Polymer Simulations with

Pruned-Enriched Rosenbluth Method

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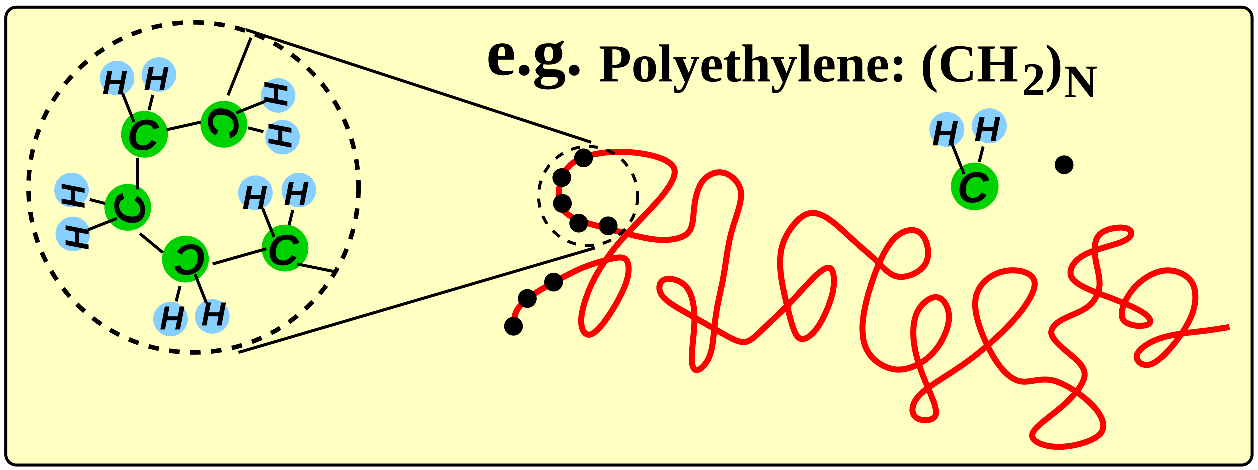
Introduction

- Polymer: a long molecule consisting of many similar or identical monomers linked together



Introduction

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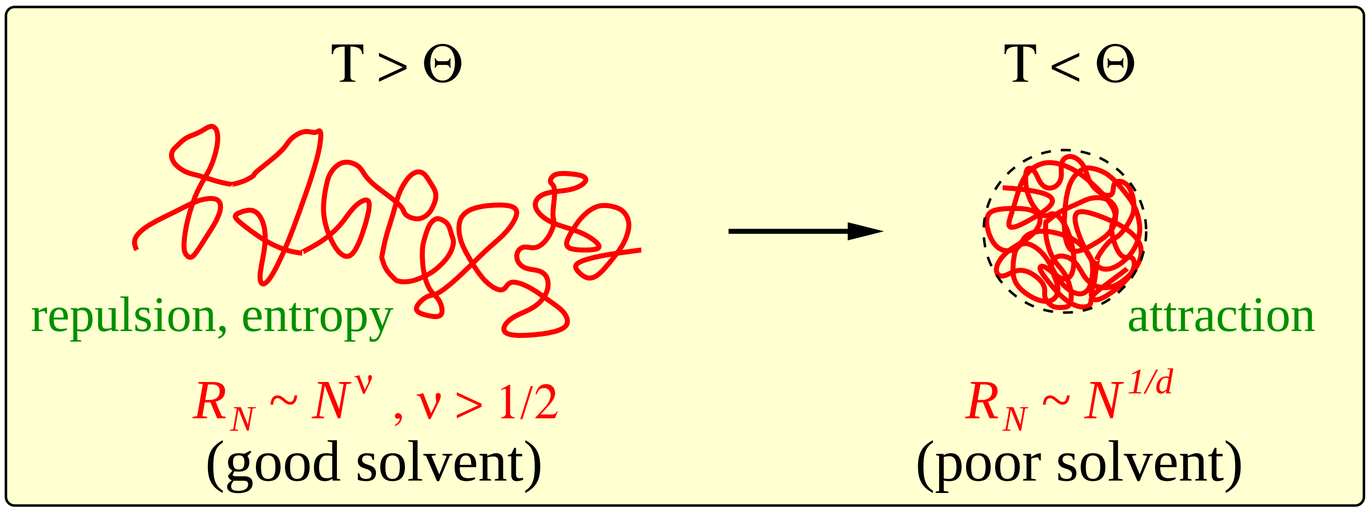
- Characteristics of a linear polymer chain in dilute solution:



Coil-globule transition at **Θ**-point

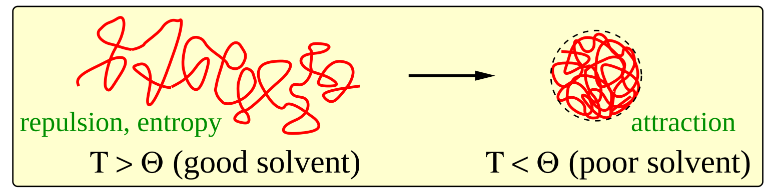
$\nu = 1/2$, Flory exponent

Introduction

- Polymer: a long molecule consisting of many similar or identical monomers linked together

- Characteristics of a linear polymer chain in dilute solution:

  In the thermodynamic limit



  - Partition sum:

$$Z \sim \begin{cases} \mu_\infty(T)^{-N} N^{\gamma-1} & \text{at } T > T_\Theta \\ \mu_\infty(T)^{-N} b^{N^s} N^{\gamma-1} & \text{at } T < T_\Theta \end{cases}$$

  - Radius of gyration: $R_g \sim N^\nu$ (chain length $N \to \infty$)

  $\mu_\infty(T)$: critical fugacity, γ: entropic exponent, $s = (d-1)/d$ in d dimension, $b > 1$, ν: Flory exponent

Algorithm: Pruned-Enriched Rosenbluth Method

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

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)

We present an algorithm for simulating flexible chain polymers. It combines the Rosenbluth-Rosenbluth method with recursive enrichment. Although it can be applied also in more general situations, it is most efficient for three-dimensional θ polymers on the simple-cubic lattice. There it allows high statistics simulations of chains of length up to $N=10^6$. For storage reasons, this is feasable only for polymers in a finite volume. For free θ polymers in infinite volume, we present very high statistics runs with $N=10\,000$. These simulations fully agree with previous simulations made by Hegger and Grassberger [J. Chem. Phys. **102**, 6681 (1995)] with a similar but less efficient algorithm, showing that logarithmic corrections to mean field behavior are much stronger than predicted by field theory. But the finite volume simulations show that the density inside a collapsed globule scales with the distance from the θ point as predicted by mean field theory, in contrast to claims in the work mentioned above. In addition to the simple-cubic lattice, we also studied two versions of the bond fluctuation model, but with much shorter chains. Finally, we show that our method can be applied also to off-lattice models, and illustrate this with simulations of a model studied in detail by Freire *et al.* [Macromolecules **19**, 452 (1986) and later work]. [S1063-651X(97)10308-7]

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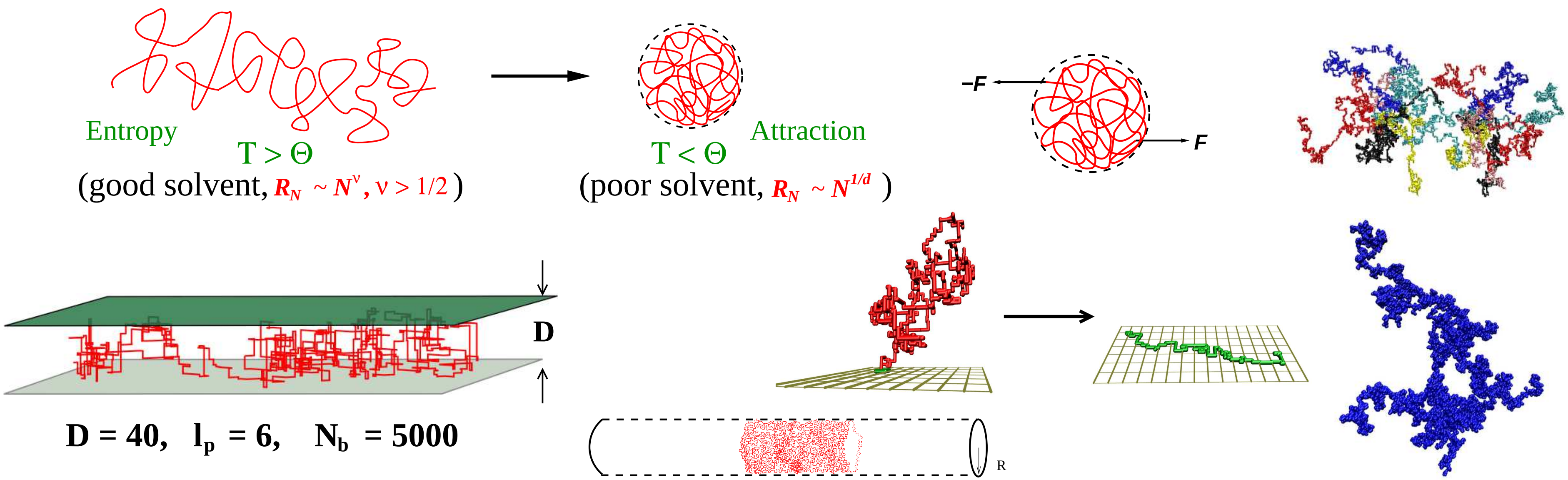
- Applications of PERM:



partition sum, scaling behavior, phase transition, ...

Statistical thermodynamics

- Partition sum for a canonical ensemble in thermal equilibrium

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

  - $\beta = 1/k_B T$, T: temperature (fixed)
  - $E(\alpha)$: the corresponding energy for the α^{th} configuration
  - $Q(\alpha)/Z$: the Gibbs-Boltzmann distribution
  - $Q(\alpha)$: the Boltzmann weight

How to estimate the partition sum $Z(\beta)$ precisely?

Statistical thermodynamics

- Partition sum for a canonical ensemble in thermal equilibrium

$$Z(\beta) = \sum_\alpha Q(\alpha) = \sum_\alpha \exp(-\beta E(\alpha))$$

- If M configurations are independently chosen according to a randomly chosen probability $p(\alpha)$ (a bias),

$$Z(\beta) = \lim_{M\to\infty} \hat{Z} \left[= \frac{1}{M} \sum_{\alpha=1}^{M} Q(\alpha)/p(\alpha) = \frac{1}{M} \sum_{\alpha=1}^{M} W(\alpha) \right]$$

with modified weights $W(\alpha) = Q(\alpha)/p(\alpha)$

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Using $p(\alpha) \propto \exp(-\beta E(\alpha))$ [Gibbs sampling]

$\Rightarrow W(\alpha) = const$ "importance sampling"

$\Rightarrow$ each contribution to $\hat{Z}_M$ has the same weight

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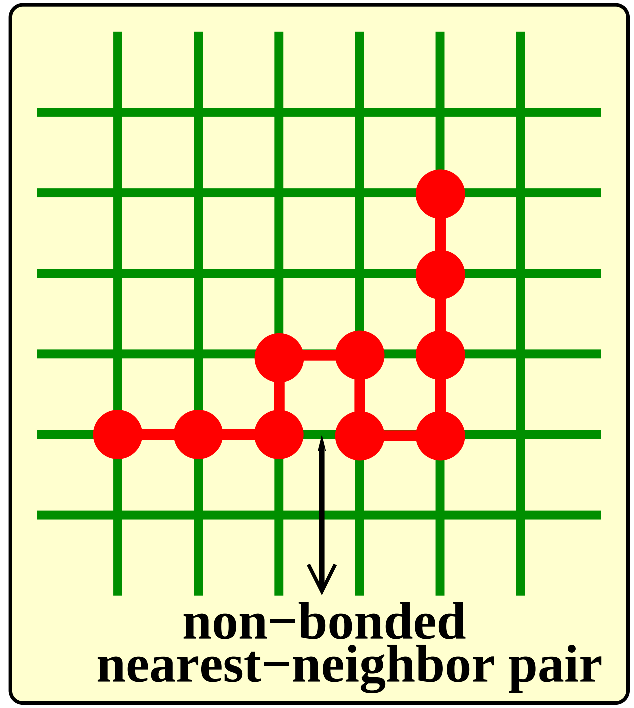
- For any observable A:

$$\langle A \rangle = \lim_{M\to\infty} \langle A \rangle_M = \lim_{M\to\infty} \frac{\sum_{\alpha=1}^{M} A(\alpha) W(\alpha)}{\sum_{\alpha=1}^{M} W(\alpha)}$$

Coarse-grained model

A linear polymer chain of $(N+1)$ monomers in an implicit solvent "=" an interacting self-avoiding walk (ISAW) of N steps on a simple (hyper-) cubic lattice of dimensions d



- Monomers are supposed to sit on lattice sites, connected by bonds of length one $(|\vec{\ell}_b| = 1)$
- Multiple visits to the same site are not allowed (excluded volume effect)
- Attractive interactions (energies $\epsilon < 0$) between non-bonded monomers occupying neighboring lattice sites are considered

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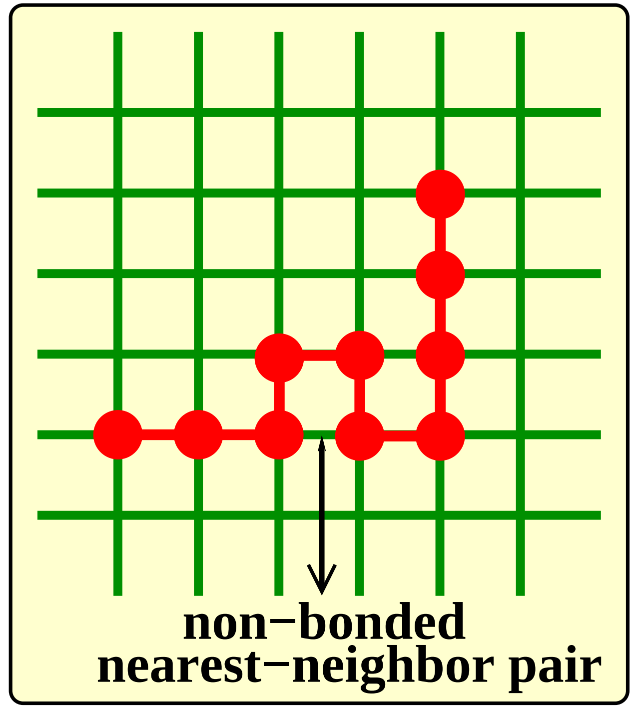

- Partition sum:

$$Z_N(q) = \sum_{walks} q^m$$

with $q = \exp(-\beta\epsilon)$, $\beta = 1/k_B T$

q: the Boltzmann factor, $\epsilon < 0$

T: temperature (solvent quality)

m: total number of non-bonded nearest neighbor pairs

As $T \to \infty$, $q = 1 \Rightarrow$ SAW (good solvent)

Algorithm: PERM

Pruned-Enriched Rosenbluth Method

- Chain growth algorithm with Rosenbluth-like bias
- Resampling ("population control")
- Depth-first implementation

Rosenbluth-Rosenbluth method, J. Chem. Phys. 23, 356 (1959)

Enrichment algorithm, J. Chem. Phys. 30, 637 (1957); 30, 634 (1959)

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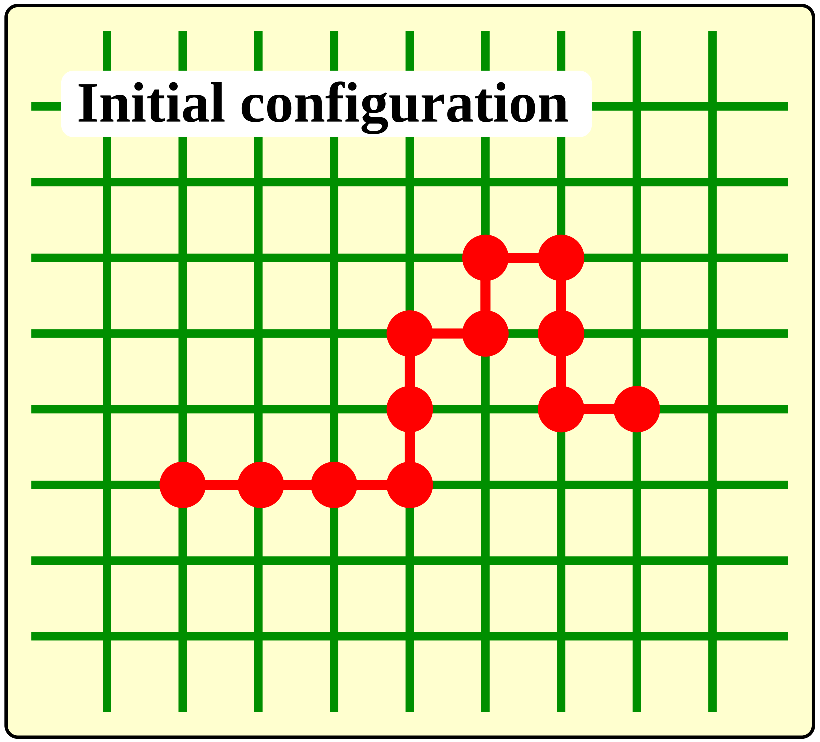
  - Polymer chains of length N are built like random walks by adding one monomer at each step



