Adsorption of 2d polymers with two- and three-body self-interactions

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Polymers

- Polymer: A linear long chain of monomers connected by chemical bonds.
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- Equilibrium properties of a single linear polymer in solution.
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Adsorption Transition

- Examples: adhesion, wetting and surface coating.
- Motivation
  - Verify numerically theoretical results.
  - Universality class hypothesis.

O'Shaugnessy & Vavylonis, *J. Phys.*, 2004
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- Key ingredient: polymer-surface interaction.
Effects of solvent conditions

- Good Solvent $\Rightarrow$ Excluded volume effect (coil).
- Poor Solvent $\Rightarrow$ Hydrophobic effect (globule).

Good Solvent Regime $\xrightarrow{\text{Collapse transition}}$ Poor Solvent Regime
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General case: Adsorption + Collapse transition.
Modelling

- Global properties $\Rightarrow$ Coarse-Grained Picture:
  - Polymers $\rightarrow$ Lattice Random-Walks
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  - Polymer surface interaction: Walk-surface interaction.
  - Canonical Model: Interacting self-avoiding walk (SAW)
Global Properties

- Critical exponents associated with the phases transitions.
- Example:
  - Collapse transition: \( R_n^2 \sim n^{2\nu(c)} f(\tau n^{\phi(c)}) \).
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- Should hold for changes in:
  - Geometry of the lattice;
  - Range and strength of interactions;
  - Occupancy restriction;
  - Surface conditions ...
Alternative Model(s)

- Occupancy restriction: self-avoiding trails (SAT)
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- Same universality class of SAW at high temperature (coil phase).
- At the collapse transition point: Exponents SAT \(\neq\) SAW.
The Model

- Trail model with bulk, $\omega = e^{\beta \epsilon_b}$, and surface, $\kappa = e^{\beta \epsilon_s}$, interaction.

$$Z_n(\kappa, \omega) = \sum_{m_s, m_b} C^{(n)}_{m_s, m_b} \kappa^{m_s} \omega^{m_b}$$
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- Three boundary scenarios:

Monomer-Surface (MS)

Bond-Surface (BS)

Diagonal-Surface (DS)
The Model

- Bond-Surface and Diagonal-Surface cases were already studied:

- Expected for SAWs:
  - Ordinary Adsorption ⇒ \( 1/\delta = \phi^{(a)} = 1/2 \)
  - Special Surface Transition ⇒ \( 1/\delta^{(s)} = \phi^{(s)} = 8/21 \)

- For SATs:
  - BS: \( 0.379 < \phi^{(s)} < 0.414 \)
  - DS: \( \phi^{(s)} \approx 0.44 \)

Numerical Simulation

- Stochastic growth methods (Rosenbluth)
- Augmented by Pruning and Enrichment Strategy (PERM)
- Extended to uniform sampling techniques (flatPERM)
Finite-size phase diagram $n_{\text{max}} = 128$

based on largest eigenvalue of covariance matrix
Phase diagram MS case $n_{\text{max}} = 1024$
Normal adsorption transition $n_{\text{max}} = 10240$
Special adsorption transition $n_{\text{max}} = 10240$

- $\omega^{(s)} = 3$: $\kappa^{(s)}_{(MS)} = 1.924(2)$, $\kappa^{(s)}_{(BS)} = 2.442(4)$ $\kappa^{(s)}_{(DS)} = 3.001(2)$
- Expected values $\kappa^{(s)}_{(BS)} = 2.45(5)$ and $\kappa^{(s)}_{(DS)} = 3$

<table>
<thead>
<tr>
<th></th>
<th>monomer-surface</th>
<th>bond-surface</th>
<th>diagonal surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi^{(s)}$</td>
<td>0.338(17)</td>
<td>0.387(10)</td>
<td>0.447(18)</td>
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<tr>
<td>$1/\delta^{(s)}$</td>
<td>0.303(22)</td>
<td>0.299(33)</td>
<td>0.449(22)</td>
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Adsorption of interacting self-avoiding trails in two dimensions

N. T. Rodrigues, T. Prellberg, and A. L. Owczarek
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Lattice trails in two dimensions are a greatly simplified system that can give insight into the complex phase diagram of polymer adsorption on a surface. The authors simulate three different adsorption scenarios in this system, and study the resulting phases and phase boundaries as well as the critical exponents.

