Lattice Polymers near a Permeable Interface

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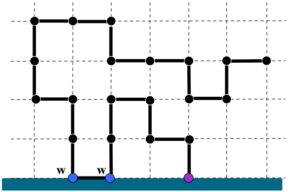
Guttmann 2025 - 80 and (still) counting

Polymer Adsorption

Polymers near a sticky impermeable wall have been studied for a long time.
(Hammersley Torrie Whittington J Phys A 15 p539 1982 and many more)

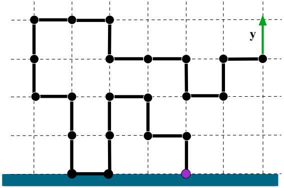
- Boltzmann weight for monomers in the surface is w
- Adsorption Transition (continuous) at $w_c > 1$: two phases
- Desorbed $\langle m \rangle = o(n)$ for $w < w_c$ and Adsorbed $\langle m \rangle \sim An$ for $w > w_c$
  - Adsorbed fraction $\langle m \rangle \sim n^{\phi}$ at $w = w_c$
  - $\phi = 1/2 \ldots$ except 3D, $\phi \approx 0.484$
  - (Diehl & Shpot *NPB* 1998, Grassberger *J Phys A* 2005, Bradly *et al.* PRE 2018)



Polymer Manipulation

Pulling of individual polymers (AFM) modelled by adding a force to one end of the polymer.

- Boltzmann weight for distance of end above the surface is $y = e^{\beta F}$
- Vertical pulling force F
- Continuous pulling transition at $y_c = 1$ (Beaton 2015)



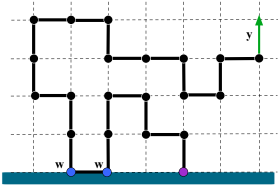
- Two phases: Desorbed for $y < 1$ and Ballistic for $y > 1$
- In Desorbed phase end point is pushed to surface
- While for $y > 1$ Ballistic phase the size exponent $\nu = 1$
- $\phi = \nu$ so in dimension two $\phi = 3/4$ (Bradly & Owczarek 2023)

Polymer Adsorption and Manipulation

Add vertical pulling force F, inducing a Boltzmann weight $y = e^{\beta F}$, and in the presence of a sticky surface with Boltzmann weight w

(Krawczyk et al J Stat Mech P10004 2004, Rensburg Whittington J Phys A 46 435003 2013)

- Three phases: Desorbed, Adsorbed and Ballistic
- Adsorption at value w_c when $y = 1$ (continuous) Desorbed to Adsorbed
- Pulling transition at $y_c(w)$
- For $w \leq w_c$ we have $y_c = 1$ (continuous) Desorbed to Ballistic
- For $w > w_c$ we have $y_c > 1$ (first order) Adsorbed to Ballistic



Polymer Adsorption and Manipulation

Let $w = a$ and "free" = "desorbed"

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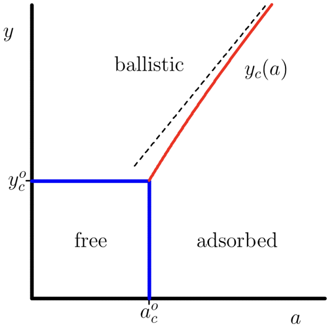


Figure 5. The phase diagram of pulled adsorbing walks. The critical curve $y_c(a)$ separating the ballistic and adsorbed phases is asymptotic to the dashed line in the sense that $\log y_c(a) = \log(a\mu_{d-1}) + o(\log(a))$. There are numerical results indicating that $y_c^o = 1$ (see also [11]). It is known that $a_c^o > 1$ [4].

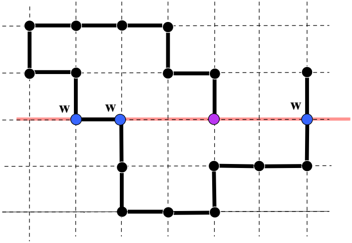
Localisation: a defect interface

Consider a sticky permeable interface - a defect line - also well studied
Add a Boltzmann weight for monomers in the interface as w

(Bray Moore J Phys A 10 p1927 1977, Hammersley et al J Phys A 15 p539 1982, Kremer J Chem Phys 83 p5882 1985, Zhao et al Phys Rev A 1990, Vrbova Whittington J Phys A 31 p7031, 1998, Madras J Phys A 50 064003, 2017)

Expectations (no proof):

- Continuous transition at $w_c = 1$ with two phases
- Delocalised $\langle m \rangle \sim o(n)$ when $w \leq 1$
- Localised $\langle m \rangle \sim A\, n$ when $w > 1$