Conventional Monte Carlo method

Self-avoiding walks (SAW) in $d = 2$

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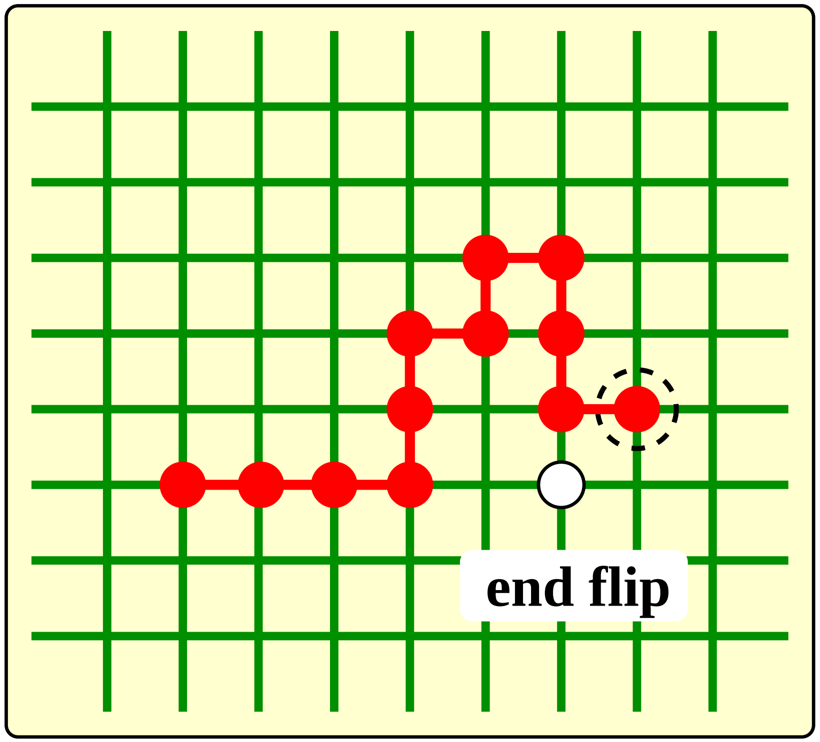

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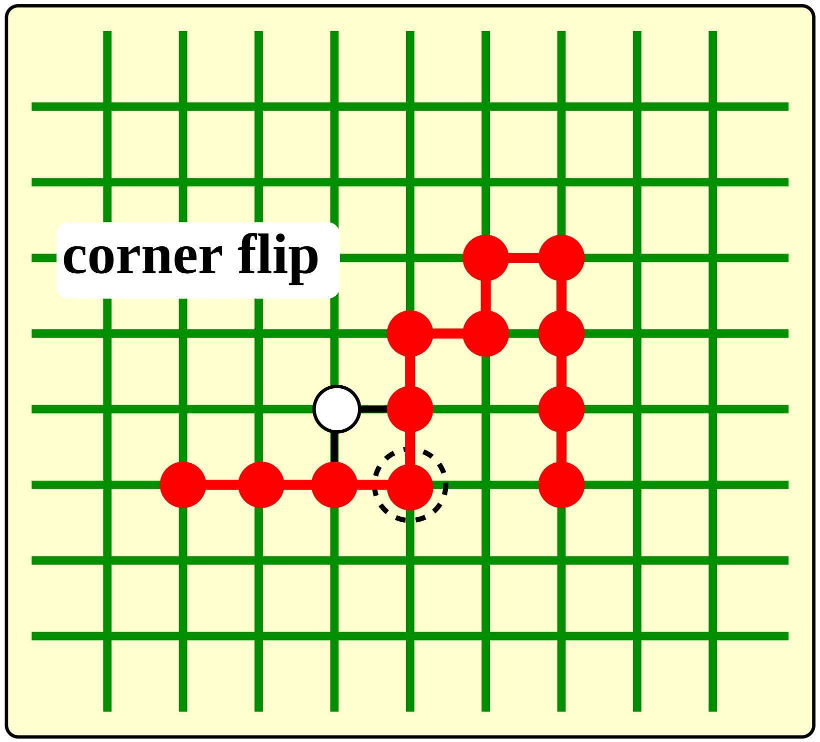

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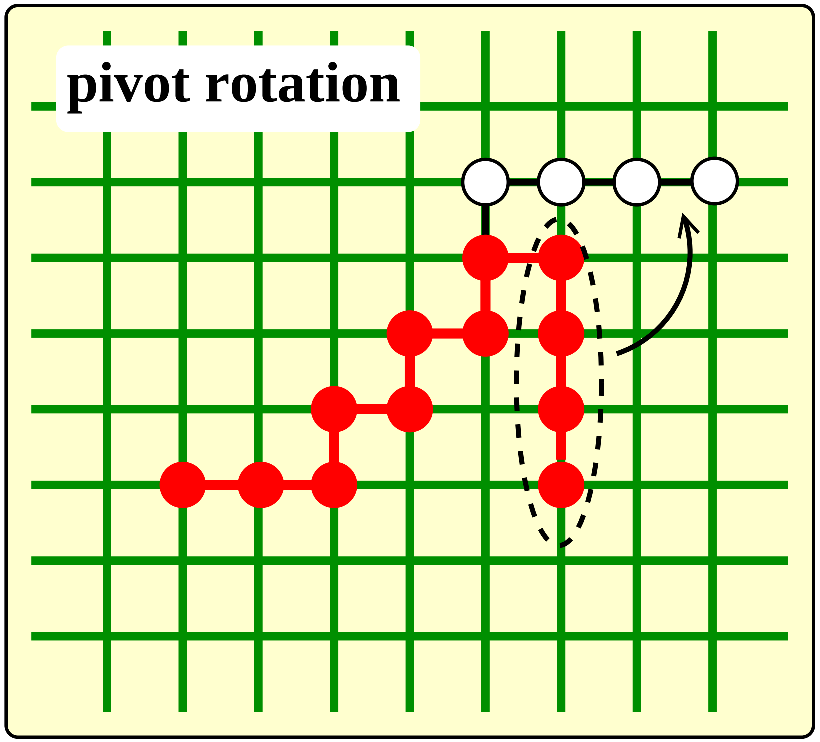

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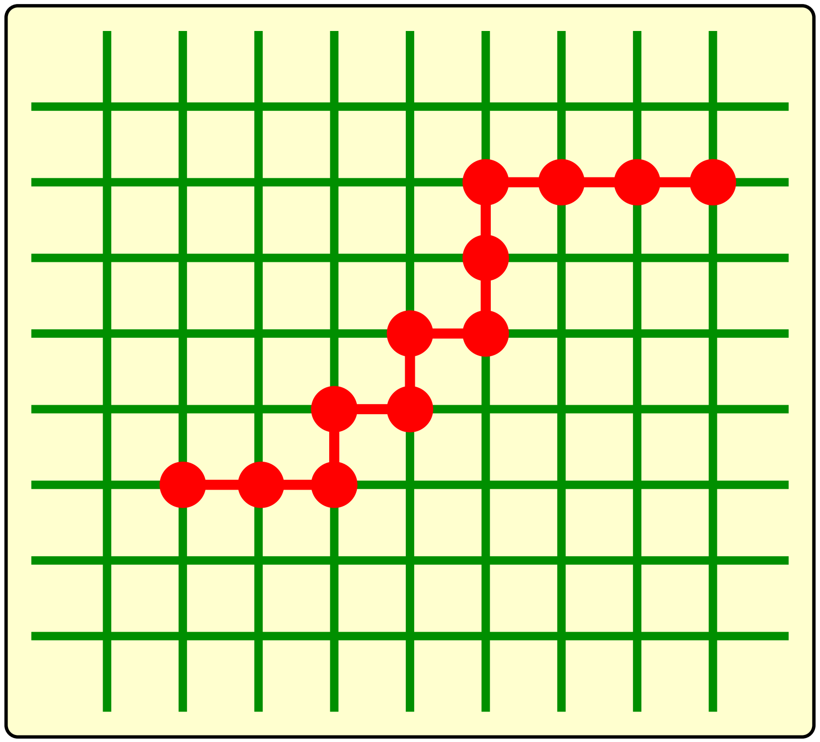

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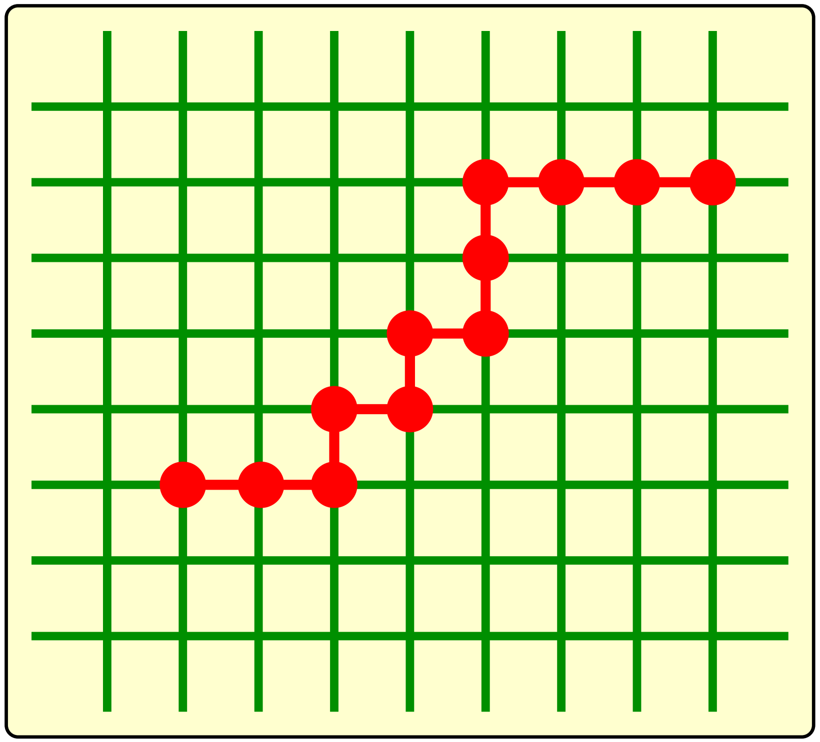

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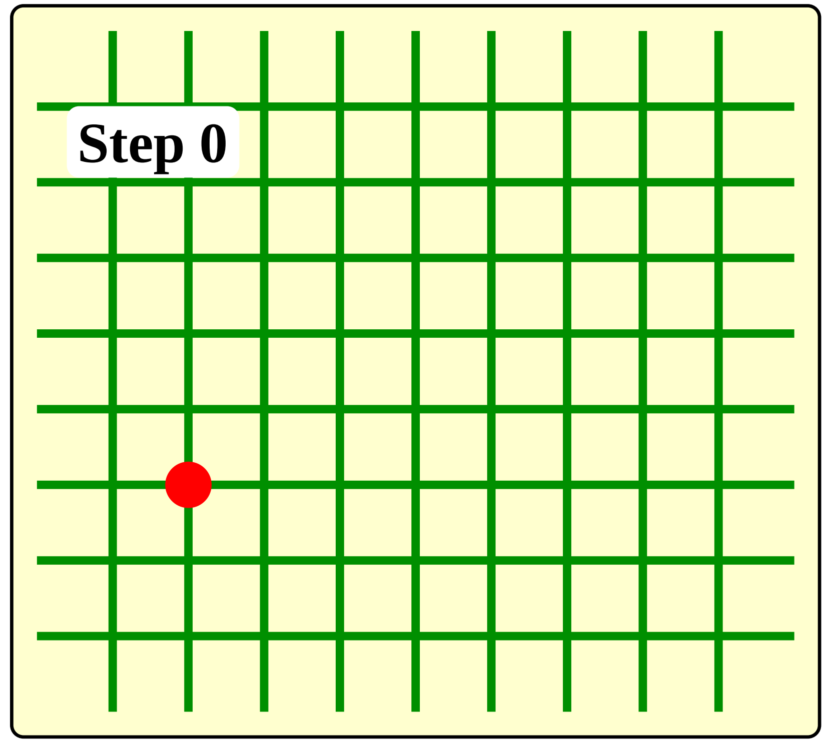

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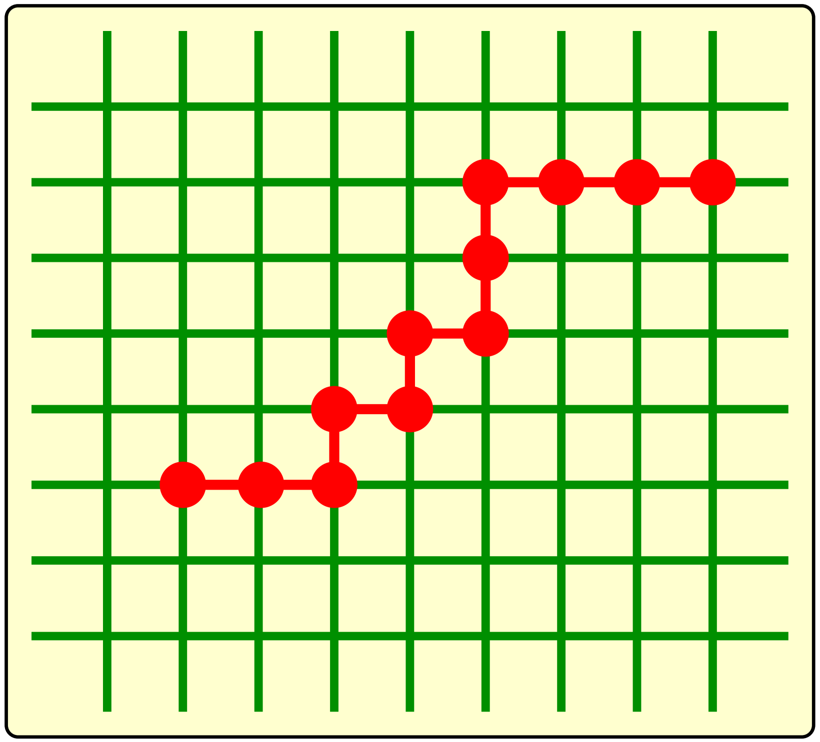

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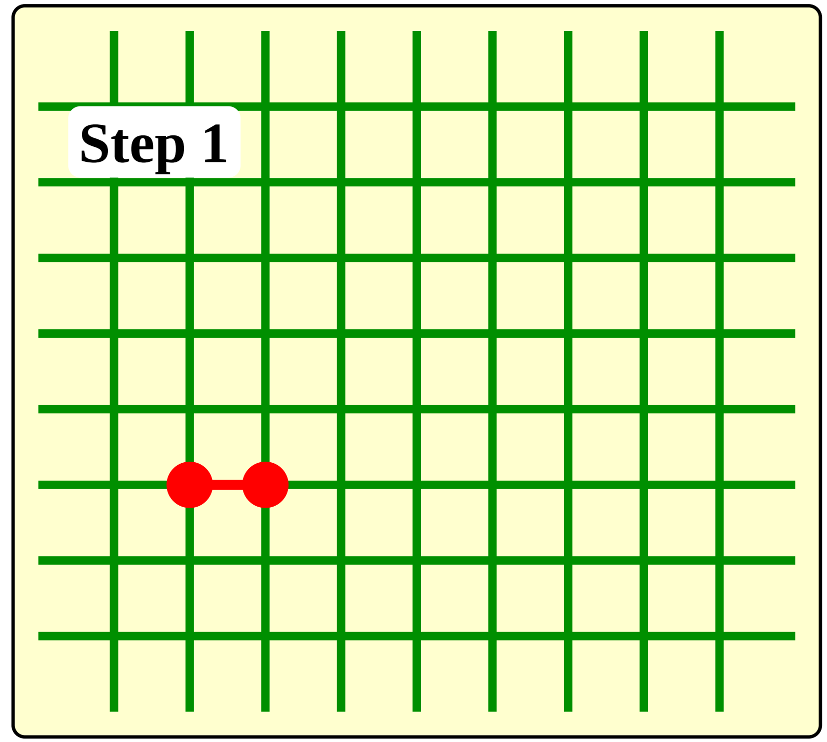

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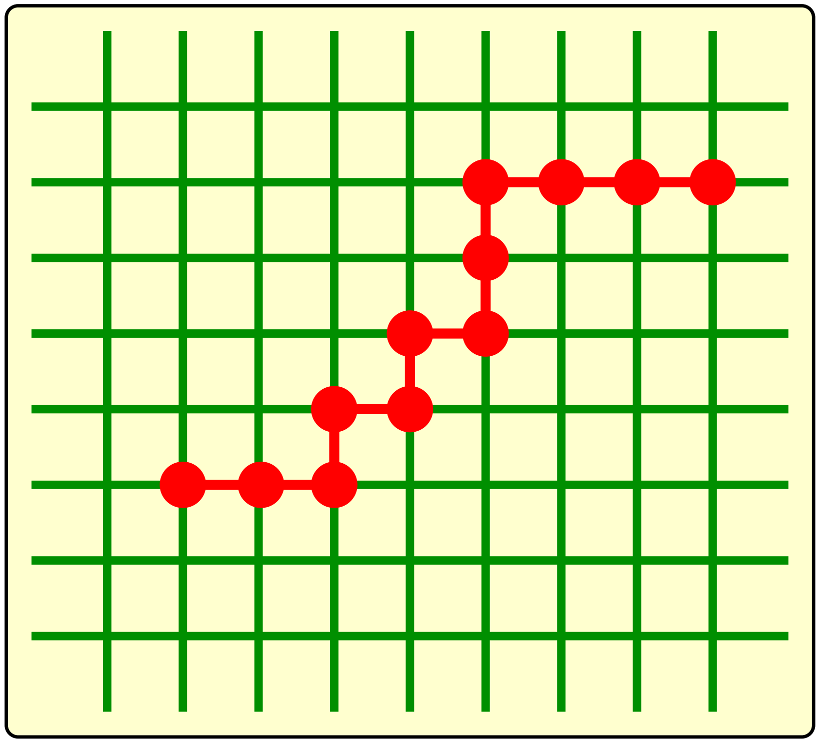

