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

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Polymers

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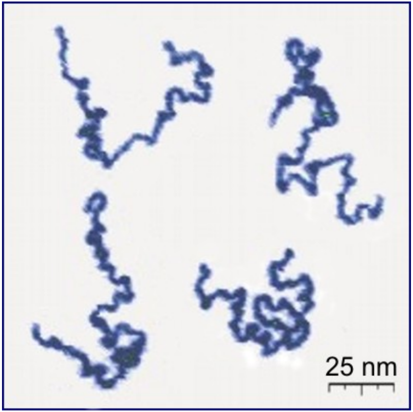
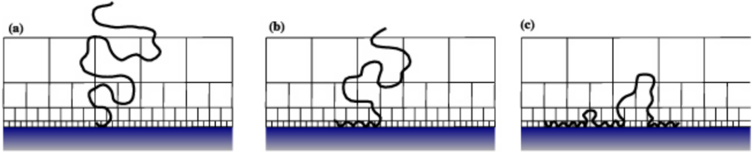


Roiter, Y.; Minko, S. Journal of the American Chemical Society. 127 (45): 15688–15689 (2005).

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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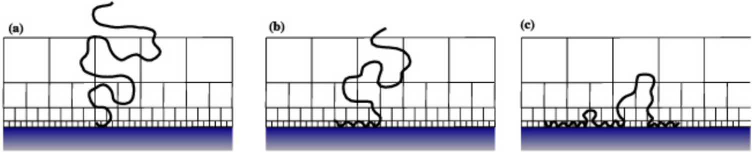

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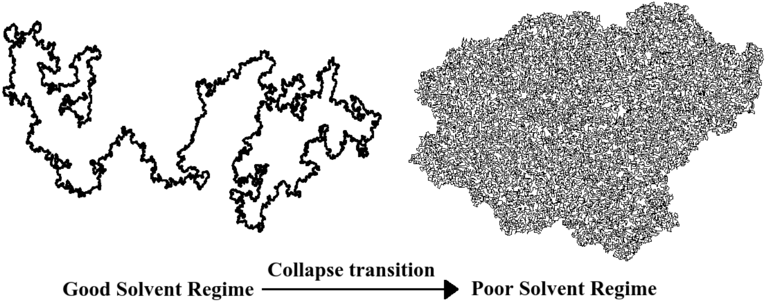
- Key ingredient: polymer-surface interaction.

Effects of solvent conditions

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



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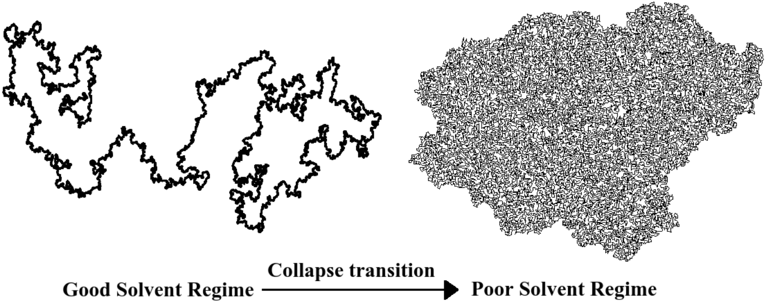

- General case: Adsorption + Collapse transition.

Modelling

- Global properties ⇒ Coarse-Grained Picture:
  - Polymers → Lattice Random-Walks

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  - Excluded volume effect: Occupancy restriction (one visit per site).
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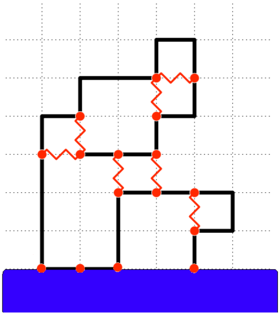
  - Polymer surface interaction: Walk-surface interaction.
  - Canonical Model: Interacting self-avoiding walk (SAW)



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- Critical exponents associated with the phases transitions.
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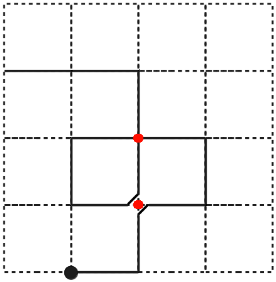
- Should hold for changes in:
  - Geometry of the lattice;
  - Range and strength of interactions;
  - Occupancy restriction;
  - Surface conditions ...

