

Polymer Simulations

From Self-Avoiding Walks to the Coil-Globule Transition

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24th april 2024





Plastics



Silicon gels



Coton, polyester



Acrylic paint

numerical approach

- Modelize the coil-globule transition
- Study the influence of forces

Outline

1 Physics of polymers and motivations

- What is a polymer ?
- First goal: the coil-globule transition
- Second goal: applying an external force

2 Model and computational methods

- Coarse-grained model
- Monte Carlo sampling and statistical thermodynamics
- Prune-enriched Rosenbluth Method (PERM)

3 Results

- Scaling laws with SAW
- Coil-globule transition
- Applying an external force

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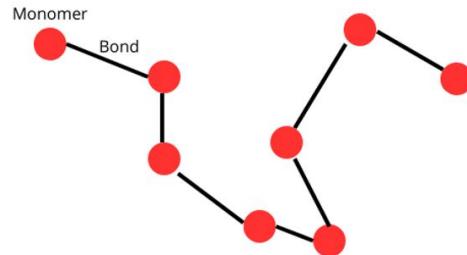
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What is a Polymer ?

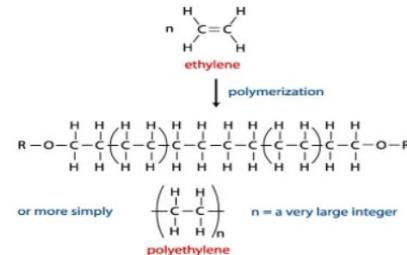
Polymer = chemical bonds + monomers

Monomers :

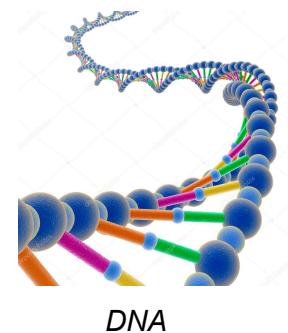
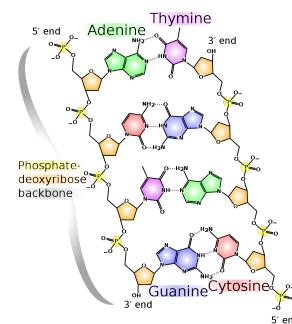
- simple molecules : ethylene \rightarrow polyethylene
- complex molecules : amino acids \rightarrow protein
- nucleotides (ATCG) \rightarrow DNA



Simple representation of polymer



Polyethylene resins



DNA

Simulation methods

Method	Characteristics
Molecular Dynamics	atomic scale, classical equations of motion
Continuous models	molecular scale, interaction potentials
Coarse-grained models	macroscopic scale, approximations

Simulation methods : Coarse-grained models

Covalent bonds = string

excluded volume = repulsion effect

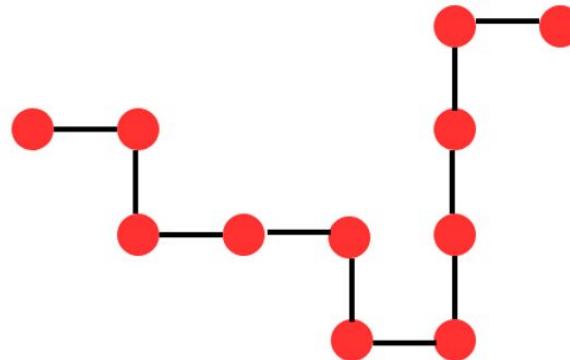
orientations are orthogonal or parallel

Système size : big size

different configurations = different properties

$$r_e^2(N) = |\mathbf{r}_N - \mathbf{r}_0|^2$$

$$r_g^2(N) = \frac{1}{N} \sum_{i=0}^N |\mathbf{r}_i - \mathbf{r}_{\text{cm}}|^2,$$