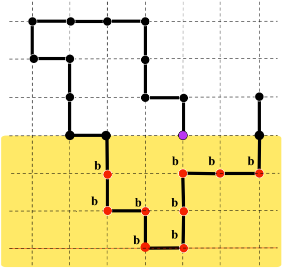


Bisolvent

Consider a polymer near an interface between two different solvents

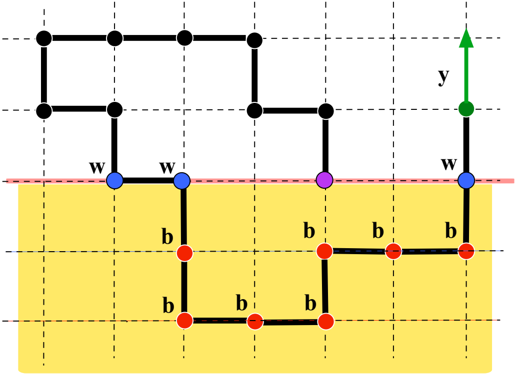
One can prove that

- Two (desorbed) phases exist
- First order transition between them
- When $b > 1$ the polymer will stay below the interface
- When $b < 1$ the polymer will stay above the interface

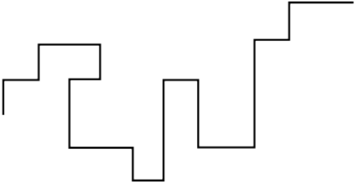


Our model

Combine all of these features into a larger model so that localisation and adsorption are limits or specialisations of our model.



Two types of lattice polymer



Self-avoiding walks:

- good model of long polymers with excluded volume,
- reproduces universal features: exponents
- one avenue to study SAW is with Monte Carlo simulations

Directed walks:

- exactly solvable
- often phase diagrams are similar to undirected SAW

Our full model

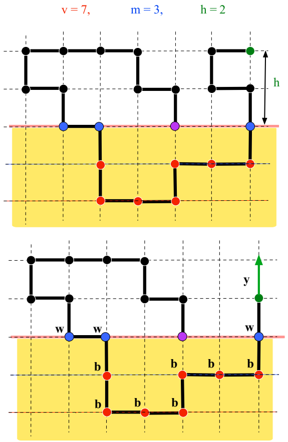
Pulling SAW vertically from a localising interface between two different solvents

Physical quantities:

- Number of vertices of the polymer in lower half space v
- Number of vertices of polymer on the surface m
- Height of endpoint above surface h

Boltzmann weights:

- Lower solvent quality (relative) b conjugate to v
- Surface interaction w conjugate to m
- Force weight y conjugate to h



Our full model II

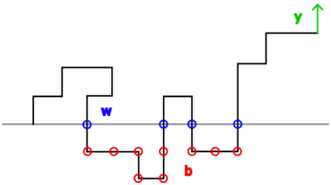
Pulling SAW vertically from a localising interface between two different solvents

Partition function

$$Z_n(b, w, y) = \sum_{vmh} s_n(v, m, h)\, b^v w^m y^h$$

Order parameters (finite size)

$$\langle v \rangle / n, \quad \langle m \rangle / n, \quad \langle h \rangle / n$$



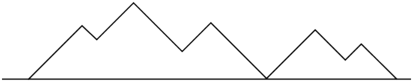
SIMULATIONS

flatPERM (Prellberg & Krawczyk *PRL* 2004)

- grow walks by random endpoint extension
- weight samples by cumulative number of possible moves: $W_n = \prod_{i=0}^{n-1} a_i$
- prune/enrich: $W_n \approx s_n$
- flat histogram, $n = 0, \ldots, n_{\max}$
- can extend to include 2 of v, m, h
- athermal (add weights later)
- parallel implementation, 10^7 iterations

Directed walks

DIRECTED WALKS



- basic Dyck path:

$$D(z) = \sum_n d_n z^n$$

Directed walks

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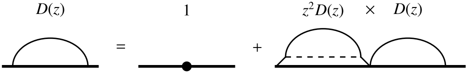
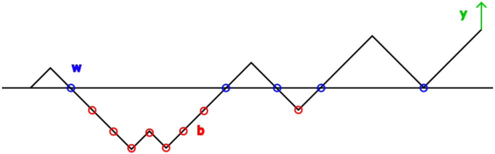
$$D(z) = \sum_n d_n\, z^n$$



