Polymers in a slabs and slits with attracting walls

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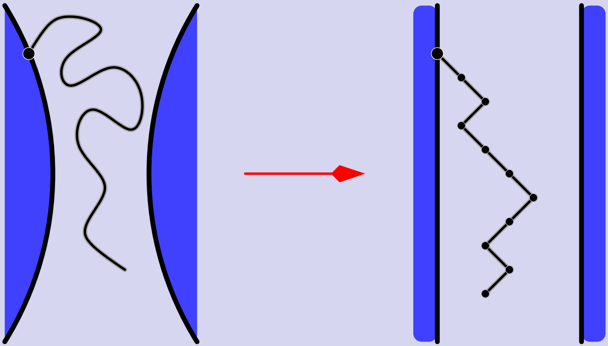
Random Polymers, EURANDOM

AUSTRALIAN RESEARCH COUNCIL
Centre of Excellence for Mathematics
and Statistics of Complex Systems

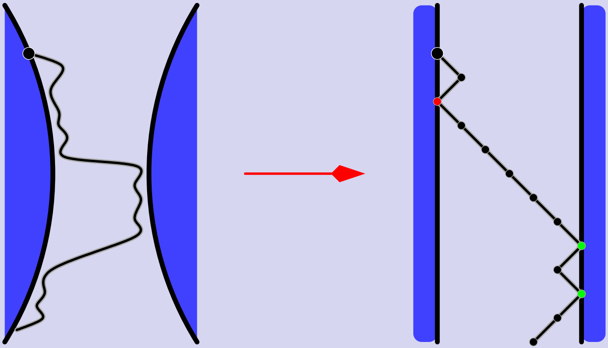
Talk outline

What is steric stabilisation?



- Entropic repulsion between the colloidal particles.

What is sensitised flocculation?



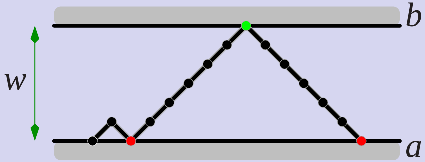
- Polymer adsorbs and pulls the particles together.

History

Paths in a slit

- R. Brak, A. L. Owczarek, A. Rechnitzer and S. Whittington *Journal of Physics A: Mathematical and General* Volume **38** (2005) pages 4309–4325.
- A directed path in a slit of width w.
- Boltzmann weights a and b for interactions with lines (walls).
- Solution: see Andrew's talk

Loops — start and end on $y = 0$.



Phase diagram for the half-plane

Consider the half-plane

- Let us take the limit $w \to \infty$ first.
- The thermodynamic limit $(n \to \infty)$ free energy $\kappa^{half-plane}(a) = \lim_{n\to\infty} \log Z_n^{1/n}(a)$ can be found exactly.
- There are 2 phases characterised by density of visits:

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

where the partition function is

$$Z_n(a) = \sum_u c_{n,u} a^u$$

with $c_{n,u}$ being the number of walks of length n with u visits to the wall.

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

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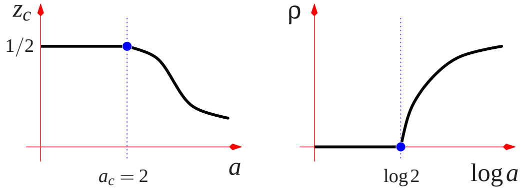
- There are 2 phases characterised by density of visits:

$$\begin{array}{llll} \text{desorbed} & a \le a_c = 2: & \kappa^{half-plane} = \log 2 & \rho = 0 \\ \text{adsorbed} & a > 2: & \kappa^{half-plane} = \log\left(a/\sqrt{a-1}\right) & \rho > 0 \end{array}$$



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- The thermodynamic limit ($n \to \infty$) free energy $\kappa^{half-plane}(a) = \lim_{n\to\infty} \log Z_n^{1/n}(a)$ can be found exactly.
- There are 2 phases characterised by density of visits:

- Jump in the specific heat
- Second order phase transition
- Crossover exponent $\phi = 1/2$ where ϕ can be found from $\langle u \rangle \sim n^{\phi}$ at $a = a_c$

Partition function

The finite slit partition function

$$Z_n(w; a, b) = \sum_{u,v} c_{n,u,v}(w) a^u b^v$$

where $c_{n,u,v}(w)$ is known as the 'density of states' and is the number of walks in a slit of width w with u visits to the bottom wall, v visits to the top wall and being of length n. Note that the free energy for the finite width slit is

$$\kappa(w; a, b) = \lim_{n\to\infty} \frac{1}{n} \log Z_n(w; a, b)$$

Analysis of the slit solution

Phase transitions

- For finite w, $\kappa(w; a, b)$ is an analytic function of a and b.
- So no phase transitions for finite w.
- However in the limit $w \to \infty$ (infinite slit) there are non-analyticities (phase transitions).

