Simulating models of polymer collapse

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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)

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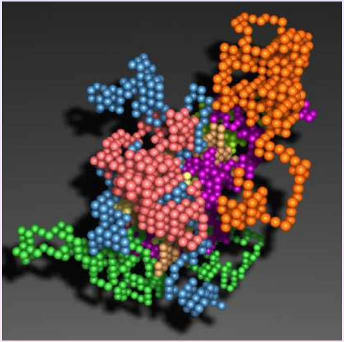
- Polymers in solution:
  - Equilibrium statistical mechanics, lattice model
- Algorithm:
  - Stochastic growth & flat histogram (PERM/flatPERM)
- Simulation of the canonical model:
  - Interacting self-avoiding walks (ISAW)
- Applications:
  - Protein groundstates (HP model)
  - Bulk vs surface phenomena: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

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



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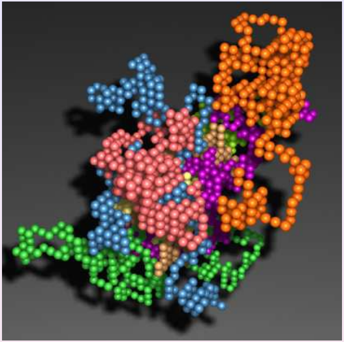
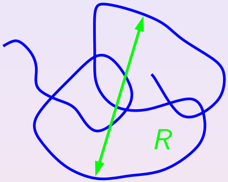
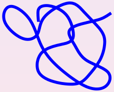


A Model of a Polymer in Solution

Random Walk + Excluded Volume + Short Range Attraction length N, spatial extension $R \sim N^{\nu}$



$T > T_c$: good solvent
swollen phase (coil)



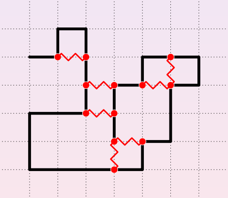
$T = T_c$:
Θ-polymer

$T < T_c$: bad solvent
collapsed phase (globule)

The Canonical Lattice Model

Interacting Self-Avoiding Walk (ISAW)

- Physical space $\longrightarrow$ simple cubic lattice $\mathbb{Z}^3$
- Polymer $\longrightarrow$ self-avoiding random walk (SAW)
- Quality of solvent $\longrightarrow$ short-range interaction ϵ



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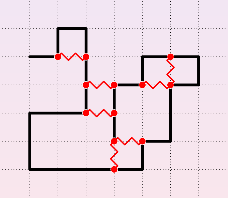
Partition function:

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



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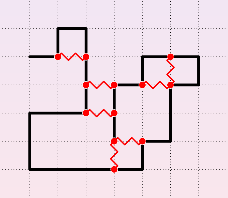

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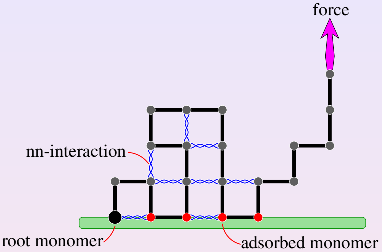
Thermodynamic Limit for a dilute solution:

$$V = \infty \quad \text{and} \quad N \to \infty$$

Extensions of the Model

- In addition to
  - solvent modelling (bulk interaction)
- add
  - adsorption (surface interaction)
  - 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

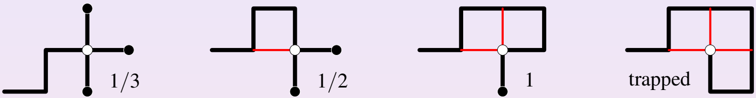
The Algorithm

PERM: "Go With The Winners"

PERM = Pruned and Enriched Rosenbluth Method

P Grassberger, Phys Rev E 56 (1997) 3682

- Rosenbluth Method: kinetic growth



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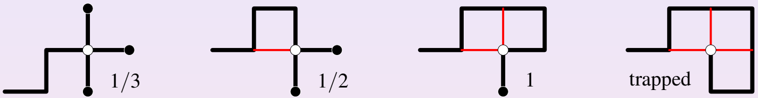

- Enrichment: weight too large → make copies of configuration
- Pruning: weight too small → remove configuration occasionally

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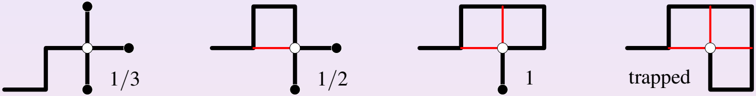