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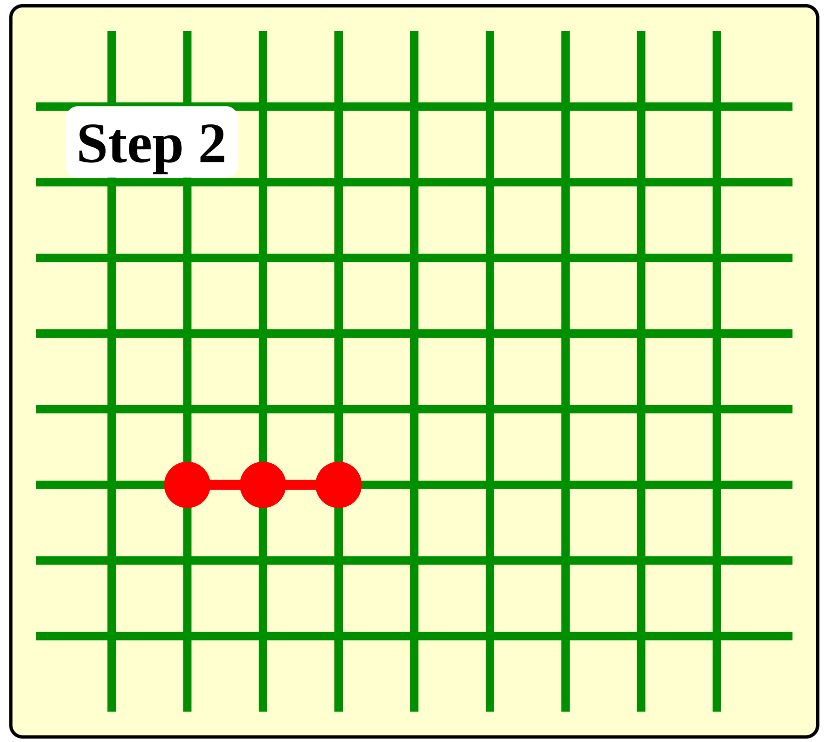

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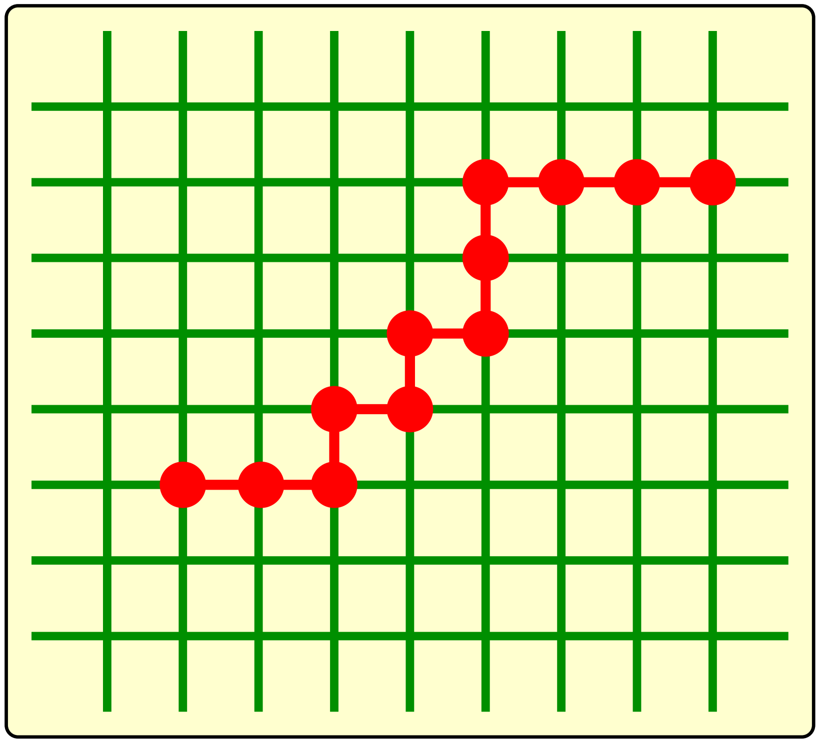

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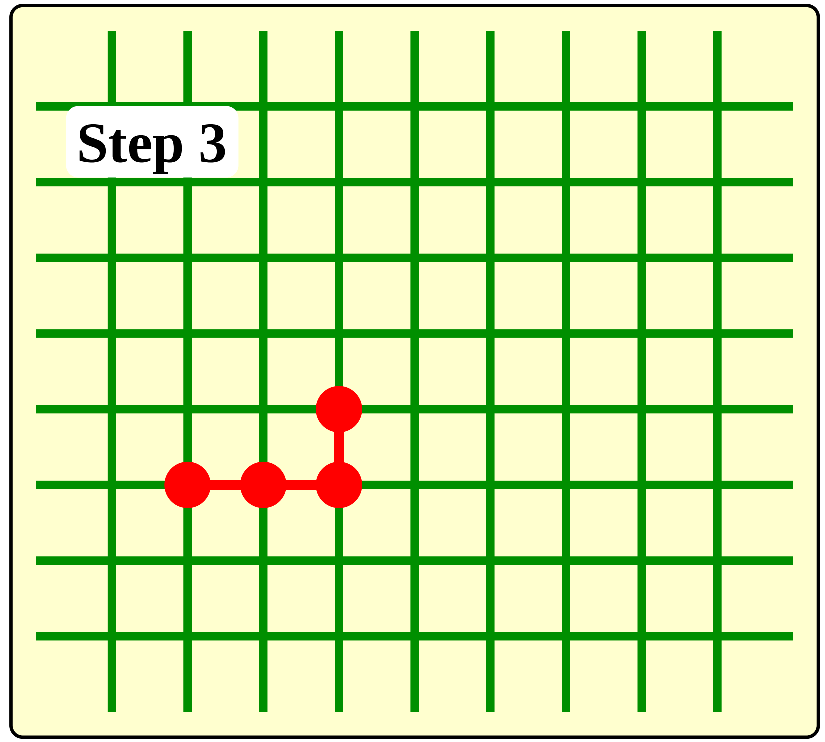

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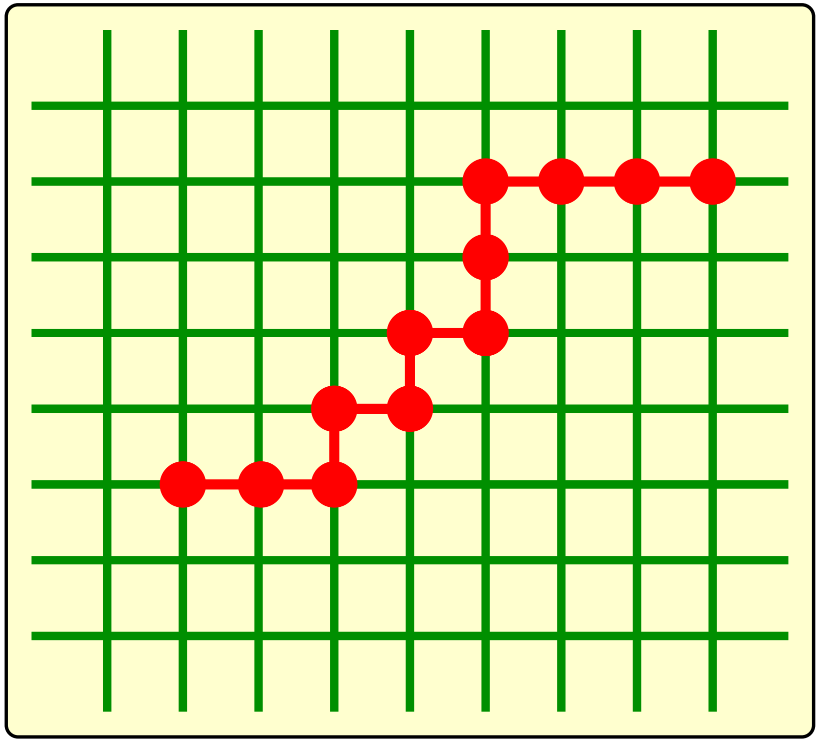

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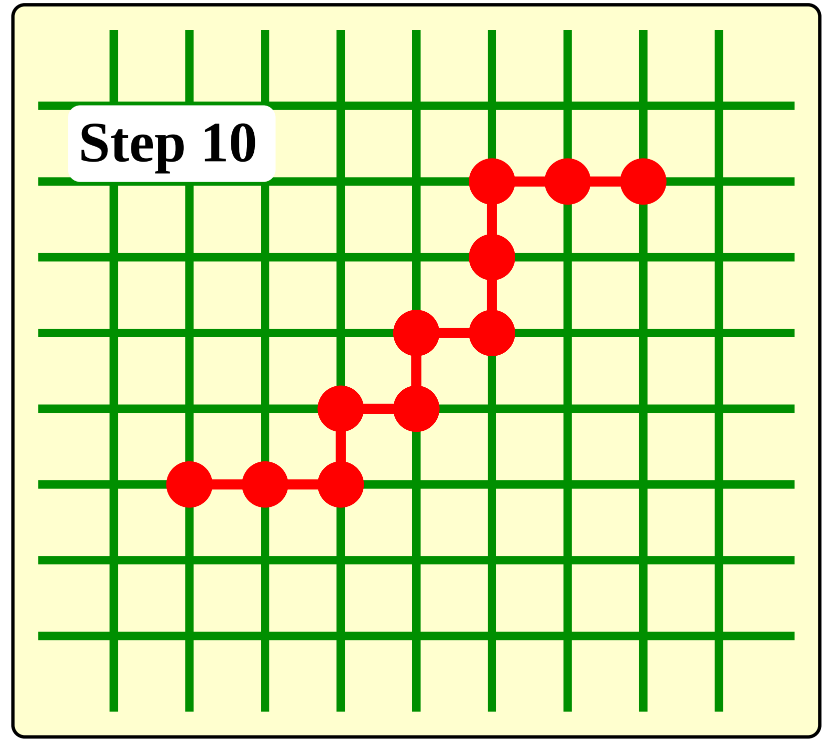

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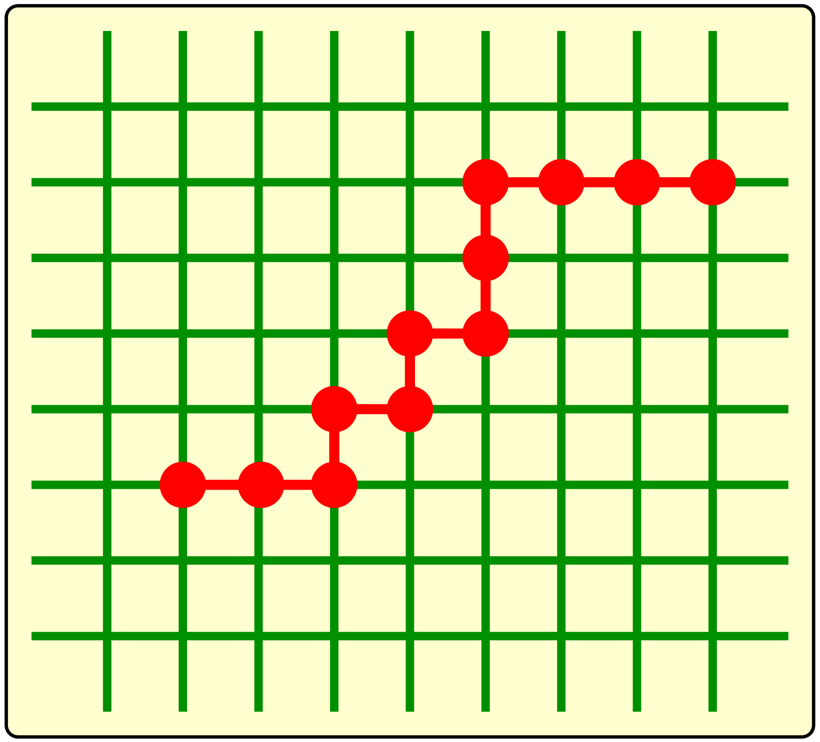

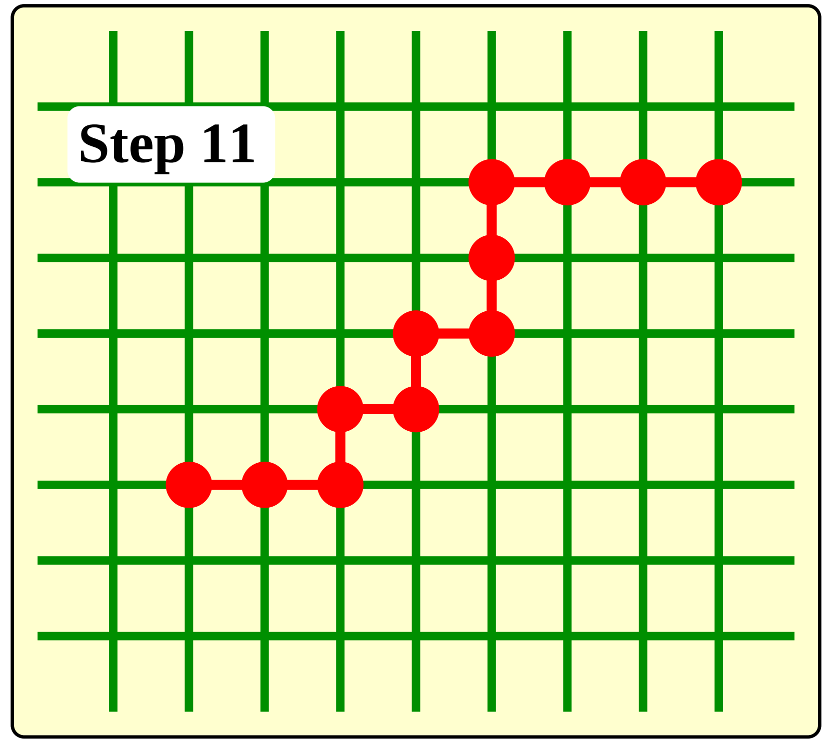

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Chain growth algorithm

Self-avoiding walks (SAW) in $d = 2$

- Rosenbluth-like bias for self-avoidance:

  a wide range of probability distributions (p_n) can be used for choosing the way to go at each step n

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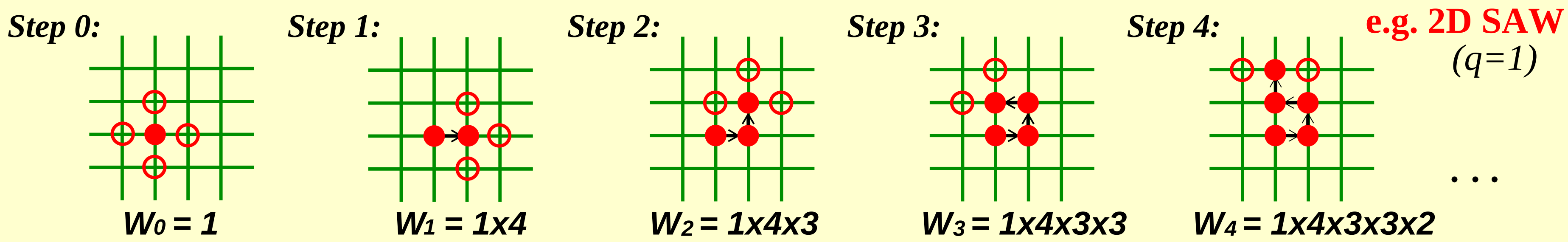

● occupied by monomers

○ nearest neighbor free sites

Each configuration carries its own weight W_n

- Rosenbluth bias: the selection probability $p_n = 1/n_{\text{free}}$

  (each nearest-neighbor free sites is chosen at equal probability)

$$W_N = W_{N-1} w_N = \prod_{n=0}^{N} w_n = \prod_{n=0}^{N} \frac{1}{p_n} = \prod_{n=0}^{N} n_{\text{free}}$$

n_{free}: # of free nearest-neighbor sites

$\Rightarrow$ Estimate the partition sum directly at the step n

$$Z_n \approx \hat{Z}_n = \frac{1}{M_n} \sum_{\alpha=1}^{M_n} W_n(\alpha)$$

$W_n(\alpha)$: total weight for the α^{th} configuration at the step n

M_n: total number of configurations

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- The estimate for any physical observable A:

$$\langle A \rangle_n = \frac{\sum_{\alpha=1}^{M_n} A(\alpha) W_n(\alpha)}{\sum_{\alpha=1}^{M_n} W_n(\alpha)}$$

$$W_n = \prod_{i=1}^{n} w_i \,, \qquad w_i = \prod_{i=1}^{n} q^{m_n} / p_n \ \text{(ISAW)}$$

- Population control: Two thresholds W_n^+ and W_n^- (overcome attrition $n_{\mathrm{free}} = 0$, reduce the fluctuation of weight W_n)

