Exact solution of long chain polymers in an attractive slit

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Talk outline

Sensitised flocculation and steric stabilisation

The model

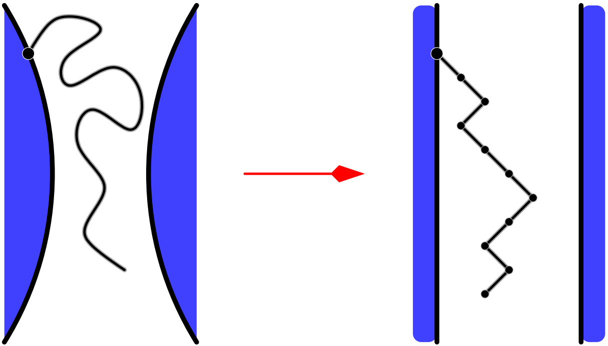
Solving the full model

Analysing the model

Mesoscopic scale

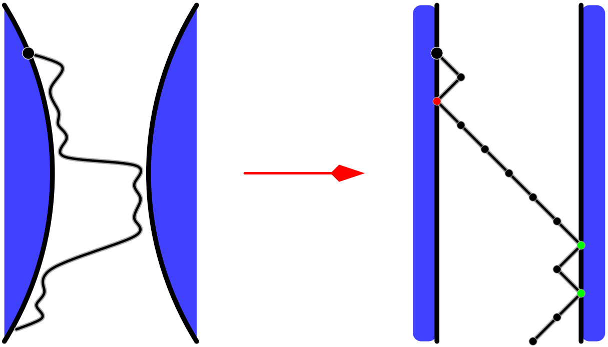
Conclusions

What is steric stabilisation?



- Entropic repulsion between the colloidal particles.

What is sensitised flocculation?



- Polymer adsorbs and pulls the particles together.

Our model

Paths in a slit

- A directed path in a slit of width w.
- Boltzmann weights a and b for interactions with lines (walls).
- Several different geometric constraints:
  loops, bridges and tails — in this talk only loops.

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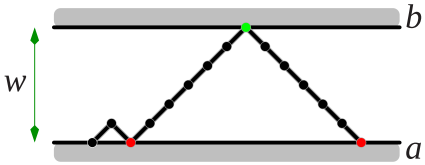
Loops — start and end on $y = 0$.



Relationship to Tony's work

History: no walls or no interactions

- Guttmann, A.J., Owczarek, A.L. and Viennot, X.G., *Vicious walkers and Young Tableaux I: Without Walls,* (1998)
- Krattenthaler, C., Guttmann, A.J. and Viennot, X. G.,*Vicious walkers, friendly walkers and Young tableaux: II With a wall* (2000)
- Guttmann, A.J. and Voege, M, *Lattice paths: vicious walkers and friendly walkers.* Journal of Statistical Inference and Planning, (2002)
- Krattenthaler, C, Guttmann, A. J., and Viennot, X. V., *Vicious walkers, friendly walkers and Young tableaux III: Between two walls.* (2003)
- Chan, Y-b and Guttmann A.J., *Some results for directed lattice walkers in a strip.* (2003)

First let $w \to \infty$; the half-plane limit

Adsorbing paths in a half plane

- Study model via its generating function

$$L(z,a) = \sum_{\varphi \in loops} z^{n(\varphi)} a^{v(\varphi)}$$

- Obtain a functional equation and solve it
- Solution is algebraic

$$L(z,a) = \frac{2}{2 - a + a\sqrt{1-4z^2}}$$

Phase diagram for the half-plane

Analyse the solution

- The free energy is $\kappa^{half-plane}(a) = -\log z_c(a)$.
- There are 2 phases characterised by density of visits:

$$\rho = \lim_{n\to\infty} \frac{\langle v \rangle}{n} = \frac{\partial \kappa(a)}{\partial \log a}$$

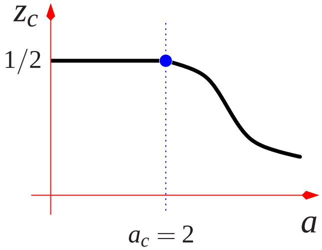
- The limit $n \to \infty$ has been taken after $w \to \infty$.