Alternative Model(s)

- Occupancy restriction: self-avoiding trails (SAT)



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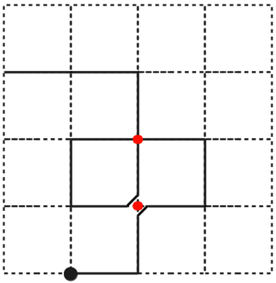

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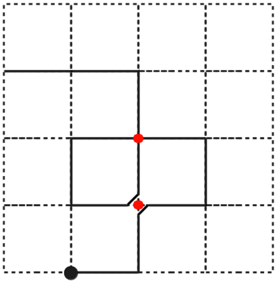

- Same universality class of SAW at high temperature (coil phase).
- At the collapse transition point: Exponents SAT $\neq$ SAW.

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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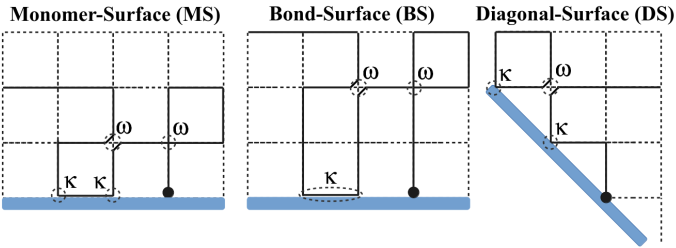
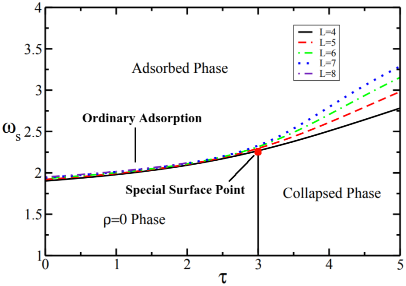
- Three boundary scenarios:



The Model

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



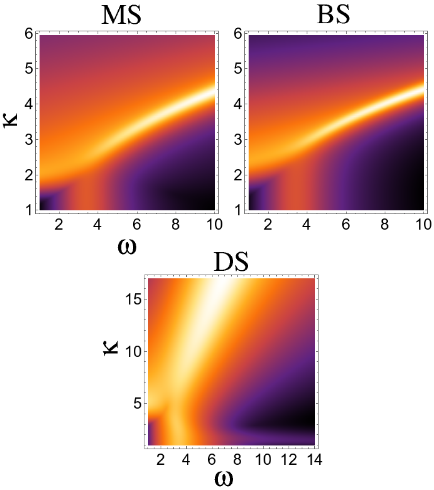
- Expected for SAWs:
  - Ordinary Adsorption $\Rightarrow 1/\delta = \phi^{(a)} = 1/2$
  - Special Surface Transition $\Rightarrow 1/\delta^{(s)} = \phi^{(s)} = 8/21$
- For SATs:
  - BS: $0.379 < \phi^{(s)} < 0.414$ [1]
  - DS: $\phi^{(s)} \approx 0.44$ [2]

[1] D. P. Foster, J. Phys. A: Math. Theor. **43**, (14pp) (2010)
[2] A. L. Owczarek and T. Prellberg, J. Stat. Phys. **79**, 951-967(1995)

Numerical Simulation

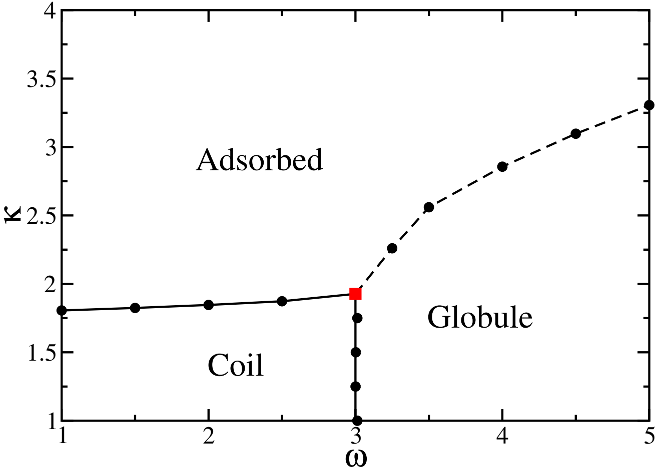
- Stochastic growth methods (Rosenbluth)
- Augmented by Pruning and Enrichment Strategy (PERM)
- Extended to uniform sampling techniques (flatPERM)