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Current work: flatPERM = flat histogram PERM

T Prellberg and J Krawczyk, PRL 92 (2004) 120602

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

Algorithm details

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- Add pruning/enrichment with respect to ratio $r = W_N^{(S+1)} / C_N^{est}$
  - Number of samples generated for each N is roughly constant
  - We have a $\boxed{\text{flat histogram algorithm}}$ in system size

From PERM to flatPERM

- Consider athermal case
  - PERM: estimate number of configurations C_N
    - $C_N^{est} = \langle W \rangle_N$
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- Consider energy E, temperature $\beta = 1/k_B T$
  - thermal PERM: estimate partition function $Z_N(\beta)$
    - $Z_N^{est}(\beta) = \langle W \exp(-\beta E) \rangle_N$
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- Consider parametrisation $\vec{m}$ of configuration space
  - flatPERM: estimate density of states $C_{N,\vec{m}}$
    - $C_{N,\vec{m}}^{est} = \langle W \rangle_{N,\vec{m}}$
    - $r = W_{N,\vec{m}}^{(i)} / C_{N,\vec{m}}^{est}$

Why Simulations?

- Most interesting open questions for dense and geometrically restricted configurations

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- Most interesting open questions for dense and geometrically restricted configurations

There is little theory and this is notoriously difficult to simulate

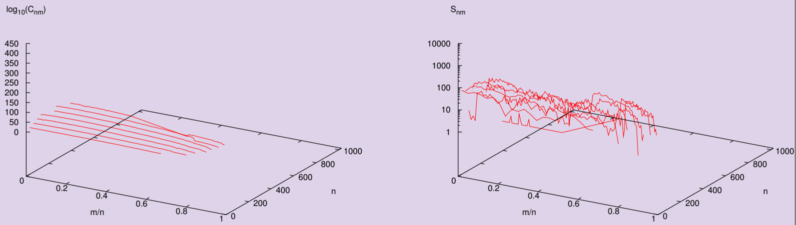
Simulations and Results

2d ISAW simulation up to $N = 1024$

To stabilise algorithm (avoid initial overflow/underflow):
Delay growth of large configurations
Here: after t tours growth up to length $10t$

