Polymer Simulation with a Flat Histogram Stochastic Growth Algorithm

Thomas Prellberg

thomas.prellberg@qmul.ac.uk

School of Mathematical Sciences

Queen Mary, University of London

joint work with

J. Krawczyk, TU Clausthal

A. Rechnitzer and A.L. Owczarek, Uni Melbourne

Queen Mary
University of London

Outline

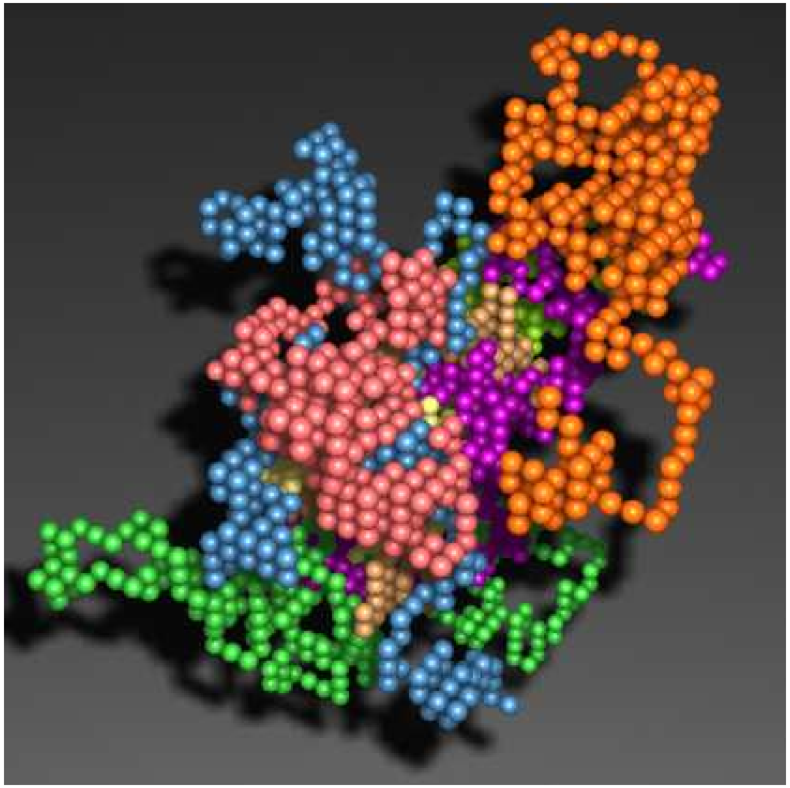
- Polymers in solution:
  - Equilibrium statistical mechanics, lattice model
- Algorithm:
  - Stochastic growth & flat histogram (flatPERM)
- Applications:
  - Bulk phenomena (previous work)
    - polymer collapse, protein groundstates
  - Surface phenomena (this talk)
    - confined polymers, force-induced desorption, interplay of collapse and adsorption
- Work in progress:
  - off-lattice models, extended Domb-Joyce model, . . .

Queen Mary
University of London

Introduction

Modelling of Polymers in Solution

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

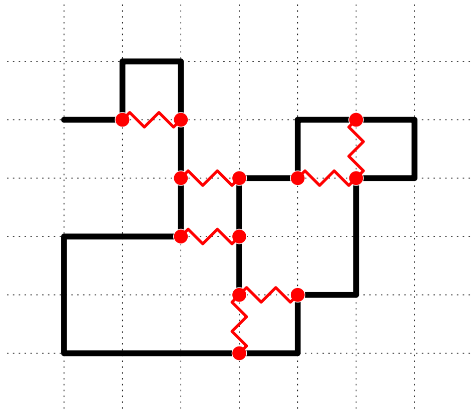


Queen Mary
University of London

Pedagogical Setting: Lattice Model

Self-Avoiding Walks with Interactions

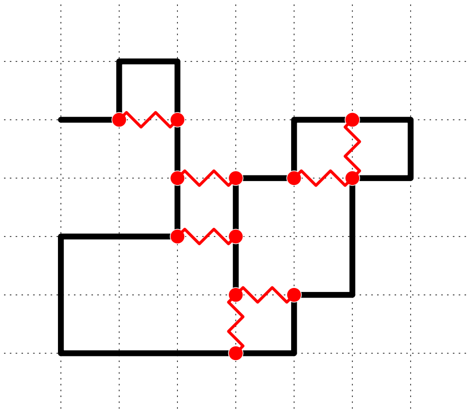
- Physical space $\rightarrow$ simple cubic lattice $\mathbb{Z}^3$
- Polymer $\rightarrow$ self-avoiding random walk (SAW)
- Quality of solvent $\rightarrow$ short-range interaction ϵ