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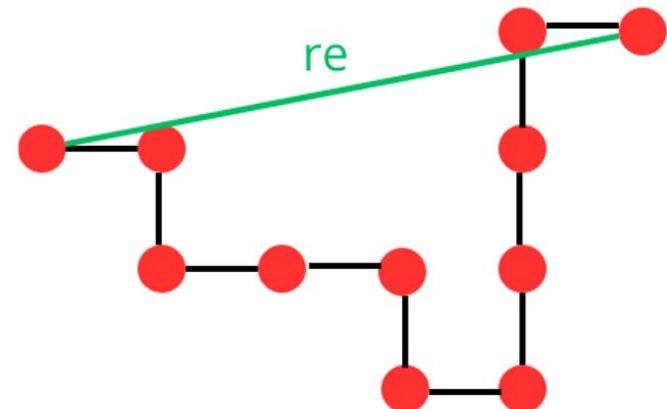
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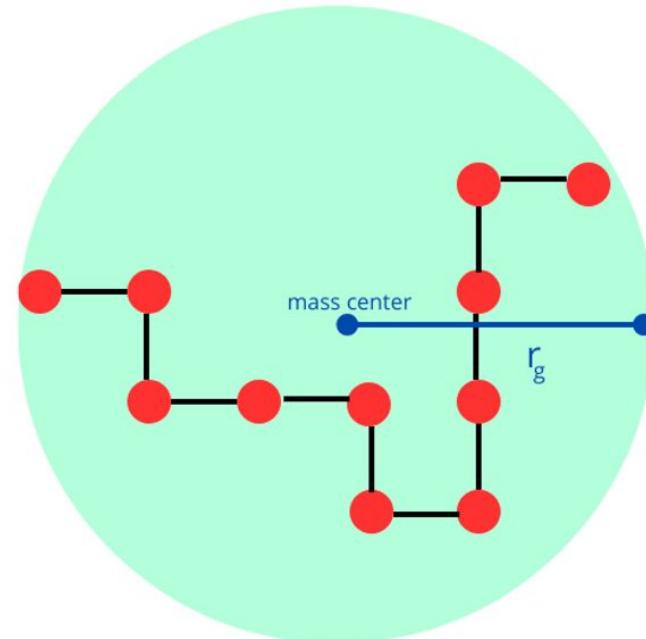
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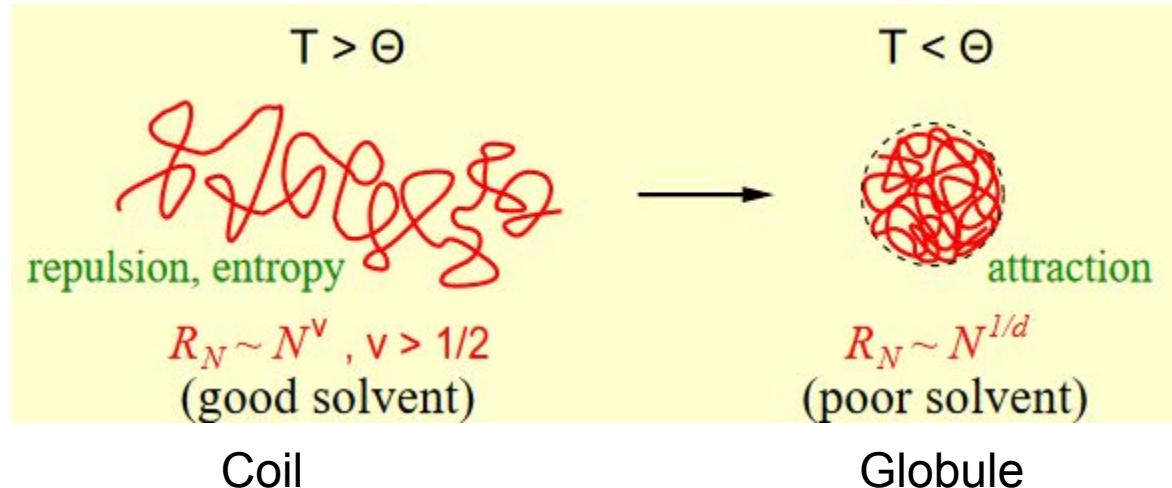
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System size : big size



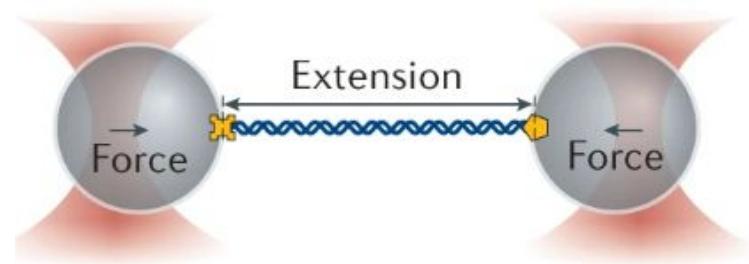
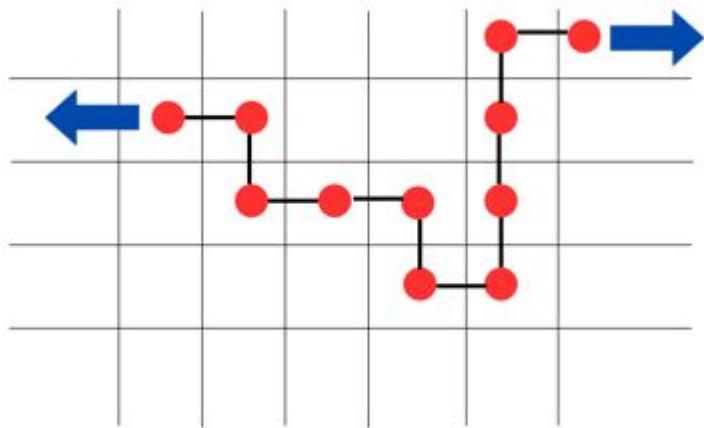
1st goal : the coil-globule transition



Practical applications :

- controlled release drugs
- studies of structure for DNA in biological cells and medical applications

2nd goal : applying an external force



Practical applications :

- Optical tweezers : to study the mechanical properties, structure, and interactions

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Coarse-grained model

A linear polymer chain of $N + 1$ monomers



An **interacting self-avoiding walk (ISAW)** of N steps on a simple cubic lattice (3D)

Coarse-grained model

A linear polymer chain of $N + 1$ monomers

$$\Leftrightarrow$$

An **interacting self-avoiding walk (ISAW)** of N steps on a simple cubic lattice (3D)

- Monomers are supposed to sit on lattice sites, connected by bonds of length one

Coarse-grained model

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An **interacting self-avoiding walk (ISAW)** of N steps on a simple cubic lattice (3D)

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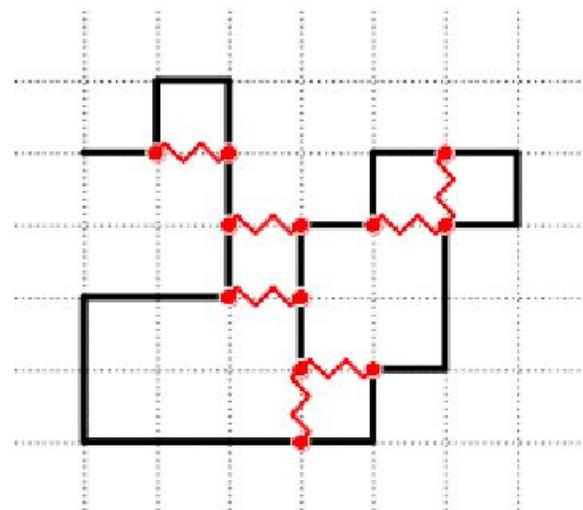
Coarse-grained model

A linear polymer chain of $N + 1$ monomers

\Leftrightarrow

An **interacting self-avoiding walk (ISAW)** of N steps on a simple cubic lattice (3D)

