Simulating models of polymer collapse

Thomas Prellberg

School of Mathematical Sciences
Queen Mary, University of London

with Jarek Krawczyk, Aleks Owczarek, Andrew Rechnitzer

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Polymers in solution:
  - Equilibrium statistical mechanics, lattice model
Algorithm:
  - Stochastic growth & flat histogram (PERM/flatPERM)
Simulation of the canonical model:
  - Interacting self-avoiding walks (ISAW)
Outline

- Polymers in solution:
  - Equilibrium statistical mechanics, lattice model
- Algorithm:
  - Stochastic growth & flat histogram (PERM/flatPERM)
- Simulation of the canonical model:
  - Interacting self-avoiding walks (ISAW)
- Applications:
  - Protein groundstates (HP model)
  - Bulk vs surface phenomena:
    - confined polymers, force-induced desorption, interplay of collapse and adsorption
  - Hydrogen-bond type interactions
- Comparison with alternative lattice models
Polymers in Solution
Modelling of Polymers in Solution

- Polymers: long chains of monomers
- “Coarse-Graining”: beads on a chain
- “Excluded Volume”: minimal distance between beads
- Contact with solvent: effective short-range interaction
- Good/bad solvent: repelling/attracting interaction
Polymers: long chains of monomers

“Coarse-Graining”: beads on a chain

“Excluded Volume”: minimal distance between beads

Contact with solvent: effective short-range interaction

Good/bad solvent: repelling/attracting interaction

A Model of a Polymer in Solution
Random Walk + Excluded Volume + Short Range Attraction
Polymer Collapse, Coil-Globule Transition, $\Theta$-Point

length $N$, spatial extension $R \sim N^{\nu}$

$T > T_c$: good solvent

swollen phase (coil)

$T = T_c$: $\Theta$-polymer

$T < T_c$: bad solvent

collapsed phase (globule)
The Canonical Lattice Model

Interacting Self-Avoiding Walk (ISAW)

- Physical space $\rightarrow$ simple cubic lattice $\mathbb{Z}^3$
- Polymer $\rightarrow$ self-avoiding random walk (SAW)
- Quality of solvent $\rightarrow$ short-range interaction $\epsilon$
The Canonical Lattice Model

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- Physical space $\rightarrow$ simple cubic lattice $\mathbb{Z}^3$
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Partition function:

$$Z_N(\omega) = \sum_m C_{N,m} \omega^m$$

$C_{N,m}$ is the number of SAWs with $N$ steps and $m$ interactions
The Canonical Lattice Model

**Interacting Self-Avoiding Walk (ISAW)**

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Thermodynamic Limit for a dilute solution:

$$V = \infty \quad \text{and} \quad N \to \infty$$
In addition to solvent modelling (bulk interaction), add adsorption (surface interaction) and micromechanical deformations e.g. force on chain end (optical tweezers). Complete description through three-dimensional density of states: (a) bulk energy, (b) surface energy, (c) position of chain end.
The Algorithm
PERM: “Go With The Winners”

PERM = Pruned and Enriched Rosenbluth Method

- Rosenbluth Method: kinetic growth

\[ P \text{ Grassberger, Phys Rev E 56 (1997) 3682} \]
PERM: “Go With The Winners”

PERM = Pruned and Enriched Rosenbluth Method

- **Rosenbluth Method**: kinetic growth

- **Enrichment**: weight too large → make copies of configuration
- **Pruning**: weight too small → remove configuration occasionally

P Grassberger, Phys Rev E 56 (1997) 3682
PERM: “Go With The Winners”

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- **Rosenbluth Method**: kinetic growth

- **Enrichment**: weight too large → make copies of configuration
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**Current work**: flatPERM = flat histogram PERM

- flatPERM samples a generalised multicanonical ensemble
- Determines the whole density of states in *one* simulation!

\( P \) Grassberger, Phys Rev E 56 (1997) 3682

T Prellberg and J Krawczyk, PRL 92 (2004) 120602
View kinetic growth as *approximate enumeration*
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- Exact enumeration: choose *all* a continuations with equal weight
- Kinetic growth: chose *one* continuation with *a*-fold weight
Algorithm details

View kinetic growth as *approximate enumeration*

- Exact enumeration: choose *all* a continuations with equal weight
- Kinetic growth: chose *one* continuation with *a*-fold weight
  - An $N$ step configuration gets assigned a weight

$$W = \prod_{k=0}^{N-1} a_k$$
View kinetic growth as *approximate enumeration*

- Exact enumeration: choose *all* a continuations with equal weight
- Kinetic growth: chose *one* continuation with *a*-fold weight
  - An $N$ step configuration gets assigned a weight
    \[ W = \prod_{k=0}^{N-1} a_k \]
  