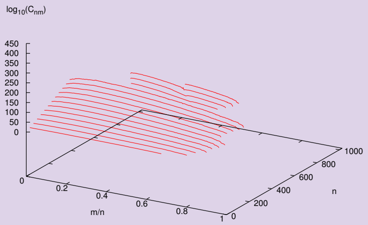
2d ISAW simulation up to $N = 1024$

Total sample size: $1,000,000$



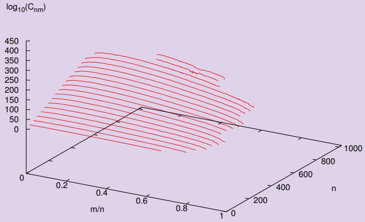
2d ISAW simulation up to $N = 1024$

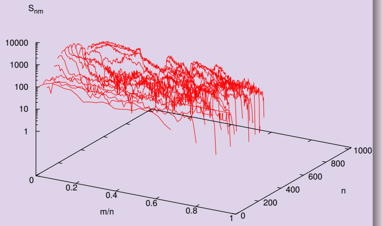
Total sample size: $10,000,000$



2d ISAW simulation up to $N = 1024$

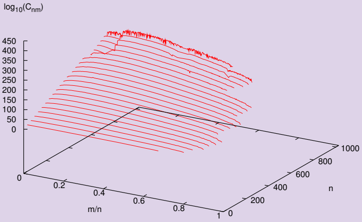
Total sample size: $20,000,000$

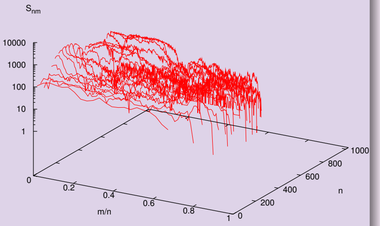




2d ISAW simulation up to $N = 1024$

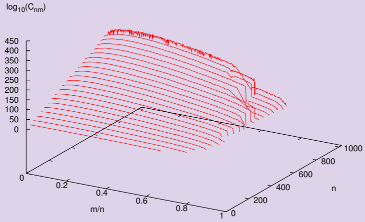
Total sample size: $30,000,000$

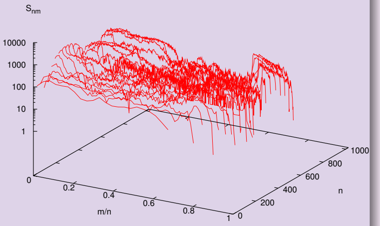




2d ISAW simulation up to $N = 1024$

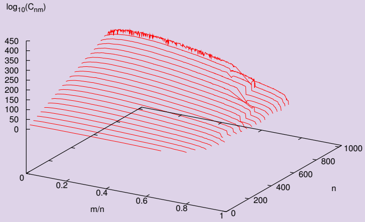
Total sample size: $40,000,000$

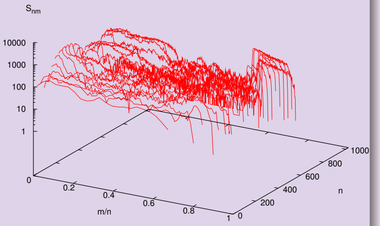




2d ISAW simulation up to $N = 1024$

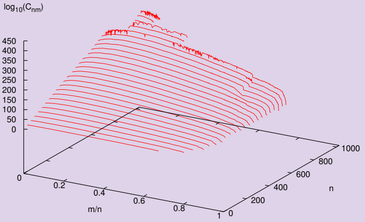
Total sample size: $50,000,000$

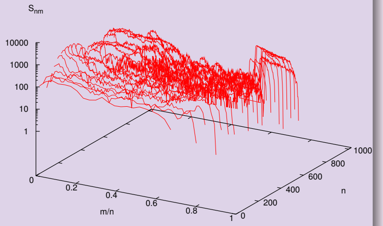




2d ISAW simulation up to $N = 1024$

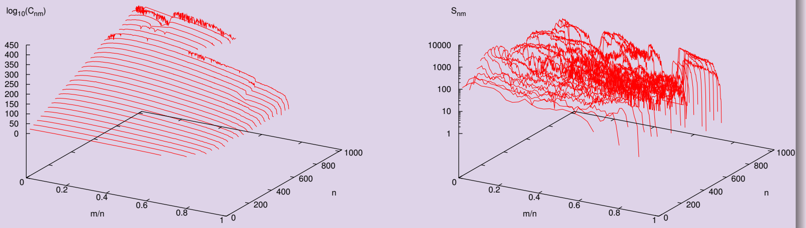
Total sample size: $60,000,000$





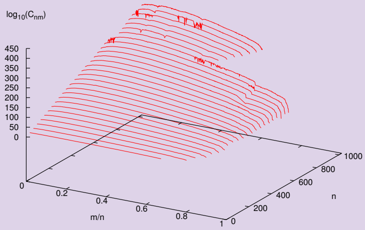
2d ISAW simulation up to $N = 1024$

Total sample size: $70,000,000$