- Monomers are supposed to sit on lattice sites, connected by bonds of length one
- Multiple visits to the same site are not allowed (**excluded volume effect**)
- Attractive interactions (energies $\epsilon < 0$) between non-bond monomers occupying neighboring lattice sites



Chain growth algorithm

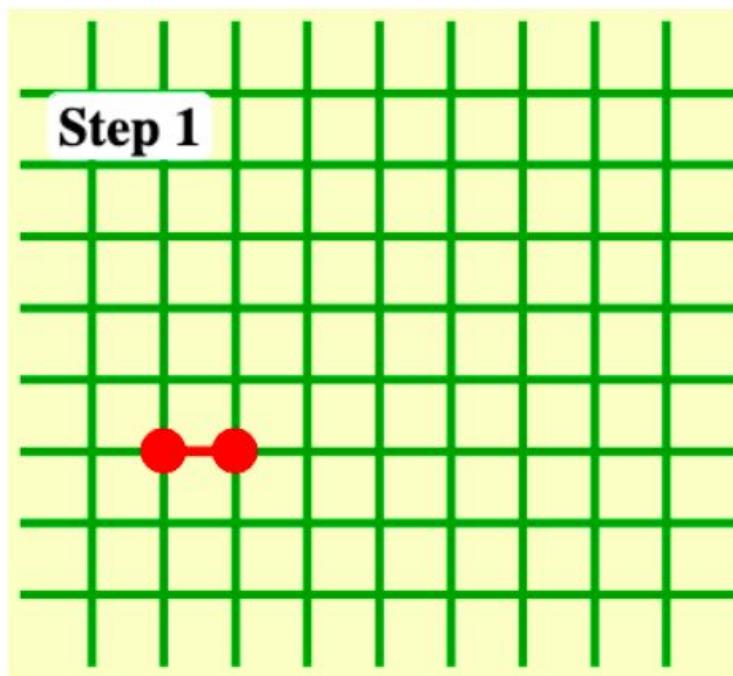
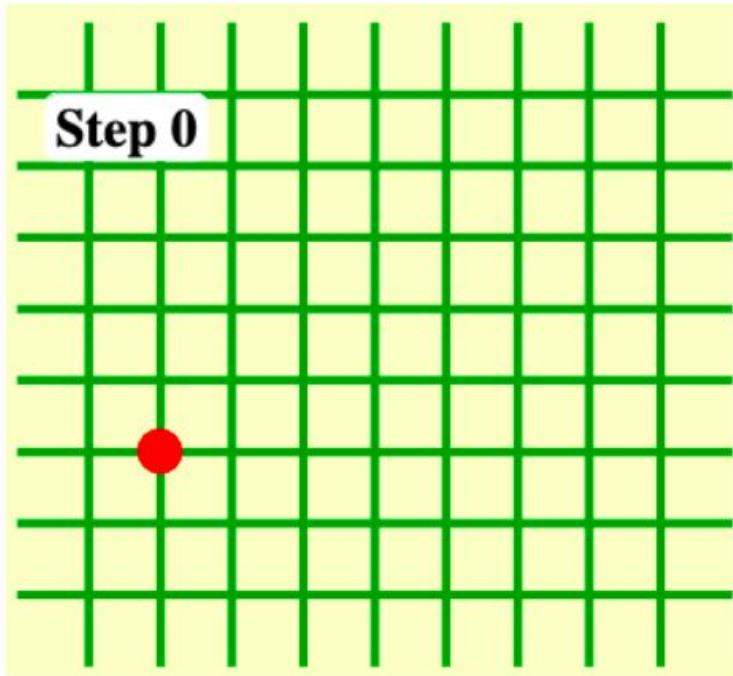
Polymer chains are built like self-avoiding walks (SAW) by adding one monomer at each step

Example in 2d

Chain growth algorithm

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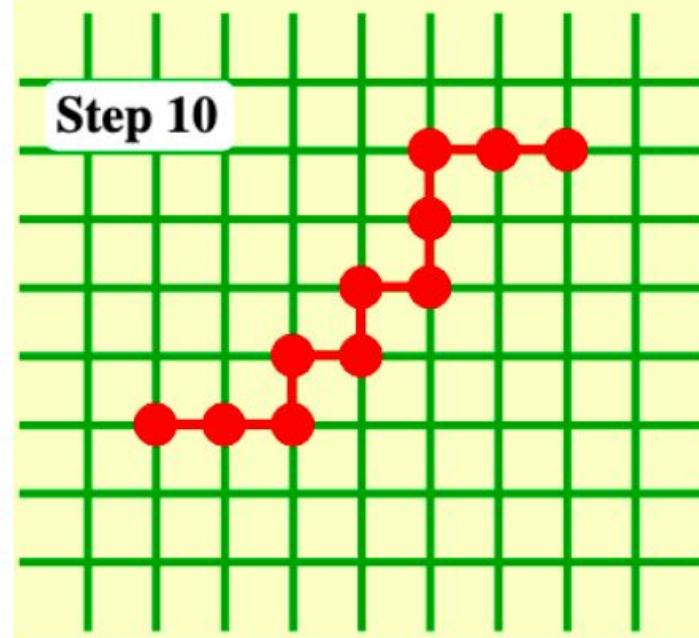
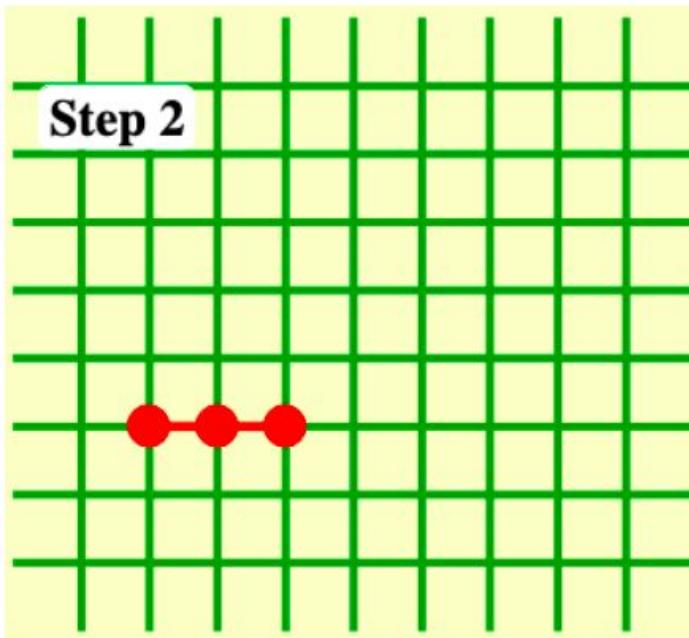
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Example in 2d



