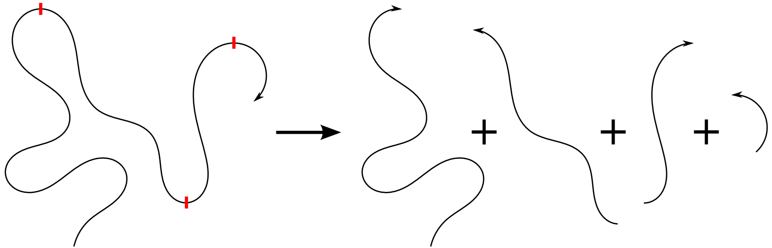
Any full-plane SAW can be split into two half-plane SAWs, with the direction of one reversed:



Thus

$$C^e(z, y) \leq U^e(x, y)U^e(x, 1/y)$$

Every half-plane SAW can be decomposed as a sequence of bridges which alternate direction and decrease in height:



So

$$U^e(z,y) \le \prod_{h\ge 1}\left(1+(y^h+y^{-h})\sum_{n\ge 1} b_n(h)z^n\right)$$

where $b_n(h)$ is the number of bridges of length n and height h.

Using $1+x\le e^x$, get

$$U^e(z,y) \le e^{B(z,y)+B(z,1/y)}$$

Combining,

$$C^e(z,y) \leq e^{2(B(z,y)+B(z,1/y))}$$

Finally, since every bridge can be written uniquely as a concatenation of irreducible bridges, we have

$$B(z,y) = \frac{I(z,y)}{1 - I(z,y)}$$

Divergence of generating functions (sketch)

$C^e(z,y)$ diverges at its critical point, $z_c^e(y)$, for the same reason as $C(z)$ (submultiplicativity):

$$C_{m+n}^e(y) \leq C_m^e(y) C_n^e(y)$$

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So $z^e_c(y) = z^e_u(y)$ is strictly decreasing for $y > 1$, and hence $y^e_c = 1$.

Further results

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Values of the critical exponents have been conjectured for some objects in some regimes: full- and half-plane walks for all values of y, bridges for $y \geq 1$.

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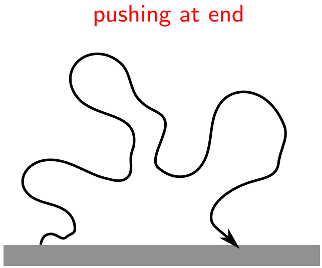
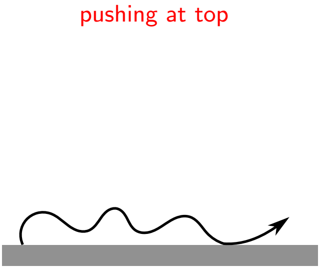
When $y > 1$, there is little or no difference between the two: walks (and bridges) are ballistic, so the endpoint is at/near the top anyway. Critical exponents should be the same.

When $y < 1$, however, things are very different:





When pushing at the endpoint, both ends must be near the surface but the rest of the walk has a lot of freedom.

$\Rightarrow$ different critical exponent for $y < 1$, $y = 1$ and $y > 1$.

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Pushing at the top looks like restricting walks to a strip of finite height, so we might even expect the critical point (and hence the growth rate $\mu_u^t(y)$) to change.

But walks with large height, even though they are heavily penalised, still contribute enough to keep the growth rate at constant μ.

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$$U_n^t(y) \sim A(y) n^{\gamma' - 1} \mu^n \tau(y)^{n^\sigma},$$

where $\tau(y) < 1$ and $\sigma \approx 0.42$.

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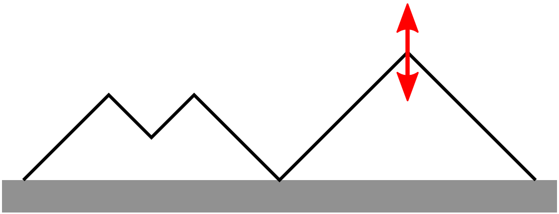
Similar for bridges when $y < 1$.

Resembles the conjectured asymptotics for collapsing partially directed walks (there, $\sigma = 1/2$) [Brak, Owczarek, Prellberg 1993].

Pushing Dyck paths

Try looking at a much simpler model to see if we observe the same behaviour.

Dyck paths take north-east $(1, 1)$ or south-east $(1, -1)$ steps, start and end on the surface, and remain above the surface.



Use z to track half-length (length is always even) and y to track height, as before. Then the generating function $D(z, y)$ can be computed in several ways.

Unfortunately, extracting detailed information from the generating function for $y < 1$ proves to be very difficult.

However, can use it to calculate the free energy $\lambda^d(y)$ exactly:

$$\lambda^d(y) = \log\left(\begin{cases} 4 & \text{if } y \le 1 \\ \frac{(y+1)^2}{y} & \text{if } y > 1 \end{cases}\right)$$

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For $y > 1$, the partition function is asymptotically

$$D_n(y) \sim \frac{(y-1)^3}{y(y+1)^2} \cdot \left(\frac{(y+1)^2}{y}\right)^n$$

For $y < 1$, Robin Pemantle and Brendan McKay use the fact that Dyck paths become reflected Brownian bridges in the scaling limit. If the distribution of the heights tends to a Gaussian, this can be asymptotically approximated and integrated. They obtain

$$D_n(y) = A(y) n^{-5/6} 4^n \tau(y)^{n^{1/3}} (1 + O(n^{-1/3})),$$

where

$$A(y) = (1-y) 2^{5/3} 3^{-1/2} \pi^{5/6} e^{2r}$$
$$\tau(y) = \exp(-3 \times 2^{-2/3} \pi^{2/3} r^{2/3})$$

and $r = -\log y$.

Matches numerical analyses of 2500-term series.

Further asymptotic terms can be calculated using the same method.

Future work

Complete the phase diagram picture for endpoint pulling when surface $a \neq 1$. Is it really the same for top-pulling?

On the honeycomb lattice, a_c is known exactly. Can other parts of the phase diagram be calculated exactly?

What kind of singularity leads to the $y < 1$ asymptotics for top-pushed SAWs and Dyck paths? Results are known for τ^{n^σ} when $\tau > 1$, but we have $\tau(y) < 1$.

This can all be repeated with a penetrable surface. Still have $y_c^e = 1$, but the surface weight a is quite different.

Thank you!