Simulating models of polymer collapse

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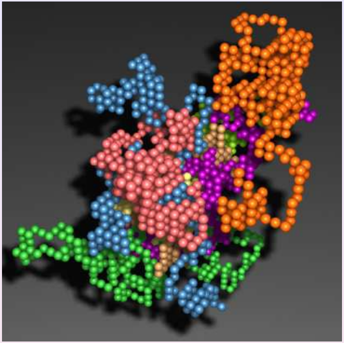
Outline

- Polymers in solution:
    - Equilibrium statistical mechanics, lattice models, exponents
- Algorithm:
    - Stochastic growth & flat histogram (PERM/flatPERM)
- Simulations and results:
    - Interacting self-avoiding walks/trails (ISAW/ISAT)
    - Site-weighted random walks (SWRW): a tale of surprises

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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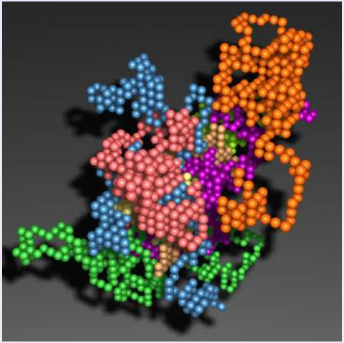
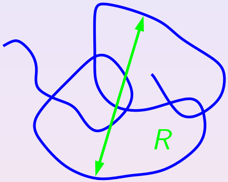


A Model of a Polymer in Solution

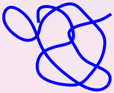
Random Walk + Excluded Volume + Short Range Attraction

Polymer Collapse, Coil-Globule Transition, Θ-Point

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)

Critical Exponents

Length scale exponent ν*:* $R_N \sim N^\nu$

d	Coil	Θ	Globule
2	$3/4$	$4/7$	$1/2$
3	$0.587\ldots$	$1/2(\log)$	$1/3$
4	$1/2(\log)$	$1/2$	$1/4$

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Entropic exponent γ: $Z_N \sim \mu^N N^{\gamma-1}$

d	Coil	Θ	Globule
2	$43/32$	$8/7$	different scaling form
3	$1.15\ldots$	$1(\log)$	$Z_N \sim \mu^N {\mu_s}^{N^\sigma} N^{\gamma-1}$
4	$1(\log)$	1	$\sigma = (d-1)/d$ (surface)

Crossover Scaling at the Θ-Point

Crossover exponent ϕ

$$R_N \sim N^{\nu} \mathcal{R}(N^{\phi} \Delta T) \qquad Z_N \sim \mu^N N^{\gamma-1} \mathcal{Z}(N^{\phi} \Delta T)$$

Specific heat of Z_N at $T = T_c$: $C_N \sim N^{\alpha\phi}$

$$2 - \alpha = 1/\phi \qquad \text{tri-critical scaling relation}$$

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Poor man's mean field theory of the Θ-Point for $d \geq 3$

Balance between "excluded volume" and attractive interaction
$\Rightarrow$ polymer behaves like random walk: $\nu = 1/2$, $\gamma = 1$
$\Rightarrow$ weak thermodynamic phase transition $\alpha = 0$, i.e. $\phi = 1/2$

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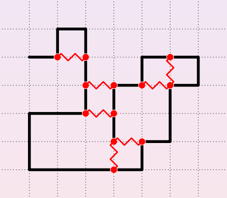
d	2	3	4
ϕ	3/7	1/2(log)	1/2

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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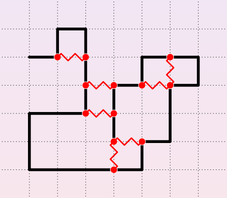
Partition function:

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



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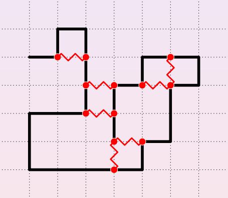

Thermodynamic Limit for a dilute solution:

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

Theory and Models

- Theoretical results from e.g.
  - $d = 2$: Coulomb gas methods, conformal invariance, SLE, ...
  - $d \geq 3$: self-consistent mean field theory
  - field theory: $\phi^4 - \phi^6$ $O(n)$-model for $n \to 0$

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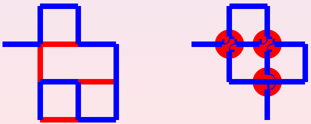
A Model of a Polymer in Solution