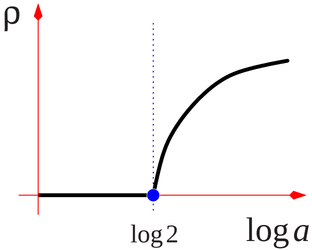
Phase diagram for the half-plane

Analyse the solution

- The free energy is $\kappa^{half-plane}(a) = -\log z_c(a)$.
- There are 2 phases characterised by density of visits:

$$\begin{array}{llll} \text{desorbed} & a \le 2: & z_c = 1/2 & \text{and} \quad \rho = 0 \\ \text{adsorbed} & a > 2: & z_c = \sqrt{a-1}/a & \text{and} \quad \rho > 0 \end{array}$$





Back to the full model — finite width slit

How to solve the full model

- Build the paths a row at a time
- Replace vertices in top row by zig-zag paths.
- Leads to (different) infinite set of functional equations

Rational form

$$L_w(z, a, b) = \frac{P_w(z, 0, b)}{P_w(z, a, b)}$$

- $P_w(z, a, b)$ satisfies a simple linear recurrence.
- Related to Fibonacci polynomials.

The solution of the full model

- This leads us to

$$L_w = \frac{(1+q)\left[(1+q-bq)-(1+q-b)q^w\right]}{(1+q-aq)(1+q-bq)-(1+q-a)(1+q-b)q^w}.$$

where

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

- A similar analysis works for tails and bridges.

Location of singularities

Zeros of P_w

- The zeros of P_w give the singularities of L_w.
- These satisfy

$$q^w = \frac{(1+q-aq)(1+q-bq)}{(1+q-a)(1+q-b)}.$$

- The closest singularity to the origin gives the free energy.

Analysis of the solution

Special points

- For certain points in the a, b plane the equation for the zeros simplifies
  - $(a, b) \in \{(1,1), (2,1), (1,2), (2,2)\}$
  - and on the curve $ab = a + b$.
- At these points we can find $q_c(w)$ and so $z_c(w)$ exactly.

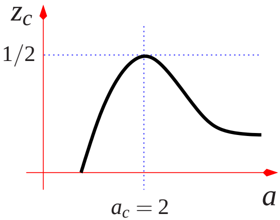
On the special curve

Zeros of P_w

- when $ab = a + b$ the zeros are given by

$$q^w = 1 \qquad \text{and} \qquad q = (a-1), \ \frac{1}{(a-1)}$$

- This implies that $z_c = \frac{\sqrt{a-1}}{a}$.
- Note, this is independent of the strip width, w.



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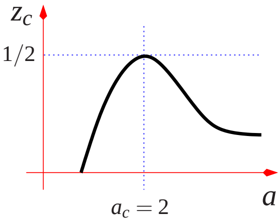
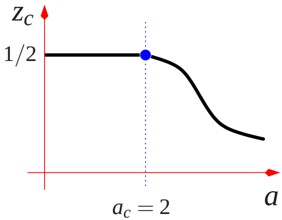




The limit $w \to \infty$ for arbitrary a, b
The infinite slit limit

The free energy

- Can find zeros of P_w in the limit $w \to \infty$.
- The smallest zero gives z_c which gives κ.
- We have the following

$$z_c(a,b) = \begin{cases} 1/2 & a, b \leq 2 \\ \frac{\sqrt{a-1}}{a} & a > 2 \text{ and } a > b \\ \frac{\sqrt{b-1}}{b} & \text{otherwise} \end{cases}$$

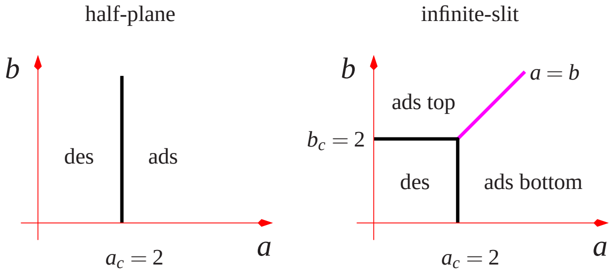
The phase diagram for loops and tails

Phase transitions

- For finite w, $z_c(a, b)$ is an analytic function of a and b.
- So no phase transitions for finite w.
- However in the limit $w \longrightarrow \infty$ there are phase transitions.