Finite-size phase diagram $n_{\text{max}} = 128$

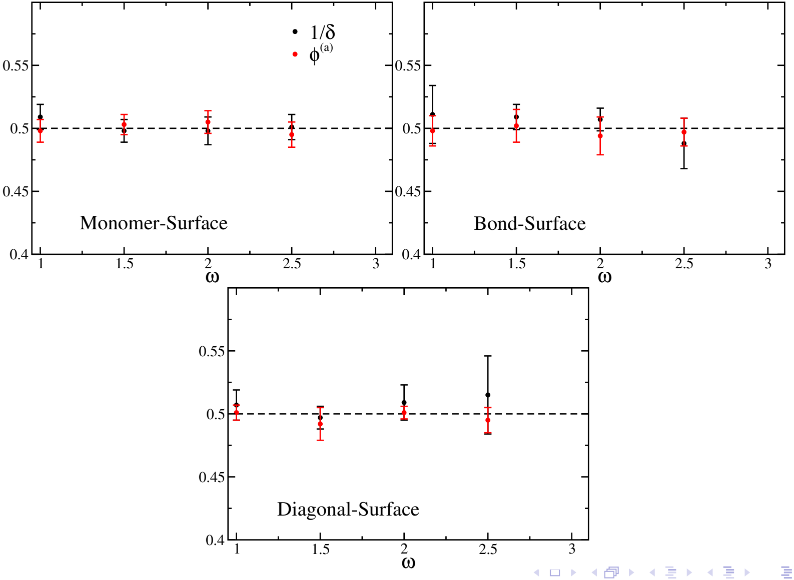


based on largest eigenvalue of covariance matrix

Phase diagram MS case $n_{\mathsf{max}} = 1024$

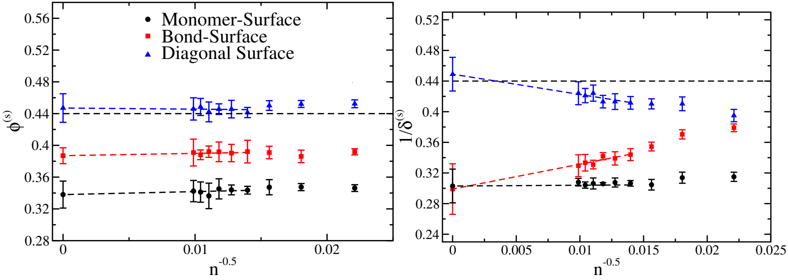


Normal adsorption transition $n_{\text{max}} = 10240$



Special adsorption transition $n_{max} = 10240$

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



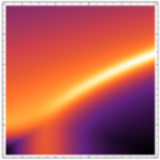
	monomer-surface	bond-surface	diagonal surface
$\phi^{(s)}$	0.338(17)	0.387(10)	0.447(18)
$1/\delta^{(s)}$	0.303(22)	0.299(33)	0.449(22)

Editors' Suggestion

Adsorption of interacting self-avoiding trails in two dimensions

N. T. Rodrigues, T. Prellberg, and A. L. Owczarek

Phys. Rev. E **100**, 022121 (2019) – Published 15 August 2019

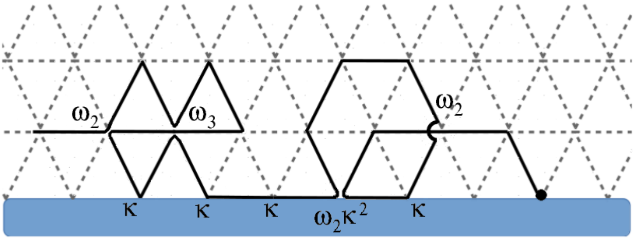


Lattice trails in two dimensions are a greatly simplified system that can give insight into the complex phase diagram of polymer adsorption on a surface. The authors simulate three different adsorption scenarios in this system, and study the resulting phases and phase boundaries as well as the critical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

Show Abstract +

Triangular Lattice Trails

- The Triangular Lattice allows for two types of bulk interactions



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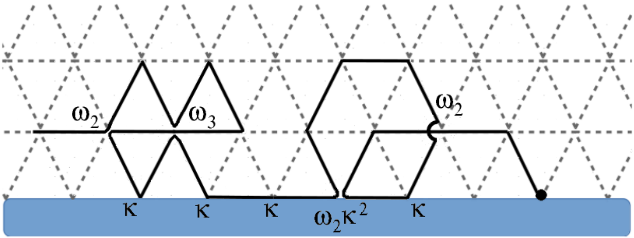

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Bulk interactions analysed in:

J. Doukas, A. L. Owczarek and T. Prellberg, *Phys. Rev. E*, **82**, 031103, 2010

The extended model of self-interacting trails (eISAT)

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 $\omega_2^{m_2}\omega_3^{m_3}$, where $\omega_j = \exp(\beta\varepsilon_j)$.

