Semi-flexible directed polymers in a strip with attractive walls

Nicholas Beaton[1] Leo Li[1] Jonathon Liu[2] Thomas Wong[3]

[1]School of Mathematics and Statistics, University of Melbourne
[2]School of Mathematics and Statistics, University of Sydney
[3]Department of Mathematics, Heriot Watt University, Edinburgh

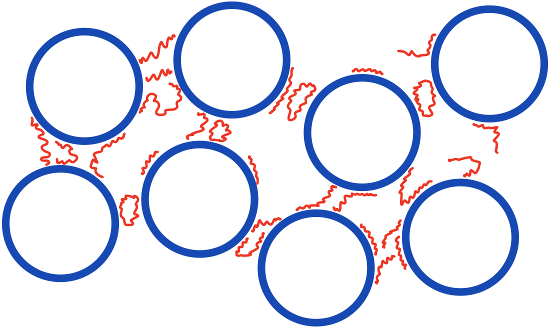
AustMS 2019
Monash University
December 3–6, 2019

THE UNIVERSITY OF MELBOURNE

Australian Government
Australian Research Council

Colloidal suspensions

Colloidal particles in suspension (eg. globules of milk) can be stabilised by polymers in the suspending solution.

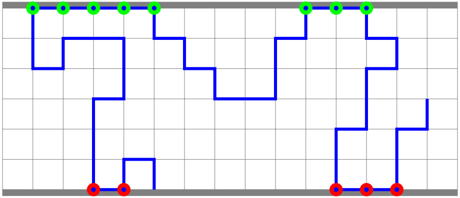


The polymers may be attracted to the colloidal particles, but this attraction is balanced by entropy which causes them to push the particles apart and prevent them from sticking together.

This process is known as **steric stabilisation**.

Modelling with SAWs

A simple but powerful model of a polymer in solution is the **self-avoiding walk** (SAW). To model polymers interacting with colloidal particles, we assume the particles are **much larger** than the polymers. Then place the SAW in a **strip** of the lattice (in 2D) or **slab** (in 3D) of finite width w:



Suppose a SAW ϕ starts on the lower wall, accrues weight a with each visit to the bottom wall and weight b with each visit to the top wall. Let $v_a(\phi)$ and $v_b(\phi)$ be the number of visits to each wall.

The partition function is

$$Z_{w,n}(a,b) = \sum_{\phi \in \mathcal{W}_{w,n}} a^{v_a(\phi)} b^{v_b(\phi)}$$

with limiting free energy

$$\kappa_w(a,b) = \lim_{n\to\infty} \frac{1}{n} \log Z_{w,n}(a,b).$$

SAW cont'd

Theorem (Janse van Rensburg et al 2006)

The free energy $\kappa_w(a, b)$

- *exists for all $a, b \geq 0$,*
- *is continuous, increasing and almost-everywhere differentiable in a and b*
- *is increasing with w if $a \leq 1$ or $b \leq 1$*
- *approaches $\mathcal{F}(a)$ as $w \to \infty$ if $b \leq 1$, where $\mathcal{F}(a)$ is the half-plane free energy (and vice versa)*

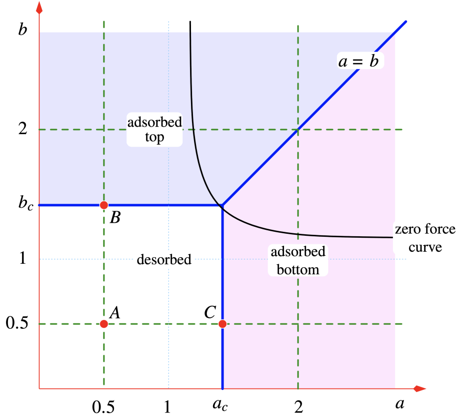
Note that there exists $a_c > 1$ such that $\mathcal{F}(a)$ is constant for $a < a_c$ and increasing for $a > a_c$.