Statistical thermodynamics

- Partition sum for a canonical ensemble in thermal equilibrium

$$Z = \sum_{\ell} \exp(-\beta E(\ell)) =: \sum_{\ell} Q(\ell)$$

- ☞ $\beta = \frac{1}{k_B T}$; T being the temperature
- ☞ $E(\ell)$: energy of ℓ -th configuration
- ☞ $Q(\ell) = \exp(-\beta E(\ell))$: Boltzmann weight

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How to estimate Z precisely ?

Statistical thermodynamics

- Partition sum for a canonical ensemble in thermal equilibrium

$$Z = \sum_{\ell} \exp(-\beta E(\ell)) =: \sum_{\ell} Q(\ell)$$

- If M configurations are independently chosen according to a sampling probability $p(\ell)$ (**bias**), the law of large number yields:

$$Z = \lim_{M \rightarrow \infty} \left[\frac{1}{M} \sum_{\ell=1}^M \frac{Q(\ell)}{p(\ell)} \right] =: \frac{1}{M} \sum_{\ell=1}^M W(\ell)$$

with $W(\ell) = \frac{Q(\ell)}{p(\ell)}$ the effective weight of the ℓ -th configuration

Statistical thermodynamics

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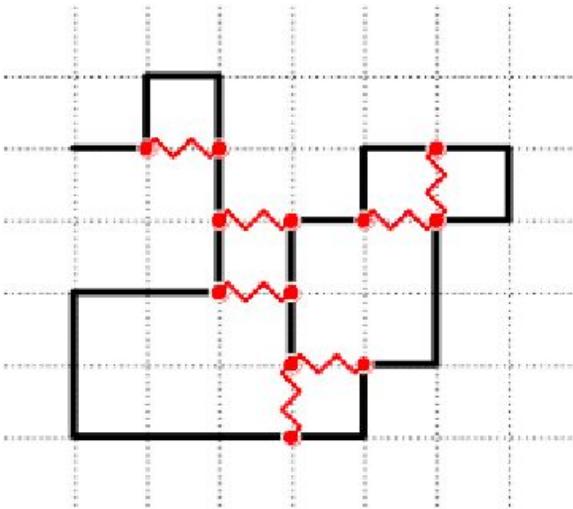
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- For any observable A :

$$\langle A \rangle = \lim_{M \rightarrow \infty} \frac{\sum_{\ell=1}^M A(\ell) W(\ell)}{\sum_{\ell=1}^M W(\ell)}$$

Partition function of ISAW

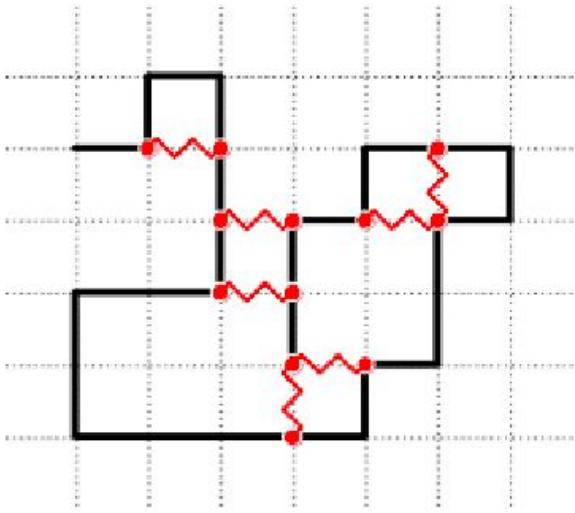


$$Z_N = \sum_{\text{walks of length } N+1} \exp(-\beta E(\ell)) =: \sum_{\ell} q^{m(\ell)}$$

with $E(\ell) = m(\ell)\epsilon$

- $q = e^{-\beta\epsilon}$: Boltzmann factor
- T : temperature (solvent quality)
- $m(\ell)$: total number of non-bonded nearest neighbor pairs