The phase diagram for loops and tails

Phase transitions



- Black $= 2^{nd}$ order and pink $= 1^{st}$ order.
- Left-hand diagram: $w \longrightarrow \infty$ and then $n \longrightarrow \infty$.
- Right-hand diagram: $n \longrightarrow \infty$ and then $w \longrightarrow \infty$.
- The order of n and w limits really does matter!

Asymptotics of free energy for large w

Special points

- We know $z_c(w)$ exactly at these points.

General a, b

- Can do asymptotic expansion of $z_c(w)$ for large w.
- e.g. For $a, b < 2$:

$$z_c(w) = \frac{1}{2} + \frac{\pi^2}{4}\frac{1}{w^2} + \frac{\pi^2(ab - a - b)}{(2-a)(2-b)}\frac{1}{w^3} + \cdots$$

- For $a > 2$ and $a > b$:

$$z_c = \frac{\sqrt{a-1}}{a} - \frac{(a-2)^2(ab-a-b)}{2a(a-b)\sqrt{a-1}}\left(\frac{1}{a-1}\right)^w + \cdots$$

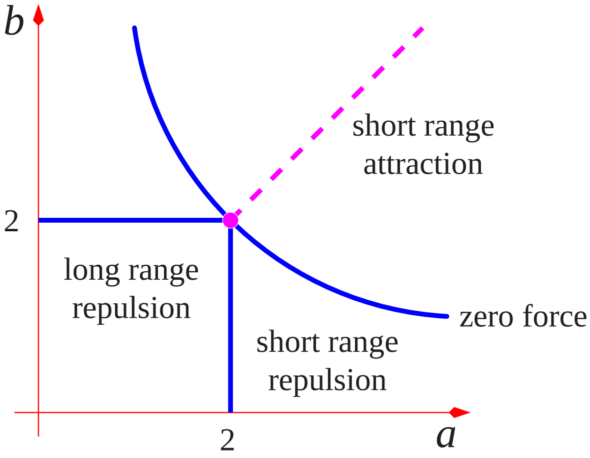
Steric stabilisation and sensitised flocculation

Forces

- Compute forces between walls from $\frac{\partial \kappa(w)}{\partial w}$.
- There are attractive and repulsive regimes.
- For various regions of the (a, b)-plane we have:
  - long-ranged repulsive force,
  - short-ranged repulsive force,
  - short-ranged attractive force,
  - and a line of zero force dividing the last two.
- The zero-force line is *not* a phase boundary.

Steric stabilisation and sensitised flocculation

Force diagram



Publication details

- The above work has been published *Journal of Physics A: Mathematical and General* Volume **38** (2005) pages 4309–4325.

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- The above work has been published *Journal of Physics A: Mathematical and General* Volume **38** (2005) pages 4309–4325.
- There is more to come.

Mesoscopic scale

Large but finite n and w

- We now consider finite but large n and w.
- To do this look at the partition function, defined via

$$L_w(z, a, b) = \sum_{n \geq 0} Z_n(w; a, b) z^n$$

- We define the finite-length free energy by

$$\kappa_n(w; a, b) = \frac{1}{n} \log Z_n(w; a, b)$$

so that $\kappa(w; a, b) = \lim_{n\to\infty} \kappa_n(w; a, b)$.

Order of limits

The order of limits matters

- The infinite slit limit is

$$\begin{aligned}\kappa^{inf-slit}(a,b) &= \lim_{w\to\infty} \kappa(w;a,b)\\ &= \lim_{w\to\infty}\lim_{n\to\infty} \kappa_n(w;a,b)\end{aligned}$$

- whereas the half-plane limit is

$$\begin{aligned}\kappa^{half-plane}(a) &= \lim_{n\to\infty} \kappa_n^{half-plane}(a)\\ &= \lim_{n\to\infty}\lim_{w\to\infty} \kappa_n(w;a,b)\end{aligned}$$

What we know

From now on we confine ourselves to $a, b \leq 2$.

- Here we have

$$\kappa^{half-plane}(a) = \kappa^{inf-slit}(a, b) = \log 2.$$

- So the limits do agree, but what about asymptotics?
- We have

$$Z_n^{half-plane} \sim A\, 2^n n^{\gamma-1}, \qquad \gamma = \begin{cases} -1/2 & a < 2 \\ +1/2 & a = 2 \end{cases}$$

- So

$$\kappa_n^{half-plane} \sim \log 2 + \frac{1}{n}\left[(\gamma - 1)\log n + \log A\right]$$

What we know

The asymptotics are different.