Conjecture (Janse van Rensburg et al 2006)

$$\lim_{w \to \infty} \kappa_w(a, b) = \max\{\mathcal{F}(a), \mathcal{F}(b)\} = \begin{cases} \mathcal{F}(a) & a \geq b \\ \mathcal{F}(b) & a < b \end{cases}$$

SAW cont'd

For each w there is a **zero-force curve** in (a, b)-space where $\kappa_w(a, b) = \kappa_{w-1}(a, b)$: the entropic loss from the strip constraint is balanced by the energy gained from visiting the walls. These curves are expected to approach a limiting curve as $w \to \infty$.

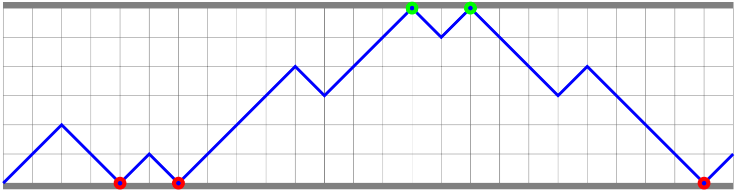


[Owczarek et al 2009]

A solvable version: directed walks

SAW model can be solved exactly for small w (finite transfer matrix) but for larger w this is untenable. Some Monte Carlo work has been done (eg. [Janse van Rensburg et al 2005]).

[Brak et al 2005] looked at a simpler model which can be solved exactly: directed walks.



Define partition function $W_{w,n}(a, b)$ for walks of length n, and then the generating function

$$G_w(z; a, b) = \sum_{n \geq 0} W_{w,n}(a, b) z^n.$$

These can be solved using either the kernel method or recurrences in w (more later).

The free energy $\delta_w(a, b)$ is then connected to the radius of convergence $z_w^*(a, b)$ of G_w via

$$\delta_w(a, b) = -\log z_w^*(a, b)$$

They defined the force to be

$$F_w(a, b) = \frac{\partial}{\partial w} \delta_w(a, b).$$

Directed paths cont'd

To solve this with the kernel method, generalise the partition functions to $W_{w,n,h}(a,b)$, where h is the height of the endpoint. Then

$$G_w(z;s;a,b) = \sum_{n,h\geq 0} W_{w,n,h}(a,b) z^n s^h.$$

Also let $G_w^{[h]}(z;a,b) = [s^h] G_w(z;s;a,b)$.

By appending one step at a time, this satisfies the **functional equation**

$$G_w = 1 + z(s+\bar{s})G_w - z\bar{s}G_w^{[0]} - zs^{w+1}G_w^{[w]} + z(a-1)G_w^{[1]} + zs^w(b-1)G_w^{[w-1]}$$

where $\bar{s} = \frac{1}{s}$.

With

$$\sigma = \frac{1-\sqrt{1-4z^2}}{2z}$$

the **kernel method** yields

$$G_w^{[0]} = \frac{(\sigma^2+1)((\sigma^2+1-b)\sigma^{2w} + (\sigma^2 b - \sigma^2 - 1))}{(\sigma^2+1-a)(\sigma^2+1-b)\sigma^{2w} - (\sigma^2 a - \sigma^2 - 1)(\sigma^2 b - \sigma^2 - 1)}$$

This is rational (not obvious from this expression).

Easy to show that the radius of convergence does not depend on final vertex height.

Directed paths cont'd

$\delta_w(a, b)$ can be computed exactly for a few values:

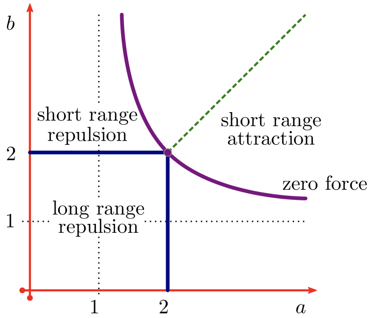
$$\delta_w(1,1) = \log 2 + \log\cos\left(\frac{2\pi}{w+2}\right)$$

$$\delta_w(1,2) = \delta_w(2,1) = \log 2 + \log\cos\left(\frac{\pi}{w+1}\right)$$

and when $ab - a - b = 0$,

$$\delta_w(a,b) = \log\left(\frac{a}{\sqrt{a-1}}\right).$$

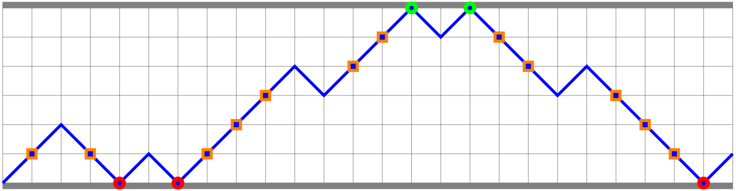
Asymptotics can be computed for other values.