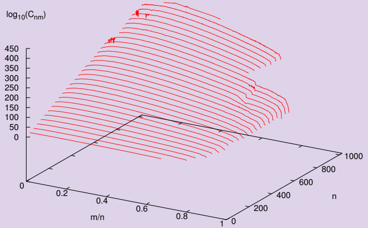
2d ISAW simulation up to $N = 1024$

Total sample size: $80,000,000$



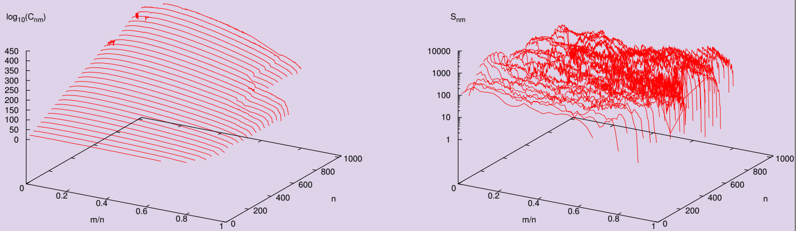
2d ISAW simulation up to $N = 1024$

Total sample size: $90,000,000$



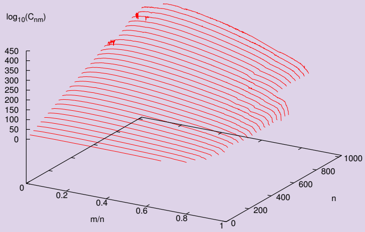
2d ISAW simulation up to $N = 1024$

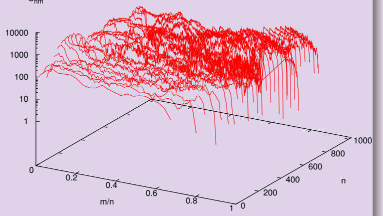
Total sample size: $100,000,000$



2d ISAW simulation up to $N = 1024$

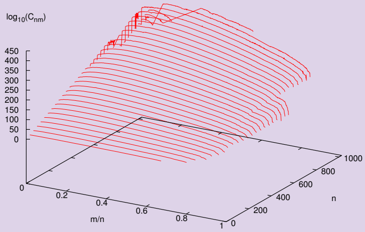
Total sample size: $110,000,000$

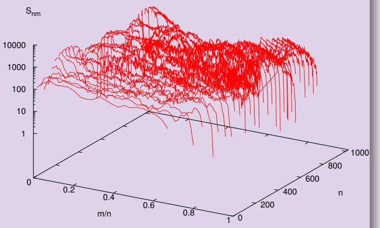




2d ISAW simulation up to $N = 1024$

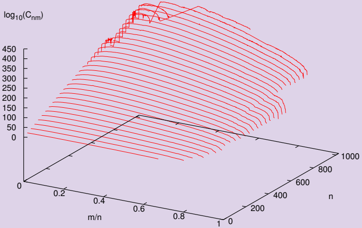
Total sample size: $120,000,000$





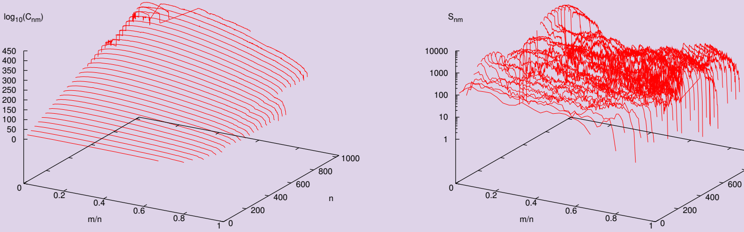
2d ISAW simulation up to $N = 1024$

Total sample size: $130,000,000$



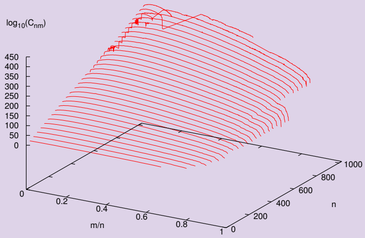
2d ISAW simulation up to $N = 1024$

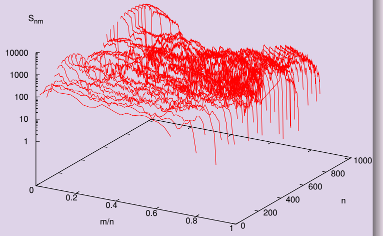
Total sample size: $140,000,000$



2d ISAW simulation up to $N = 1024$

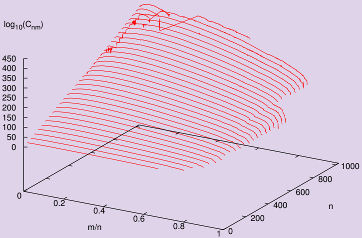
Total sample size: $150,000,000$

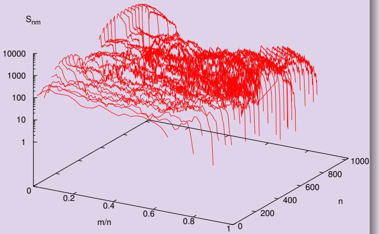




2d ISAW simulation up to $N = 1024$