- The free energy $\kappa(w; a, b)$ in the limit $w \to \infty$ can be found
- The free energy $\kappa(w; a, b)$ for large widths w can be found asymptotically
- Special points exist where more can be done

Special points

- For certain points in the a, b plane namely
  - $(a, b) \in \{(1, 1), (2, 1), (1, 2), (2, 2)\}$
  - and on the curve $ab = a + b$.
- we can find $\kappa(w; a, b)$ exactly at any width w at these points.

On the special curve

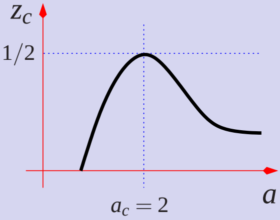
Special curve

- when $ab = a + b$ the free energy is given by

$$\kappa = \log\left(\frac{a}{\sqrt{a-1}}\right)$$

.

- Importantly, this is independent of the strip width, w.



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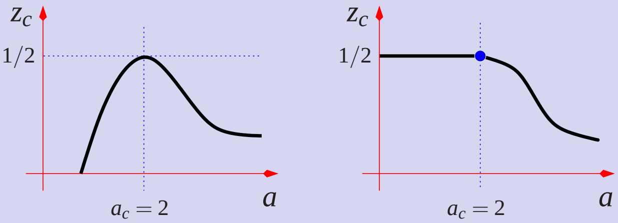


The limit $w \to \infty$ for arbitrary a, b
The infinite slit limit

The free energy of the infinite slit

- In the limit $w \to \infty$ one can calculate exactly

$$\kappa^{inf-slit}(a,b) = \lim_{w \to \infty} \kappa(w;a,b)$$

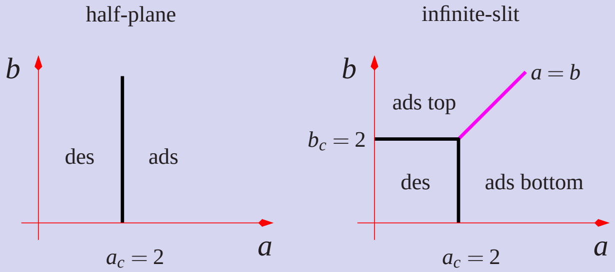
- We have the following

$$\kappa^{inf-slit}(a,b) = \begin{cases} \log 2 & a,b \le 2 \\ \log\left(\frac{a}{\sqrt{a-1}}\right) & a > 2 \text{ and } a > b \\ \log\left(\frac{b}{\sqrt{b-1}}\right) & \text{otherwise} \end{cases}$$

- The free energy depends on b !
- Free energy of infinite slit and half plane are not equal if $b > 2$ and $a < b$

The phase diagram for directed model

Phase transitions



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

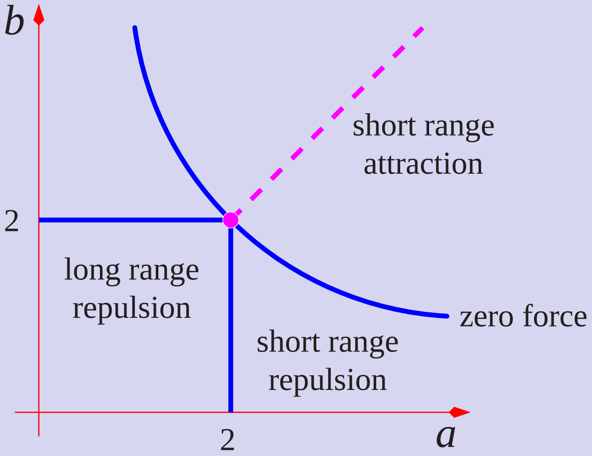
Steric stabilisation and sensitised flocculation

Forces

- Compute forces between walls from $\frac{\partial \kappa(w)}{\partial w}$ from large w expansion of $\kappa(w; a, b)$.
- 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

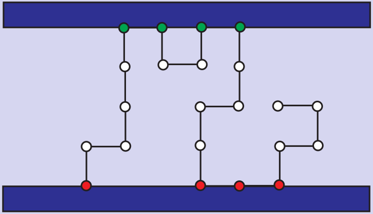


The SAW model in three dimensions

Self-avoiding walks in a slab

- A self-avoiding walk in a slab of width w.
- Boltzmann weights a and b for interactions with planes (walls).