The partition function of the eISAT model is then given by

$$Z_n(\omega_2, \omega_3) = \sum_{SAT} \omega_2^{m_2(\varphi_n)} \omega_3^{m_3(\varphi_n)} \ .$$

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We can define a one temperature family paramerized by k, where $\omega_3 = \omega_2^k$, with

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

Fluctuations

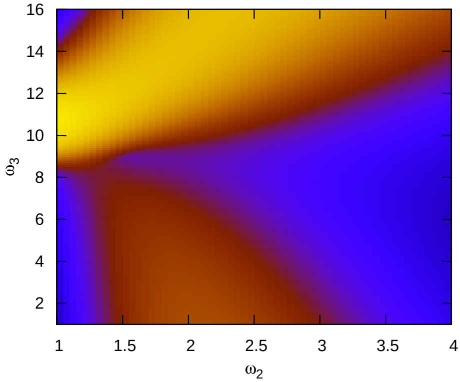


Figure: Density plot of the logarithm of the largest eigenvalue λ_{max} of the matrix of second derivatives of the free energy with respect to ω_2 and ω_3 at length $n = 128$ (the lighter the shade, the larger the value).

Phase diagram

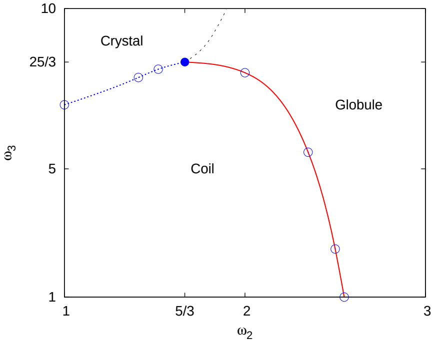
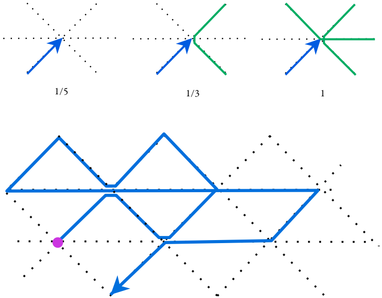


Figure: Schematic of the proposed phase diagram of the extended ISAT model on the triangular lattice. The open circles represent estimates of the collapse transition for various values of k.

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 $(\frac{1}{6})(\frac{1}{5})(\frac{1}{5})(\frac{1}{5})(\frac{1}{5})(\frac{1}{3})(\frac{1}{5})(\frac{1}{5})(1)(\frac{1}{3})(\frac{1}{5})(\frac{1}{5})(\frac{1}{3})$.

KGT to eISAT mapping

The KGT progress gives SAT configurations with Boltzmann weights

$$\omega_2 = 5/3 \qquad \text{and} \qquad \omega_3 = 25/3$$

Alternatively

$$\omega = 5/3 \qquad \text{with} \qquad k = k_G \equiv \frac{\log(25/3)}{\log(5/3)} \approx 4.15$$

Phase diagram

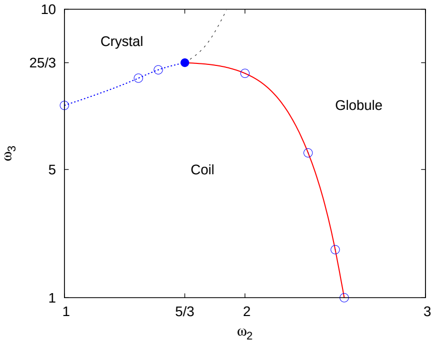


Figure: Schematic of the proposed phase diagram of the extended ISAT model on the triangular lattice. The filled circle is at the location of the kinetic growth point.

