Polymer adsorption on the honeycomb lattice

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36th Conference on Stochastic Processes and their Applications
Boulder, Colorado
31 July 2013

Outline

- Introduction
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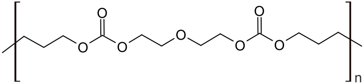
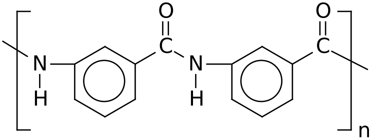
Work with Tony Guttmann, Jan de Gier, Mireille Bousquet-Mélou & Hugo Duminil-Copin.

Introduction I: Polymer adsorption

A polymer is a large molecule made of many repeated parts.





Polymers in solution interact with one another, themselves and their environment.

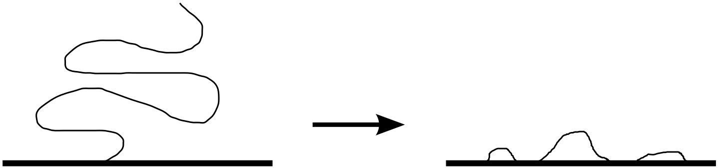
These interactions depend on solvent quality, temperature, pressure, etc.

Polymer adsorption is the interaction with a surface:

- impenetrable
- penetrable

and this interaction can be attractive or repulsive.

At an impenetrable surface, sometimes observe a phase transition: as temperature is decreased, polymers transition from a desorbed to an adsorbed state:



Want a mathematical model to help understand this behaviour.

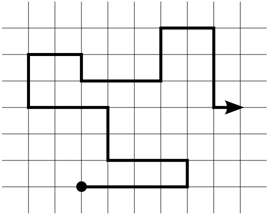
Random walks?

- Nice mathematically
- Lots of existing theory
- But don't encapsulate the excluded volume effect

Want to forbid monomers from lying on top of one another.

$\Rightarrow$ Self-avoiding walks!

Introduction II: Self-avoiding walks (reminder)



For a given lattice, c_n is the number of n-step SAWs.
eg. square lattice: $c_0 = 1,\ c_1 = 4,\ c_2 = 12,\ c_3 = 36,\ c_4 = 100, \ldots$

The limit

$$\kappa = \lim_{n\to\infty} n^{-1} \log c_n$$

exists. κ is called the connective constant of the lattice.

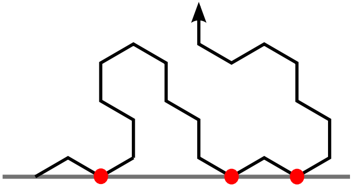
$$c_n = \exp(\kappa n + o(n))$$

In general, κ is also not known exactly (numerical estimates). Except for the honeycomb lattice, where

$$\mu = e^{\kappa} = \sqrt{2+\sqrt{2}}.$$

Introduction III: The model

To model polymer adsorption, restrict SAWs to a half-space. Interactions occur when walks visit the boundary. (Except the origin.)



Define $c_n^+(\nu)$ to be number of n-step SAWs which visit boundary ν times.

Then associate a fugacity (Boltzmann weight) y with each visit. Define the partition function

$$Z_n^+(y) = \sum_{\nu} c_n^+(\nu) y^{\nu}$$

Physically, $y = \exp(\epsilon / kT)$, where

- ϵ is energy gain per contact (determined experimentally)
- k is Boltzmann's constant, $1.38 \times 10^{-23} \mathrm{JK}^{-1}$
- T is absolute temperature

When y is small (large T), walks with few contacts dominate the partition function, but when y is large (small T), walks with lots of contacts dominate. So

- small $y \Rightarrow$ surface is repulsive
- large $y \Rightarrow$ surface is attractive

Like c_n, can prove

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

exists. For $y > 0$, $\kappa(y)$ is

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

By comparison with walks which never touch the surface, can show

$$\kappa(y) = \kappa \qquad \text{for } 0 \le y \le 1.$$

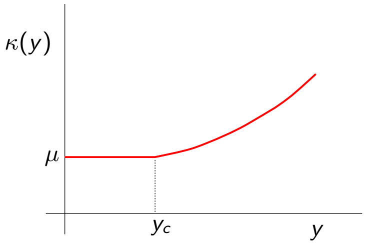
By comparison with the walk which never leaves the surface, can show

$$\kappa(y) \ge \log y^r$$

where $r = 1$ for square/triangular lattice and $r = 1/2$ for honeycomb lattice.

So there must be a critical point y_c with

$$\kappa(y) \begin{cases} = \kappa & \text{if } y \le y_c \\ > \kappa & \text{if } y > y_c \end{cases}$$



This is the location of the phase transition:

$$T_c = \frac{\epsilon}{k \log y_c}$$

In the limit of polymer length:

- $y < y_c$ $(T > T_c) \Rightarrow$ polymers are desorbed
- $y > y_c$ $(T < T_c) \Rightarrow$ polymers are adsorbed

What does this really mean?