Start on $z = 0$ and finish anywhere



Half-space for 3d SAW

Self-avoiding walks in a half-space

- A self-avoiding walk in a half-space has been studied rigorously and numerically.
- Free energy is known to exist
- A phase transition has been proved to exist
- The adsoption transition has been seen numerically
- The crossover exponent $\phi = 1/2$ as for directed 2d walks but other exponents are different (eg entropic exponents).

Partition function

The partition function

$$Z_n(w; a, b) = \sum_{u,v} c_{n,u,v}(w) a^u b^v$$

where $c_{n,u,v}(w)$ is known as the 'density of states' and is the number of walks in a slab of width w with u visits to the bottom wall, v visits to the top wall and being of length n. Note that the free energy for the slab is

$$\kappa(w; a, b) = \lim_{n \to \infty} \frac{1}{n} \log Z_n(w; a, b)$$

Rigourous results

Rigorous work

- E. J. Janse Van Rensburg, E. Orlandini and S. G. Whittington *Journal of Physics A: Mathematical and General* Volume **39** (2006) pages 13869-902.
- Concatenation arguments and new pattern theorem (Kesten patterns) for walks in slabs lead to a number of results.

Rigorous results continued

Rigorous work

- Existence of the limiting free energy: that is. $\kappa(w; a, b)$ exists for all a, b and all w.
- Montonic properties of the free energy: the limiting free energy is a strictly increasing function of the width w in some region of the phase diagram: implies repulsive force exerted by polymer
- Equality of half-plane and slit free energies in certain parts of phase diagram
- Bounds on the location of the zero force curve
- Points to the structure of phase diagram similar as directed walks in 2d

Self-avoiding walks in slabs using numerical techniques

Self-avoiding walks in slabs

- E. J. Janse Van Rensburg, E. Orlandini, A. L. Owczarek, A. Rechnitzer and S. G. Whittington *Journal of Physics A: Mathematical and General* Volume **38** (2005) pages L823–L828.
- Monte Carlo and series analysis found phase diagram of same shape as the two-dimensional directed walk model!
- E. J. Janse Van Rensburg, E. Orlandini, A. L. Owczarek, A. Rechnitzer and S. G. Whittington *Journal of Physics A: Mathematical and General* soon
- Monte Carlo and series analysis now verifies that most aspects of the phase diagram are the same as the exactly solved two-dimensional directed walk model!
- Proposes and confirms a scaling theory

Exact enumeration and series analysis

Exact enumeration

Exact enumeration of $c_{n,u,v}(w)$ for $n \leq 22$ and $w \leq 8$.
Use Ratio method to infer movement of free energy with changing width

The estimated adsorption transition for the half-plane is $a = a_c \approx 1.33$.

Exact enumeration and series analysis

Define

$$R_n(a, b; w) = \sqrt{Z_n(a, b; w)/Z_{n-2}(a, b; w)}$$

which one expects behaves as

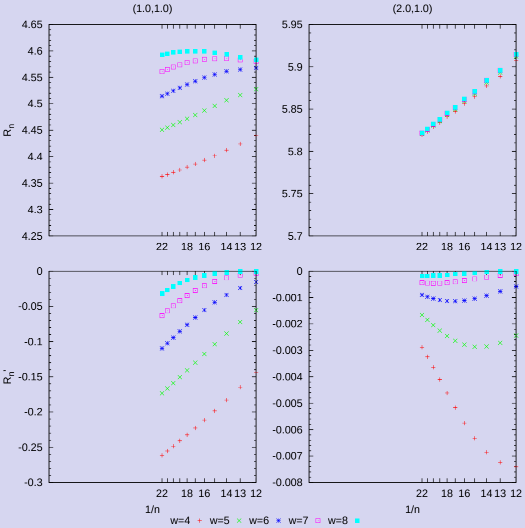
$$R_n(a, b; w) = \exp(\kappa(w, a, b))[1 + B/n + o(1/n)].$$