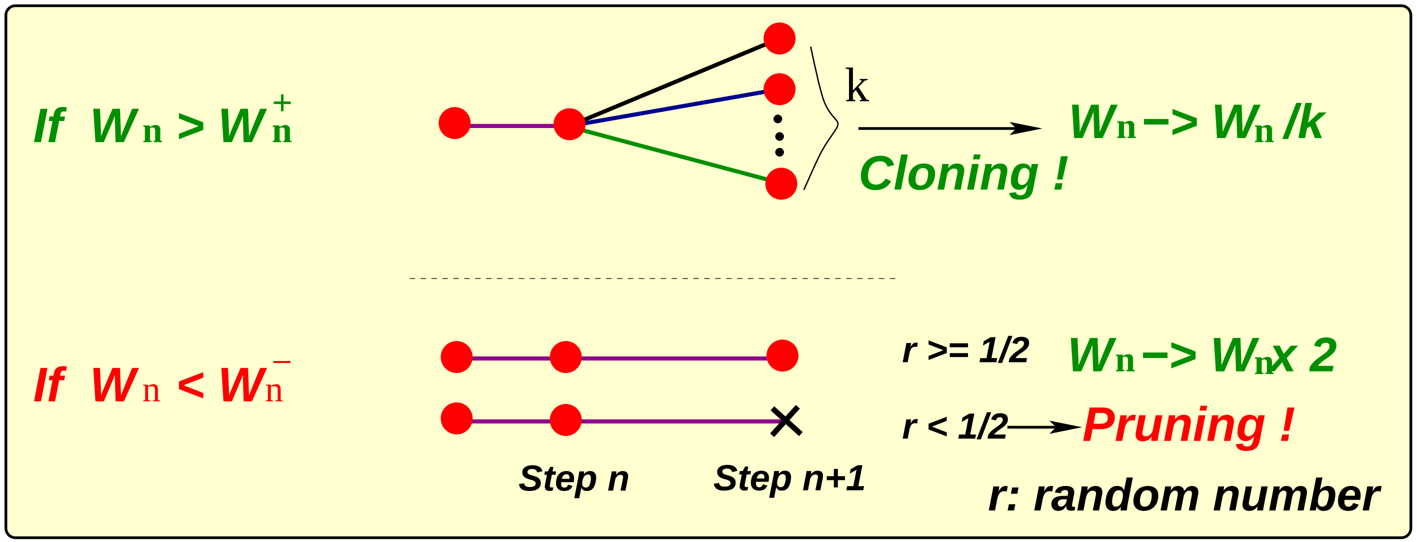
In the original Rosenbluth-Rosenbluth method

e.g. SAW "simple sampling"

$$W_N = \prod_0^N n_{\mathrm{free}}$$

- If $n_{\mathrm{free}} = 0$ ("attrition") $\longrightarrow$ the walk is killed
- If $N \gg 1 \longrightarrow$ huge fluctuations of the full weight (The total weight is dominated by a single configuration)

- Population control: Two thresholds W_n^+ and W_n^-
  (overcome attrition $n_{\mathbf{free}} = \mathbf{0}$, reduce the fluctuation of weight W_n)



$$W_n^+ = C_+ \hat{Z}_n \text{ and } W_n^- = C_- \hat{Z}_n, \; C_+/C_- \sim \mathcal{O}(10)$$

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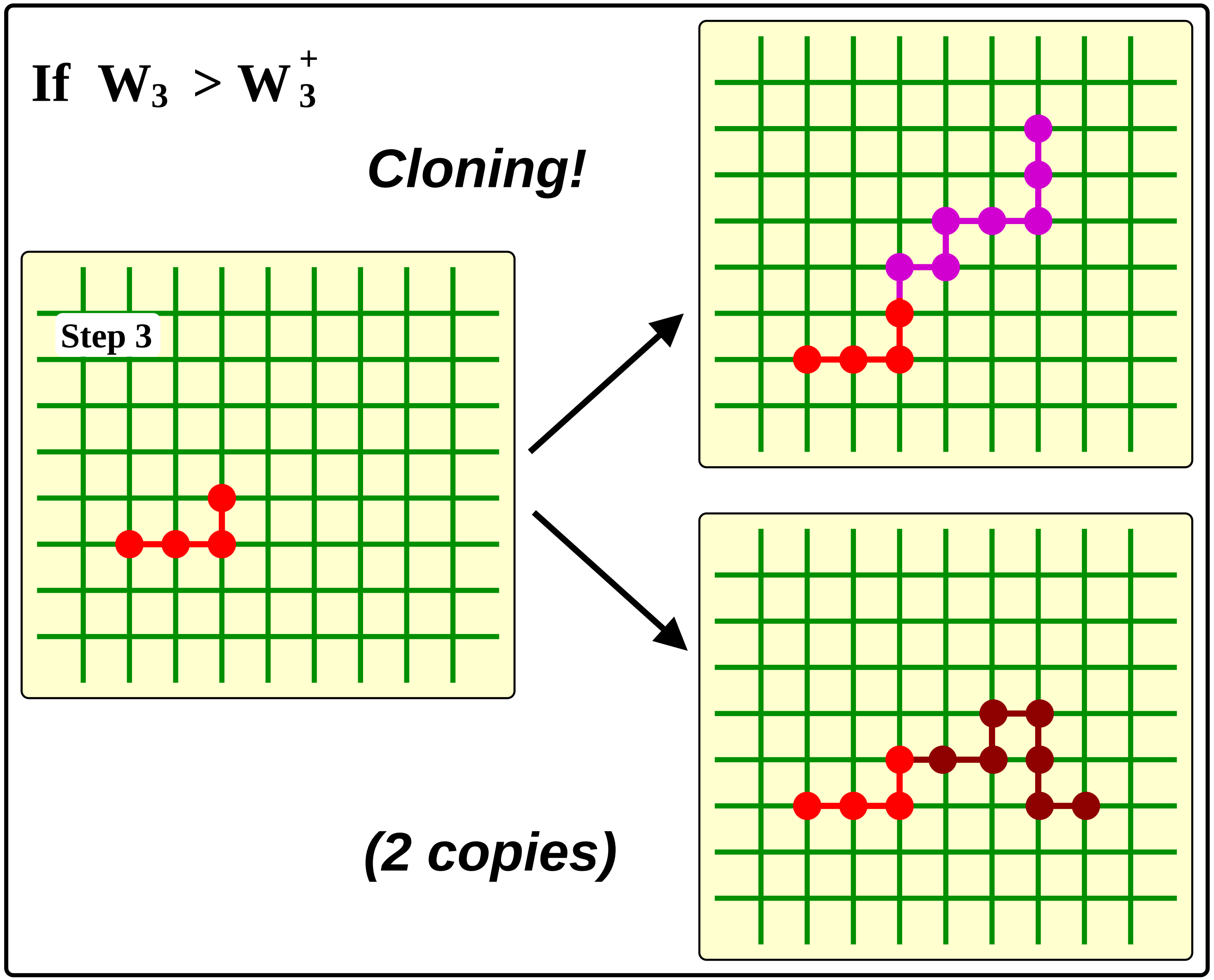

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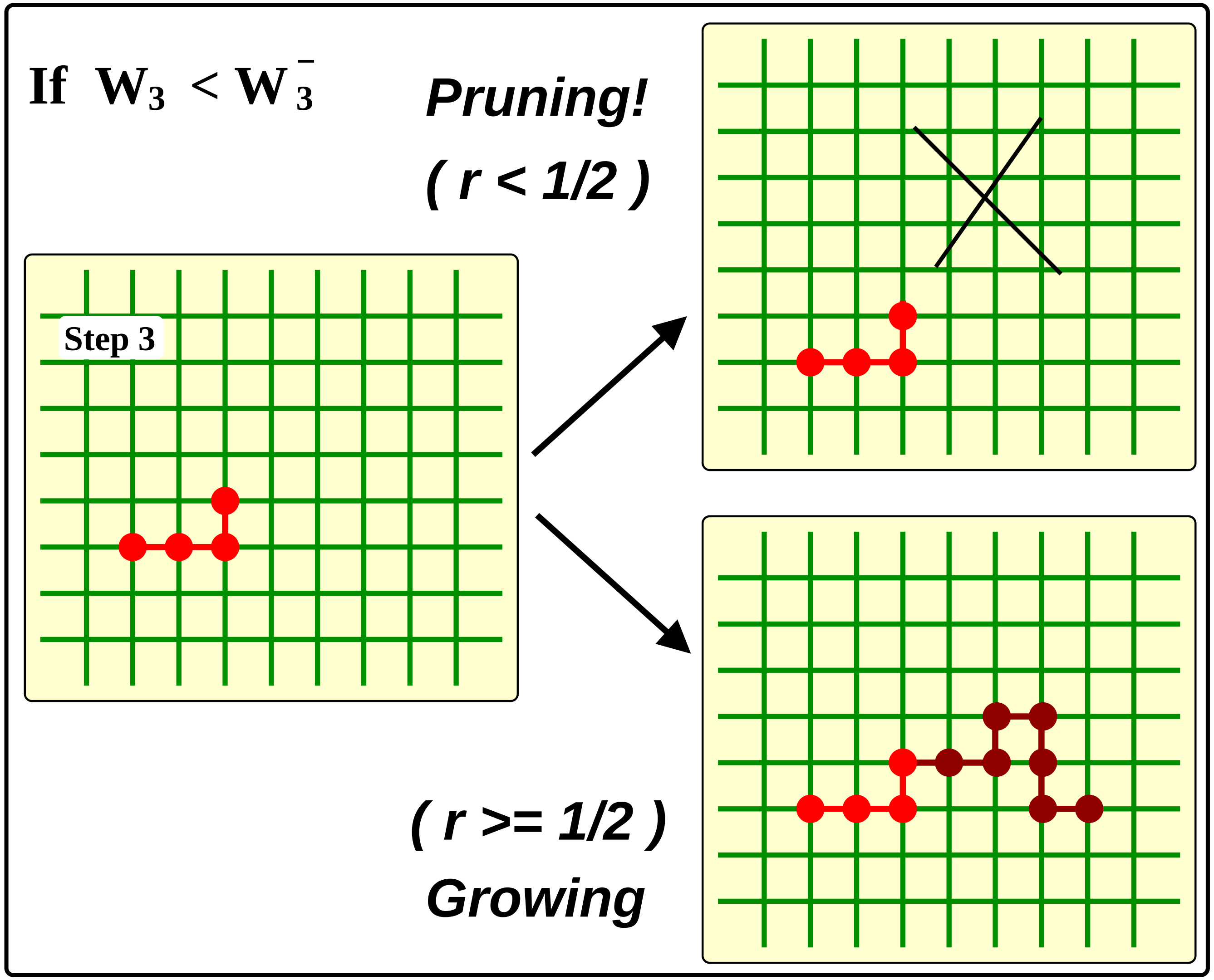

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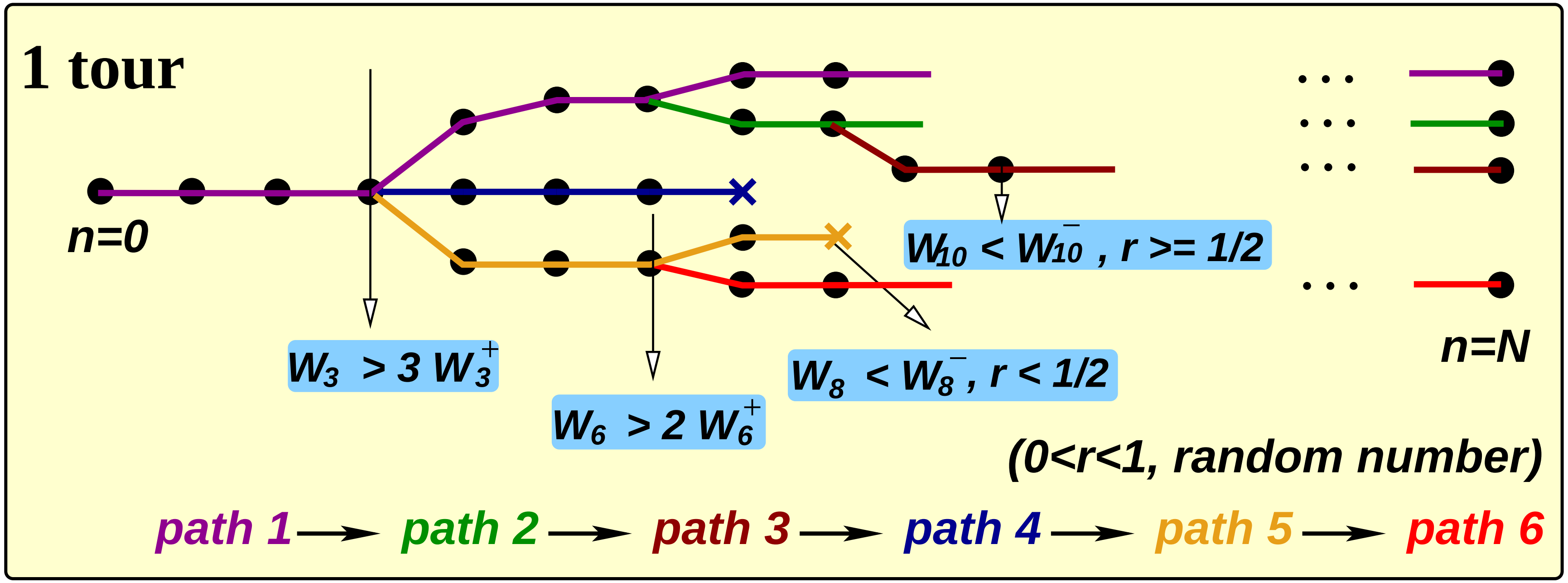
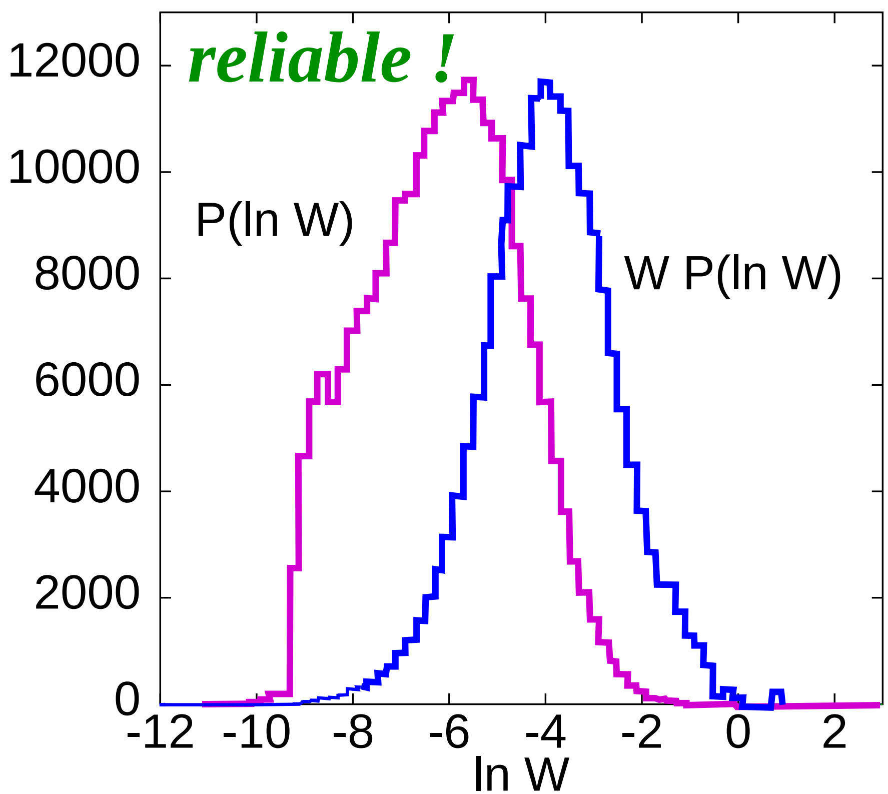
Depth-first implementation:

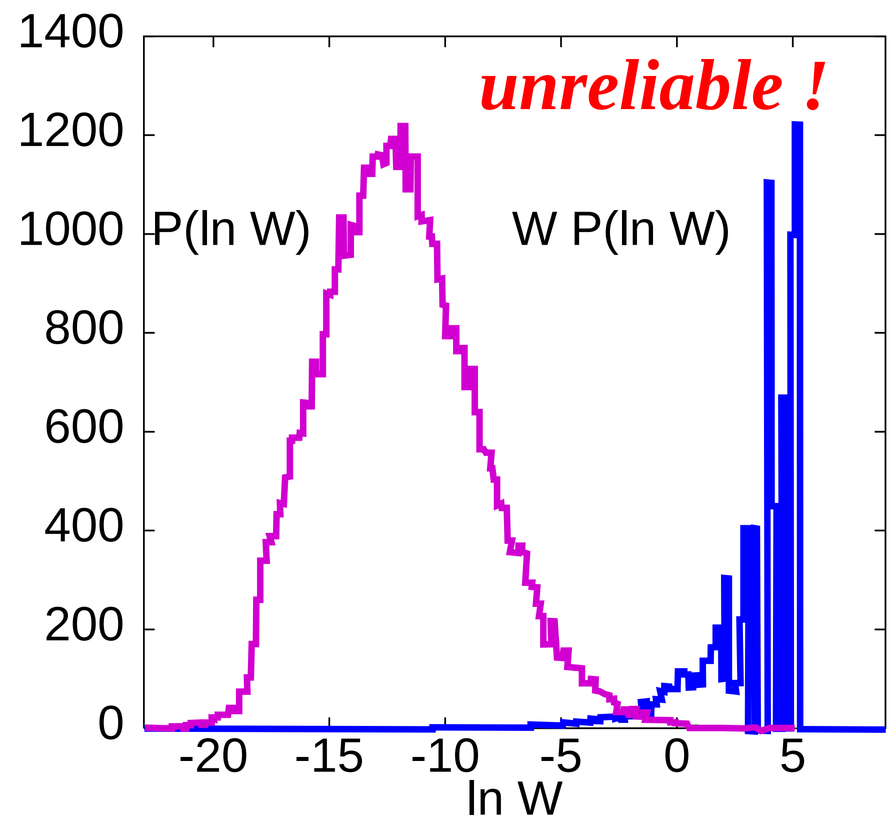


- Last-in first-out stack
- Only a single configuration is stored during the run
- Configurations generated within a tour are correlated
- Different tours are uncorrelated