- However for any finite w we have

$$Z_n(w;a,b) \sim B(w)\mu(w)^n,$$

where $\mu(w) = \exp(\kappa(w;a,b))$, $\lim_{w\to\infty} \mu(w) = 2$.

- So

$$\begin{aligned}\kappa_n(w;a,b) &\sim \log 2 + \log\left(\mu(w)/2\right) + \frac{\log B(w)}{n} \\ &\sim \log 2 + \frac{1}{n} f(n,w)\end{aligned}$$

The scaling regime

Is there a scaling regime?

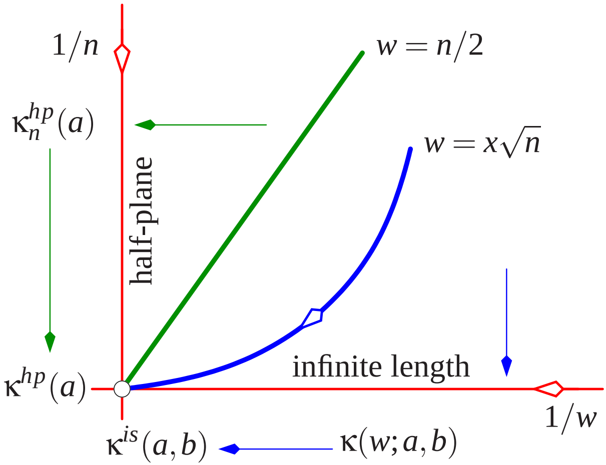
- Can we write $f(n, w)$ as a function of a single variable?
- Does it match the various limiting asymptotic cases?
- A case of finite-size scaling.
- The mean vertex height at $a = b = 1$ is

$$\text{mean height of vertex} \sim \sqrt{\frac{\pi n}{8}} + O(1),$$

- Hence we expect the scaling variable

$$\frac{w}{\xi_\perp} \propto \frac{w}{\sqrt{n}}.$$

The scaling regime



The scaling Ansatz

Scaling of κ and $\mathcal{F}$

- For $a, b \leq 2$ and as $w, n \to \infty$ with fixed $x = \frac{w}{\sqrt{n}}$, we propose the Ansatz for the free energy:

$$\kappa_n(w; a, b) \sim \log 2 + \frac{1}{n} X\left(gx\right).$$

- Differentiating wrt w gives an expression for the force

$$\mathcal{F}_n(w; a, b) \sim \frac{1}{n^{3/2}} Y\left(gx\right).$$

- The universal functions $X(x)$ and $Y(x)$ change if a or b equal 2.
- The constant g is a non-universal factor.

Matching the infinite-slit

Scaling of κ

- Reiterating the Ansatz

$$\kappa_n(w; a, b) \sim \log 2 + \frac{1}{n} X\left(gx\right).$$

- For w fixed and large and $n \to \infty$ we recall that

$$\kappa(w; a, b) = \log 2 + \frac{e_1}{w^2} + O(w^{-3})$$

Matching the infinite-slit

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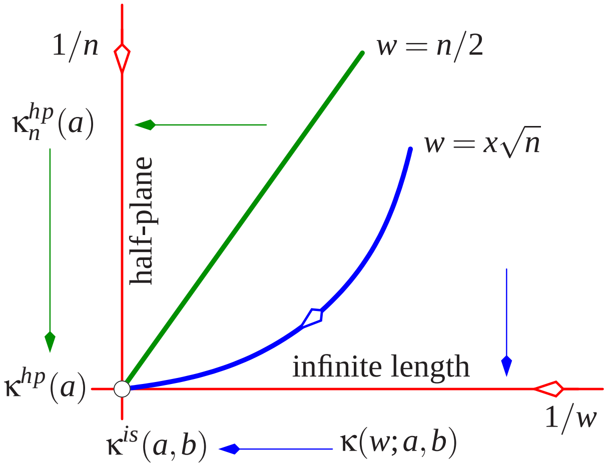
- So if

$$X(x) \sim \frac{e_1}{x^2} = \frac{e_1 n}{w^2} \qquad \text{as } x \to 0^+$$

  then the scaling Ansatz matches the infinite-slit asymptotics.