Let $Q_n(a)$ be the partition function for the half-space problem. Suppose that $a \geq b$. Define

$$R'_n(a, b; w) = R_n(a, b; w) - \sqrt{Q_n(a)/Q_{n-2}(a)}.$$

Free energy changes

Ratio plots

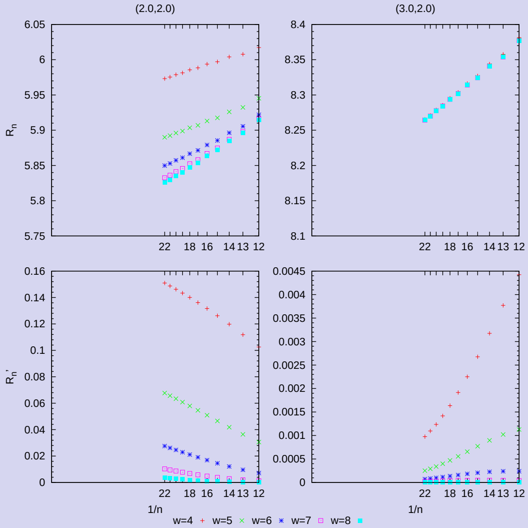


Free energy changes

- For $a = 1,\ b = 1$ the ratio plots for the different values of w are well separated and the values for small w are below those for larger w, consistent with the limiting free energy being an increasing function of w or, equivalently, with the force being repulsive.
- For $a = 2,\ b = 1$ the curves are very much closer together though the ratios for small w are still below those for larger w, corresponding to a repulsive force.
- These results then allow us to infer a force which decreases like a power law for $a = 1,\ b = 1$ and exponentially for $a = 2,\ b = 1$.

Free energy changes

Ratio plots

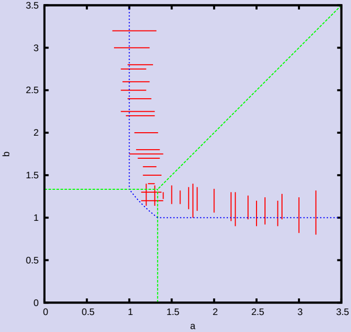


Free energy changes

- For $a = 2,\ b = 2$ (*ie* on the diagonal in the (a, b)-plane) the values of the ratios (and their estimated intercepts) are decreasing as w increases so the force is attractive.
- For $a = 3,\ b = 2$ we see the same behaviour but now the ratios are very close together (*ie* depend only weakly on w).
- The values still decrease as w increases so the force is attractive and the weak w-dependence is consistent with exponential decay of the force as found for a directed walk model.
- For the directed case the behaviour on the diagonal is predicted to be different from that elsewhere in the attractive regime, and this is seen clearly in the plots.

Location of the zero-force curve

Zero Force curve



Estimates of the location of the zero force curve. Note that it passes through or close to the point (a_c, a_c) and is asymptotic to the lines $a = 1$ and $b = 1$. The phase boundaries are also displayed: that is, the lines $a = a_c$ for $0 \leq b \leq a_c$, $b = a_c$ for $0 \leq a \leq a_c$ and $a = b$ for $a \geq a_c$. Note that $a_c \approx 1.33$.

Monte Carlo technique

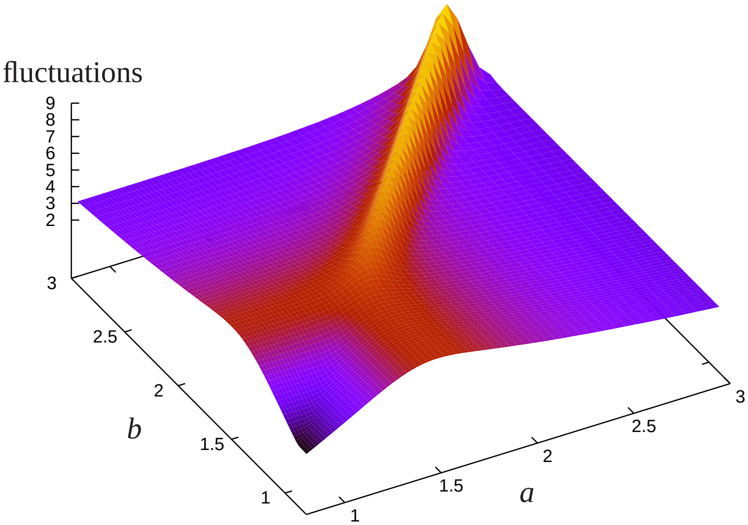
Simulate with FlatPERM algorithm

- Not Markov Chain Monte Carlo
- Growth algorithm with ‘pruning’ and ‘enrichment’
- Flat Histogram method: performs a random walk in the space of parameters (u, v, n) for all u and v and n up to an n_{max}
- Algorithm operates so as to obtain approximately an equal number of samples for any (u, v, n)