Collapsed phase for canonical model — globule

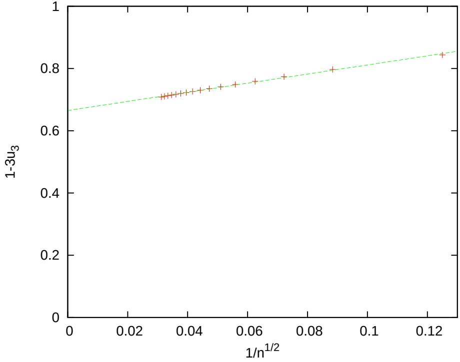


Figure: Plot of $1 - 3u_3(n)$, which measures the proportion of steps that are not involved with triply-visited sites per unit length, against $1/\sqrt{n}$ at a point $(\omega_2, \omega_3) = (4, 16)$ in the collapsed liquid-drop-like globule phase. As the length increases this reaches a non-zero value.

A globule when $k = 0$

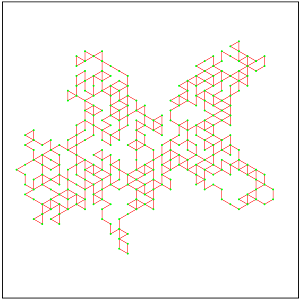


Figure: A typical configuration at length 512 produced at $(\omega_2, \omega_3) = (5, 1)$, which is in the globule phase: it looks disordered and rather more like a liquid-like globule than a crystal.

Collapsed phase when $k = 6$

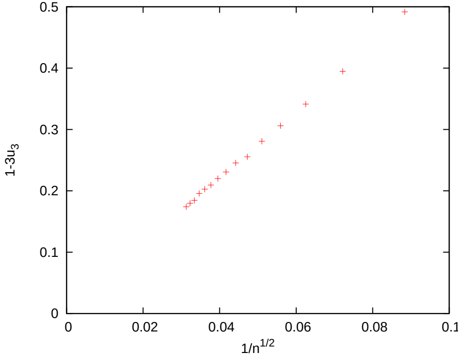


Figure: Plot of $1 - 3u_3(n)$, which measures the proportion of steps that are not involved with triply-visited sites per unit length, against $1/\sqrt{n}$ at a point $(1.58, 15.6)$ in the hypothesised frozen (crystal-like) phase. As the length increases this quantity vanishes.

A 'crystal' in the Triple model

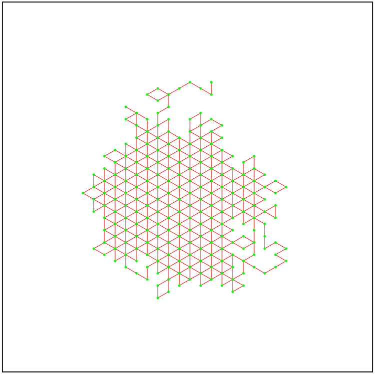
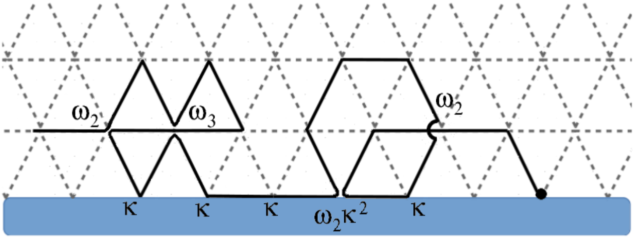


Figure: A typical configuration at length 512 produced at $(\omega_2, \omega_3) = (1, 10)$ which looks like an ordered crystal.

Triangular Lattice Trails

- Include interaction with surface



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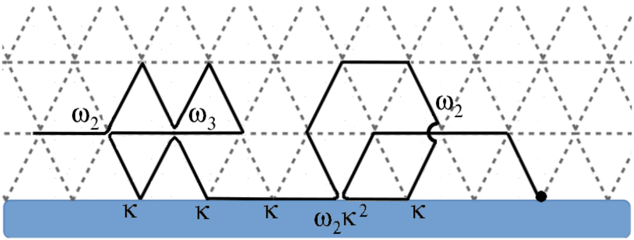

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Full model analysed in:
N. T. Rodrigues, T. J. Oliveira, T. P. and A. L. Owczarek, *Phys. Rev. E* in print (accepted yesterday)

Bulk interactions revisited ($\kappa = 1$)