The scaling regime



Matching the half-plane

- What about $w \to \infty$ with n fixed and large?
- Reiterating the Ansatz

$$\kappa_n(w; a, b) \sim \log 2 + \frac{1}{n} X\left(gx\right).$$

and the half-plane result

$$\kappa_n^{half-plane} \sim \log 2 + \frac{1}{n}\left[(\gamma - 1)\log n + \log A\right]$$

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- After $w > n/2$, $Z_n(w; a, b)$ is a constant function of w.
- So which limit do we really want?

$$w \to \frac{n}{2} \qquad \text{or} \qquad w \to \infty$$

Analytic results in progress?

An expression for the partition function

- We can write

$$Z_n(w; a, b) = \frac{1}{2\pi i} \oint L_w(z; a, b) \frac{\mathrm{d}z}{z^{n+1}},$$

where L_w is a rational function.

- So Z_n is a sum over residues at the zeros of the denominator of L_w — in the q variable these satisfy:

$$q^w = \frac{(1 + q - aq)(1 + q - bq)}{(1 + q - a)(1 + q - b)}.$$

- This is equivalent to a partial fraction expansion of L_w.
- However where are all the zeros?

A nice trick

A different expression

- There is a 'trick' which is equivalent to moving the integration contour which gives the following expression for arbitrary a and b.

$$Z_{2\ell}(w; a, b) = \sum_{r=0}^{w} \sum_{s=0}^{\ell} {\sum_{s_0,\ldots,s_w}}' C_{2\ell,\ell^*} \binom{s}{s_0, \ldots, s_w} \alpha_r \prod_{m=0}^{w} \beta_m^{s_m}$$

where the multinomial sum is simply constrained,
$C_{n,m}$ is a generalised Catalan number,
ℓ^* is a simple function of ℓ and
α_i and β_i are simple functions of a and b.

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- We have summed over all Bethe roots without knowing them!
- This is pretty, but an asymptotic challenge!
- We are currently analysing the special cases $a, b \in \{1, 2\}$ where Z_n simplifies.

Numerical analysis

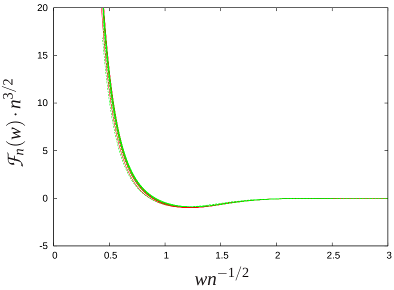
Scaling function $Y(x)$ for the force

- The scaling Ansatz tells us that

$$\mathcal{F}_n(w;a,b)n^{3/2} \sim Y(gx) = Y\left(g\frac{w}{\sqrt{n}}\right),$$

  in the limit $n \to \infty$ with x fixed.
- So $Y(x)$ should be the same for all $a, b < 2$ — seems to be the case
- and also same for other models in the universality class — e.g. Motzkin paths in a slit.
- $Y(x)$ different for $(1,1)$, $(1,2)$, $(2,1)$ and $(2,2)$ since there is a phase transition at $a = 2$ and also at $b = 2$.

$Y(x)$ is universal.



- Scaled force at $(1, 2)$ for Dyck paths and $(1, \frac{3}{2})$ for Motzkin paths.
- Data collapse for $w \in \{8, 16, \ldots, 80\}$.
- Same scaling function (up to some constants) for both models.
- Note that $Y(x)$ changes sign and is non-monotonic!

Conclusions

- We have found an exact solution for the g.f.
- The thermodynamic limits now well understood.
- The half-plane is not the same as the infinite-slit.
- The force-diagram has been mapped out.

Conclusions

- Finite-size scaling analysis in progress.
- Matching for small x (infinite-slit) appears to hold.
- Matching for large x (half-plane) as yet undetermined.
- Scaling analysis of partition function and generating function at special points $a, b \in \{1, 2\}$ is proceeding.
- Numerical analysis for $a, b > 2$ also underway.
- Some preliminary work for self-avoiding walks using FlatPERM.
- Of course we stand on Tony's shoulders...