Random Walk + Excluded Volume + Short Range Attraction

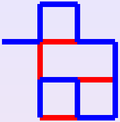
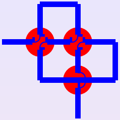
- Canonical model: interacting self-avoiding walks (ISAW)
- Alternative model: interacting self-avoiding trails (ISAT)

vertex avoidance (walks) $\Leftrightarrow$ edge avoidance (trails)



nearest-neighbour interaction $\Leftrightarrow$ contact interaction

ISAW versus ISAT

ISAW   ISAT

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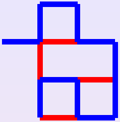
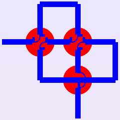
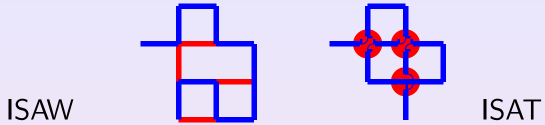
ISAW   ISAT

- simulations of ISAW confirm the theoretical predictions
- simulations of ISAT confound the theoretical predictions

ISAW versus ISAT



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Length scale exponent ν for $\mathbb{Z}^2$:

Model	Coil	Θ	Globule
ISAW	3/4	4/7	1/2
ISAT	3/4	1/2(log)	1/2

Entropic exponent γ for $\mathbb{Z}^2$:

Model	Coil	Θ
ISAW	43/32	8/7
ISAT	43/32	1(log)

Crossover exponent ϕ for $\mathbb{Z}^2$:

Model	
ISAW	3/7
ISAT	0.84(3)

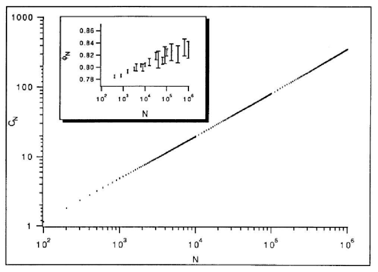
Simulations of ISAT

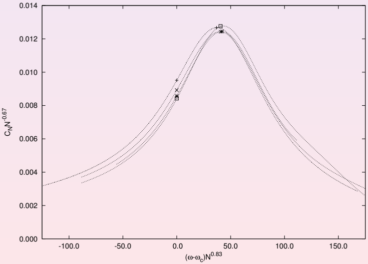
- At critical T_c, ISAT can be modelled as kinetic growth; simulations up to $N = 10^6$

AL Owczarek and T Prellberg, J. Stat. Phys. 79 (1995) 951-967

- Pruned Enriched Rosenbluth Method enables simulations for $T \neq T_c$; new simulations up to $N = 2 \cdot 10^6$

AL Owczarek and T Prellberg, Physica A, in print





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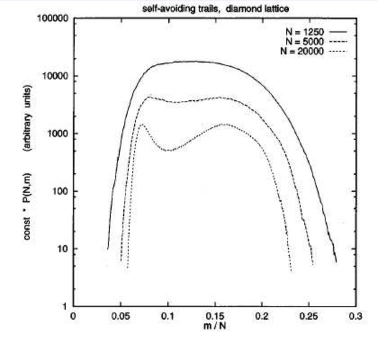

T Prellberg and AL Owczarek, Phys. Rev. E 51 (1995) 2142-214

(figure from) P Grassberger and R Hegger, J. Phys. A 29 (1996) 279-288

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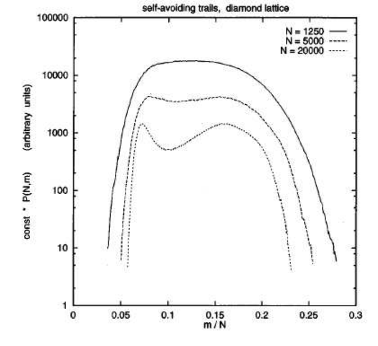

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10 years later, this is still not understood!