- Reliability of DATA:

Compare the distribution $P(\ln W)$ of logarithms of tour weights W with the weighted distribution $W\,P(\ln W)$





Self-avoiding walks in $d = 3$

In the thermodynamic limit, $N \to \infty$

- Partition sum: $Z_N \sim \mu_\infty^{-N} N^{\gamma-1}$
  - Critical fugacity μ_∞:

    $\mu_\infty = 0.213491(4)$

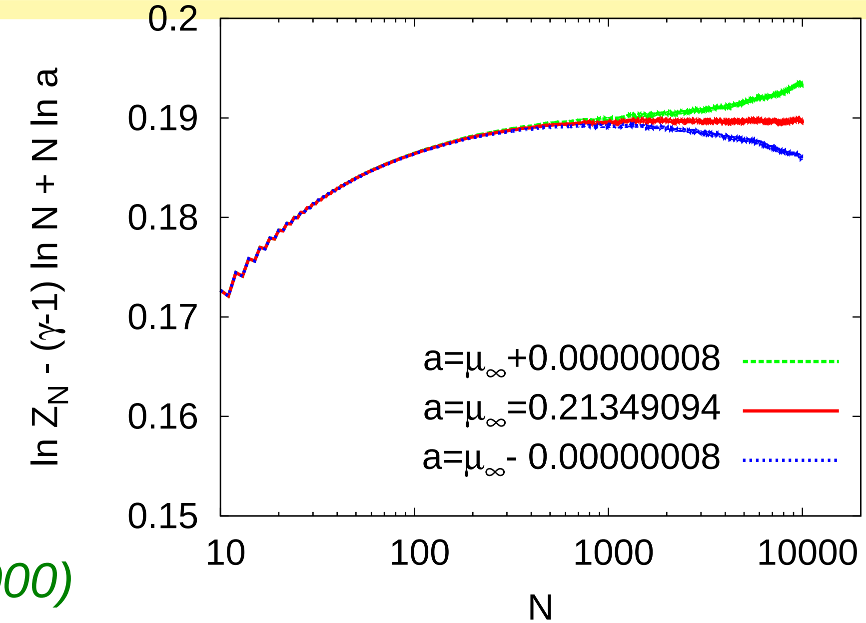
    (exact enumerations)

    MacDonald et al. J. Phys. A33, 5973 (2000)

    $\mu_\infty = 0.2134910(3)$

    (Monte Carlo simulations)

    Grassberger et al., J. Phys. A 30, 7039 (1997)



  - Entropic exponent γ:

    $\gamma = 1.1575(6)$ (Monte Carlo simulations)

    Caracciolo et al., Phys. Rev. E 57, R1215 (1998)

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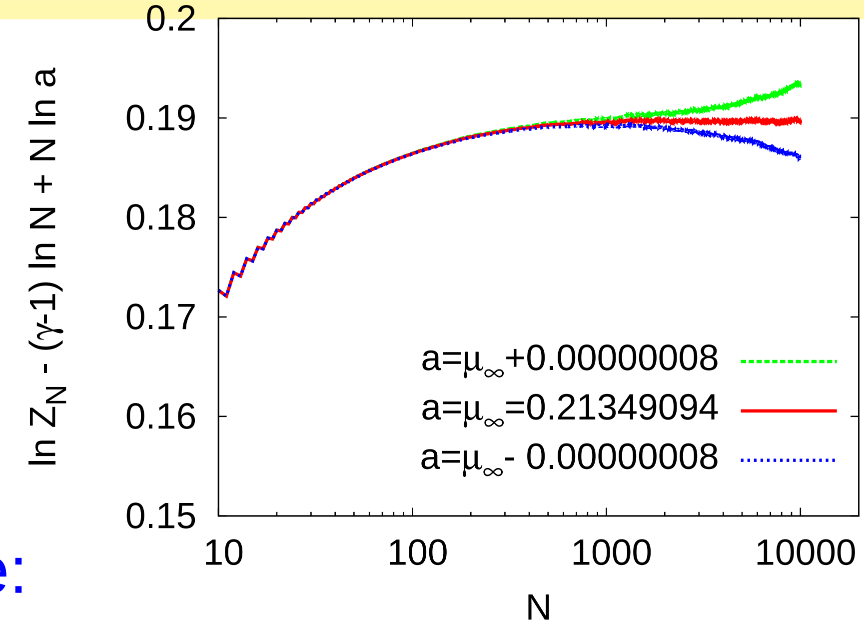


- Mean square end-to-end distance:

  $R_N^2 = \langle (\sum_{j=1}^{N} \vec{a}_j)^2 \rangle \sim N^{2\nu}$

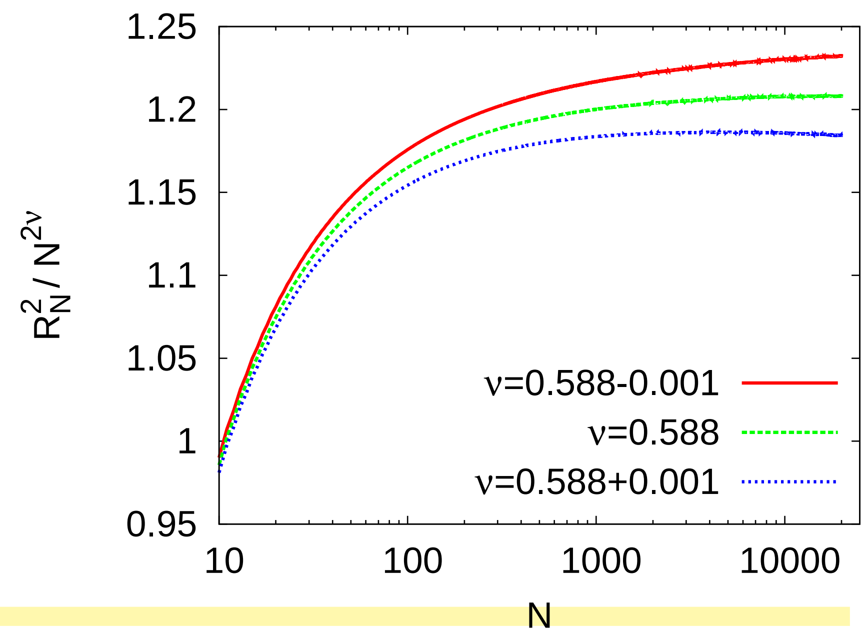
  - $\nu = 0.58765(20)$

    (Monte Carlo simulations)

    Hsu & Grassberger

    J. Chem. Phys. 120, 2034 (2004)

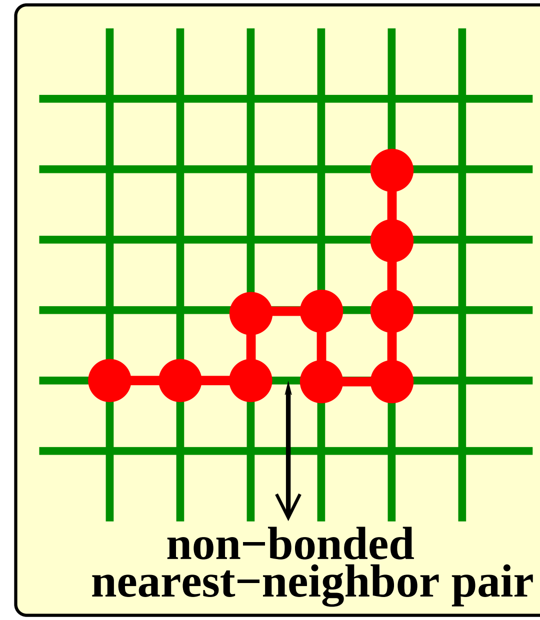
    Macromolecules 37, 4658 (2004)

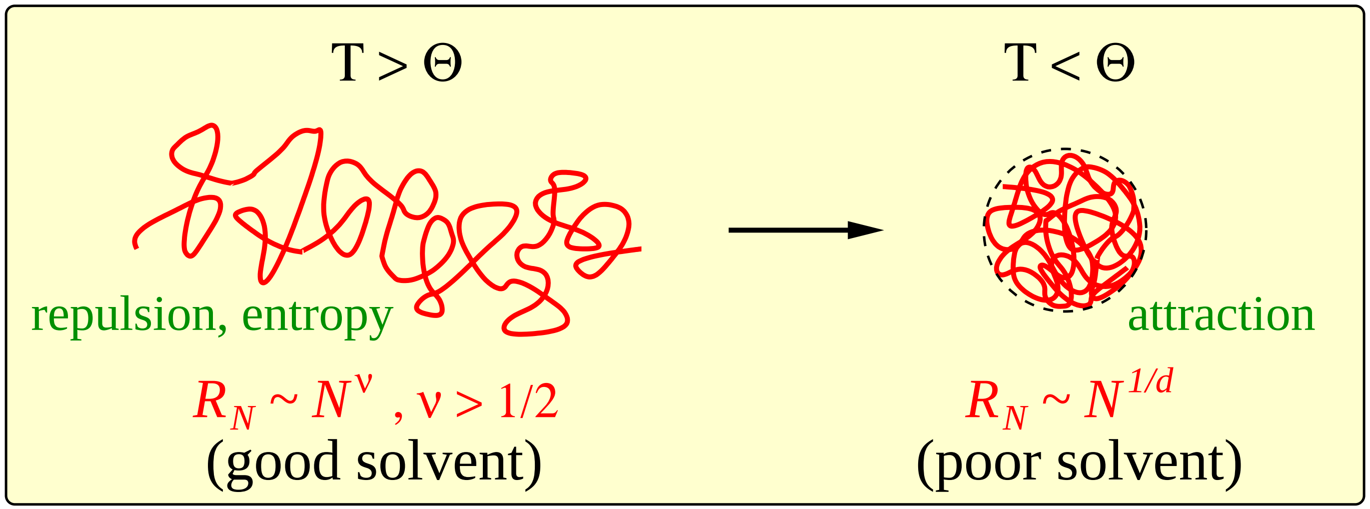


Θ-polymers

- Model: Interacting self-avoiding walk (ISAW)

  Partition sum: $Z_N(q) = \sum_{walks} q^m \, , q = e^{-\beta\epsilon}$





Coil-globule transition at Θ-point

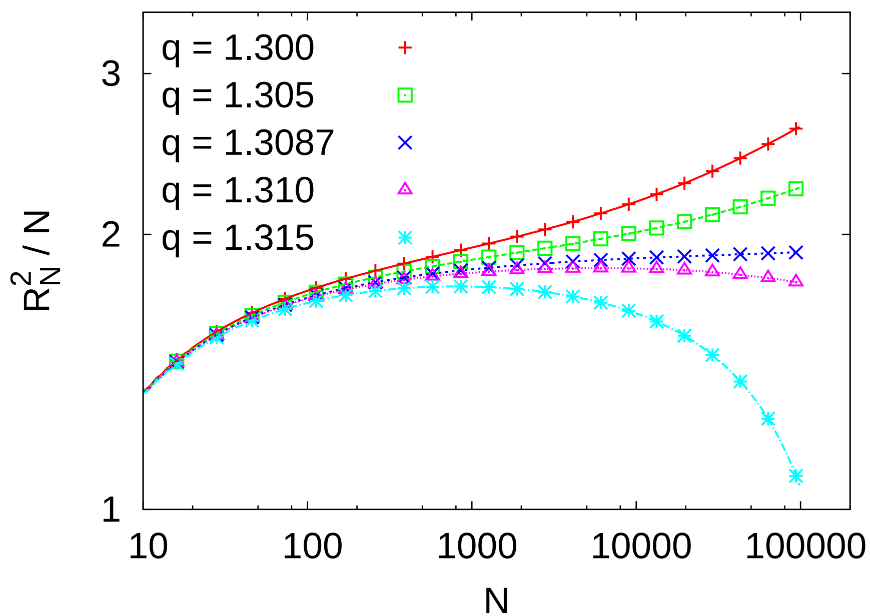
$\nu = 1/2$, Flory exponent

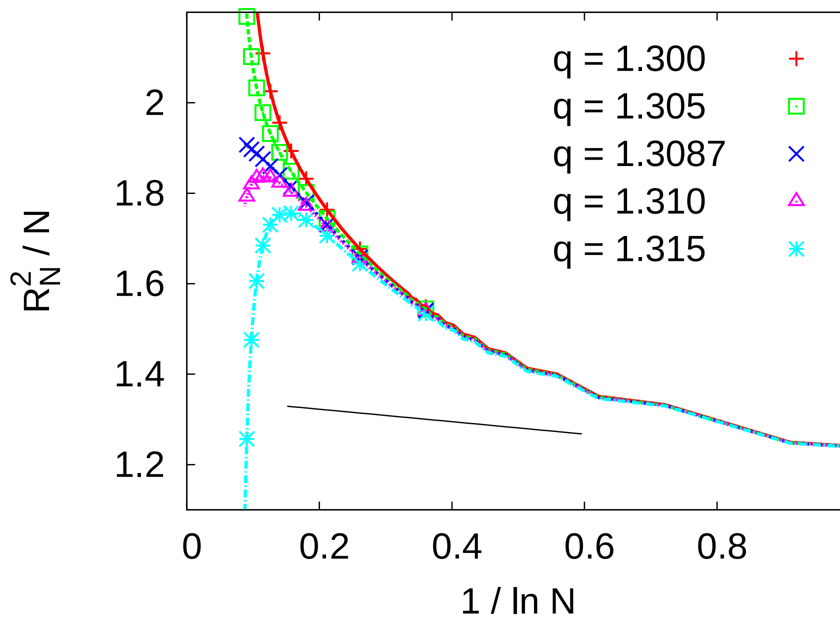
Θ-polymers

- Model: Interacting self-avoiding walk (ISAW)
- Rescaled mean square end-to-end distance R_N^2/N

$$R_N^2/N = const \times \left(1 - \frac{37}{363 \ln N}\right)$$

Theoretical prediction (field theory)

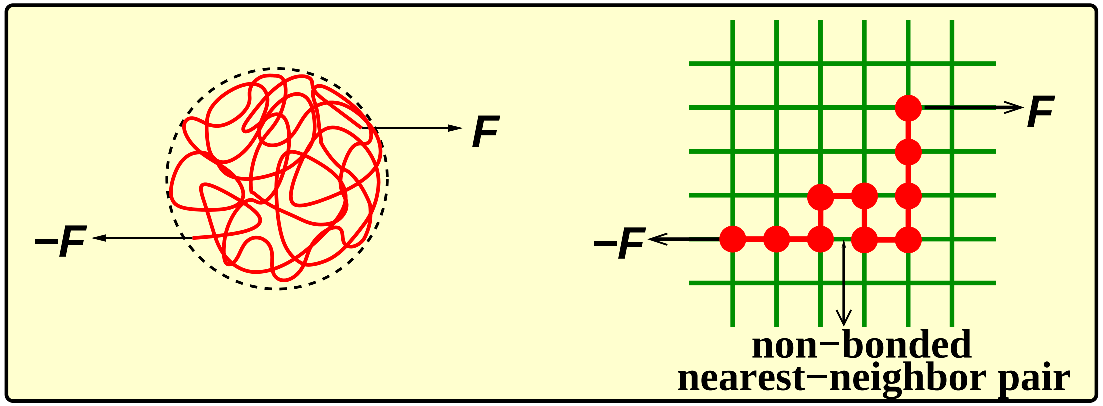




Stretching collapsed polymers

under poor solvent conditions

- Model: Biased interacting self-avoiding walk (BISAW)



- Partition sum:

$$Z_N(q,b) = \sum_{walks} q^m b^x \,, \ (q = e^{-\beta\epsilon}, \, b = e^{\beta a F}, \, a = 1)$$

  - $\vec{F} = F\hat{x}$: stretching force
  - x: end-to-to end distance in the stretching direction
  - m: # of non-bonded nearest-neighbor (NN) pairs

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- Algorithm: PERM
  - Poor solvent condition: choosing $q = 1.5$, $(q > q_\Theta,\ q_\Theta = \exp(-\beta/k_B T_\Theta) \approx 1.3087(3))$
  - Biased samplings: each step of a walk is guided to the stretching direction with higher probability, i.e.,

$$p_{+\hat{x}} : p_{-\hat{x}} : p_{\pm\hat{y}\,\mathrm{or}\,\pm\hat{z}} = \sqrt{b} : \sqrt{1/b} : 1$$