  - $S$ growth chains with weights $W_N^{(i)}$ give an estimate of the total number of configurations, \( C_N^{\text{est}} = \langle W \rangle_N = \frac{1}{S} \sum_i W_N^{(i)} \)
View kinetic growth as *approximate enumeration*

- **Exact enumeration:** choose *all* a continuations with equal weight
- **Kinetic growth:** chose *one* continuation with $a$-fold weight
  - An $N$ step configuration gets assigned a weight  
    \[
    W = \prod_{k=0}^{N-1} a_k
    \]
  - $S$ growth chains with weights $W_N^{(i)}$ give an estimate of the total number of configurations,  
    \[
    C_N^{est} = \langle W \rangle_N = \frac{1}{S} \sum_i W_N^{(i)}
    \]
- Add pruning/enrichment with respect to ratio  
  \[
  r = \frac{W_N^{(S+1)}}{C_N^{est}}
  \]
Algorithm details

View kinetic growth as *approximate enumeration*

- Exact enumeration: choose *all* a continuations with equal weight
- Kinetic growth: chose *one* continuation with *a*-fold weight
  - An \( N \) step configuration gets assigned a weight
  \[
  W = \prod_{k=0}^{N-1} a_k
  \]

- \( S \) growth chains with weights \( W_N^{(i)} \) give an estimate of the total number of configurations, \( C_N^{\text{est}} = \langle W \rangle_N = \frac{1}{S} \sum_i W_N^{(i)} \)
- Add pruning/enrichment with respect to ratio
  \[
  r = \frac{W_N^{(S+1)}}{C_N^{\text{est}}}
  \]
  - Number of samples generated for each \( N \) is roughly constant
  - We have a flat histogram algorithm in system size

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Simulating models of polymer collapse
Consider athermal case

PERM: estimate number of configurations $C_N$

- $C_N^{est} = \langle W \rangle_N$
- $r = W^{(i)}_N / C_N^{est}$
Consider athermal case

PERM: estimate number of configurations $C_N$

- $C_N^{est} = \langle W \rangle_N$
- $r = W_N^{(i)} / C_N^{est}$

Consider energy $E$, temperature $\beta = 1/k_B T$

thermal PERM: estimate partition function $Z_N(\beta)$

- $Z_N^{est}(\beta) = \langle W \exp(-\beta E) \rangle_N$
- $r = W_N^{(i)} \exp(-\beta E^{(i)}) / Z_N^{est}(\beta)$
Consider athermal case

PERM: estimate number of configurations $C_N$

- $C_N^{est} = \langle W \rangle_N$
- $r = W_N^{(i)}/C_N^{est}$

Consider energy $E$, temperature $\beta = 1/k_B T$

thermal PERM: estimate partition function $Z_N(\beta)$

- $Z_N^{est}(\beta) = \langle W \exp(-\beta E) \rangle_N$
- $r = W_N^{(i)} \exp(-\beta E^{(i)})/Z_N^{est}(\beta)$

Consider parametrisation $\vec{m}$ of configuration space

flatPERM: estimate density of states $C_{N,\vec{m}}$

- $C_{N,\vec{m}}^{est} = \langle W \rangle_{N,\vec{m}}$
- $r = W_{N,\vec{m}}^{(i)}/C_{N,\vec{m}}^{est}$
Most interesting open questions for dense and geometrically restricted configurations
Most interesting open questions for dense and geometrically restricted configurations

There is little theory and this is notoriously difficult to simulate
Simulations and Results
To stabilise algorithm (avoid initial overflow/underflow):
Delay growth of large configurations
Here: after $t$ tours growth up to length $10t$
2d ISAW simulation up to $N = 1024$

Total sample size: 1,000,000

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2d ISAW simulation up to $N = 1024$

Total sample size: 10,000,000

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2d ISAW simulation up to $N = 1024$

Total sample size: 20,000,000

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2d ISAW simulation up to $N = 1024$

Total sample size: 30,000,000

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Simulating models of polymer collapse
2d ISAW simulation up to $N = 1024$

Total sample size: 40,000,000
2d ISAW simulation up to $N = 1024$

Total sample size: 50,000,000

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Simulating models of polymer collapse
2d ISAW simulation up to $N = 1024$

Total sample size: 60,000,000
2d ISAW simulation up to $N = 1024$

Total sample size: 70,000,000
2d ISAW simulation up to $N = 1024$

Total sample size: 80,000,000

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2d ISAW simulation up to $N = 1024$