Partition function of ISAW



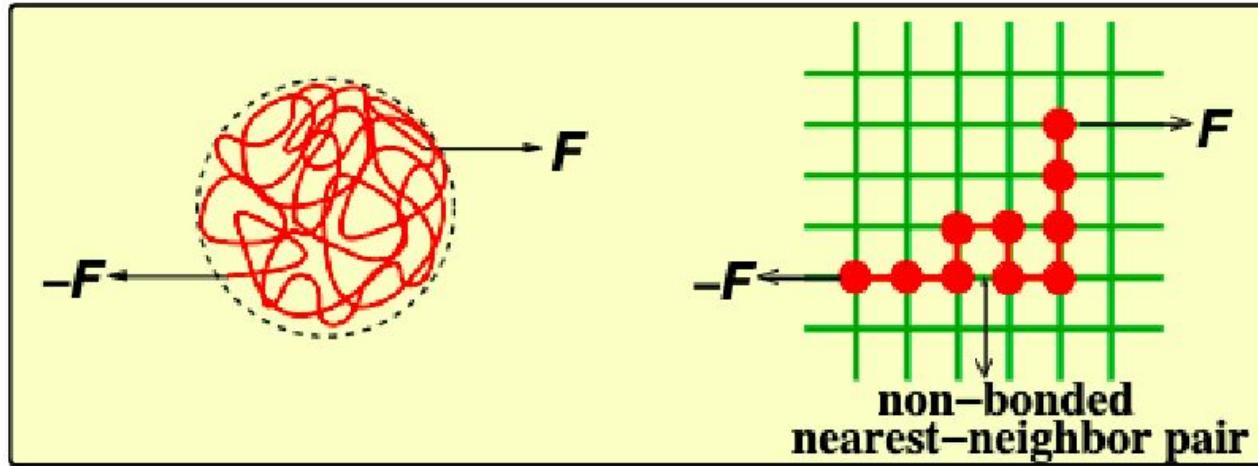
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Note: for $T \rightarrow \infty$, $q \rightarrow 1$ and the model becomes a Self-Avoiding Walk (SAW)

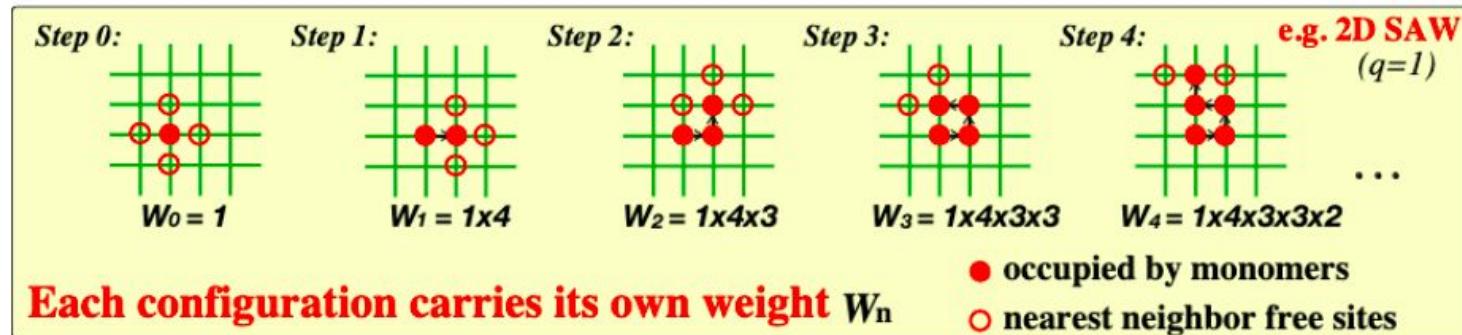
Biased Interacting Self-Avoiding Walk (BISAW)



$$Z = \sum_{\ell} q^{m(\ell)} b^{x(\ell)} \left(q = e^{-\beta\epsilon}, b = e^{\beta F} \right)$$

- $\mathbf{F} = F\mathbf{e}_x$: stretching force
- $x(\ell)$: end-to-end distance in the x direction
- $m(\ell)$: number of non-bonded nearest-neighbor pairs

Rosenbluth sampling

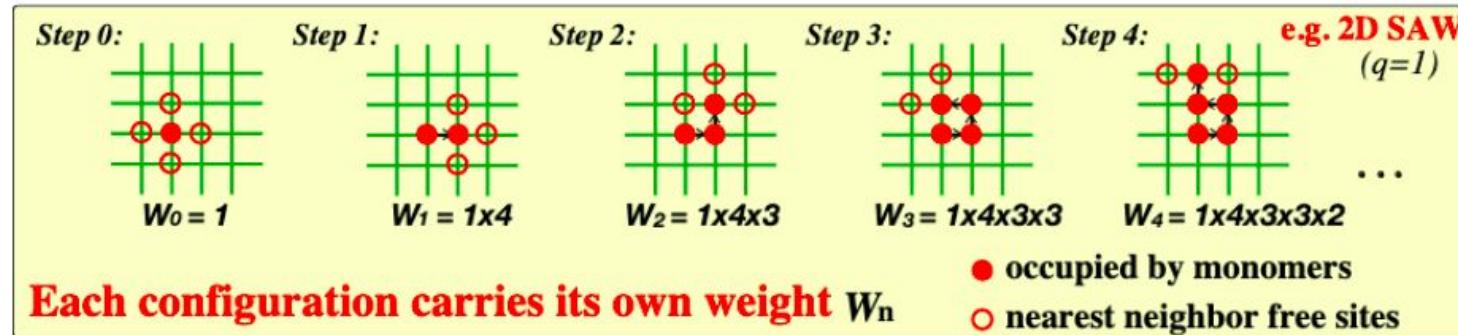


The k -th step is chosen between the last monomer's free-neighboring sites n_k

$$p_k = \frac{1}{n_k} \text{ & } W_N = W_{N-1} w_N = \prod_{k=0}^N w_k$$

- p_k : sampling probability at step k
- W_k : polymer-weight after k steps
- w_k : k -th step contribution to the weight

Rosenbluth sampling



The k -th step is chosen between the last monomer's free-neighboring sites n_k
For us

$$p_k = \frac{1}{n_k} \text{ & } W_N = W_{N-1} w_N = \prod_{k=0}^N w_k$$

$$W(\ell) \stackrel{\text{def}}{=} \frac{Q(\ell)}{p(\ell)} = \frac{q^{m(\ell)}}{p(\ell)}$$

- p_k : sampling probability at step k
- W_k : polymer-weight after k steps
- w_k : k -th step contribution to the weight

$$p = \prod_{k=0}^N p_k \text{ & } m = \sum_{k=0}^N m_k$$

$$w_k = n_k q^{m_k}$$

Why Rosenbluth sampling fails at $N \gg 1$?