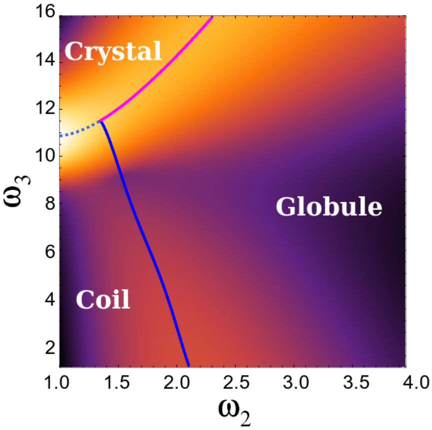
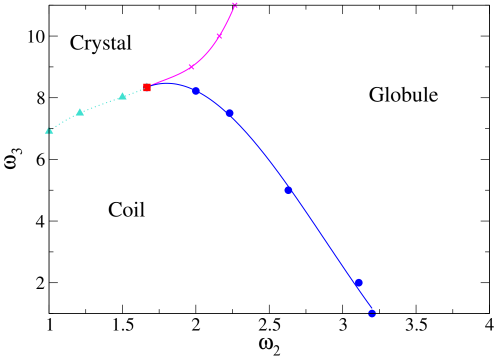


Figure: Fluctuation map for the plane $(\omega_2, \omega_3, 1)$. The lighter (darker) colors indicates regions of larger (smaller) fluctuations. The lower (higher) solid lines are approximations for the continuous coil-globule and crystal-globule transition lines, while the dashed line is the discontinuous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

$\omega_2 - \omega_3$ Phase Diagram



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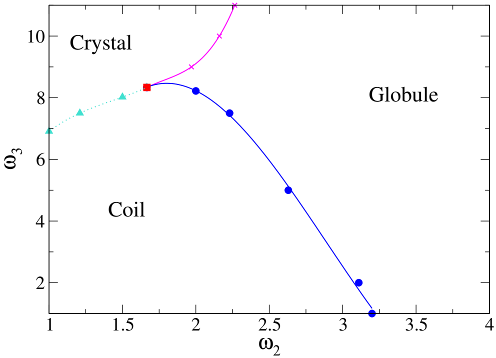

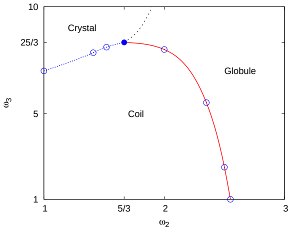

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Adsorption for $\omega_2 = 1$

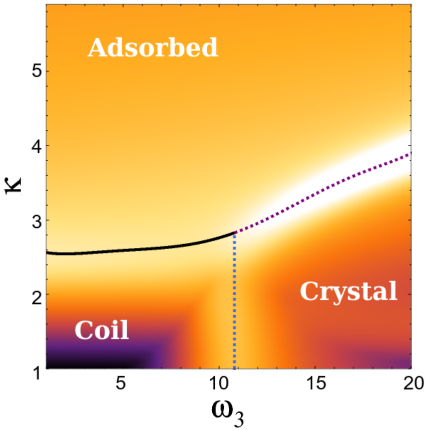
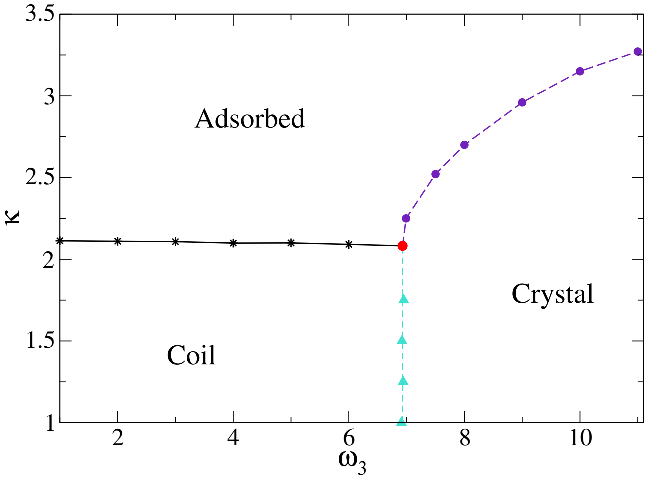


Figure: Fluctuation map for the plane $(1, \omega_3, \kappa)$. The lighter (darker) colors indicate regions of larger (smaller) fluctuations. The solid line is the continuous coil-adsorbed line, while the slanted and vertical dashed lines are the discontinuous crystal-adsorbed and coil-crystal transition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