Total sample size: 90,000,000
2d ISAW simulation up to $N = 1024$

Total sample size: 100,000,000

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2d ISAW simulation up to $N = 1024$

Total sample size: 110,000,000

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2d ISAW simulation up to $N = 1024$

Total sample size: 120,000,000

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2d ISAW simulation up to $N = 1024$

Total sample size: 130,000,000

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Total sample size: 140,000,000
2d ISAW simulation up to $N = 1024$

Total sample size: 150,000,000
2d ISAW simulation up to $N = 1024$

Total sample size: 160,000,000

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2d ISAW simulation up to $N = 1024$

Total sample size: 170,000,000

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2d ISAW simulation up to $N = 1024$

Total sample size: 180,000,000

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2d ISAW simulation up to $N = 1024$

Total sample size: 190,000,000

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2d ISAW simulation up to $N = 1024$

Total sample size: 200,000,000
2d ISAW simulation up to $N = 1024$

Total sample size: 210,000,000

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2d ISAW simulation up to $N = 1024$

Total sample size: 220,000,000
2d ISAW simulation up to $N = 1024$

Total sample size: 230,000,000
2d ISAW simulation up to $N = 1024$

Total sample size: 240,000,000

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2d ISAW simulation up to $N = 1024$

Total sample size: 250,000,000
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Total sample size: 260,000,000

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Total sample size: 270,000,000

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2d ISAW simulation up to $N = 1024$

Total sample size: 280,000,000
2d ISAW simulation up to $N = 1024$

Total sample size: 290,000,000

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2d ISAW simulation up to $N = 1024$

Total sample size: 300,000,000
2d ISAW up to $n = 1024$
- One simulation suffices
- 400 orders of magnitude
  (only 2d shown, 3d similar)
Simulation results: SAW in a strip


- 2d SAW in a strip: strip width 64, up to $n = 1024$

- Scaled endpoint density

![Graphs showing simulation results](image-url)
Engineered sequence HPHHPHPHHPPH in $d = 3$:

- Investigated other sequences up to $N \approx 100$ in $d = 2$ and $d = 3$
- Collapsed regime accessible
- Reproduced known ground state energies
- Obtained density of states $C_{n,m}$ over large range ($\approx 10^{30}$)
- Force-induced desorption of adsorbed polymers
  - Relevance: optical tweezers, AFM; related to DNA unzipping

- 3-dim polymer in a half space, one simulation, up to $n = 256$
  - Fluctuations of surface coverage

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**2-Dimensional Density of States**

*J Krawczyk et al, JSTAT (2004) P10004*

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Layering transitions of adsorbed polymers in poor solvents

- whole phase diagram at once
- low temperatures accessible
- hierarchy of layering transitions
- resolved controversy over “surface attached globule”
Pulling adsorbing and collapsing polymers off a surface

\[ \epsilon_s = \alpha, \epsilon_b = 1 - \alpha \]

- Simulations up to \( n = 91 \) (4-dimensional histogram)
- Interplay of (both force-induced and thermal) desorption (\( \alpha = 1 \)) and stretching (\( \alpha = 0 \))
Hydrogen-bond type interactions

Hydrogen-like interactions between *straight* segments of the walk

Distinguish parallel and orthogonal interactions: layering of \( \beta \)-sheets
Hydrogen-bond type interactions (ctd.)

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Hydrogen-bond type interactions (ctd.)

1.0e-12
1.0e-10
1.0e-08
1.0e-06
1.0e-04
1.0e-02
1.0e+00
1.0e+02

\( p(x) \)

\( x = \frac{m}{n} \)

\( n = 1024 \)

\( \beta \)

\( \beta \)-sheets

swollen coil

parallel \( \beta \)-lines

orthogonal \( \beta \)-sheets

triple point

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Simulating models of polymer collapse
Interplay of hydrogen-bond interactions (equal strength parallel and orthogonal) with isotropic interactions

First-order globule-crystal transition
Alternative Lattice Models
Alternative lattice models

General “universality” assumption:

A Model of a Polymer in Solution

Random Walk + Excluded Volume + Short Range Attraction
Alternative lattice models

General “universality” assumption:

A Model of a Polymer in Solution
Random Walk + Excluded Volume + Short Range Attraction

- Canonical model: interacting self-avoiding walks (ISAW)
- Alternative model: interacting self-avoiding trails (ISAT)

vertex avoidance (walks) ⇔ edge avoidance (trails)

nearest-neighbour interaction ⇔ contact interaction
Alternative lattice models

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nearest-neighbour interaction ⇔ contact interaction