Queen Mary
University of London

Pedagogical Setting: Lattice Model

Self-Avoiding Walks with Interactions



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

Why Simulations?

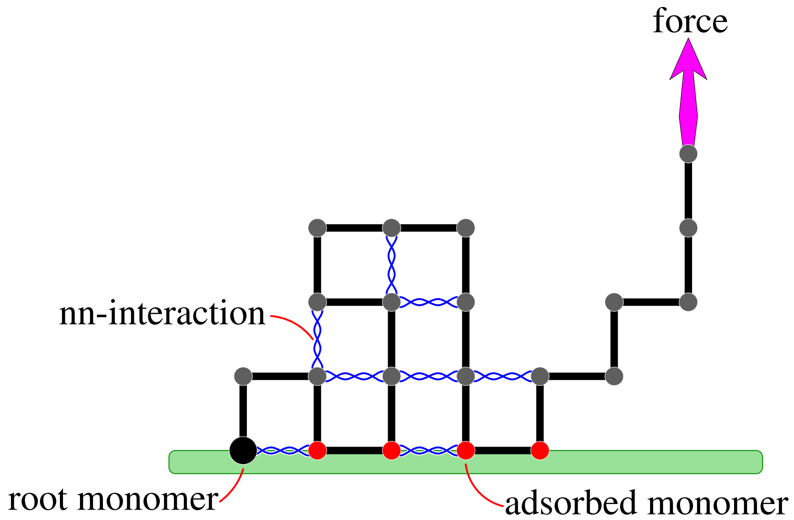
- Most interesting open questions for dense and geometrically restricted configurations
- There is little theory and

$\boxed{\text{this is notoriously difficult to simulate}}$

Queen Mary
University of London

Application: Pulling of Collapsed and Adsorbed Polymers

- 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



Stochastic Growth Algorithm

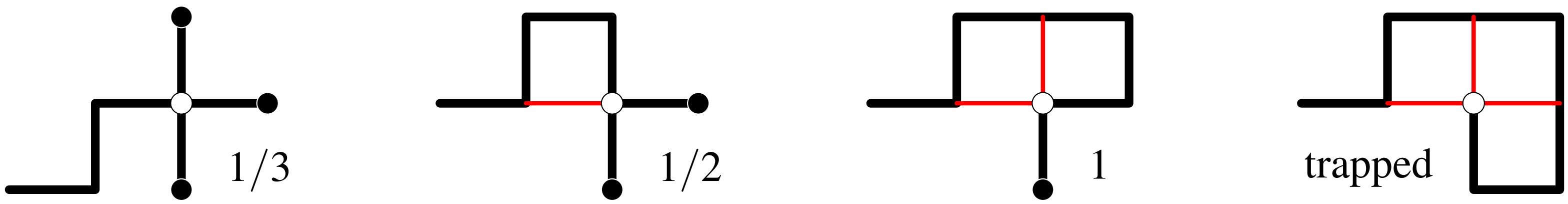
Queen Mary
University of London

PERM: "Go With The Winners"