[Owczarek et al 2009]

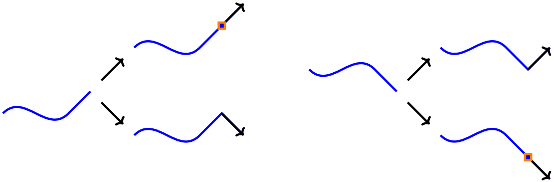
Varying the flexibility

We can introduce a parameter c to control the **flexibility** or **stiffness** of the polymers: each consecutive pair of collinear steps gets weight c.



Partition functions become $W_{w,n,h}(a,b,c)$ and generating function $G_w(z;s;a,b,c)$.

But now when appending a step we need to know what the previous step was:



Solving the system

Need to separately count paths according to whether the last step was down or up:

$$G_w(z;s;a,b,c) = D_w(z;s;a,b,c) + U_w(z;s;a,b,c)$$

Then we get a pair of functional equations:

$$D_w = 1 + z\bar{s}\big(cD_w + U_w\big) - z\bar{s}cD_w^{[0]} + z(a-1)\big(cD_w^{[1]} + U_w^{[1]}\big)$$
$$U_w = zs\big(D_w + cU_w\big) - zs^{w+1}cU_w^{[w]} + zs^w(b-1)\big(D_w^{[w-1]} + cU_w^{[w-1]}\big)$$

Can still be solved with the kernel method, but more complicated now:

$$D_w^{[0]} = \frac{1}{B_w}\left(\tau^{2w}(\tau - cz)(1 - b + bcz\tau) + \tau^2(cz\tau - 1)((1-b)\tau + bcz)\right)$$
$$U_w^{[w]} = \frac{1}{B_w} bc\tau^{w+1}(\tau^2 - 1)z^2$$

where

$$B_w = \tau^{2w}(\tau - cz)(1 - a + acz\tau)(1 - b + bcz\tau) + \tau(cz\tau - 1)((1-a)\tau + acz)((1-b)\tau + bcz)$$
$$\tau = \frac{1 - z^2 + c^2z^2 \pm \sqrt{(1 - z^2 + c^2z^2)^2 - 4c^2z^2}}{2cz}$$

Easy to show that the radius of convergence does not depend on final step height or direction, so we can focus on $U_w^{[w]}$

$\Rightarrow$ interested in roots of B_w.

Zero-force surface

If there are (a, b, c) values where the radius of convergence is independent of w, this is where the force is 0.

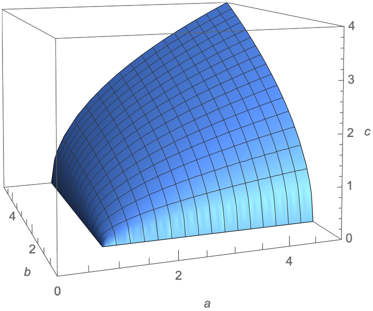
Turns out this happens iff

$$(\tau - cz)(1 - a + acz\tau)(1 - b + bcz\tau) = \tau(cz\tau - 1)((1-a)\tau + acz)((1-b)\tau + bcz) = 0,$$

which has solution

$$ab - a - b - c^2 + 1 = 0 \qquad \text{and} \qquad z = z^* = \frac{\sqrt{a-1}}{\sqrt{a(a+c^2-1)}}$$

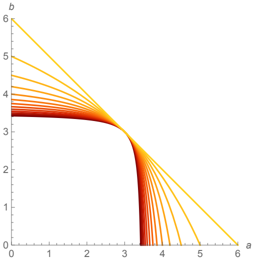
if $a, b > 1$. This defines a **zero-force surface** in (a, b, c)-space:



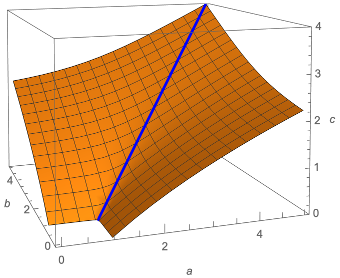
Long-ranged force

Can show that the force is long-ranged (and positive) when $|\tau(z_w)| = 1$. This happens for small a, b:

$$a < \frac{(c+1)(w-1)}{w-c-1} \qquad \text{and} \qquad b < \frac{(c+1)(a-aw+(c+1)(c+w-1))}{a(c-w+1)+(c+1)(w-1)}$$



(a) $c = 2$, $w = 3, \ldots, 15$



(b) $w = 5$

As $w \to \infty$ the boundary becomes piecewise planar: $a = c + 1$ and $b = c + 1$.

Inside this region

$$z_w = \frac{1}{c+1} + \frac{\pi^2 c}{2(c+1)w^2} + \frac{\pi^2 c\left(ab - a - b - c^2 + 1\right)}{(c-a+1)(c-b+1)w^3} + O\left(\frac{1}{w^4}\right)$$

$$F_w = \frac{\pi^2 c}{w^3} + \frac{3\pi^2 c(c+1)\left(ab - a - b - c^2 + 1\right)}{(c-a+1)(c-b+1)w^4} + O\left(\frac{1}{w^5}\right).$$

Short-ranged force

On the boundary between long- and short-ranged, the force is also long-ranged but with slightly different asymptotics.

In the short-ranged region, can deduce the exponential rate of decay, and then substitute to obtain coefficients.

If $a > b$, set

$$\Lambda = \frac{\sqrt{a}c}{\sqrt{(a-1)(a+c^2-1)}}.$$

Then

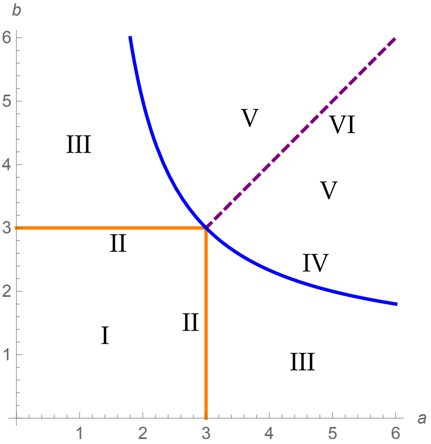
$$z_w = \frac{\sqrt{a-1}}{\sqrt{a(a+c^2-1)}}\left(1 - \frac{((a-1)^2-c^2)^2(ab-a-b-c^2+1)}{2ac^2(a-1)(a-b)(a+c^2-1)}\Lambda^{2w} + O(\Lambda^{4w})\right)$$

$$F_w = \frac{((a-1)^2-c^2)^2(ab-a-b-c^2+1)\log\Lambda}{ac^2(a-1)(a-b)(a+c^2-1)}\Lambda^{2w} + O(\Lambda^{4w})$$

If $a < b$ then just swap a and b.

If $a = b$ then the force is still short-ranged but with different asymptotics.

Force diagram for fixed c



$c = 2$

I & II: long-ranged positive force

III: short-ranged positive force

IV: zero-force surface

V: & VI: short-ranged negative force

Future work

Could use Motzkin paths instead (diagonal up, diagonal down, and horizontal steps). Should still be exactly solvable.

Alternatively could move to directed paths in $\mathbb{Z}^3$, taking steps $+x, +y, +z$ and confined to

$$\frac{x+y}{2} \leq z \leq \frac{x+y}{2} + w.$$

Or partially directed walks (N, S, E).

Instead of weighting for stiffness/flexibility, can use SAWs or PDWs and put a weight u on nearest-neighbour contacts. As u increases, polymers form globules $\Rightarrow$ still push harder on walls, but scaling should be totally different. Much harder to solve...

Or (eek!) use weights for both stiffness and nearest-neighbour contacts.

Reference

arXiv:1912.00151

Thank you!