Problems with origin rosenbluth sampling:

Why Rosenbluth sampling fails at $N \gg 1$?

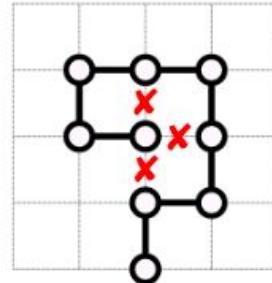
Problems with origin rosenbluth sampling:

- Huge fluctuations of the weight between all configurations

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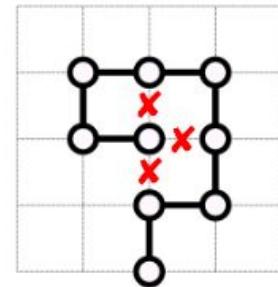
- Huge fluctuations of the weight between all configurations
- The surviving rate decreases with N



Why Rosenbluth sampling fails at $N \gg 1$?

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PHYSICAL REVIEW E

VOLUME 56, NUMBER 3

SEPTEMBER 1997

Pruned-enriched Rosenbluth method: Simulations of θ polymers of chain length up to 1 000 000

Peter Grassberger

HLRZ, Kernforschungsanlage Jülich, D-52425 Jülich, Germany

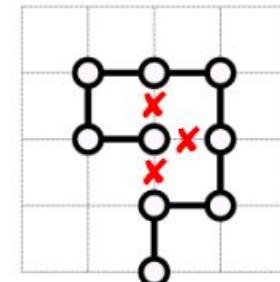
and Department of Theoretical Physics, University of Wuppertal, D-42097 Wuppertal, Germany

(Received 16 December 1996)

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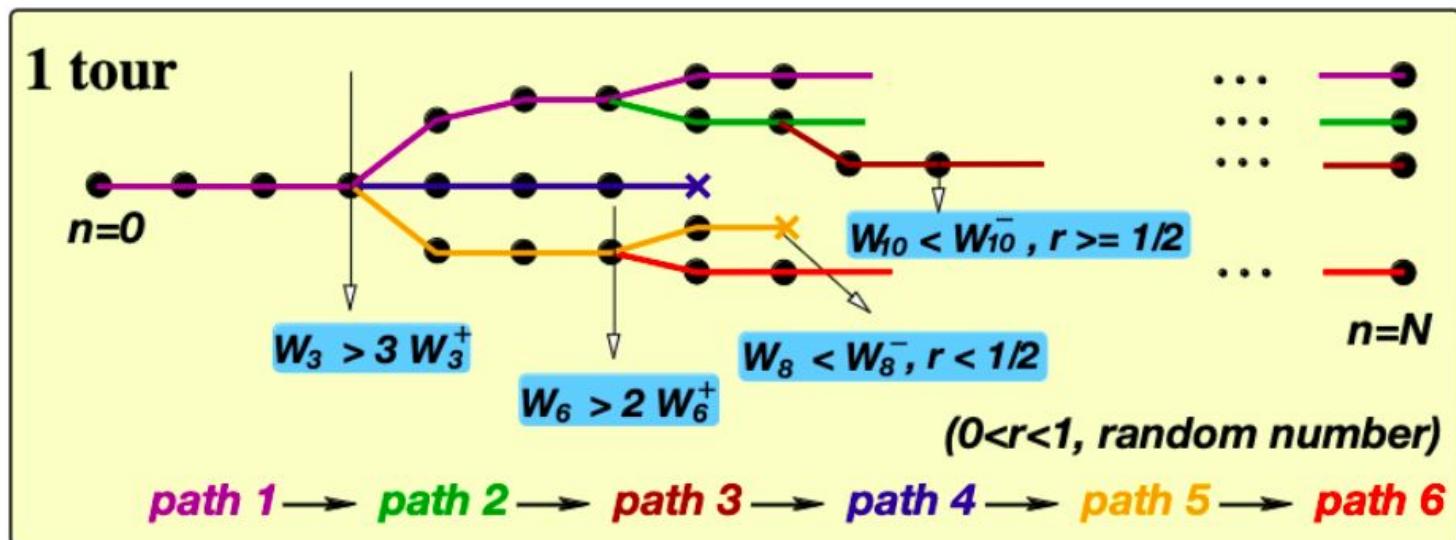
(Received 16 December 1996)

- Flexible Rosenbluth-like biased chain growth
 - Population control \Rightarrow Eliminate attrition and reduce weight fluctuations
 - Effective for **stretched polymers**, confined geometries, protein folding, and much more ...
- Hsu *et al.*, Journal of Statistical Physics, 144, (2011)

Prune-enriched Rosenbluth Method (PERM)

Population control is implemented with two thresholds:

$$W_n^+ = c_+ Z_n \text{ and } W_n^- = c_- Z_n.$$



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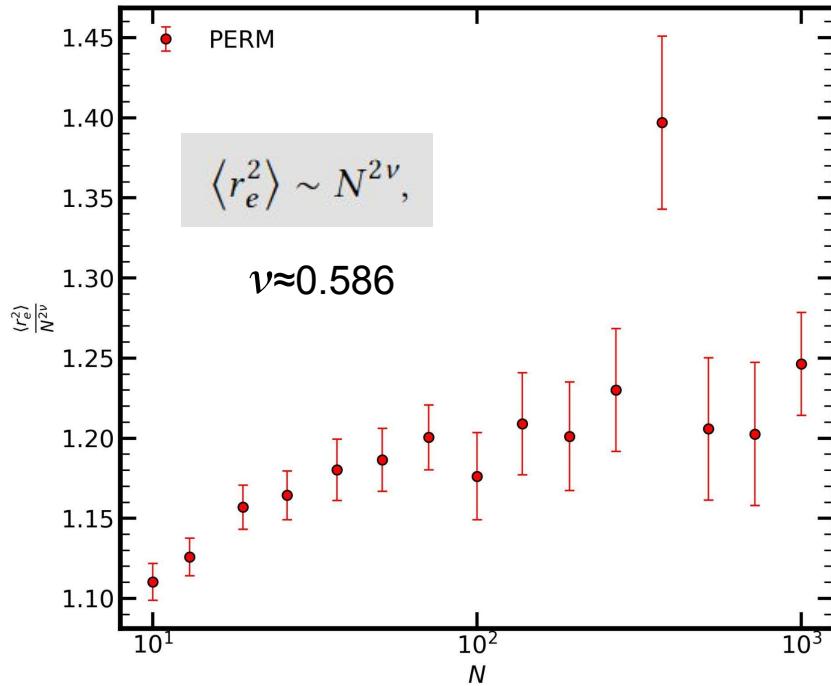
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Scaling laws with SAW