$\omega_3 - \kappa$ Phase Diagram



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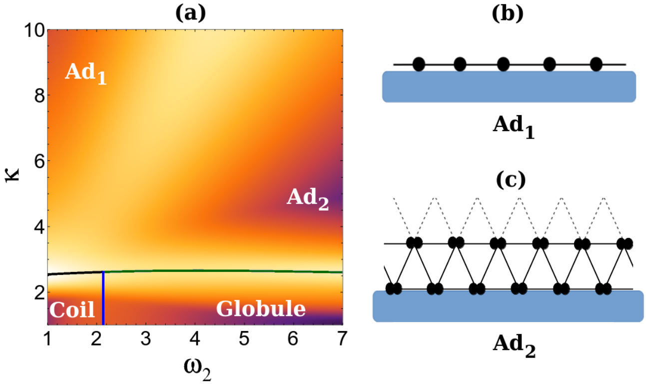


Figure: Fluctuation map for the plane $(\omega_2, 1, \kappa)$. While the adsorbed phase is a single phase, it has two regions where the ground state differs. Illustrations of the two different ground state configurations for the Ad_1 region and Ad_2 region.

Crossover between Ad_1 and Ad_2

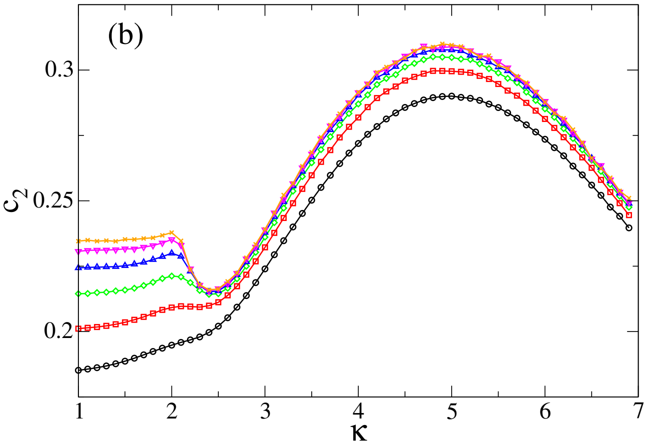


Figure: Fluctuation in the number of doubly visited sites $c_2^{(n)}$ versus κ for $\omega_3 = 1$, $\omega_2 = 2.4$.

$\omega_2 - \kappa$ Phase Diagram

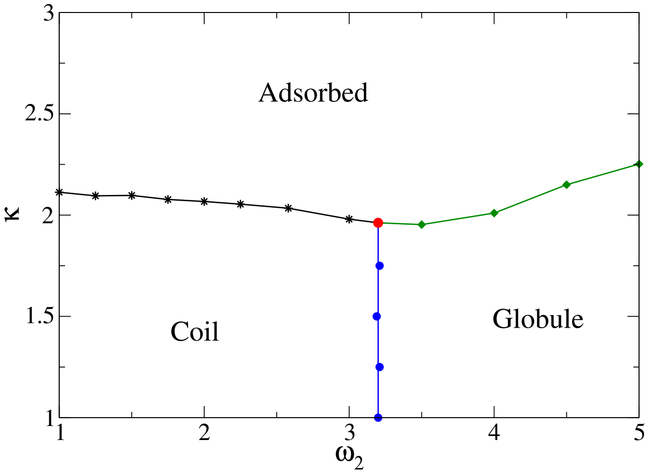


Figure: Phase diagram for the plane $(\omega_2, 1, \kappa)$.

Towards a 3-dimensional phase diagram

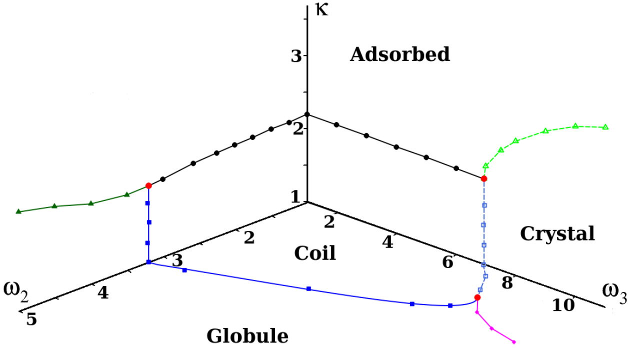


Figure: Phase diagram in the boundary planes plotted together.