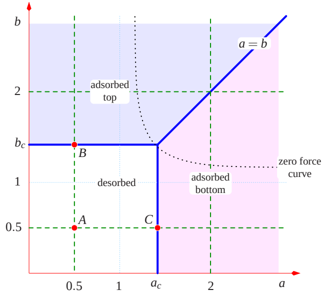
Our simulations

- Simulated walks up to length 512 and for various widths up to $w = 40$
- Calculated fluctuations in visits to the two walls: used largest eigenvalue of matrix of second derivatives to search for phase transitions

Fluctuations in the SAW slab model

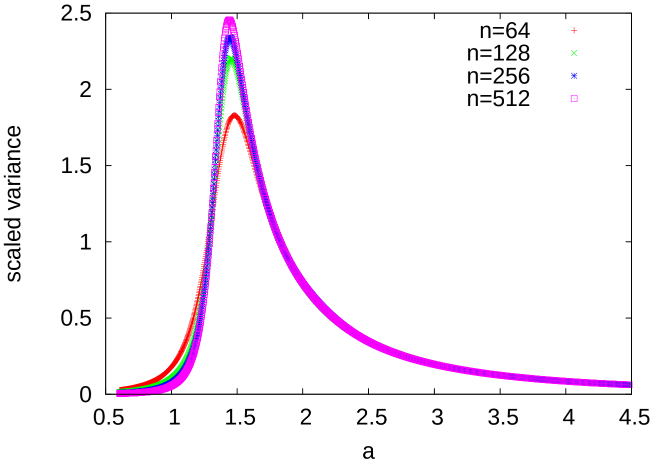


Phase diagram



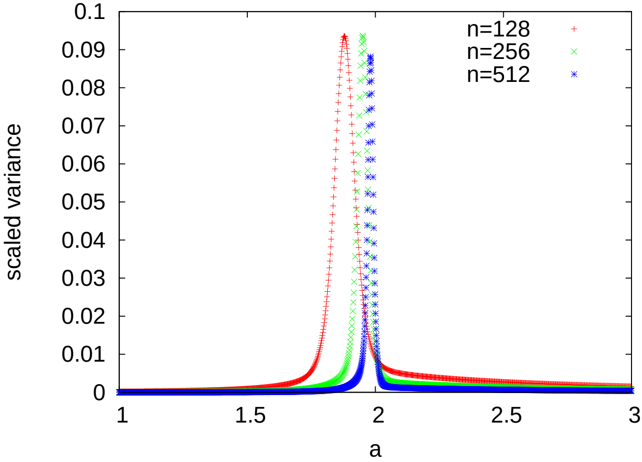
The conjectured infinite-slab phase diagram contains three phases in which the polymer is desorbed, adsorbed to the bottom surface and adsorbed to the top surface. The corresponding phase boundaries are indicated with solid lines. We have simulated the system along the lines $\{(a, 1/2), (a, 2), (1/2, b), (2, b)\}$ (indicated with dashed lines). The three points A, B and C are those at which we estimate the scaling function.

Transitions I



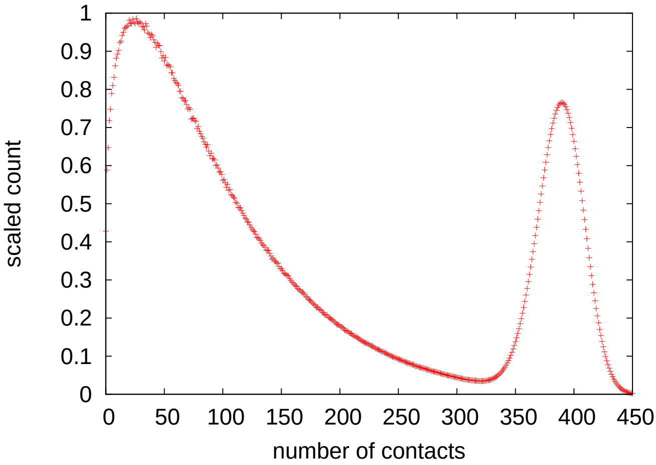
The variance of contacts with the bottom surface per length along the line $(a, 1/2)$ for width 20 and lengths 64, 128, 256 and 512.

Transitions II



The variance of contacts with the bottom surface per length squared along the line $(a, 2)$ for width 12 and lengths 128, 256 and 512. Note that the peak height stays approximately constant implying that the peak height $h_n \sim n^2$.

Transitions III



The distribution of contacts with the bottom surface from the simulations at a point $(a_t, 2)$ where a_t was chosen to be at the peak of the variance of contacts with the bottom surface. The value of a_t used was 1.975, for data produced from simulations at width 12 and polymer length 512.