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

$$\mathbb{P}(\gamma) = \frac{y^{c(\gamma)}}{Z_n^+(y)}$$

where $c(\gamma)$ is the number of γ's surface contacts.

Then the mean density of contacts for walks of length n is

$$\frac{1}{n}\frac{\sum_\nu \nu c_n^+(\nu) y^\nu}{Z_n^+(y)} = \frac{y}{n}\frac{\partial \log Z_n^+(y)}{\partial y}.$$

As $n \to \infty$, this becomes

$$y\frac{\partial \kappa(y)}{\partial y} \begin{cases} = 0 & \text{if } y < y_c \\ > 0 & \text{if } y > y_c. \end{cases}$$

Define the bivariate generating function

$$C^+(x,y) = \sum_{n,\nu} c_n^+(\nu) x^n y^\nu = \sum_n Z_n^+(y) x^n.$$

Then if $\mu(y) = e^{\kappa(y)}$, the radius of convergence of $C^+(x,y)$ for a given y is $\mu(y)^{-1}$.

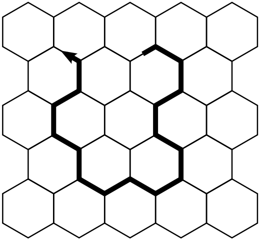
Honeycomb lattice: Connective constant

For the honeycomb lattice, $\mu = \sqrt{2+\sqrt{2}}$.

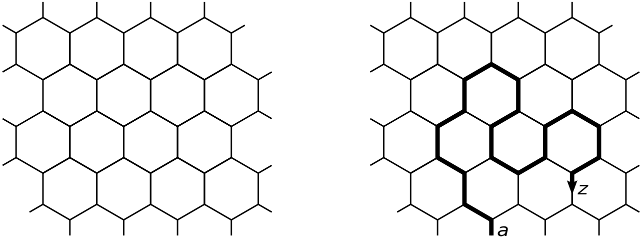
Conjectured by Nienhuis in 1982, using methods from statistical physics ($O(n)$ loop model, Coulomb gas).

Proof announced in 2010 by Duminil-Copin and Smirnov. They use ideas in discrete holomorphicity.

Convenience: SAWs start and end at mid-edges, rather than vertices.



Let a domain $\Omega = (V_\Omega, M_\Omega)$, where V_Ω induces a connected graph on the lattice, and M_Ω is all the mid-edges adjacent to V_Ω.



$\delta_\Omega \subseteq M_\Omega$ is mid-edges on the boundary.

For $a \in \delta_\Omega$ and $z \in M_\Omega$, define the observable

$$F(\Omega, a, z; x, \sigma) \equiv F(z) = \sum_{\gamma: a \to z} x^{|\gamma|} e^{-i\sigma w(\gamma)}$$

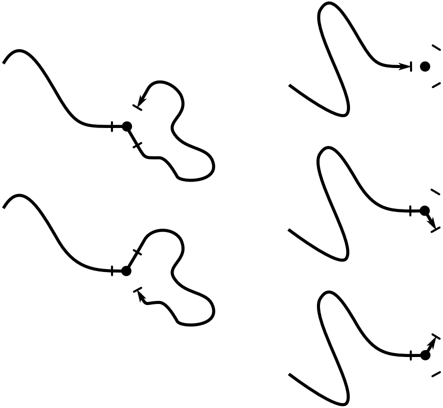
where γ is a SAW from a to z, $|\gamma|$ is the length and $w(\gamma)$ is the winding angle:

$$w(\gamma) = \frac{\pi}{3}(\#\text{left turns} - \#\text{right turns})$$

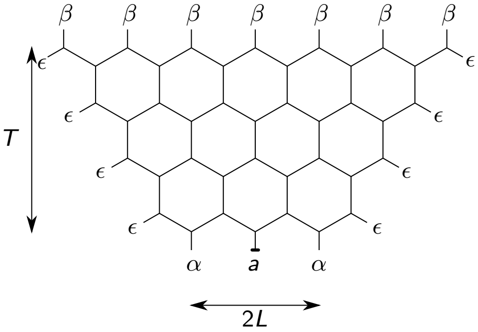
Theorem. (Smirnov) Let $v \in V_\Omega$ and $p, q, r \in M_\Omega$ adjacent to v. Then if $x = x^* = 1/\sqrt{2+\sqrt{2}}$ and $\sigma = 5/8$,

$$(p - v)F(p) + (q - v)F(q) + (r - v)F(r) = 0.$$

Idea of proof. SAWs ending at p, q, r can be grouped into pairs or triples, then show contribution of each group is 0.