- Comparison with universal laws (y axis is divided by universal law)
- $q=1$ ($q = e^{-\beta\epsilon}, \epsilon=0$)
- Benchmark law valid for large N
- Different behavior at small N
- Benchmark passed ✓

Mean end-to-end distance square $\langle r_e^2 \rangle$ as a function of the number of monomers N with SAW.



The coil globule transition : expected results for ISAW

Expected graph taken from Hsu paper

Five different q's

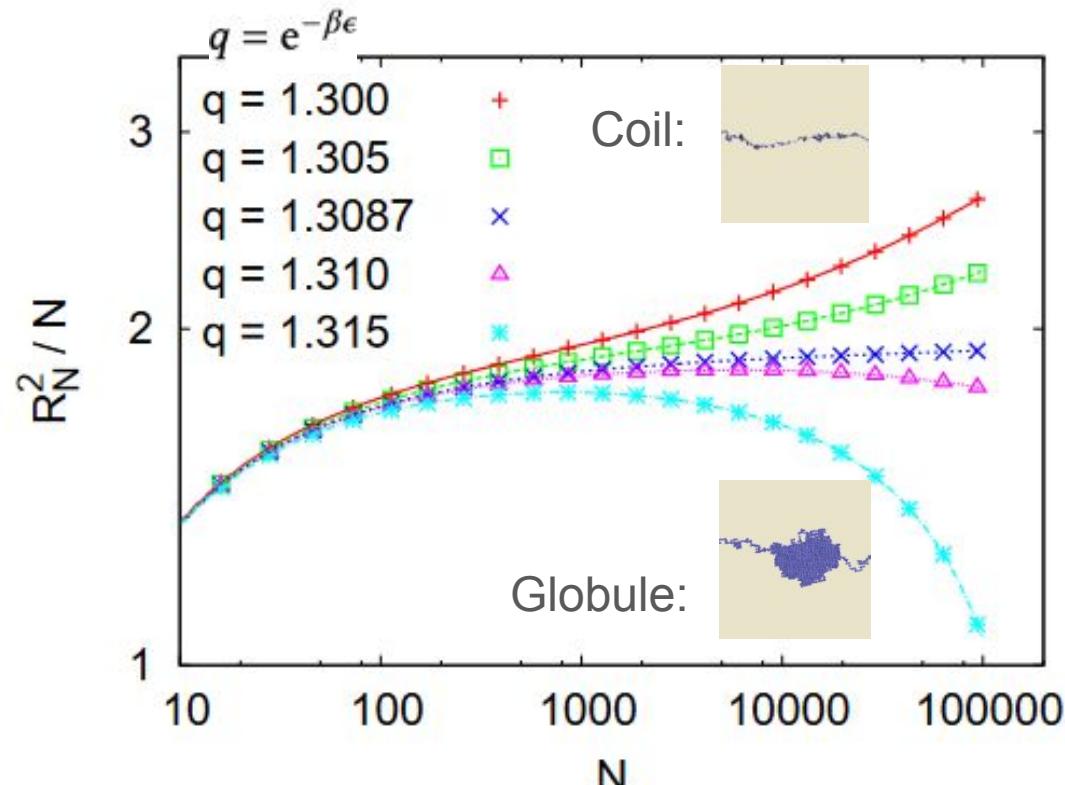
θ point : Temperature at the transition point

Three behaviors:

- $T < \theta$: low temperature => globule
- $T > \theta$: high temperature => coil
- $T = \theta$: logarithmic evolution of R_e^2

Entropy implications:

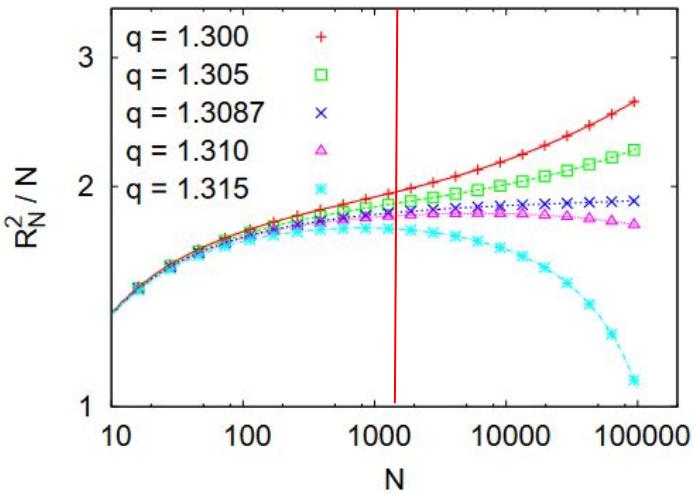
- Stretched => High entropy (more configurations)
- Globule => Low entropy (less configurations)