- simulations of ISAW confirm predictions from theory
- simulations of ISAT confound predictions from theory:
  $\text{SAW} = \text{SAT}$, but $\text{ISAW} \neq \text{ISAT}$ (different collapse exponents)
Simulations of ISAT

- At critical $T_c$, ISAT can be modelled as kinetic growth; simulations up to $N = 10^6$
  

- Pruned Enriched Rosenbluth Method enables simulations for $T \neq T_c$; new simulations up to $N = 2 \cdot 10^6$
  
ISAW/ISAT contain on-site and nearest-neighbour interactions

- The field-theory is formulated with purely local interactions
- Field theory is equivalent to Edwards model:
  - Brownian motion + suppression of self-intersections + attractive interactions
  - Field theory is $\phi^4 - \phi^6$ $O(n)$-model for $n \to 0$
A Proposal of a New Model


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Formulate a lattice model with purely local interactions
A Proposal of a New Model


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Formulate a lattice model with purely local interactions

- Site-weighted random walk:
  - lattice random walk weighted by multiple visits of sites
  - few visits to same site are favoured (attractive interaction)
  - too many visits are disfavoured (excluded volume)
ISAW/ISAT contain on-site and nearest-neighbour interactions

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**Formulate a lattice model with purely local interactions**

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(technically, this is an extension of a Domb-Joyce model)
An $N$-step random walk $\xi = (\vec{\xi}_0, \vec{\xi}_1, \ldots, \vec{\xi}_N)$ induces a density-field $\phi_{\xi}$ on the lattice sites $\vec{x}$ via

$$
\phi_{\xi}(\vec{x}) = \sum_{i=0}^{N} \delta_{\vec{\xi}_i, \vec{x}}
$$
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$$\phi_\xi(\vec{x}) = \sum_{i=0}^{N} \delta_{\vec{\xi}_i, \vec{x}}$$

Define the energy as a functional of the field $\phi = \phi_\xi$

$$E(\xi) = \sum_{\vec{x}} f (\phi(\vec{x}))$$
Site-Weighted Random Walk

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- Define the energy as a functional of the field $\phi = \phi_\xi$

$$E(\xi) = \sum_{\vec{x}} f(\phi(\vec{x}))$$

- Incorporate self-avoidance and attraction via choice of $f(t)$. For example, $f(0) = f(1) = 0$, $f(2) = \varepsilon_1$, $f(3) = \varepsilon_2$, and $f(t \geq 4) = \infty$. 
Site-Weighted Random Walk (ctd)
Partition function

\[ Z_N(\beta) = \sum_{m_1, m_2} C_{N, m_1, m_2} e^{-\beta (m_1 \epsilon_1 + m_2 \epsilon_2)} \]

with density of states \( C_{N, m_1, m_2} \)
Partition function

\[ Z_N(\beta) = \sum_{m_1, m_2} C_{N,m_1,m_2} e^{-\beta(m_1\varepsilon_1 + m_2\varepsilon_2)} \]

with density of states \( C_{N,m_1,m_2} \)

Simulate two variants of the model on the square and simple cubic lattice

- random walks with immediate reversal allowed (RA2, RA3)
- random walks with immediate reversal forbidden (RF2, RF3)
Phase diagram

SWRW in 3d, reversal forbidden (RF3)

β1
β2
SAW
collapsed
SWRW in 3d, reversal forbidden (RF3)

Phase diagram

\[ \beta_2 = -1.0: \]

2nd order transition

\[ \beta_1 = -1.0: \]

1st order transition
SWRW in 3d, reversal forbidden (RF3)

Phase diagram

\( \beta_2 = -1.0: \)

\( \beta_1 = -1.0: \)

bimodal distribution

1st order transition

2nd order transition

collapsed

SAW

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Simulating models of polymer collapse
We find a smooth crossover:

Both 1st order and 2nd order transitions have disappeared!
We find a smooth crossover:

Both 1st order and 2nd order transitions have disappeared!

RA3 and RF2

2nd order transition disappears as in RA2
1st order transition weakens
## SWRW summarised

<table>
<thead>
<tr>
<th>Model</th>
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<th>3d</th>
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<tbody>
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### Unexpected and intriguing behaviour

Changing the dimension and/or allowing reversals removes the phase transition

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Unexpected and intriguing behaviour

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Many open questions remain . . .
The algorithm (and pedagogical applications):

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Bulk vs surface:

References

**The algorithm (and pedagogical applications):**

**Bulk vs surface:**

**Hydrogen-bond type interactions:**
References

- **The algorithm (and pedagogical applications):**

- **Bulk vs surface:**

- **Hydrogen-bond type interactions:**

- **Alternative lattice models:**

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The End