Slices for increasing κ

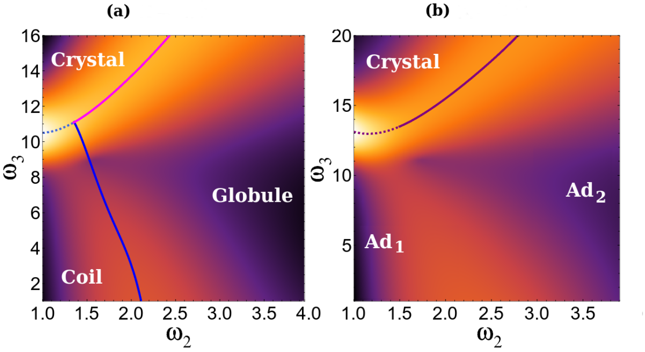


Figure: Fluctuation maps in spaces $(\omega_2, \omega_3, 2)$ and $(\omega_2, \omega_3, 3)$.

Slices for increasing ω_2

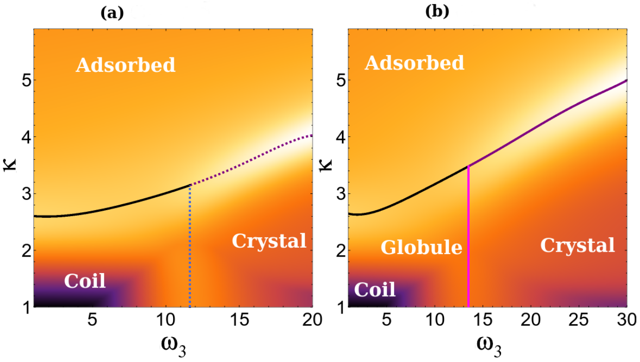


Figure: Fluctuation maps in spaces $(1.5, \omega_3, \kappa)$ and $(2.0, \omega_3, \kappa)$.

Slices for increasing ω_3

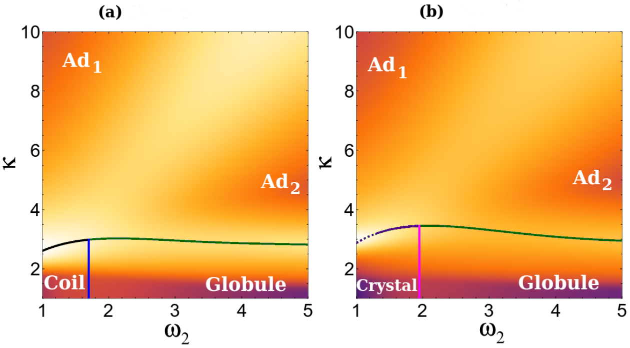


Figure: Fluctuation maps in spaces $(\omega_2, 8, \kappa)$ and $(\omega_2, 12, \kappa)$.

Putting it all together: the full phase diagram

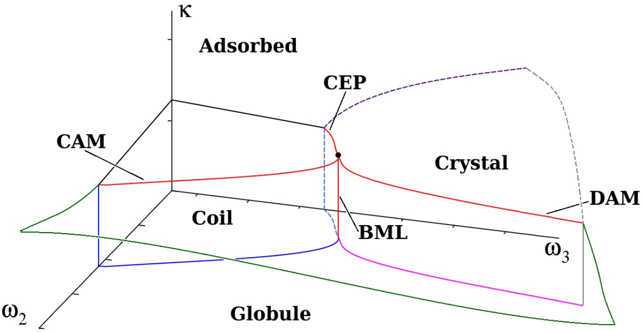


Figure: Qualitative representation of the full phase diagram, presenting the four phases found (regarding the regions Ad_1 and Ad_2 simply as the adsorbed phase), the critical-end-point (CEP) line, as well as the bulk (BML), collapsed-adsorbed (CAM) and dense-adsorbed (DAM) multicritical lines.

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

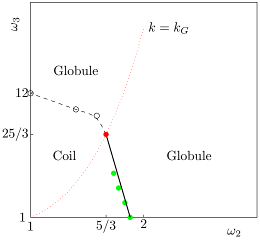
What next?

- Collapse and adsorption in 3d
- Much more complicated:
  - Surface-attached globule
  - Finite-size layering transitions
  - Adsorbed polymers collapse in 2d

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
- Most work done on walks
- 3d trail collapse done
- still to do: adsorption in 3d



Thanks!

CAPES

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