PERM = Pruned and Enriched Rosenbluth Method

Grassberger, Phys Rev E 56 (1997) 3682

- Rosenbluth Method: kinetic growth



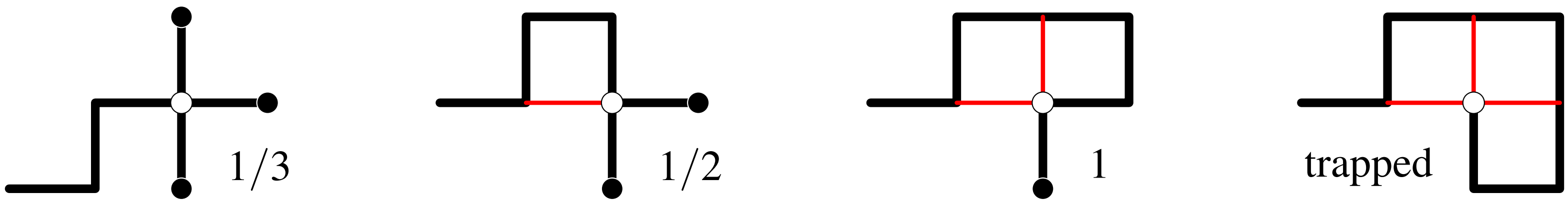
Queen Mary
University of London

PERM: "Go With The Winners"

PERM = Pruned and Enriched Rosenbluth Method

Grassberger, Phys Rev E 56 (1997) 3682

- Rosenbluth Method: kinetic growth



- Enrichment: weight too large $\rightarrow$ make copies of configuration
- Pruning: weight too small $\rightarrow$ remove configuration occasionally

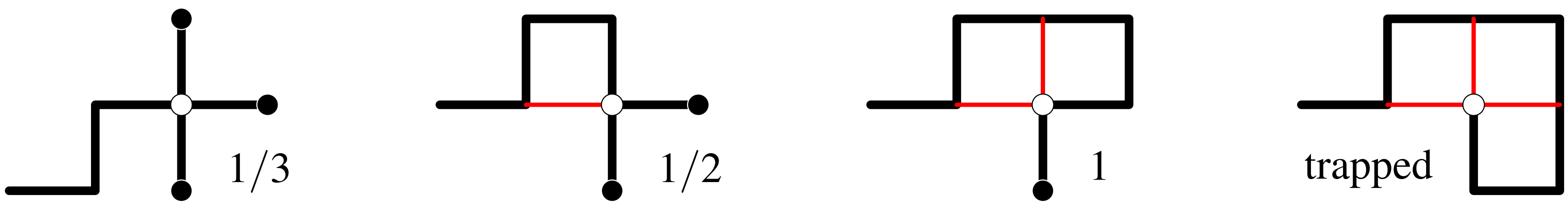
Queen Mary
University of London

PERM: “Go With The Winners”

PERM = Pruned and Enriched Rosenbluth Method

Grassberger, Phys Rev E 56 (1997) 3682

- Rosenbluth Method: kinetic growth



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

Current work: flatPERM = flat histogram PERM

TP and JK, PRL 92 (2004) 120602, TP, JK, and AR, Athens Proceedings 2004

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

Queen Mary University of London

Algorithm details

View kinetic growth as *approximate enumeration*

Queen Mary
University of London

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

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

$$W = \prod_{k=0}^{n-1} a_k$$

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, $C_n^{\rm est} = \langle W \rangle_n = \frac{1}{S} \sum_i W_n^{(i)}$

Queen Mary
University of London

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, $C_n^{\mathrm{est}} = \langle W \rangle_n = \frac{1}{S} \sum_i W_n^{(i)}$
- Add pruning/enrichment with respect to ratio $r = W_n^{(S+1)} / C_n^{est}$

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, $C_n^{\mathrm{est}} = \langle W \rangle_n = \frac{1}{S} \sum_i W_n^{(i)}$
- 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
    - $C_n^{est} = \langle W \rangle_n$
    - $r = W_n^{(i)} / C_n^{est}$

Queen Mary
University of London

From PERM to flatPERM

- 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 $Z_n(\beta)$
    - $Z_n^{est}(\beta) = \langle W \exp(-\beta E) \rangle_n$
    - $r = W_n^{(i)} \exp(-\beta E^{(i)}) / Z_n^{est}(\beta)$