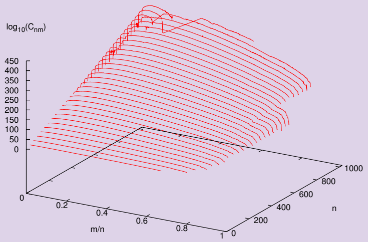
Total sample size: $160,000,000$





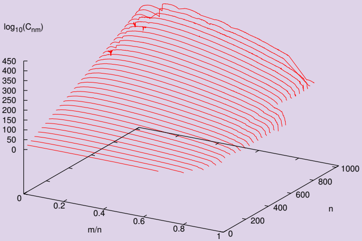
2d ISAW simulation up to $N = 1024$

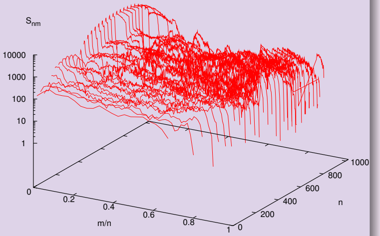
Total sample size: $170,000,000$



2d ISAW simulation up to $N = 1024$

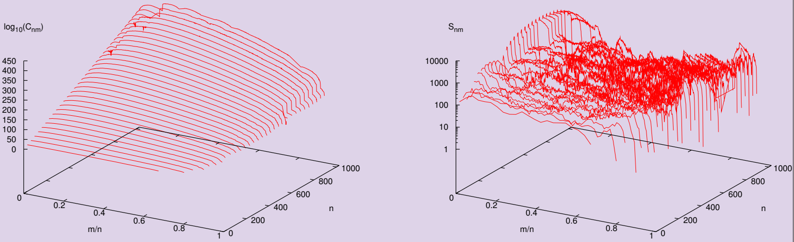
Total sample size: $180,000,000$





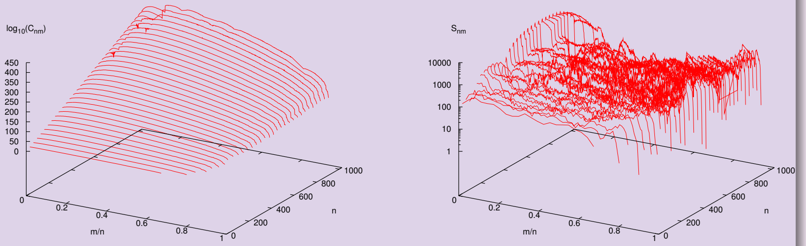
2d ISAW simulation up to $N = 1024$

Total sample size: $190,000,000$



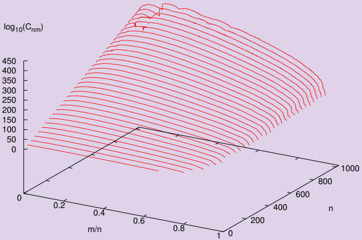
2d ISAW simulation up to $N = 1024$

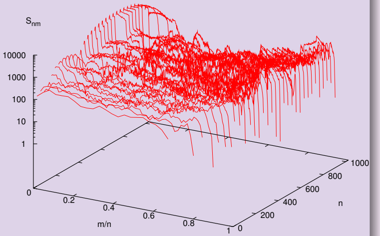
Total sample size: $200,000,000$



2d ISAW simulation up to $N = 1024$

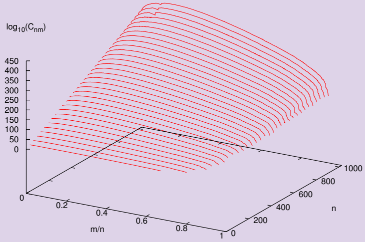
Total sample size: $210,000,000$

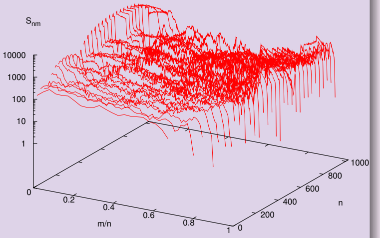




2d ISAW simulation up to $N = 1024$

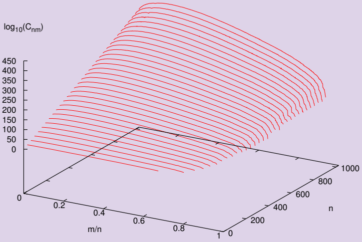
Total sample size: 220, 000, 000

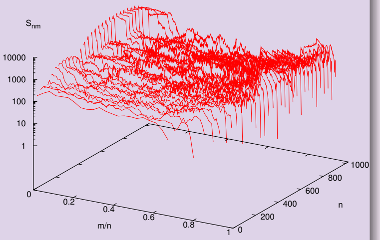




2d ISAW simulation up to $N = 1024$

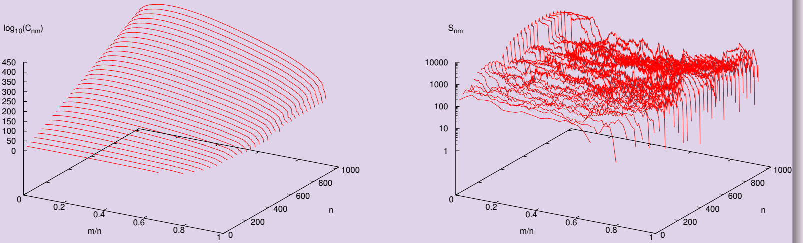
Total sample size: $230,000,000$





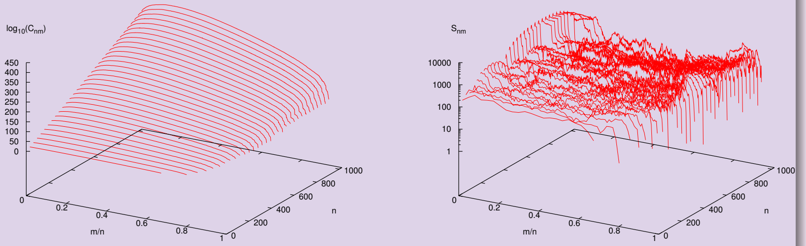
2d ISAW simulation up to $N = 1024$