Show Abstract +
The Triangular Lattice allows for two types of bulk interactions

- doubly visited sites carry a Boltzmann weight $\omega_2$
- triply visited sites carry a Boltzmann weight $\omega_3$
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- Doubly visited sites carry a Boltzmann weight $\omega_2$
- Triply visited sites carry a Boltzmann weight $\omega_3$

Bulk interactions analysed in:
We associate an energy $-\varepsilon_2$ with each doubly-visited site and a different energy $-\varepsilon_3$ with each triply-visited site. For each SAT we assign a Boltzmann weight $\omega_2^m \omega_3^m$, where $\omega_j = \exp(\beta \varepsilon_j)$.

The partition function of the eISAT model is then given by

$$Z_n(\omega_2, \omega_3) = \sum_{\text{SAT}} \omega_2^m(\varphi_n) \omega_3^m(\varphi_n).$$
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We can define a one temperature family parameterized by $k$, where $\omega_3 = \omega_2^k$, with

$$Z_n^k(\omega) = \sum_{\text{SAT}} \omega^{m_2(\varphi_n) + km_3(\varphi_n)}.$$
Fluctuations

Figure: Density plot of the logarithm of the largest eigenvalue $\lambda_{max}$ of the matrix of second derivatives of the free energy with respect to $\omega_2$ and $\omega_3$ at length $n = 128$ (the lighter the shade, the larger the value).
Figure: Schematic of the proposed phase diagram of the extended ISAT model on the triangular lattice. The open circles represent estimates of the collapse transition for various values of $k$. 
An aside: Kinetic growth trails on the triangular lattice

An example of a trail with 13 steps on the triangular lattice. This trail has six singly visited sites, two doubly-visited sites and one triply-visited site (with probability $\frac{1}{5} \frac{1}{3} 1$).

This trail is produced by the growth process with probability $\left(\frac{1}{6}\right)\left(\frac{1}{5}\right)\left(\frac{1}{5}\right)\left(\frac{1}{5}\right)\left(\frac{1}{3}\right)\left(\frac{1}{5}\right)\left(\frac{1}{5}\right)\left(\frac{1}{5}\right)\left(1\right)\left(\frac{1}{3}\right)\left(\frac{1}{5}\right)\left(\frac{1}{5}\right)$.
KGT to eISAT mapping

The KGT progress gives SAT configurations with Boltzmann weights

\[ \omega_2 = \frac{5}{3} \quad \text{and} \quad \omega_3 = \frac{25}{3} \]

Alternatively

\[ \omega = \frac{5}{3} \quad \text{with} \quad k = k_G = \frac{\log(\frac{25}{3})}{\log(\frac{5}{3})} \approx 4.15 \]
Phase diagram

Figure: Schematic of the proposed phase diagram of the extended ISAT model on the triangular lattice. The filled circle is at the location of the kinetic growth point.
Figure: Plot of $1 - 3u_3(n)$, which measures the proportion of steps that are not involved with triply-visited sites per unit length, against $1/\sqrt{n}$ at a point $(\omega_2, \omega_3) = (4, 16)$ in the collapsed liquid-drop-like globule phase. As the length increases this reaches a non-zero value.
A globule when $k = 0$

**Figure:** A typical configuration at length 512 produced at $(\omega_2, \omega_3) = (5, 1)$, which is in the globule phase: it looks disordered and rather more like a liquid-like globule than a crystal.
Collapsed phase when $k = 6$

Figure: Plot of $1 - 3u_3(n)$, which measures the proportion of steps that are not involved with triply-visited sites per unit length, against $1/\sqrt{n}$ at a point $(1.58, 15.6)$ in the hypothesised frozen (crystal-like) phase. As the length increases this quantity vanishes.
A ‘crystal’ in the Triple model

Figure: A typical configuration at length 512 produced at \((\omega_2, \omega_3) = (1, 10)\) which looks like an ordered crystal.
Triangular Lattice Trails

- Include interaction with surface

- doubly visited sites carry a Boltzmann weight $\omega_2$
- triply visited sites carry a Boltzmann weight $\omega_3$
- surface sites carry a Boltzmann weight $\kappa$