In the beginning

Arguments from the past

There was Daoud and de Gennes 1977 who conjectured

$$F_{\infty}(a, b; w) \sim \frac{1}{w^{(1+1/\nu)}}$$

where the Radius of Gyration scales as n^{ν} as n becomes large. We note that $\nu = 1/2$ for the directed model and has been estimated as approximately 0.588 for three-dimensonal SAW

Mesoscopic scale

Large but finite n and w

- We now consider finite but large n and w.
- We define the finite-length free energy by

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

so that the finite slit/slab free energy is

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

.

Order of limits

We already know that 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

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

- Only expect $\kappa^{inf-slit}(a,b) = \kappa^{half-plane}(a)$ if either $a, b \leq a_c$ where a_c is the adsorption point of the half-plane or $a > a_c$ with $a > b$.
- So when can we expect similar scaling for finite systems: that is asymptotics?

What we know

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

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

where $\mu(d)$ is the d-dimensional connective constant for SAW.

So the limits do agree, but what about asymptotics?

$$Z_n^{half-plane} \sim A\, \mu(d)^n n^g, \qquad g = \begin{cases} \gamma_1(d) - 1 & a < a_c \\ \gamma_{1,s}(d) - 1 & a = a_c \end{cases}$$

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

$\gamma_1(3) - 1 \approx -0.32$ while estimates of $\gamma_{1,s}(3) - 1$ are poor $(-0.5(2))$

Finite slit

The asymptotics are different for the finite slit.

- For any finite w we have

$$Z_n(w;a,b) \sim B(a,b;w) e^{\kappa(w;a,b)n} n^h,$$

where $h = \gamma(d-1) - 1$. Note that $\gamma(2) - 1 = 11/32$.

- Can rewrite this as

$$\kappa_n(a,b;w) \sim \kappa(a,b;w) + h\frac{\log n}{n} + \frac{B(a,b;w)}{n}$$

- What happens to this asymptotic form as w becomes large?
- Compare to half-plane result

$$\kappa_n^{half-plane}(a) \sim \kappa^{half-plane}(a) + g\frac{\log n}{n} + \frac{A(a)}{n}$$

The scaling regime

Is there a scaling regime?

- Can we write the asymptotics of $\kappa_n(a, b; w)$ as a function of a single variable?
- Does it match the various limiting asymptotic cases?
- A case of finite-size scaling.
- A scaling distance (length scale) to which compare the width is

$$\text{mean height of vertex} \sim \text{Radius of Gyration} \sim n^{\nu},$$

- Hence we expect the scaling variable

$$\frac{w}{\xi_\perp} \propto \frac{w}{n^{\nu}}.$$

Conjectured scaling form for the free energy

Our *conjectured* scaling form of the free energy is

$$\kappa_n(a, b; w) \sim \log \mu(d) + g \frac{\log n}{n} + \frac{1}{n}\mathcal{K}(d\, n^\nu / w) \qquad \text{as } n, w \to \infty$$

with n^ν / w fixed,

- Expansion around half-plane
- It is important to understand that the scaling function depends on whether the underlying infinite-slab/slit system is critical or not as the temperature is varied.
- Hence there are four different scaling functions: one for $a, b < a_c$, one for $a = a_c, b < a_c$, one for $a < a_c, b = a_c$ and one for $a = a_c, b = a_c$.

Matching the half-plane an infinite slit

The scaling function $\mathcal{K}(x)$ should obey

$$\mathcal{K}(x) \sim A(a) \qquad \text{as } x \to 0$$

and

$$\mathcal{K}(x) \sim cx^{1/\nu} + \frac{(h-g)}{\nu}\log(x) \qquad \text{as } x \to \infty$$

with c and d being generic constants here — note that d is a non-universal factor.
This second assumption matches with (large width) finite-slit.

Scaling of the force

While a scaling form for the force is

$$F_n(a,b;w) \sim \frac{1}{n^{(1+\nu)}}\mathcal{F}(d\ n^{\nu}/w) \qquad \text{as } n, w \to \infty$$