A Proposal of a New Model

- 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 $n \to 0$

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  - lattice random walk weighted by multiple visits of sites
  - few visits to same site are favoured (attractive interaction)
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(technically, this is an extension of a Domb-Joyce model)

Site-Weighted Random Walk

- An N-step random walk $\xi = (\vec{\xi}_0, \vec{\xi}_1, \ldots, \vec{\xi}_N)$ induces a density-field ϕ_ξ on the lattice sites $\vec{x}$ via

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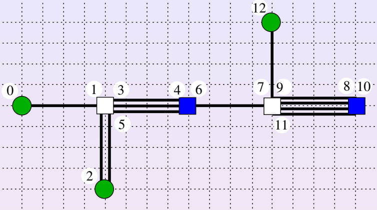
- Incorporate self-avoidance and attraction via choice of $f(t)$. For example, $f(0) = f(1) = 0$,

$$f(2) = \varepsilon_1 \ , \quad f(3) = \varepsilon_2 \ ,$$

and $f(t \geq 4) = \infty$.

Site-Weighted Random Walk (ctd)



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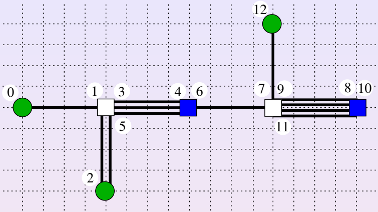

- Partition function

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

with density of states C_{N,m_1,m_2}

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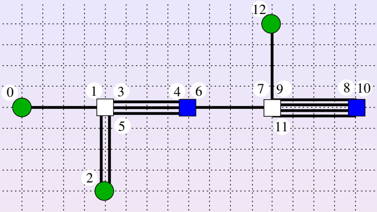

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  with density of states C_{N,m_1,m_2}
- Simulate two variants of the model on the square and simple cubic lattice
  - random walks with immediate reversal allowed (RA2, RA3)
  - random walks with immediate reversal forbidden (RF2, RF3)

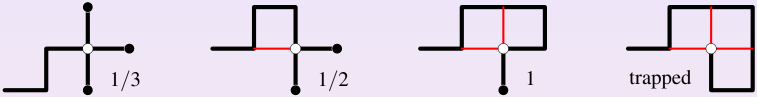
The Algorithm and Simulations

PERM: “Go With The Winners”

PERM = Pruned and Enriched Rosenbluth Method

Grassberger, Phys Rev E 56 (1997) 3682

- Rosenbluth Method: kinetic growth



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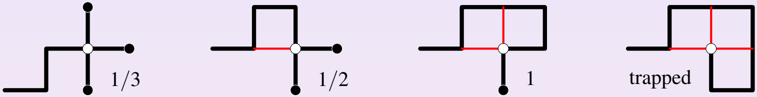

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- Pruning: weight too small → remove configuration occasionally

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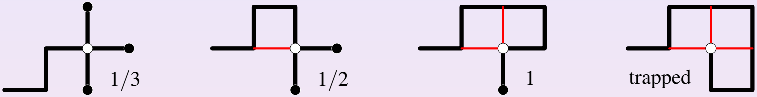

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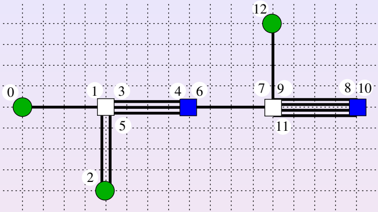
State-of-the-art: flatPERM = flat histogram PERM

M Bachmann and W Janke, PRL 91 (2003) 208105

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

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

SWRW simulations



- Four simulations: reversal allowed/forbidden, 2d/3d

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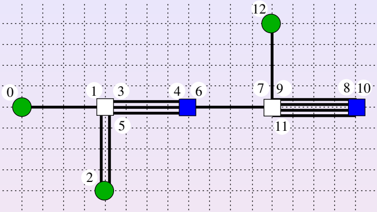

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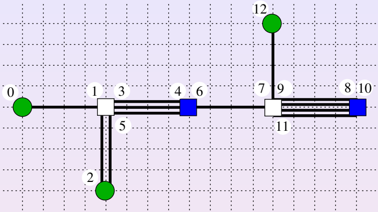

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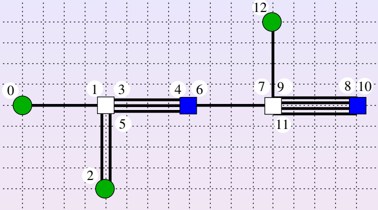
SWRW simulations