Queen Mary
University of London

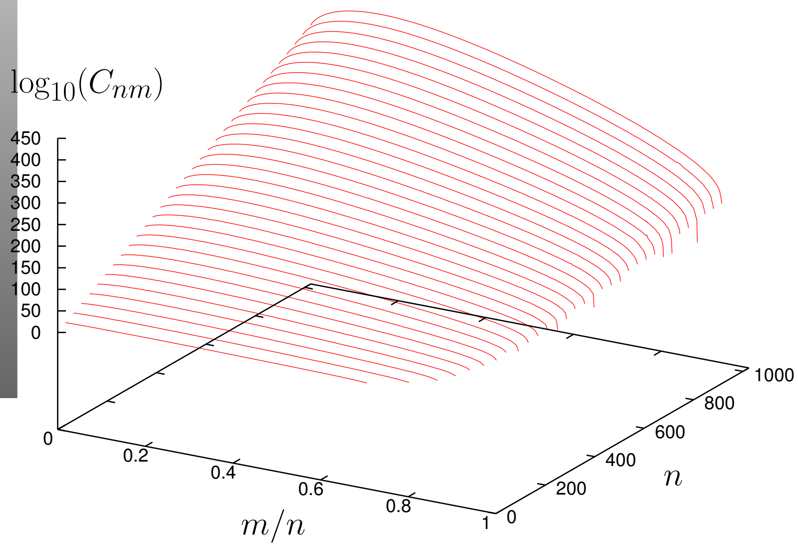
From PERM to flatPERM

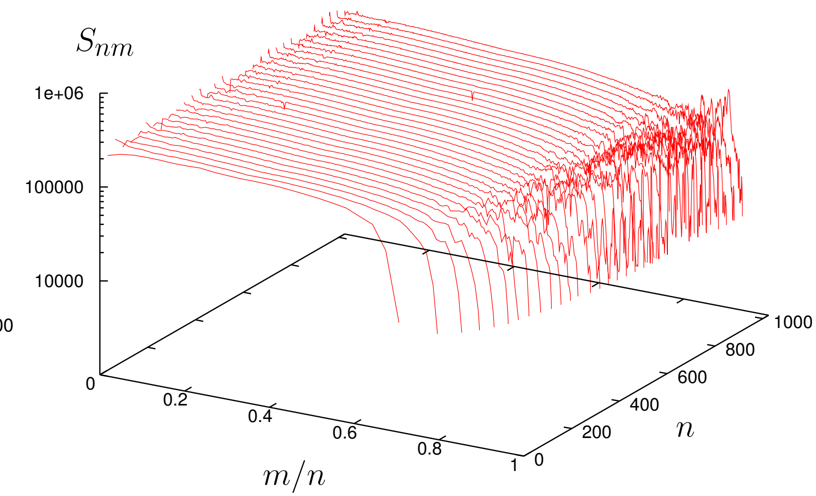
- Consider athermal case
  - PERM: estimate number of configurations C_n
    - $C_n^{est} = \langle W \rangle_n$
    - $r = W_n^{(i)} / C_n^{est}$
- Consider energy E, temperature $\beta = 1/k_B T$
  - thermal PERM: estimate partition function $Z_n(\beta)$
    - $Z_n^{est}(\beta) = \langle W \exp(-\beta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

Queen Mary
University of London

Simulation Results

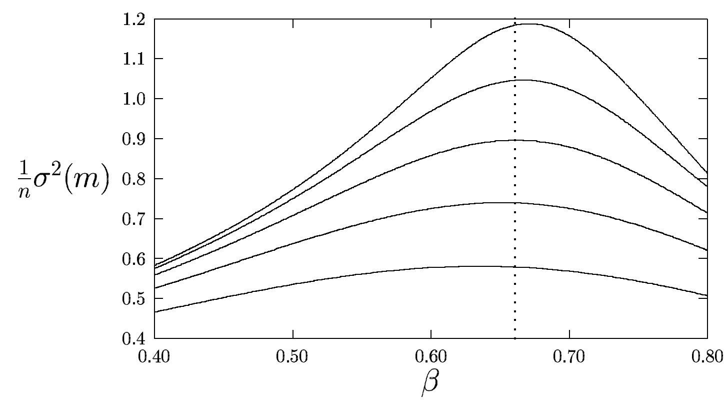
Simulation results: ISAW





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

(only 2d shown, 3d similar)