Special domain $D_{T,L}$:



Sum Smirnov's identity over all vertices → get an identity relating generating functions of walks which start at a and end on the boundary:

$$1 = \cos\left(\frac{3\pi}{8}\right) A_{T,L}(x^*) + \cos\left(\frac{\pi}{4}\right) E_{T,L}(x^*) + B_{T,L}(x^*)$$

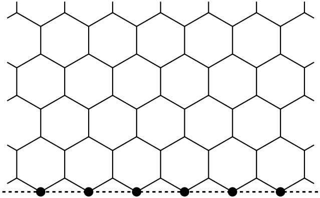
Take appropriate limits in T, L → can show

$$C(x) \begin{cases} < \infty & \text{if } x < x^* \\ = \infty & \text{if } x \geq x^*. \end{cases}$$

So x^* is the radius of convergence of $C(x)$, and $\mu = \sqrt{2 + \sqrt{2}}$.

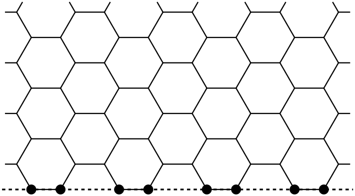
Honeycomb lattice: Critical surface fugacity

Two "natural" ways to orient the surface, and conjectures for y_c for each:



$$y_c = 1 + \sqrt{2}$$

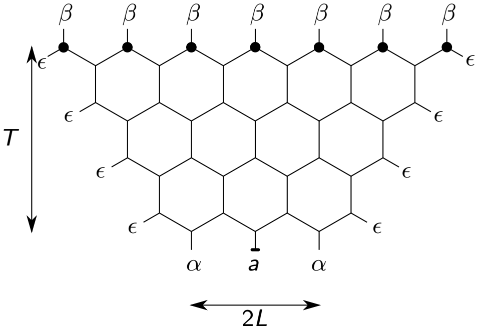
(Batchelor & Yung, 1995)



$$y_c = \sqrt{\frac{2+\sqrt{2}}{1+\sqrt{2}-\sqrt{2+\sqrt{2}}}}$$

(Batchelor, Bennett-Wood & Owczarek, 1998)

First orientation: Take same domain $D_{T,L}$, but put y weights on the β boundary:



Why not the α boundary?

- Just doesn't work! Maybe because there are two different winding angles on α boundary?

Same process:

$$1 = \cos\left(\frac{3\pi}{8}\right) A_{T,L}(x_c, y) + \cos\left(\frac{\pi}{4}\right) E_{T,L}(x_c, y) + \frac{y^* - y}{y(y^* - 1)} B_{T,L}(x_c, y)$$

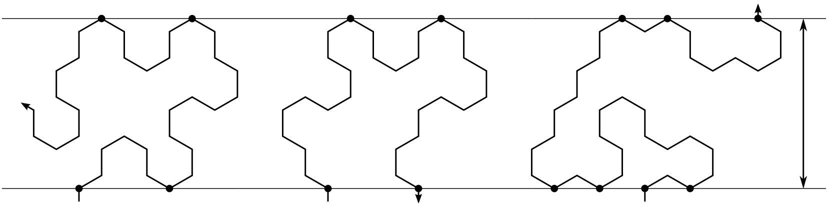
where $x_c = 1/\sqrt{2+\sqrt{2}}$ and $y^* = 1 + \sqrt{2}$.

Take $L \to \infty$, get a strip

$$1 = \cos\left(\frac{3\pi}{8}\right) A_T(x_c, y) + \cos\left(\frac{\pi}{4}\right) E_T(x_c, y) + \frac{y^* - y}{y(y^* - 1)} B_T(x_c, y).$$

In a strip, can

- let walks end on the top, bottom, or anywhere
- put y weights on top, bottom, or both



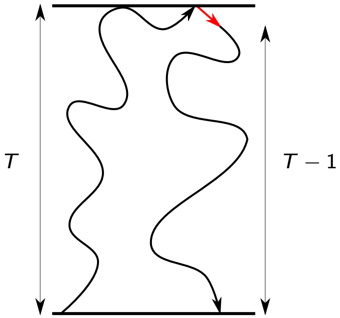
and the free energy $\kappa_T(y)$ is always the same!

Also, in the limit strip $\to$ half-plane:

$$\lim_{T \to \infty} \kappa_T(y) = \kappa(y).$$

To show that $y_c \geq y^*$ is fairly straightforward – need to adapt some results for walks in a strip of the square lattice to the honeycomb lattice.