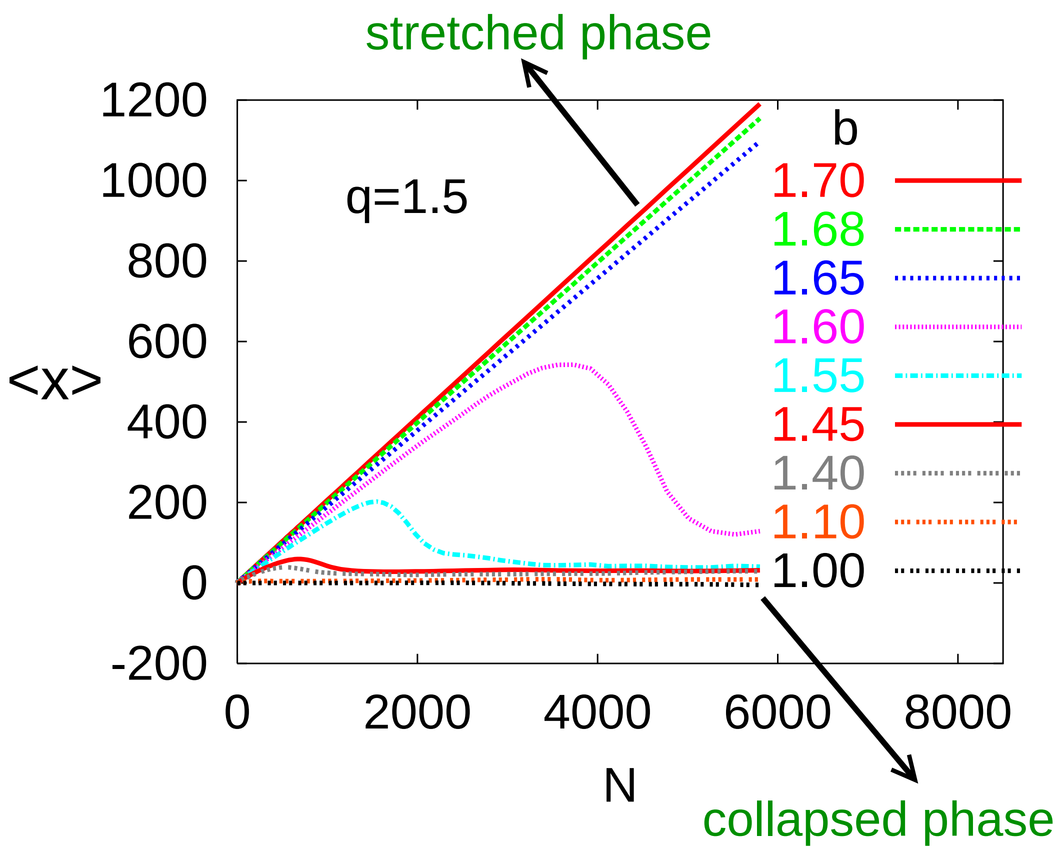
  - The corresponding weight factor at the n^{th} step is

$$w_{i_n} = \frac{q^{m_n} b^{\Delta x_i}}{p_i}$$

    m_n: # of non-bonded NN pairs of the $(n+1)^{\mathrm{th}}$ monomer
    Δx_i: displacement $((\vec{r}_{n+1} - \vec{r}_n) \cdot \hat{x})$, $\Delta x_i = 0$, 1, or -1
  - Two thresholds: $W_n^+ = 3\hat{Z}_n$ and $W_n^- = \hat{Z}_n/3$

Average displacement $\langle x \rangle$

- Transition point $b_c = \exp(\beta a F_c)$
  $(b < b_c)$ collapsed phase $\Leftrightarrow$ stretched phase $(b > b_c)$
- $1.60 < b_c < 1.65$ finite-size effects?



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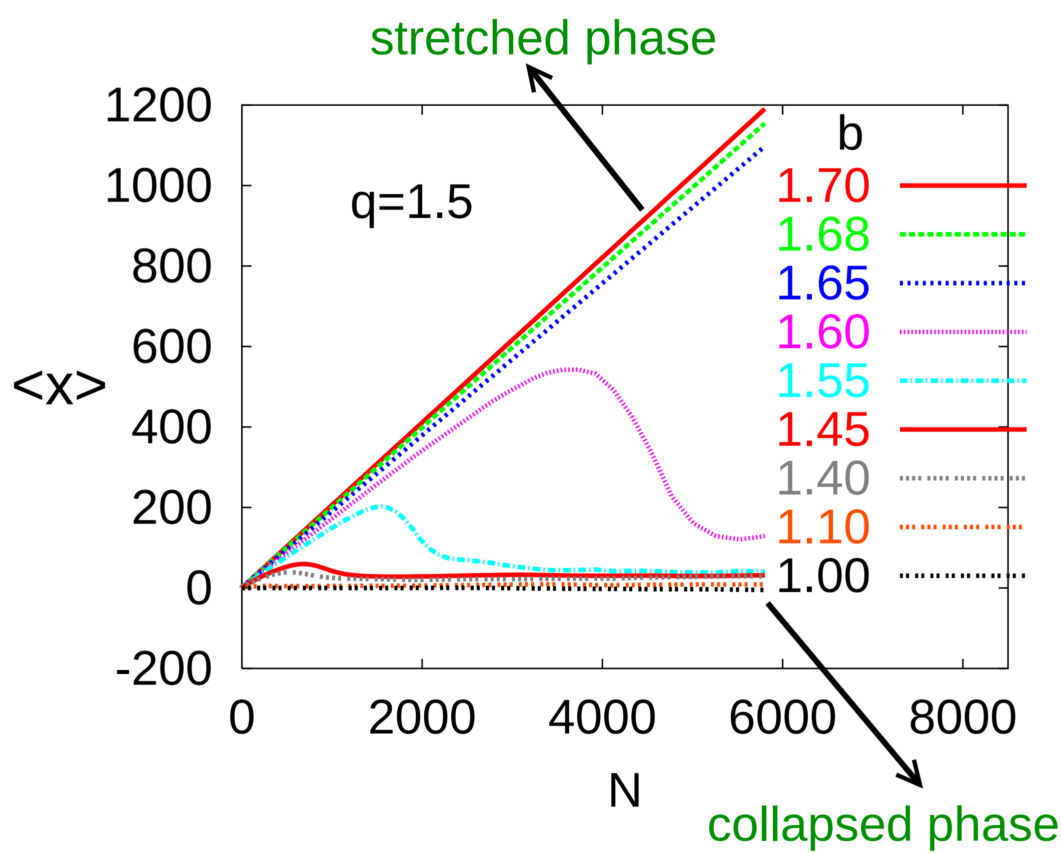

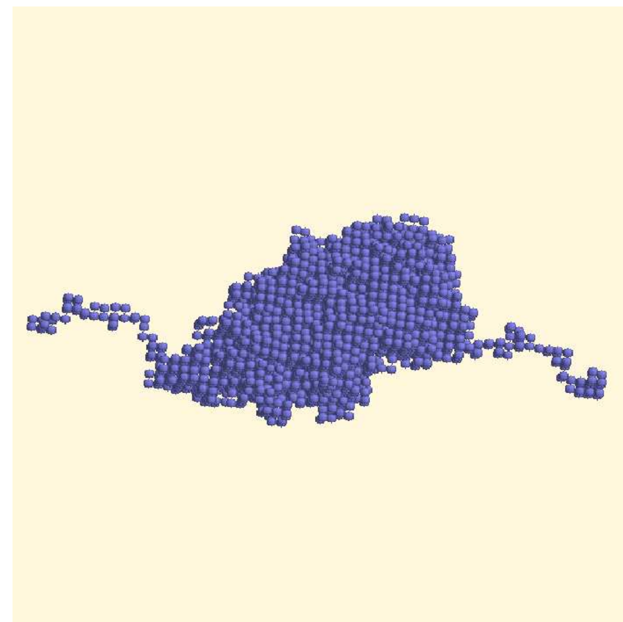

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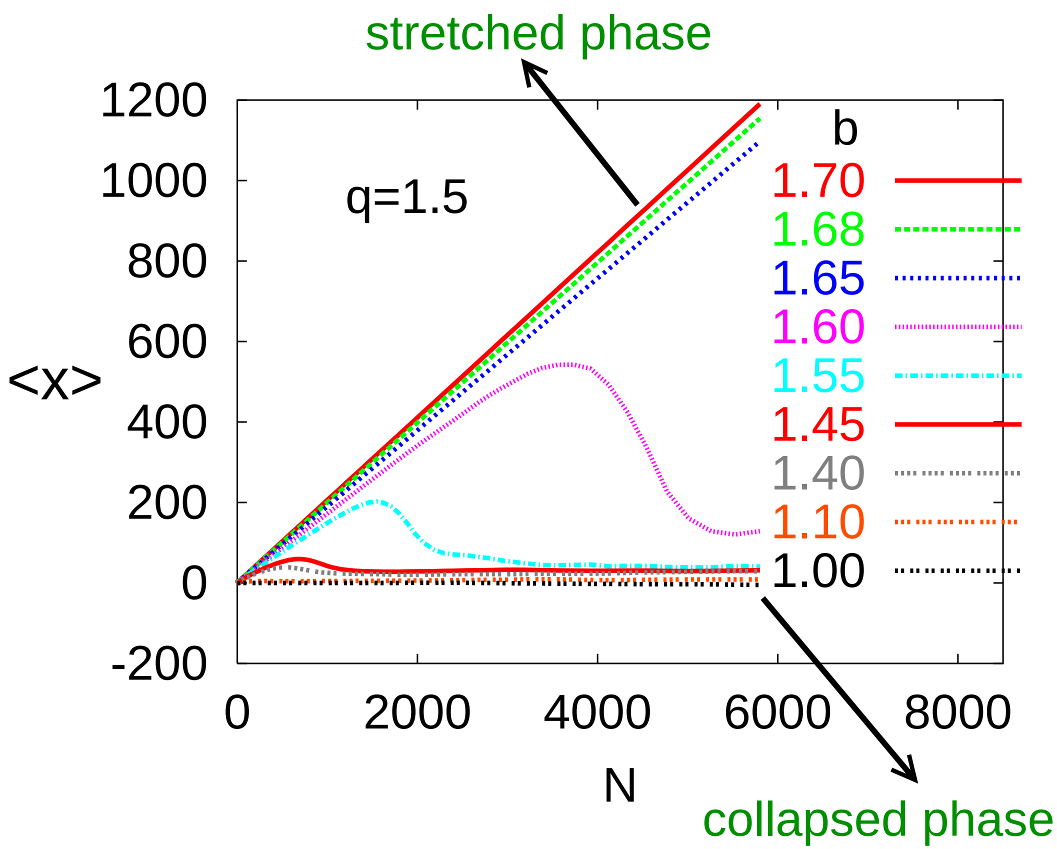

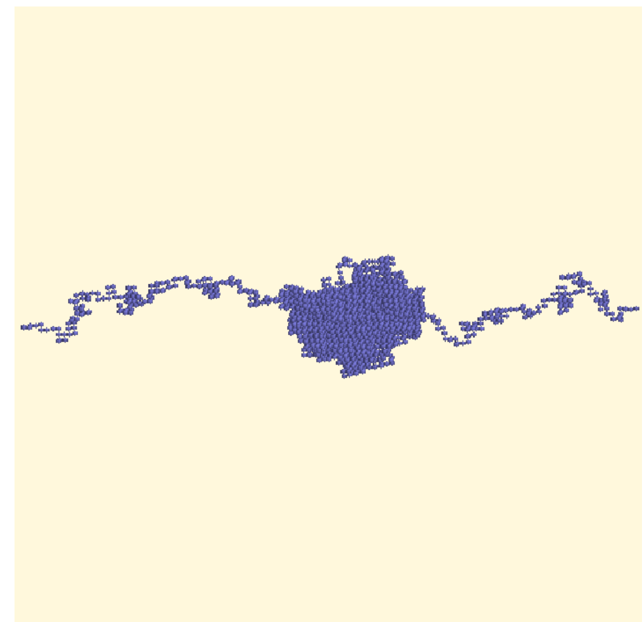

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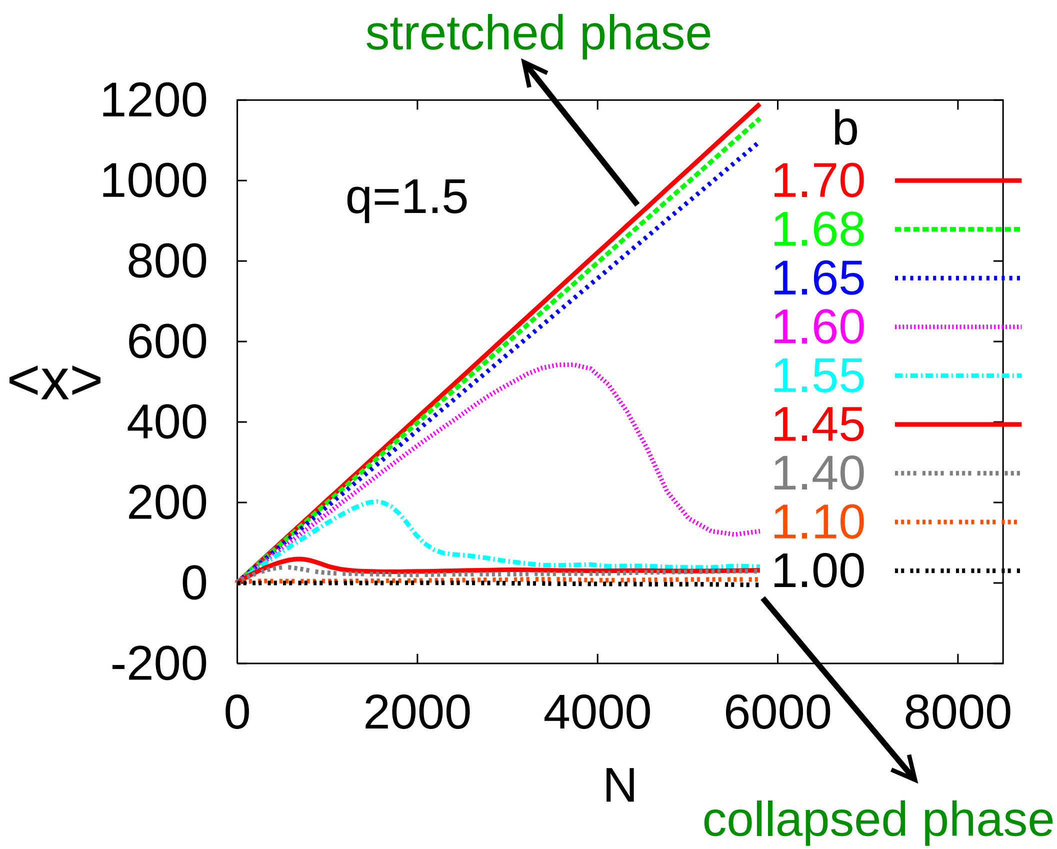

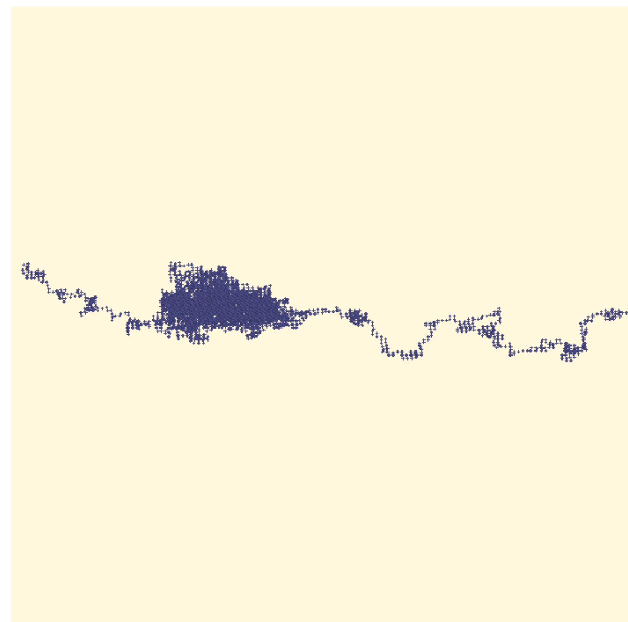

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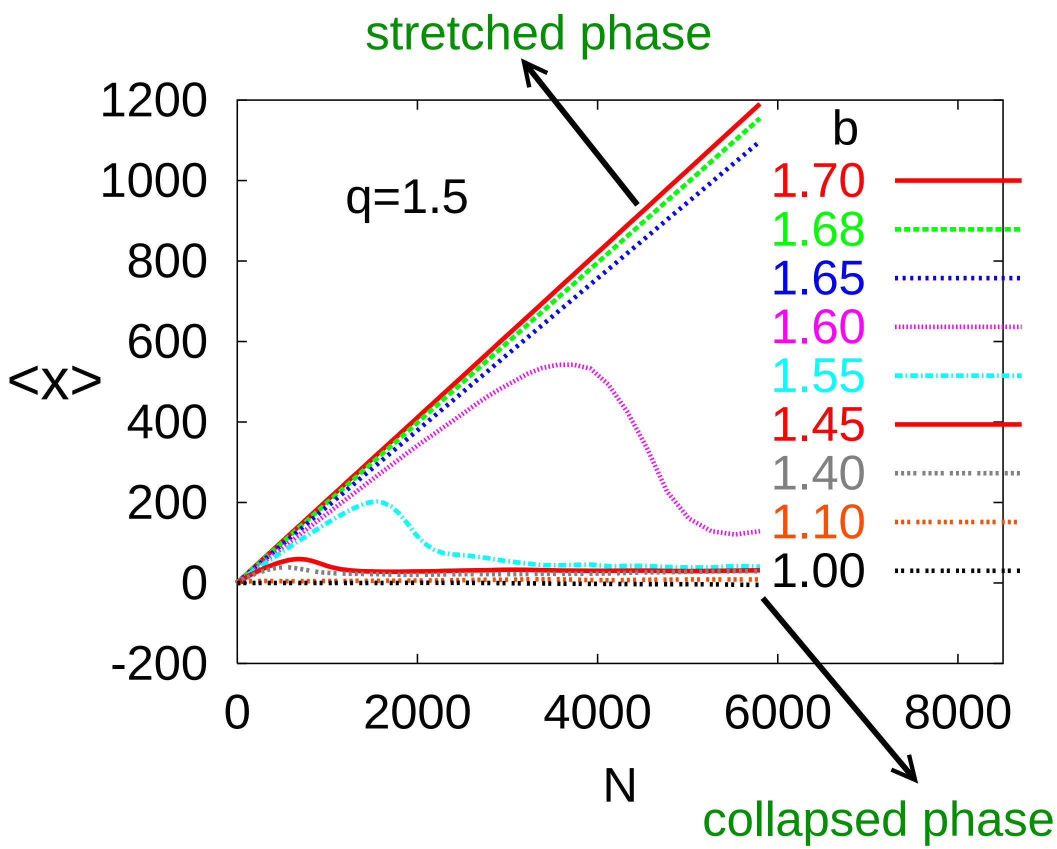