Total sample size: $240,000,000$



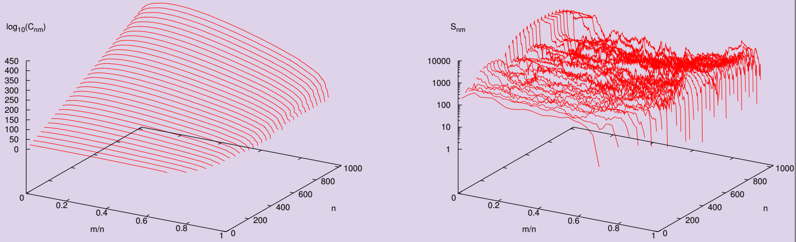
2d ISAW simulation up to $N = 1024$

Total sample size: $250,000,000$



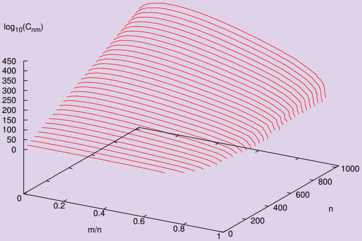
2d ISAW simulation up to $N = 1024$

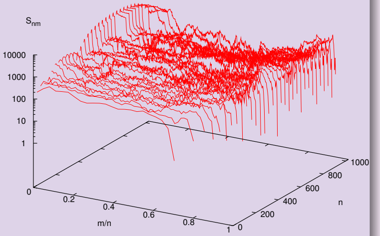
Total sample size: $260,000,000$



2d ISAW simulation up to $N = 1024$

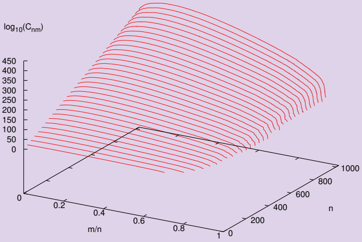
Total sample size: $270,000,000$

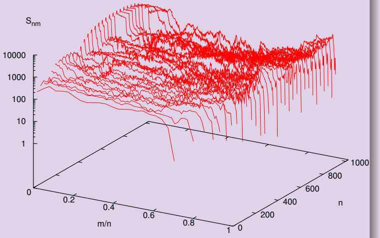




2d ISAW simulation up to $N = 1024$

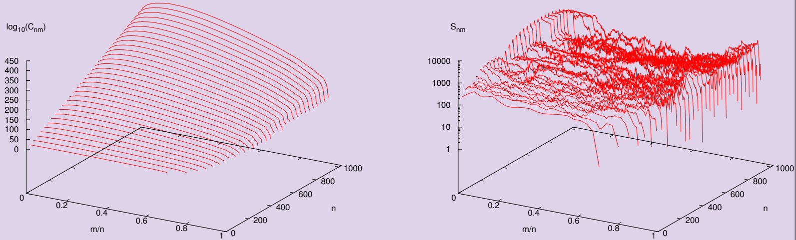
Total sample size: $280,000,000$





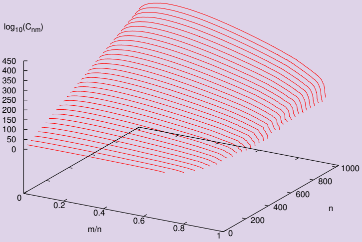
2d ISAW simulation up to $N = 1024$

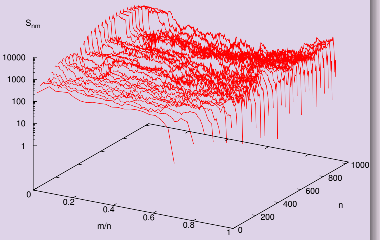
Total sample size: $290,000,000$



2d ISAW simulation up to $N = 1024$

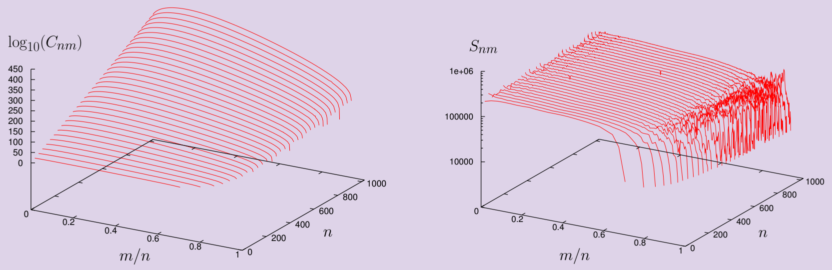
Total sample size: $300,000,000$





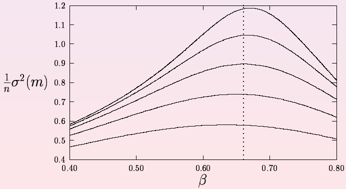
ISAW simulations

T Prellberg and J Krawczyk, PRL 92 (2004) 120602



- 2d ISAW up to $n = 1024$
- One simulation suffices
- 400 orders of magnitude

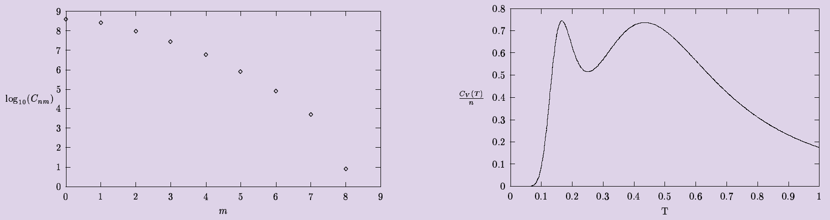
(only 2d shown, 3d similar)



HP model simulations