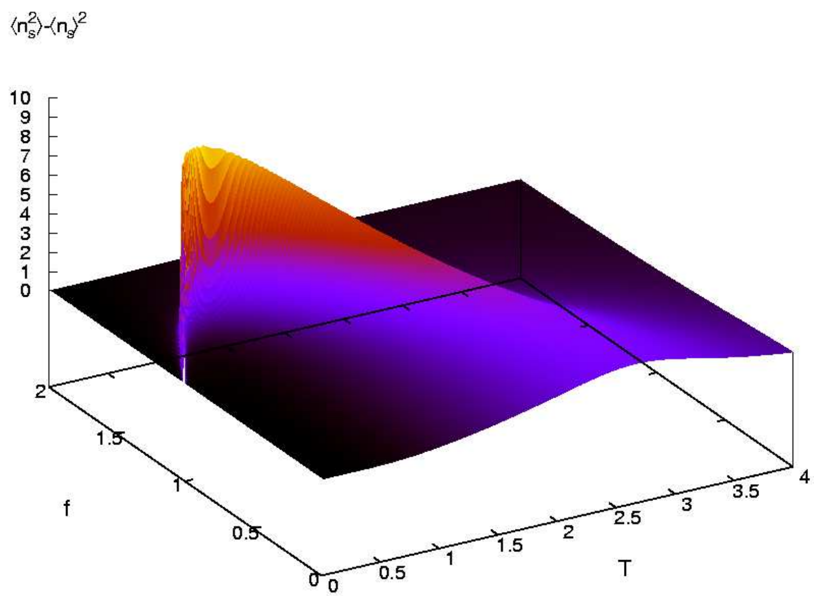


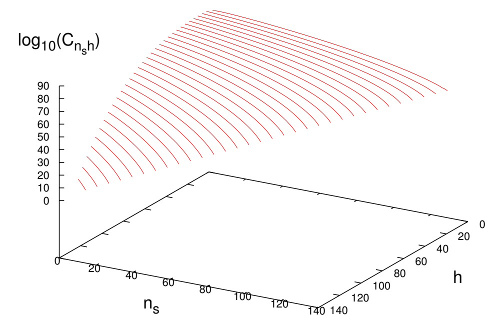
TP and JK, PRL 92 (2004) 120602

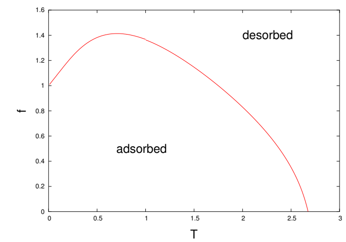
Queen Mary
University of London

2-Dimensional Density of States

- 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 $n = 256$





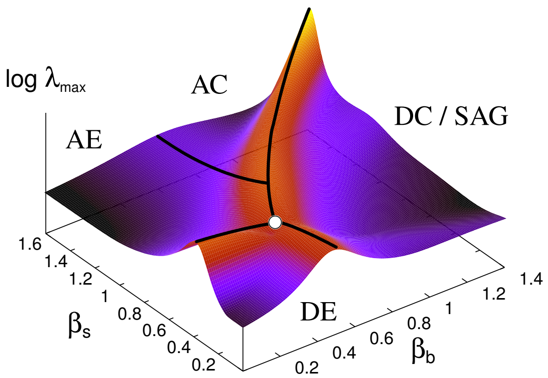


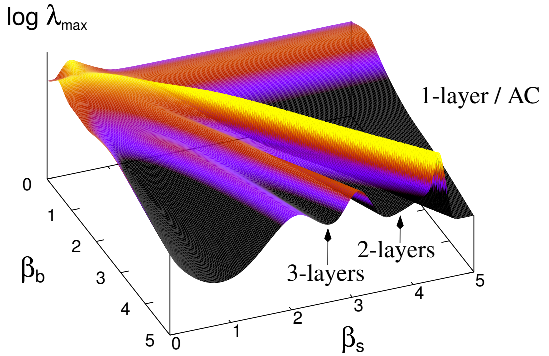
JK et al, JSTAT (2004) P10004

Queen Mary
University of London

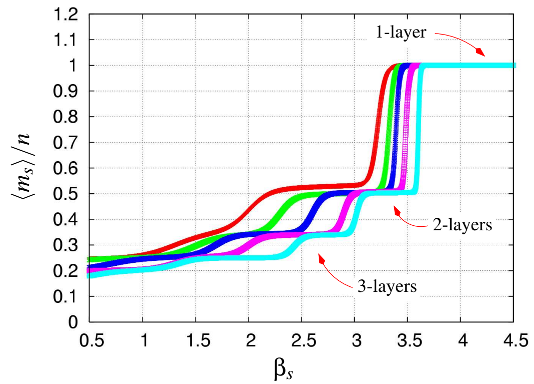
2-Dimensional Density of States

- 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"

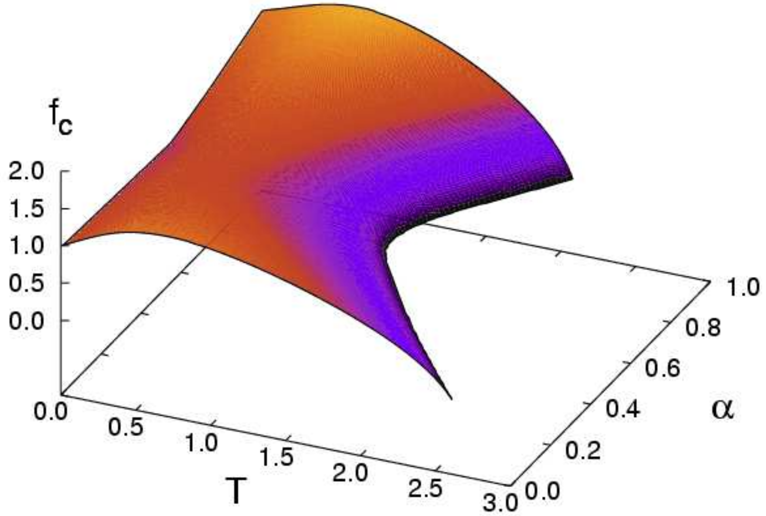


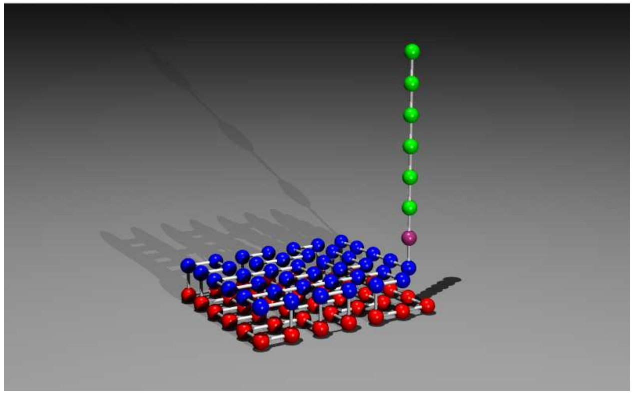
JK et al, Europhys Lett, in print

Queen Mary
University of London

3-Dimensional Density of States

- 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 ($\alpha = 0$)

JK et al, JSTAT, in print

Summary and Outlook

Conclusion: A Promising New Algorithm

- Presented “flat histogram” version of PERM
  - *One* simulation for complete density of states!
    (the range can also be selectively restricted)

Queen Mary
University of London

Conclusion: A Promising New Algorithm

- Presented “flat histogram” version of PERM
  - *One* simulation for complete density of states!
    (the range can also be selectively restricted)
- Simulations of polymers:
  - collapsed polymers
  - force-induced desorption of adsorbed polymers
  - interplay adsorption/collapse
  - force-induced stretching/desorption

Conclusion: A Promising New Algorithm

- Presented “flat histogram” version of PERM
  - *One* simulation for complete density of states!
    (the range can also be selectively restricted)
- Simulations of polymers:
  - collapsed polymers
  - force-induced desorption of adsorbed polymers
  - interplay adsorption/collapse
  - force-induced stretching/desorption
- Outlook: applications to further models, e.g.
  - off-lattice simulations
  - extended Domb-Joyce model

The End