To show $y_c \leq y^*$, can factorise A_T walks into pairs of B_T walks:



$$A_T(x_c, y) - A_{T-1}(x_c, 1) \leq x_c B_{T-1}(x_c, 1) B_T(x_c, y).$$

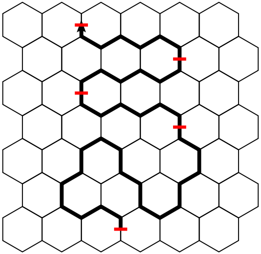
Leads to inequality which is contradicted if $y_c > y^*$.

However, this requires the assumption that

$$B(x_c, 1) := \lim_{T \to \infty} B_T(x_c, 1) = 0.$$

Proof of $B_T(x_c) \to 0$

Bridges can be decomposed into irreducible bridges (iSABs):



Theorem. (Kesten)

$$\sum_{\gamma \in \text{iSAB}} x_c^{|\gamma|} = 1.$$

$\to$ Probability distribution on iSABs: $\mathbb{P}_{\text{iSAB}}(\gamma) = x_c^{|\gamma|}$.

Define a discrete "time" renewal process by repeatedly sampling and concatenating irreducible bridges. The interarrival "times" are the heights of the irreducible bridges.

Then

$$B_T(x_c) = \mathbb{P}(T \text{ is an arrival time}).$$

The (discrete time) renewal theorem:

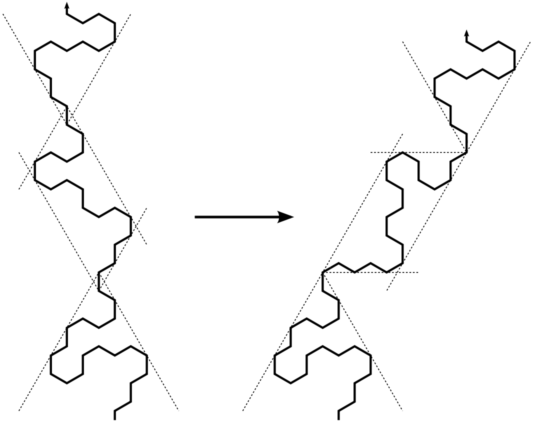
$$\lim_{T\to\infty} B_T(x_c) = \frac{1}{\mathbb{E}(\text{interarrival time})} = \frac{1}{\mathbb{E}_{\text{iSAB}}(H(\gamma))}$$

where $H(\gamma)$ is height.

So to show $B_T(x_c) \to 0$, we need to show $\mathbb{E}_{\text{iSAB}}(H(\gamma)) = \infty$.

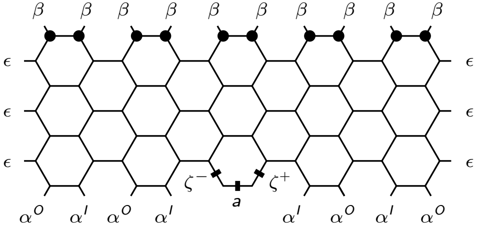
To show $\mathbb{E}_{\text{iSAB}}(H(\gamma)) = \infty$:

- Assume otherwise (for contradiction)
- Show $\mathbb{E}_{\text{iSAB}}(W(\gamma)) < \infty$
- Define a Stickbreak operation:



- Show we can (w.p. 1) perform Stickbreak many times on long bridges.
- Contradicts $\mathbb{E}_{\text{iSAB}}(W(\gamma)) < \infty$

Second orientation: Domain looks a little different:



Identity:

$$c_A^O A_{T,L}^O(x_c, y) + c_A^I A_{T,L}^I(x_c, y) + c_E E_{T,L}(x_c, y) + c_P P_{T,L}(x_c, y) + c_B(y) B_{T,L}(x_c, y) = c_G$$

where $c_B(y) = 0$ at

$$y = y^\dagger = \sqrt{\frac{2+\sqrt{2}}{1+\sqrt{2}-\sqrt{2+\sqrt{2}}}}.$$

Rest of proof is mostly the same. Some symmetry arguments don't work.

Other work

- How does $\kappa(y)$ behave near y_c? Order of the phase transition, crossover exponents...
- Penetrable surfaces (conjectured $y_c = 1$)
- Imhomogeneous surfaces
- Other geometries (quarter-plane, wedge)

References

NRB, M Bousquet-Mélou, J de Gier, H Duminil-Copin & A J Guttmann, The critical fugacity for surface adsorption of self-avoiding walks on the honeycomb lattice is $1 + \sqrt{2}$. To appear in *Comm. Math. Phys.*, arXiv:1109.0358.

NRB, The critical surface fugacity of self-avoiding walks on a rotated honeycomb lattice. In preparation, arXiv:1210.0274.