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

- non-analyticities in the generating function indicate phase boundaries

Directed walks + interactions



$$Q(b, w, y, z) = \sum_{nvmh} d_n(v, m, h)\, z^n b^v w^m y^h$$

- $b = w = 1$ — pulled tail: $T(y, z)$
- $y = w = 1$ — bisolvent: $B(b, z)$

E. Orlandini and S. G. Whittington *J.Phys. A* **37** 5305 2004

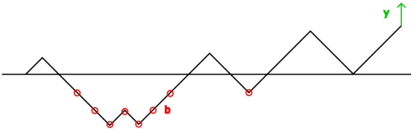
- $b = y = 1$ — interaction with interface: $I(w, z)$

A. Rechnitzer and E. J. Janse van Rensburg *Discrete Appl. Math* **140** 49-71 2004

Pulled endpoint and bisolvent: Directed walks

$$G(b, y, z) = [1 + B(b, z)]\,[1 + T(y, z)]$$

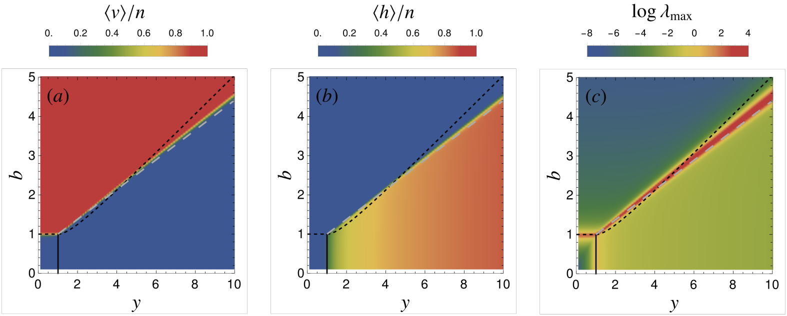
$$z_1 = \frac{1}{2}, \quad z_2 = \frac{1}{2b}$$
$$z_3 = \frac{y}{y^2 + 1}$$

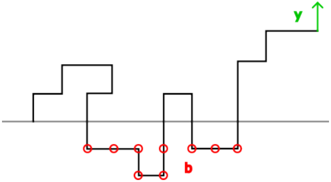


deloc.-above – ballistic (continuous):	$y_c = 1,$	$b < 1$
deloc.-above – deloc.-below (first-order):	$b_c = 1,$	$y < 1$
ballistic – deloc.-below (first-order):	$b_c = \frac{y^2+1}{2y},$	$y > 1$

E. Orlandini and S. G. Whittington *J.Phys. A* **37** 5305 2004

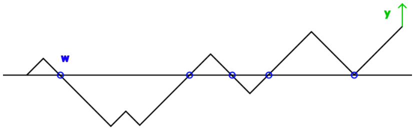
Pulled endpoint and bisolvent in SAW





Pulled endpoint and interacting interface: Directed model

$$G(w,y,z) = I(w,z)\left[1 + T(y,z)\right]$$



$$z_1 = \frac{1}{2}, \quad z_2 = \frac{\sqrt{2w-1}}{2w}$$

$$z_3 = \frac{y}{y^2+1}$$

delocalised – ballistic (continuous):	$y_c = 1,$	$w \leq 1$
delocalised – localised (continuous):	$w_c = 1,$	$y \leq 1$
ballistic – localised (first-order):	$w_c = \frac{1}{2}\left(y^2+1\right),$	$y > 1$

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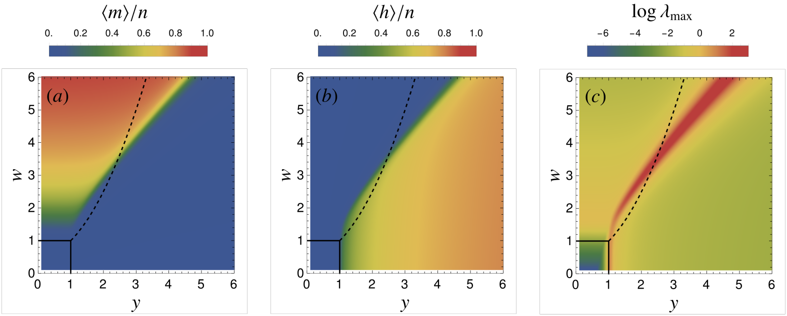
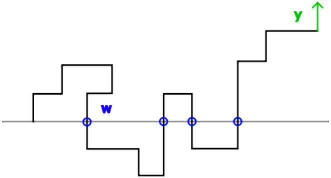
Pulled endpoint and interacting interface: SAW model