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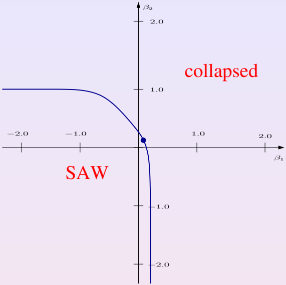
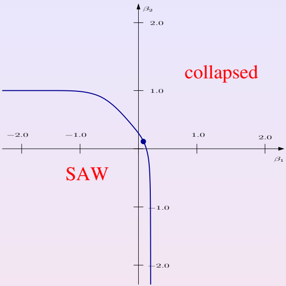
- Density of states $\bar{C}_{N,m_1}(\beta_2)$ accessible up to $N = 1024$ (for β_2 fixed)

SWRW in 3d, reversal forbidden (RF3)



Phase diagram

SWRW in 3d, reversal forbidden (RF3)



Phase diagram

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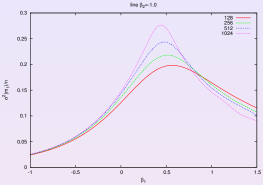
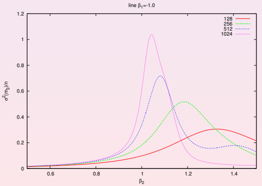
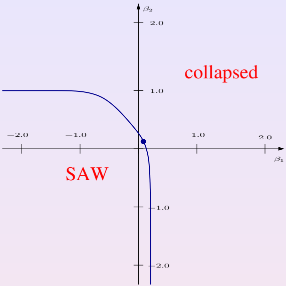


2nd order transition

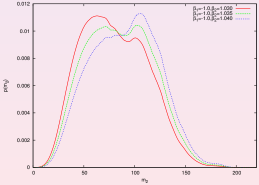
$\beta_1 = -1.0$:



1st order transition

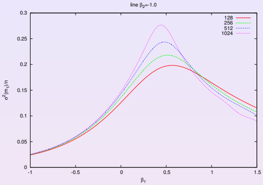


Phase diagram



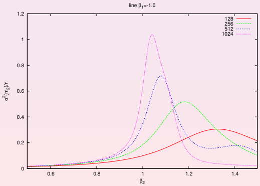
bimodal distribution

$\beta_2 = -1.0$:



2nd order transition

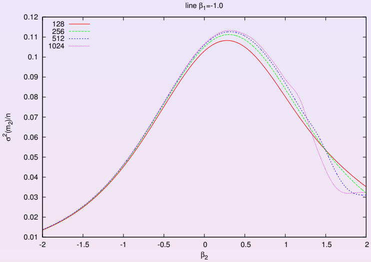
$\beta_1 = -1.0$:

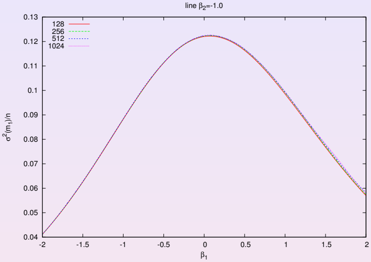


1st order transition

SWRW in 2d, reversal allowed (RA2)

We find a smooth crossover:





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

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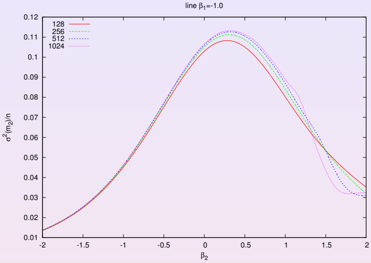

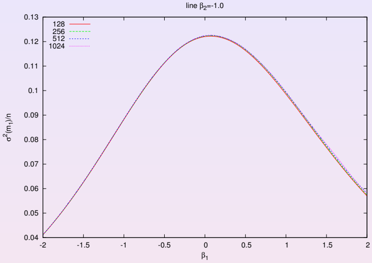

Both 1st order and 2nd order transitions have disappeared!

RA3 and RF2

2nd order transition disappears as in RA2

1st order transition weakens

SWRW summarised

Model	2d	3d
RA	no transitions	one transition
RF	one transition	two transitions

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Unexpected and intriguing behaviour

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Many open Questions remain . . .

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An unfinished story!

Acknowledgements

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- Things to come:
  - J. Krawczyk, A. L. Owczarek, T. Prellberg, and A. Rechnitzer, "Simulation of Lattice Polymers with Hydrogen-Like Bonding," preprint

The End