where

$$\mathcal{F}(x) \sim c x^{1+1/\nu} \qquad \text{as } x \to \infty.$$

This gives the Daoud and De Gennes result that

$$F(a,b;w) \sim \frac{1}{w^{(1+1/\nu)}}$$

Back briefly to directed walks: numerically

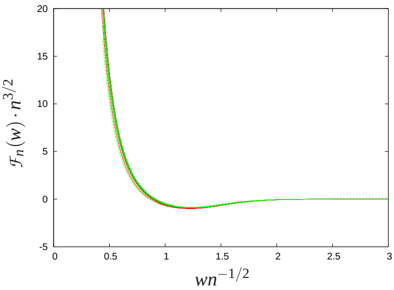
Scaling function $Y(x)$ for the force

- The scaling Ansatz tells us that

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

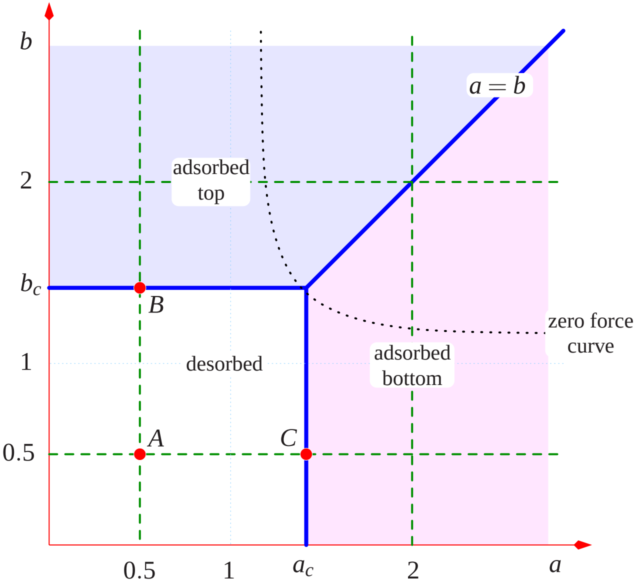
  in the limit $n \to \infty$ with x fixed.
- So $Y(x)$ should be the same for all $a, b < 2$ — seems to be the case
- and also same for other models in the universality class — e.g. Motzkin paths in a slit.
- $Y(x)$ different for $(1, 1)$, $(1, 2)$, $(2, 1)$ and $(2, 2)$ since there is a phase transition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

$Y(x)$ is universal for directed walks in 2 dimensions.

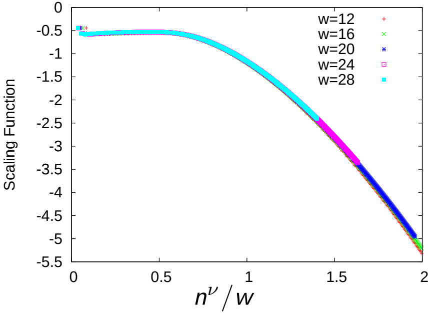


- Scaled force at $(1, 2)$ for Dyck paths and $(1, \frac{3}{2})$ for Motzkin paths.
- Data collapse for $w \in \{8, 16, \ldots, 80\}$.
- Same scaling function (up to some constants) for both models.
- Note that $Y(x)$ changes sign and is non-monotonic!

Recall Phase diagram

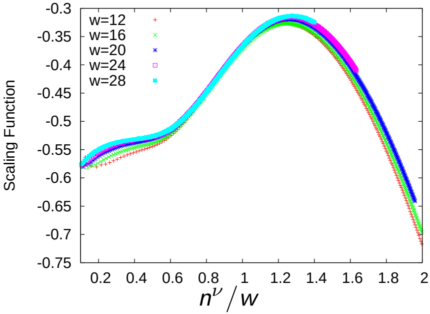


SAW Scaling Functions I



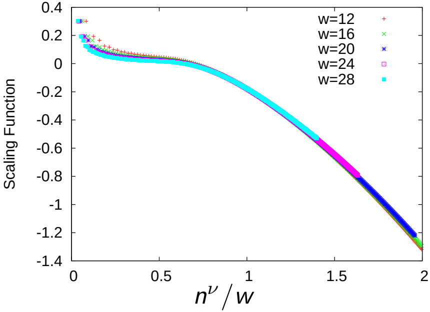
A plot of the scaled free energy at the point $A(1/2, 1/2)$ for widths $12, 16, 20, 24$ and 28 and lengths from 0 to 512. The horizontal axis is n^ν / w and the vertical axis is $n\left(\frac{\log Z_n(w)}{n} - \log\mu(3) - (\gamma_1 - 1)\frac{\log n}{n}\right)$. We have used the values $\mu(3) = 4.684$, $\nu = 0.588$ and $(\gamma_1 - 1) = -0.32$.