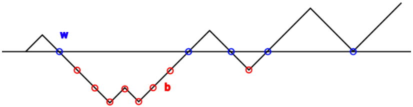


Interacting interface and bisolvent: Directed Model

$$B(b,w,z) = 1+wz^2\left[D(z)+bD(bz)\right]B(b,w,z)$$

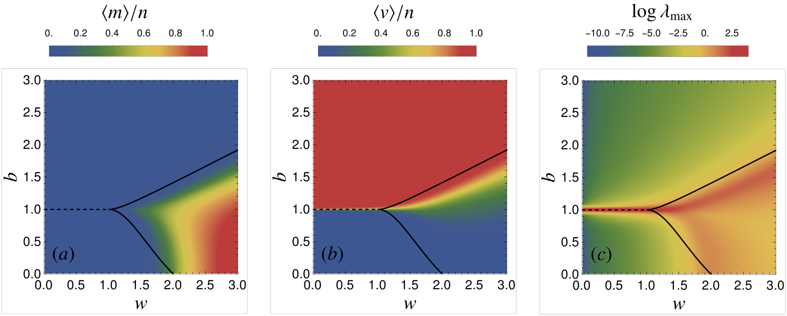
$$z_1 = \frac{1}{2}, \quad z_2 = \frac{1}{2b}$$

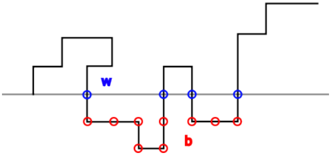
$$z_3 = \frac{\sqrt{w-1}\sqrt{w-b}\sqrt{w+bw-b}}{w\,(w+bw-2b)}$$



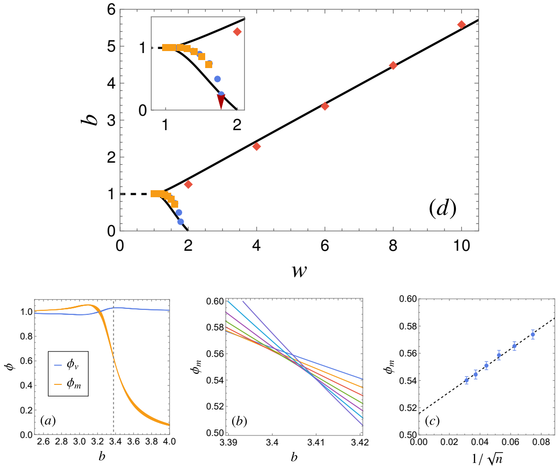
deloc.-above – deloc.-below (first-order):	$b_c = 1,$	$w<1$
localised – deloc.-above (continuous):	$b_c = \frac{-w^2+2w}{w^2-2w+2},$	$w>1$
localised – deloc.-below (continuous):	$b_c = \frac{w^2+w\left(\sqrt{w^2+4w-4}-2\right)}{4w-4},$	$w>1$

Interacting interface and bisolvent: SAW Model





LOCALISED–DELOCALISED-BELOW TRANSITION



$$\frac{\langle m\rangle}{n} \sim n^{\phi_m - 1}$$

$$\frac{\langle v\rangle}{n} \sim n^{\phi_v - 1}$$

$$\phi_m^{(n)} = 1 + \log_2 \frac{u_n}{u_{n/2}}$$

Consider transition at $w = 6$

Symmetry in delocalised phases (SAWs)

- As $b \to 0$: localisation $\to$ adsorption
- As $b \to \infty$: interface also impermeable

$$f_{\text{half}}(b) = \log(\mu_d b)$$

- localised walks:

$$f_{\text{interface}}(w) = \log(\mu_{d-1} w)$$

- free energy for localisation and bisolvent:

$$f(b,w) \begin{cases} = \log(\mu_d) & b \text{ small}, w < w_c(b), \\ = \log(\mu_d b) & b \text{ large}, w < w_c(b), \\ \sim \log(\mu_{d-1} w) & w \to \infty, w > w_c(b). \end{cases}$$