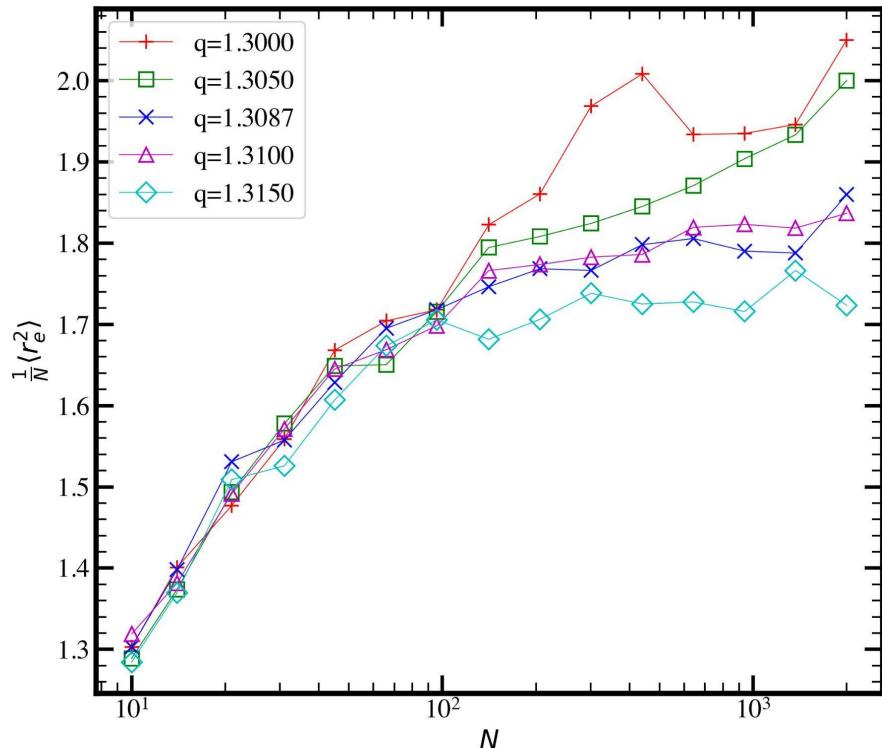
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The coil globule transition : our results for ISAW

- Scale of N, results up to red line
- 4-8 hours of computing time for each q
- Similarities with expected results



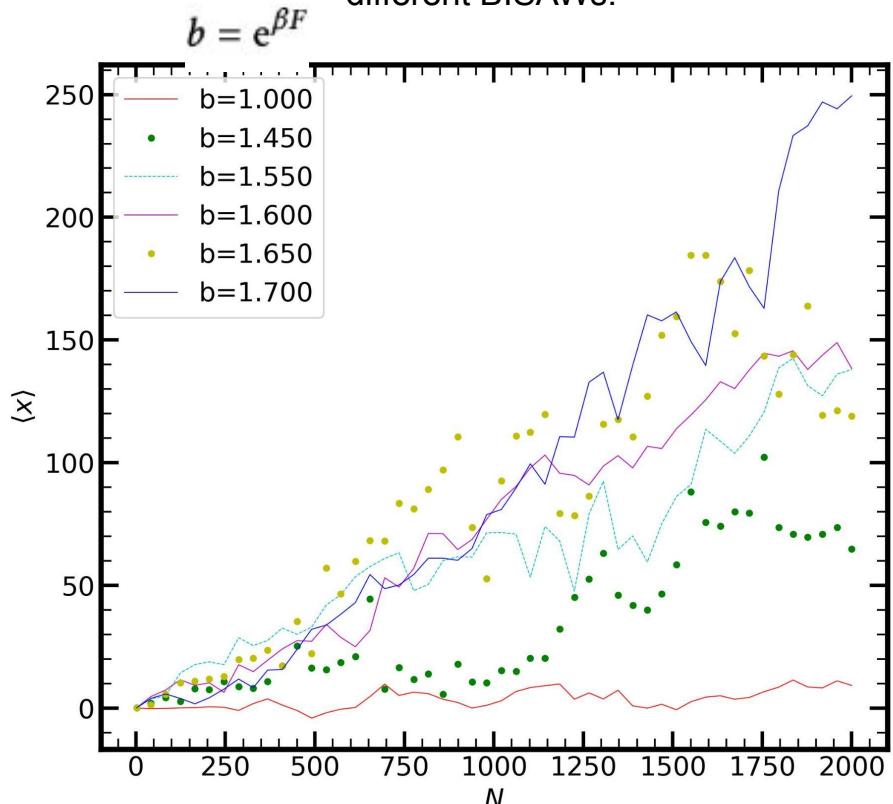
Mean end-to-end squared distance as a function of N with different ISAWs.



Applying an external force

- Really expensive
- Phase transition visible at $N=6000$
- Fixed q
- Extension $\langle X \rangle$ depends on b
- Low b : no bias towards $x>0$
- High b : high bias towards $x>0$

Mean extension in the x direction as a function of N with different BISAWs.



Conclusion

[PolyPy](https://github.com/crecric/PolyPy) Public

main 14 Branches 0 Tags Go to file Add file Code

NikitaY69 Minor 2851402 · 3 weeks ago 95 Commits

.gitignore Mac OS files ignored 3 weeks ago

README.md Minor 3 weeks ago

main.py Miscs 3 weeks ago

mc_polymers.py Packaged 3 weeks ago

requirements.txt Packaged 3 weeks ago

results.py Miscs 3 weeks ago

setup.py Packaged 3 weeks ago

visualisation.py Packaged 3 weeks ago

README

Static Monte Carlo Lattice Polymer simulation program

This package provides a Monte Carlo computational approach to simulate 3-dimensional polymers on cubic lattices.

Description

About

No description, website, or topics provided.

Readme Activity 0 stars 1 watching 0 forks Report repository

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Contributors 3

NikitaY69 Nikita Allaglo
crecric
ELoiseeeeeeee

<https://github.com/crecric/PolyPy>

-What we intended with this project

-Difficulties encountered: finding the right parameters, dealing with big numbers

-How we could expand the project: converting to C++, better parameters for bisaw