Scaling Functions II



A plot of the scaled free energy at the point $B(1/2, b_c)$ using $b_c = 1.33$, for widths $12, 16, 20, 24$ and 28 and lengths from 0 to 512. The horizontal axis is n^ν/w and the vertical axis is $n\left(\frac{\log Z_n(w)}{n} - \log\mu(3) - (\gamma_1 - 1)\frac{\log n}{n}\right)$. We have used the values $\mu(3) = 4.684$, $\nu = 0.588$. We have used $(\gamma_1 - 1) = -0.32$.

SAW Scaling Functions III



Plots of the scaled free energy at the points $C(a_c, 1/2)$ using $a_c = 1.33$, for widths $12, 16, 20, 24$ and 28 and lengths from 0 to 512. The horizontal axis is n^ν / w and the vertical axis is

$$n\left(\frac{\log Z_n(w)}{n} - \log\mu(3) - (\gamma_{1,s} - 1)\frac{\log n}{n}\right).$$

We have used the values $\mu(3) = 4.684$, $\nu = 0.588$. We have used $(\gamma_{1,s} - 1) = 0.25$

Discussion

- While $\mathcal{K}$ is monotonic at points A and C, we find that it is distinctly unimodal at point B.
- We conclude that at points A and C, the polymer exerts a repulsive force on the plates at all lengths and widths.
- Whereas at point B we see that there is a combination of length and width such that the free energy has derivative (with respect to w) equal to zero.
- At point A the interactions with both confining planes are repulsive and the entropy loss due to confinement leads to a repulsive force.
- Point C corresponds to a critical value of the attraction at the plane where the walk is tethered and there is no attractive force with the other plane, so the force is repulsive.
- At point B the walk is tethered to one plane but attracted to the other.

Discussion

- If $n \to \infty$ at fixed w it is known rigorously that the force is repulsive (rigorous work) and this corresponds roughly to the case where $n^{\nu}/w >> 1$.
- If $n^{\nu} << w$ the walk extends to allow vertices in the top plane and this leads to an attractive force.

Confirmation by calculation on the directed model

Owczarek, Prellberg, and Rechnitzer, *Finite-Size scaling functions for directed polymers confined bewteen attractive walls*, To be submitted *J.Phys. A.* in September, 2007.

What one needs to do

Recall the generating function for the directed model

$$L_w(z) = \frac{(1+q)[(1+q-bq)-(1+q-b)q^w]}{(1-q-aq)(1+q-bq)-(1+q-a)(1+q-b)q^w} \; ,$$

where $z = \sqrt{q}/(1+q)$, and so the asymptotics of the finite size partition function $Z_{n,w}(a,b)$ is given by finding

$$Z_{w,n}(a,b) = \frac{1}{2\pi i} \oint L_w(z,a,b) \frac{dz}{z^{n+1}}$$

The problem is to evaluate this contour integral for large but finite n and finite w.

Partition function asymptotics

We note that $g = 3/2$ for $a < 2$ and $g = 1/2$ for $a = 2$.
We recall that $\nu = 1/2$.
For n even, n and w large, we calculate

$$Z_{w,n}(1,1) \sim \frac{2^n}{n^{3/2}} f_{1,1}(\sqrt{n}/w) \;,$$

$$Z_{w,n}(1,2) \sim \frac{2^n}{n^{3/2}} f_{1,2}(\sqrt{n}/w) \;,$$

$$Z_{w,n}(2,1) \sim \frac{2^n}{n^{1/2}} f_{2,1}(\sqrt{n}/w) \;,$$

$$Z_{w,n}(2,2) \sim \frac{2^n}{n^{1/2}} f_{2,2}(\sqrt{n}/w)$$

Scaling Functions

The scaling functions are given by elliptic θ-functions as

$$f_{1,1}(x) = 4\pi^2 x^3 \sum_{k=0}^{\infty} k^2 e^{-\frac{\pi^2 k^2}{2} x^2} \; ,$$

$$f_{1,2}(x) = 4\pi^2 x^3 \sum_{k=0}^{\infty} (k+1/2)^2 e^{-\frac{\pi^2 (k+1/2)^2}{2} x^2} \; ,$$

$$f_{2,1}(x) = 2x \sum_{k=0}^{\infty} e^{-\frac{\pi^2 (k+1/2)^2}{2} x^2} \; ,$$

$$f_{2,2}(x) = 2x \sum_{k=0}^{\infty} e^{-\frac{\pi^2 k^2}{2} x^2}$$

Conclusions

Conclusions

- Using series analysis and Monte Carlo have confirmed phase and force diagrams look like directed 2d model
- Force can be attractive with moderate length walks and repulsive for long walks
- Scaling Theory conjectured and confirmed numerically
- Soon analytic verification... another talk