- choice of side is arbitrary

$$(a = 1, b, w) \mapsto (1/b, 1, w/b)$$

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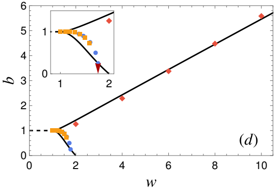
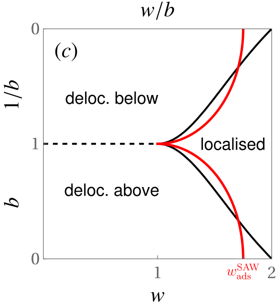
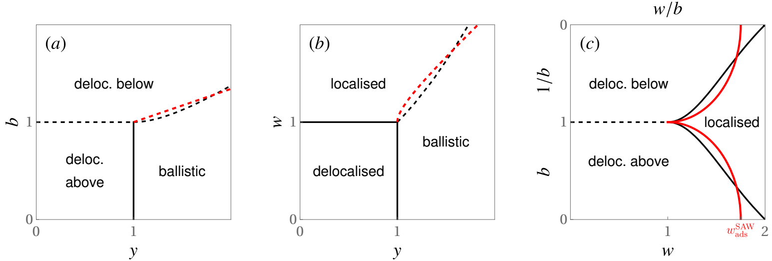
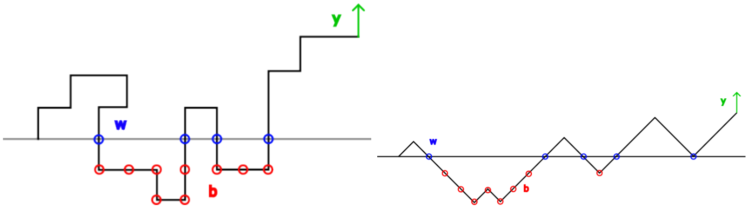


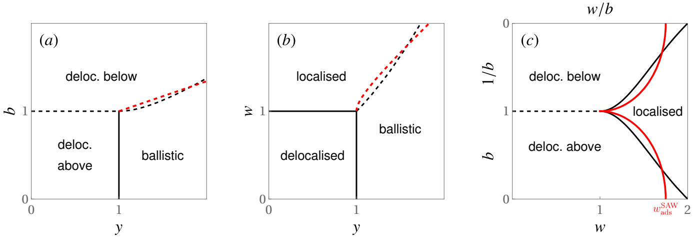


Schematic phase diagram





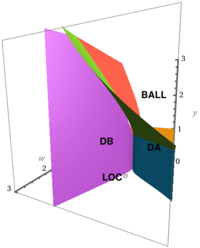
Exponents



- We have numerical evidence to suggest that for decol.below-localised that $\phi_m = 1/2$ for $b > 1$: see figure (c)
- Presumably the same for $b < 1$ by symmetry: see figure (c)
- This compares to the result that $\phi_m = 1 - \nu = 1/4$ for $b = 1$ (Bray Moore J Phys A 10 p1927 1977, Zhao et al Phys Rev A 1990)
- For $b \leq 1$ in (a) and $w \leq 1$ in (b) we predict $\phi_y = \nu = 3/4$ for decol. above - ballistic transition, extends $b = 0, w = 1$ (Bradly & Owczarek 2023)

Summary

We studied localisation and pulling at a permeable interface with a bisolvent as a generalisation of adsorption with an impermeable surface



C. J. Bradly, N. R. Beaton and A. L. Owczarek, *J. Phys. A: Math. Theor.* **57** 445004 (17 pp) (2024)

Localisation in higher dimensions

Consider a d-dimensional lattice with a permeable hypersurface of dimension d_h, and difference
Let $\Delta = d - d_h$

- For $\Delta = 1$: expect $w_c = 1$ (line in 2D, plane in 3D, etc.)
- For $\Delta = 2$: also $w_c = 1$ (plane in 4D)
- For $\Delta > 2$: conjecture $w_c > 1$ (line in 4D)
  - Self-avoiding walks: MC simulations
  - Directed walks (line in 4D):
    - Project to $(d-1)$-dimensional orthogonal hyperplane
    - Without interactions: simple random walk; recurrent if $d - 1 \leq 2$ but transient if $d - 1 > 2$.
    - Interaction weight $w_c > 1$ is required to induce a positive density of returns to the origin.
  - More generally, w_c may be sensitive to orientation of d_h-dimensional hypersurface

Looking Forward

- We studied localisation and pulling at a permeable interface with a bisolvent as a generalisation of adsorption with an impermeable surface
  - Phase diagrams similar between SAW and directed walks
  - Order of transitions (not exponents) are the same
  - Some curvature and asymptotics of phase boundaries differ
  - Crossover exponent for the continuous localised to delocalised-below transition looks like it is $1/2$ for $b > 1$
- Also looked at Motzkin paths
- Higher dimensions: both full space in dimension d and attractive hypersurface
- Will need to consider exponents more fully
- In particular, localisation near $b = w = 1$ case more closely