T Prellberg et al, Computer Simulation Studies in Condensed Matter Physics XVII, pages 122-135, Springer Verlag, 2006

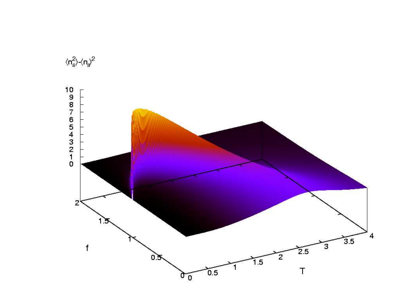
- Engineered sequence HPHPHHPHPHHPPH in $d = 3$:

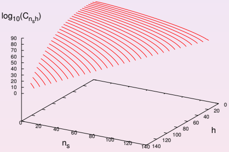


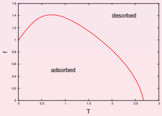
- Investigated other sequences up to $N \approx 100$ in $d = 2$ and $d = 3$
- Collapsed regime accessible
- Reproduced known ground state energies
- Obtained density of states $C_{n,m}$ over large range ($\approx 10^{30}$)

J Krawczyk et al, JSTAT (2004) P10004

- 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



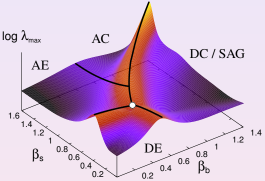


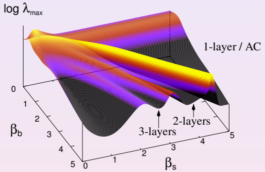


2-Dimensional Density of States

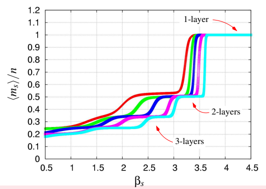
J Krawczyk et al, Europhys. Lett. 70 (2005) 726-732

- Layering transitions of adsorbed polymers in poor solvents



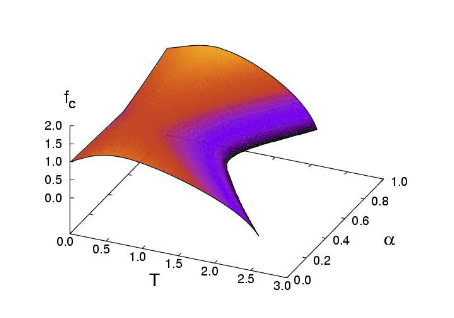


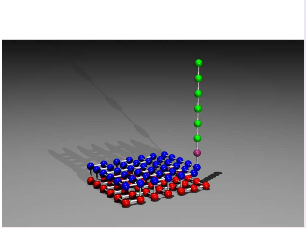
- whole phase diagram at once
- low temperatures accessible
- hierarchy of layering transitions
- resolved controversy over "surface attached globule"