Introduction

Adsorbing and Collapsing Square Lattice Trails

Collapsing Triangular Lattice Trails

Adsorbing and Collapsing Triangular Lattice Trails

Triangular Lattice Trails

Include interaction with surface

- doubly visited sites carry a Boltzmann weight $\omega_2$
- triply visited sites carry a Boltzmann weight $\omega_3$
- surface sites carry a Boltzmann weight $\kappa$

Full model analysed in:

in print (accepted yesterday)
Bulk interactions revisited ($\kappa = 1$)

Figure: Fluctuation map for the plane ($\omega_2, \omega_3, 1$). The lighter (darker) colors indicate regions of larger (smaller) fluctuations. The lower (higher) solid lines are approximations for the continuous coil-globule and crystal-globule transition lines, while the dashed line is the discontinuous coil-crystal transition line.
$\omega_2 - \omega_3$ Phase Diagram

Figure: Phase diagram for the plane $(\omega_2, \omega_3, 1)$. 
$\omega_2 - \omega_3$ Phase Diagram

**Figure:** Phase diagram for the plane $(\omega_2, \omega_3, 1)$. 
Adsorption for $\omega_2 = 1$

**Figure:** Fluctuation map for the plane $(1, \omega_3, \kappa)$. The lighter (darker) colors indicate regions of larger (smaller) fluctuations. The solid line is the continuous coil-adsorbed line, while the slanted and vertical dashed lines are the discontinuous crystal-adsorbed and coil-crystal transition lines, respectively.
Figure: Phase diagram for the plane $(1, \omega_3, \kappa)$. 
Adsorption for $\omega_3 = 1$

Figure: Fluctuation map for the plane $(\omega_2, 1, \kappa)$. While the adsorbed phase is a single phase, it has two regions where the ground state differs. Illustrations of the two different ground state configurations for the Ad$_1$ region and Ad$_2$ region.
Crossover between $\text{Ad}_1$ and $\text{Ad}_2$

**Figure:** Fluctuation in the number of doubly visited sites $c_2^{(n)}$ versus $\kappa$ for $\omega_3 = 1$, $\omega_2 = 2.4$. 

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\( \omega_2 - \kappa \) Phase Diagram

**Figure:** Phase diagram for the plane \((\omega_2, 1, \kappa)\).
Towards a 3-dimensional phase diagram

Figure: Phase diagram in the boundary planes plotted together.
Slices for increasing $\kappa$

**Figure:** Fluctuation maps in spaces $(\omega_2, \omega_3, 2)$ and $(\omega_2, \omega_3, 3)$. 

- **(a)**: 
  - **Crystal**
  - **Globule**
  - **Coil**

- **(b)**: 
  - **Crystal**
  - **Ad$_1$**
  - **Ad$_2$**
Slices for increasing $\omega_2$

**Figure:** Fluctuation maps in spaces $(1.5, \omega_3, \kappa)$ and $(2.0, \omega_3, \kappa)$. 

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Adsorption of 2d polymers with two- and three-body self-interactions
Slices for increasing $\omega_3$

Figure: Fluctuation maps in spaces $(\omega_2, 8, \kappa)$ and $(\omega_2, 12, \kappa)$.
Putting it all together: the full phase diagram

**Figure:** Qualitative representation of the full phase diagram, presenting the four phases found (regarding the regions $Ad_1$ and $Ad_2$ simply as the adsorbed phase), the critical-end-point (CEP) line, as well as the bulk (BML), collapsed-adsorbed (CAM) and dense-adsorbed (DAM) multicritical lines.
Summary and Outlook

Today’s talk

- Polymer collapse and adsorption
- 2d adsorbing and interacting trails
- canonical trail model: square lattice
- many-body interactions: triangular lattice
Summary and Outlook

What next?

- Collapse and adsorption in 3d
- Much more complicated:
  - Surface-attached globule
  - Finite-size layering transitions
  - Adsorbed polymers collapse in 2d
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- Collapse and adsorption in 3d
- Much more complicated:
  - Surface-attached globule
  - Finite-size layering transitions
  - Adsorbed polymers collapse in 2d
- Most work done on walks
- 3d trail collapse done
- still to do: adsorption in 3d
Thanks!