J Krawczyk et al, JSTAT (2005) P05008

- Pulling adsorbing and collapsing polymers off a surface



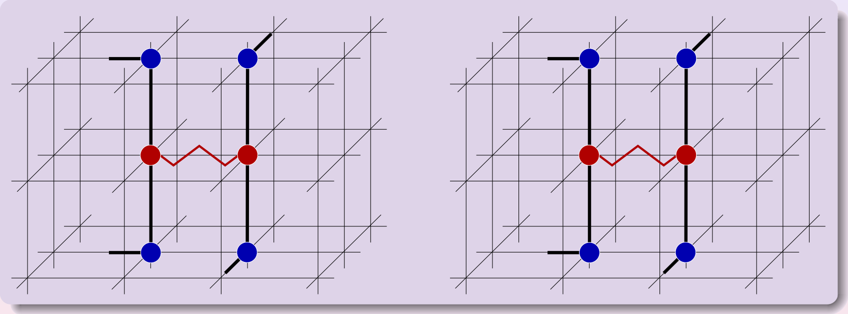


$\epsilon_s = \alpha$, $\epsilon_b = 1 - \alpha$

- simulations up to $n = 91$ (4-dimensional histogram)
- interplay of (both force-induced and thermal) desorption ($\alpha = 1$) and stretching ($\alpha = 0$)

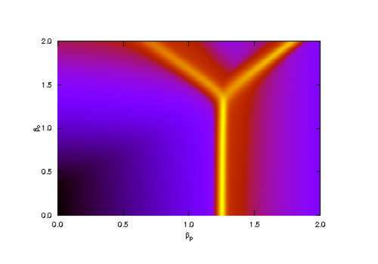
Hydrogen-bond type interactions

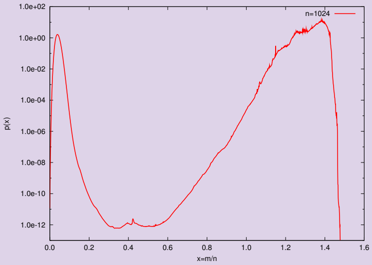
J Krawczyk et al, in preparation



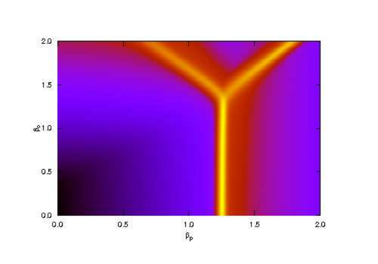
Introduce orientation-dependent (parallel/orthogonal) interactions between *straight* segments of the walk

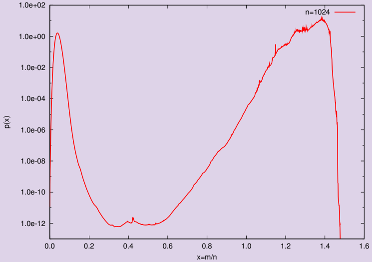
Hydrogen-bond type interactions (ctd.)

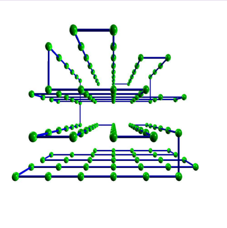


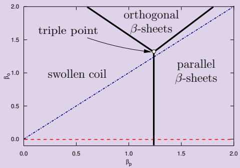


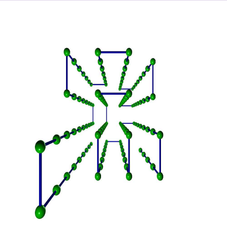
Hydrogen-bond type interactions (ctd.)











Acknowledgements

Joined work with A.L. Owczarek, A. Rechnitzer, J. Krawczyk

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  - J. Krawczyk, T. Prellberg, A. L. Owczarek, and A. Rechnitzer, "On a type of self-avoiding random walk with multiple site weightings and restrictions," Phys. Rev. Lett. 96 (2006) 240603; selected for Virt. J. Biol. Phys. Res. 12 (2006)

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- Hydrogen-bond type interactions:
  - J. Krawczyk, A. L. Owczarek, T. Prellberg, and A. Rechnitzer, "Simulation of Lattice Polymers with Hydrogen-Like Bonding," preprint

The End