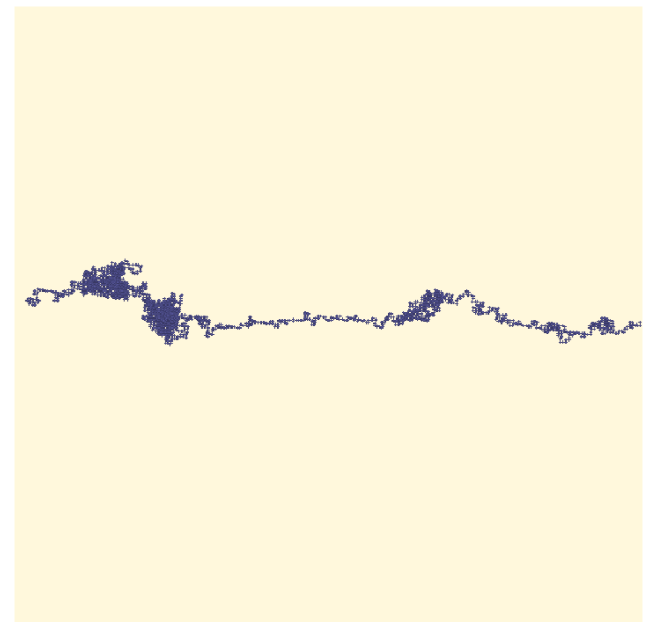

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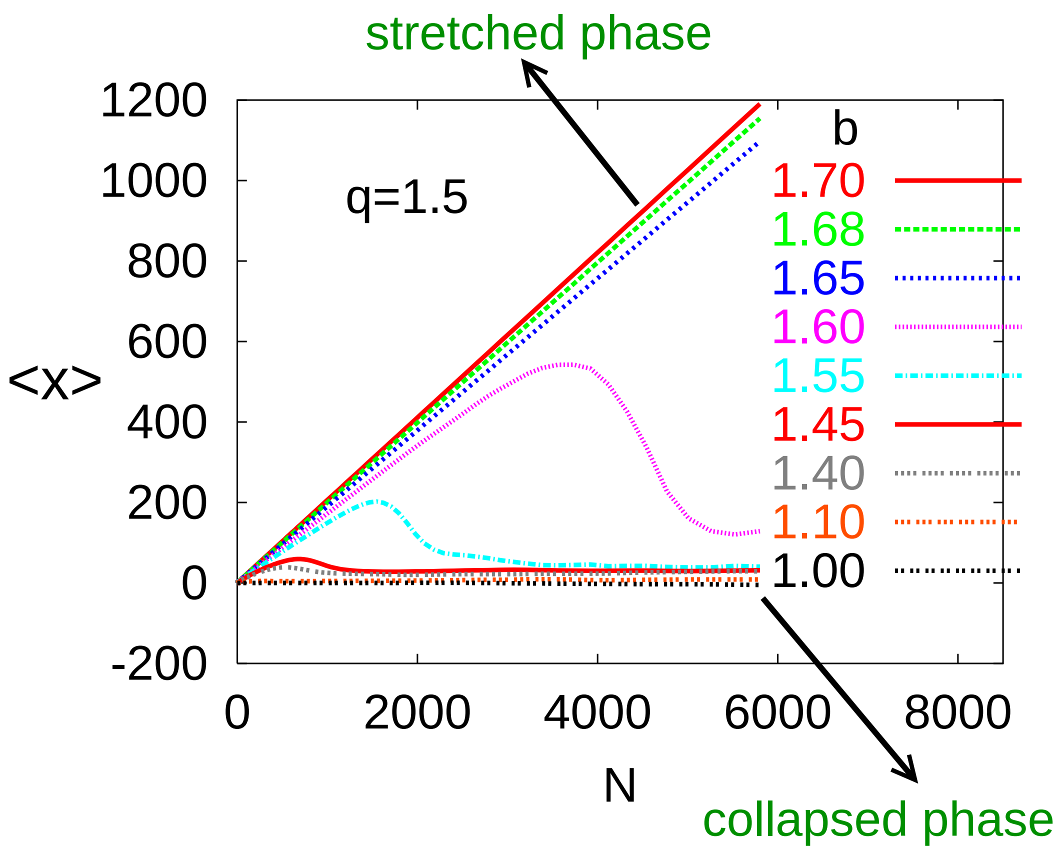

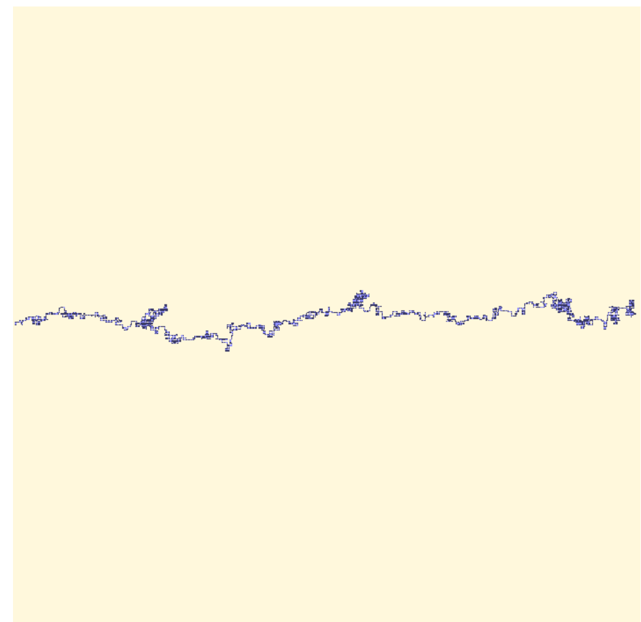

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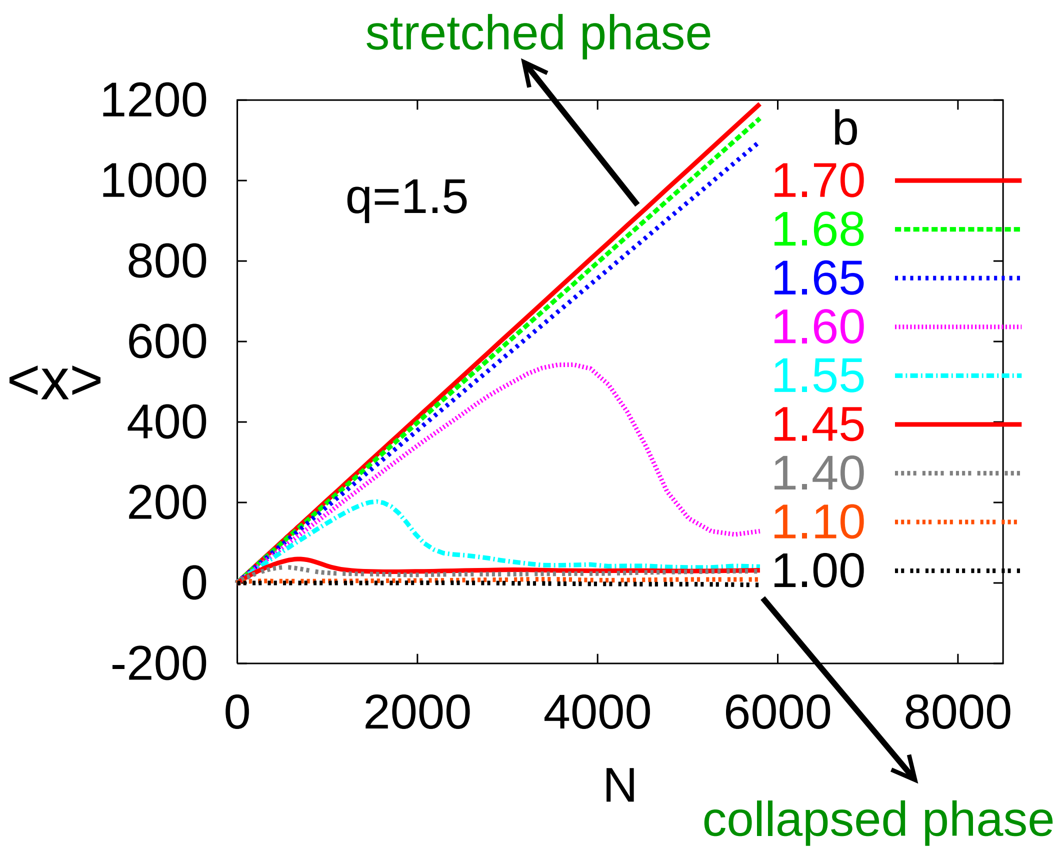
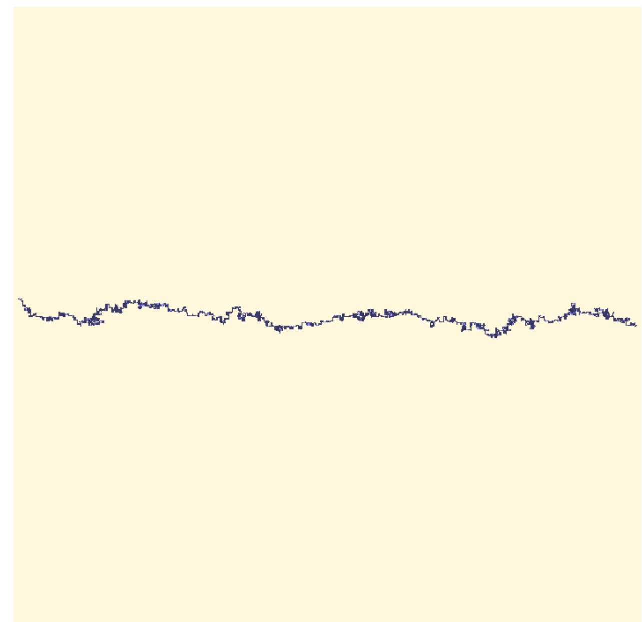
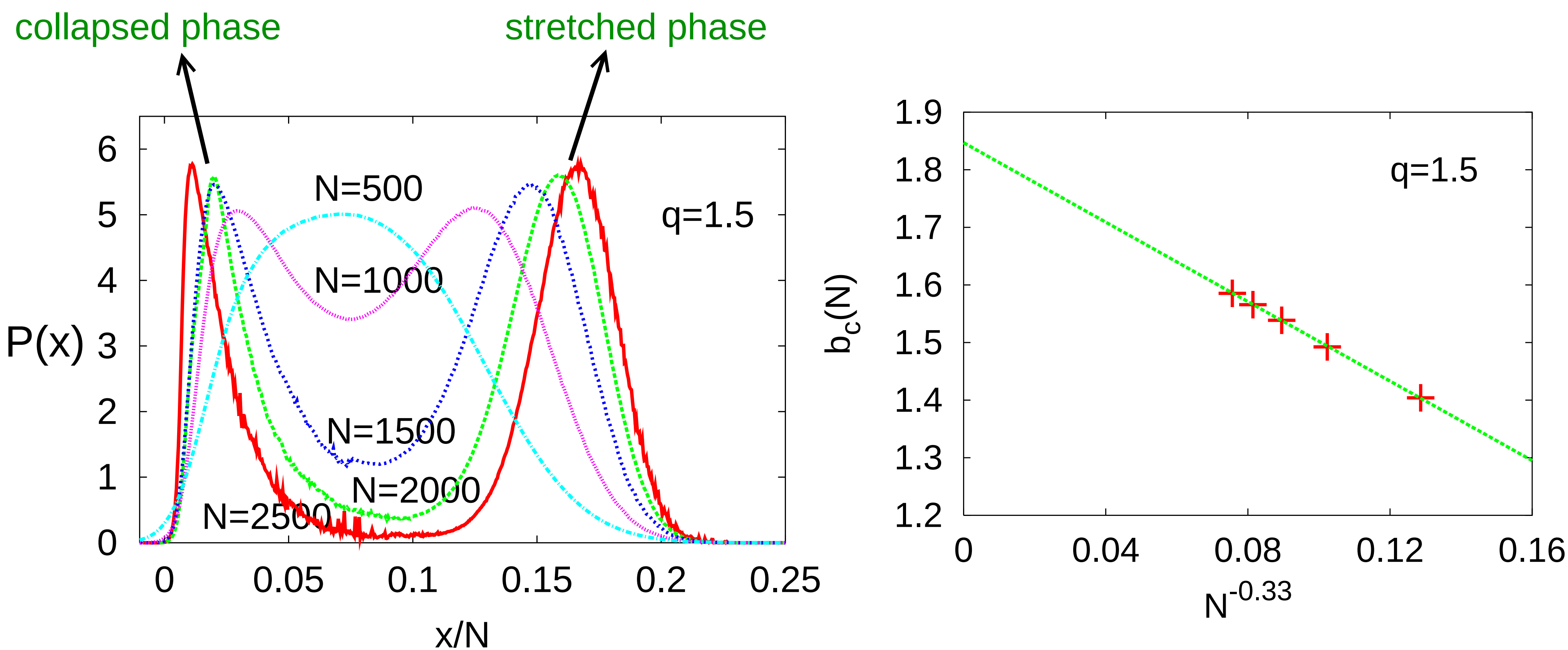




First-order phase transition

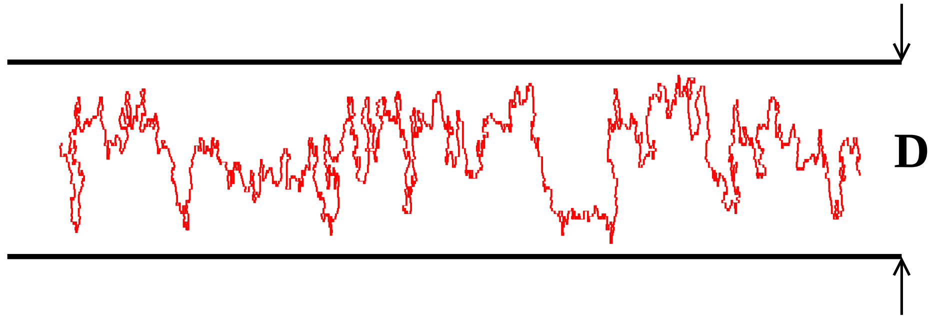
- Histogram of x: $P_{q,b}(m,x) = \sum_{walks} q^{m'} b^{x'} \delta_{m,m'} \delta_{x,x'}$
- Reweighting histograms:

$$P_{q',b'}(m,x) = P_{q,b}(m,x)(q'/q)^m (b'/b)^x$$



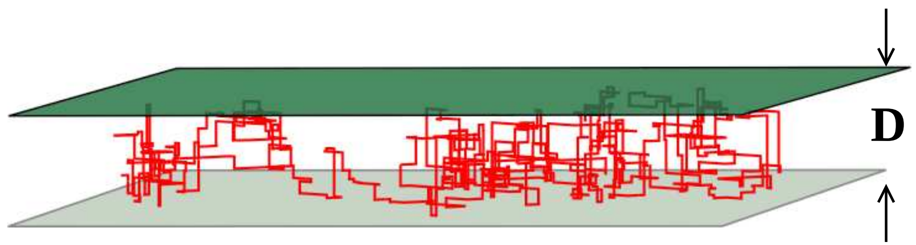
Polymers in confining geometries

- A slit of width D:



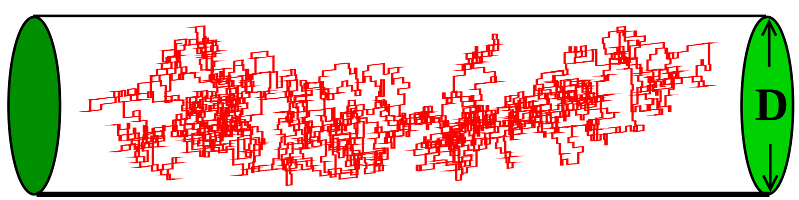
$$d = 2 \longrightarrow d = 1$$

- Two parallel hard walls separated by a distance D:



$$d = 3 \longrightarrow d = 2$$

- A tube of diameter D:



$$d = 3 \longrightarrow d = 1$$

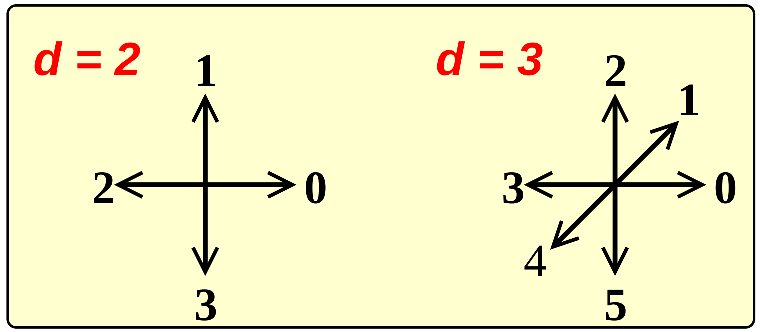
K-step Markovian anticipation

The $(k+1)^{th}$ step of walk is biased by the history of the previous k steps

A walk on a d-dimensional hypercubic lattice

- All possible moving directions at each step i:

  $s_i = 0, \ldots, 2d-1$



- A sequence of $(k+1)$ steps:

  (all possible configurations)

  $$\mathcal{S} = (s_{-k}, \ldots, s_{-1}, s_0) = (\mathrm{s}, s_0)$$

  s: configurations of the previous k steps

  s_0: configurations of the $k+1^{th}$ step

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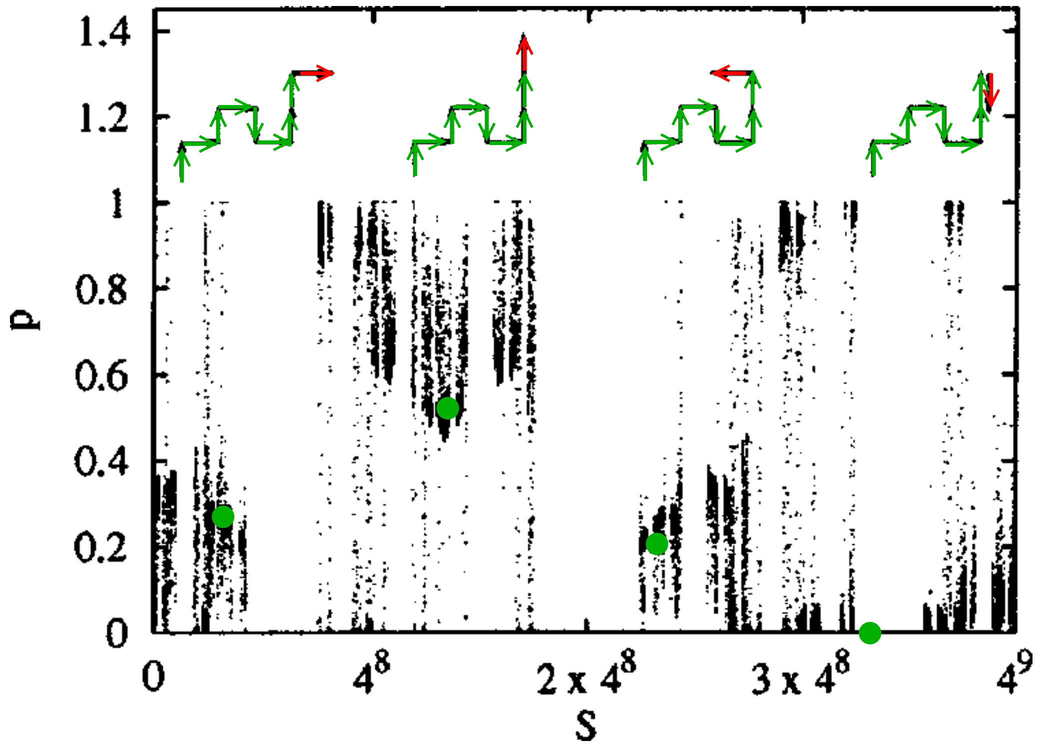
- The bias in k-step Markovian anticipation for the next step

$$P(s_0 \mid \mathrm{s}) = \frac{H_m(\mathrm{s}, s_0)/H_0(\mathrm{s}, s_0)}{\sum_{s_0'=0}^{2d-1} H_m(\mathrm{s}, s_0')/H_0(\mathrm{s}, s_0')}$$

  - $H_m(\mathrm{s}, s_0)$: sum of all contributions to $\hat{Z}_{n+m}$ of configurations that had the same sequence $S = (s, s_0)$ during the steps $n-k$, $n-k+1, \ldots$, and n
  - $H_m(s, s_0)/H_0(s, s)$: measuring how successful configurations ending with S were in contributing to the partition sum m step later
  - Accumulating histograms at step n and at step $n+m$ (e.g. $n > 300$, $m = 100$)

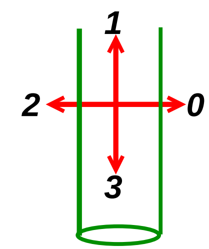
- The bias in k-step Markovian anticipation for the next step

$$P(s_0 \mid \mathrm{s}) = \frac{H_m(\mathrm{s}, s_0)/H_0(\mathrm{s}, s_0)}{\sum_{s_0'=0}^{2d-1} H_m(\mathrm{s}, s_0')/H_0(\mathrm{s}, s_0')}$$

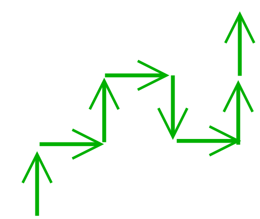


$k = 8$

$S = s + s_0 \times 4^8$



$s_0 = 0, 1, 2, 3$



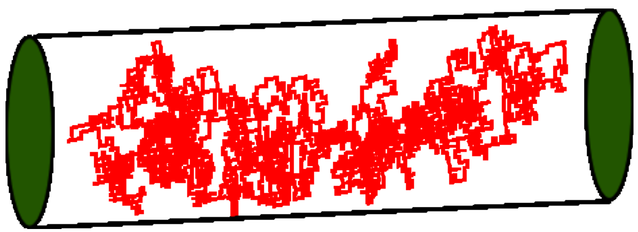
$s = 1 + 0 \times 4 + 1 \times 4^2 + 0 \times 4^3 + 3 \times 4^4 + 0 \times 4^5 + 1 \times 4^6 + 1 \times 4^7$

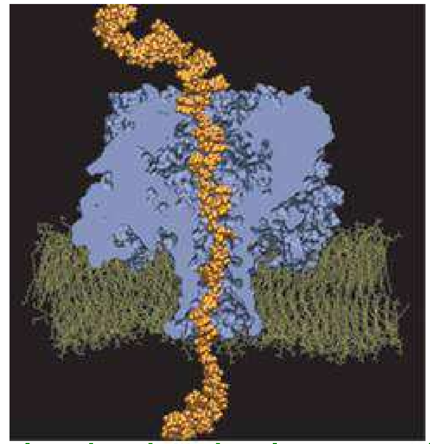
"Two-dimensional self-avoiding walks on a cylinder"

Frauenkron, Causo, & Grassberger, Phys. Rev. E 59, R16, (1999)

Polymers confined in a tube

- The confinement/escape problem of polymer chains confined in a finite cylindrical tube





Aksimentiev et al, Biophysical Jouranl 88, 3745 (2005)

  - Polymer translocation through pores in a membrane
  - DNA confined in artificial nanochannels

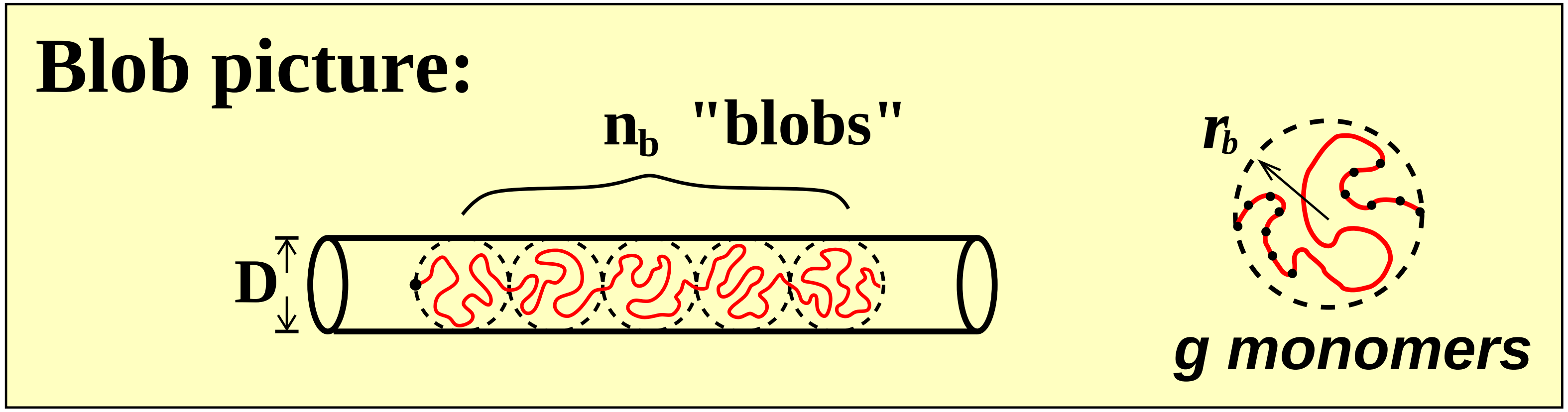
Hsu, Binder, Klushin, & Skvortsov

Phys. Rev. E 76, 021108 (2007); 78, 041803 (2008)

Macromolecules 41, 5890 (2008)

Fully confined polymer chains

- Polymer chains of size N in an imprisoned state



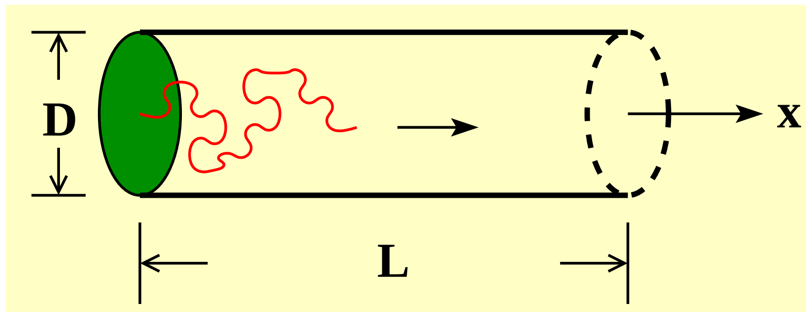
- Total number of monomers: $N = g n_b$
- End-to-end distance: $R_{\rm imp} = n_b(2r_b) = n_b D$ || tube

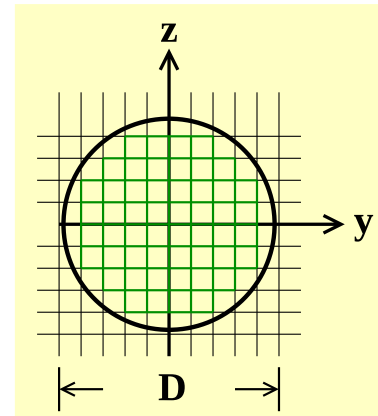
  within a blob, $D = a g^{\nu} = 2r_b$, $\nu = 0.588$ (3DSAW)

  $\Rightarrow R_{\rm imp}/a = N(D/a)^{1-1/\nu}$
- Free energy: $F_{\rm imp} = n_b[k_B T] = N(D/a)^{-1/\nu}$

Simulations

- Model: Self-avoiding random walks on a simple cubic lattice





Monomers are forbidden to sit on

$\{1 \le x \le L,\ y^2 + z^2 = D^2/4\}$ and $\{x = 0,\ y^2 + z^2 = D^2/4\}$

- Algorithm: PERM with k-step Markovian anticipation

weak confinement regime $\leftrightarrow$ strong confinement regime

$1 \ll R_F \ll D$ $\qquad$ $1 \ll D \ll R_F$

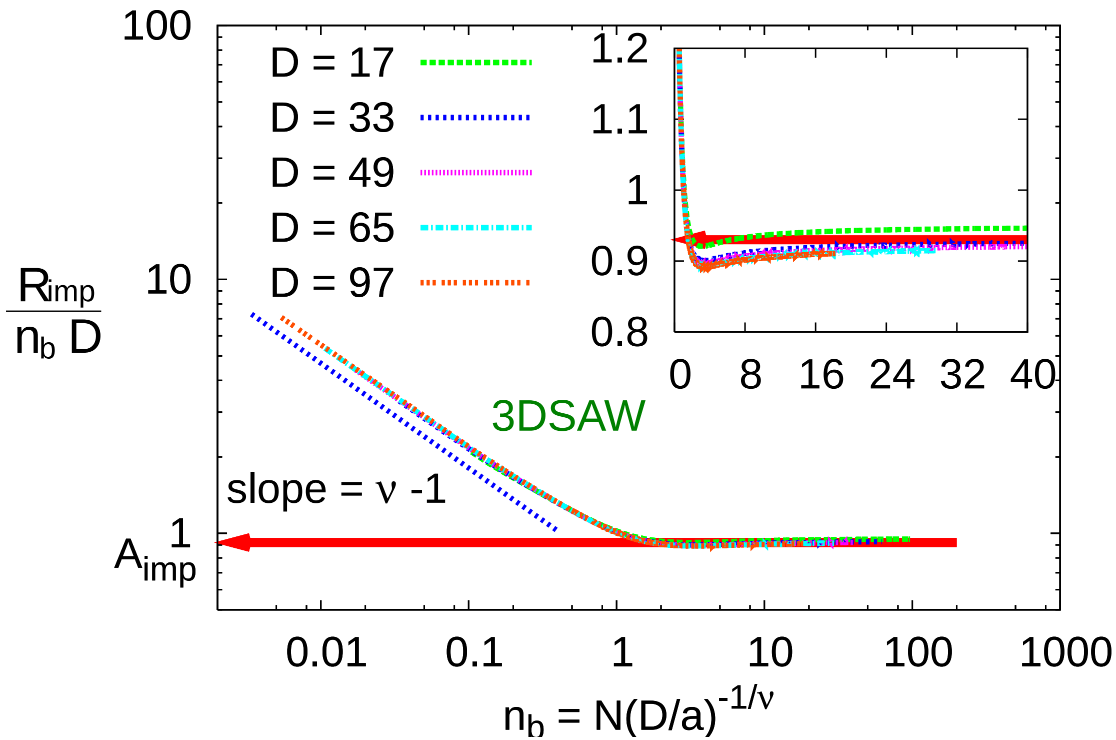
$R_F \sim N^\nu$: Flory radius, $\nu \approx 0.588$

$R_{\rm imp}$ and $F_{\rm imp}$

In the strong confinement regime:

$n_b = N(D/a)^{-1/\nu}$: # of blobs, $N_{\rm max} = 44000$

- End-to-end distance: $R_{\rm imp} = A_{\rm imp} D n_b$, $A_{\rm imp} = 0.92 \pm 0.03$

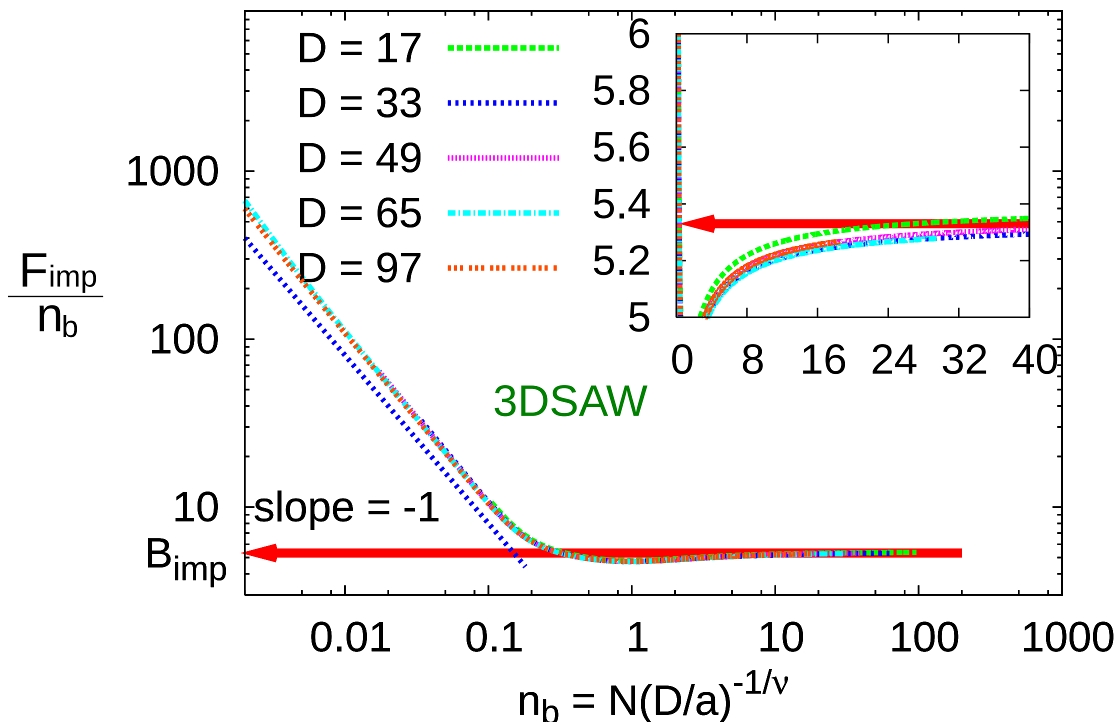


$R_{\rm imp}$ and $F_{\rm imp}$

In the strong confinement regime:

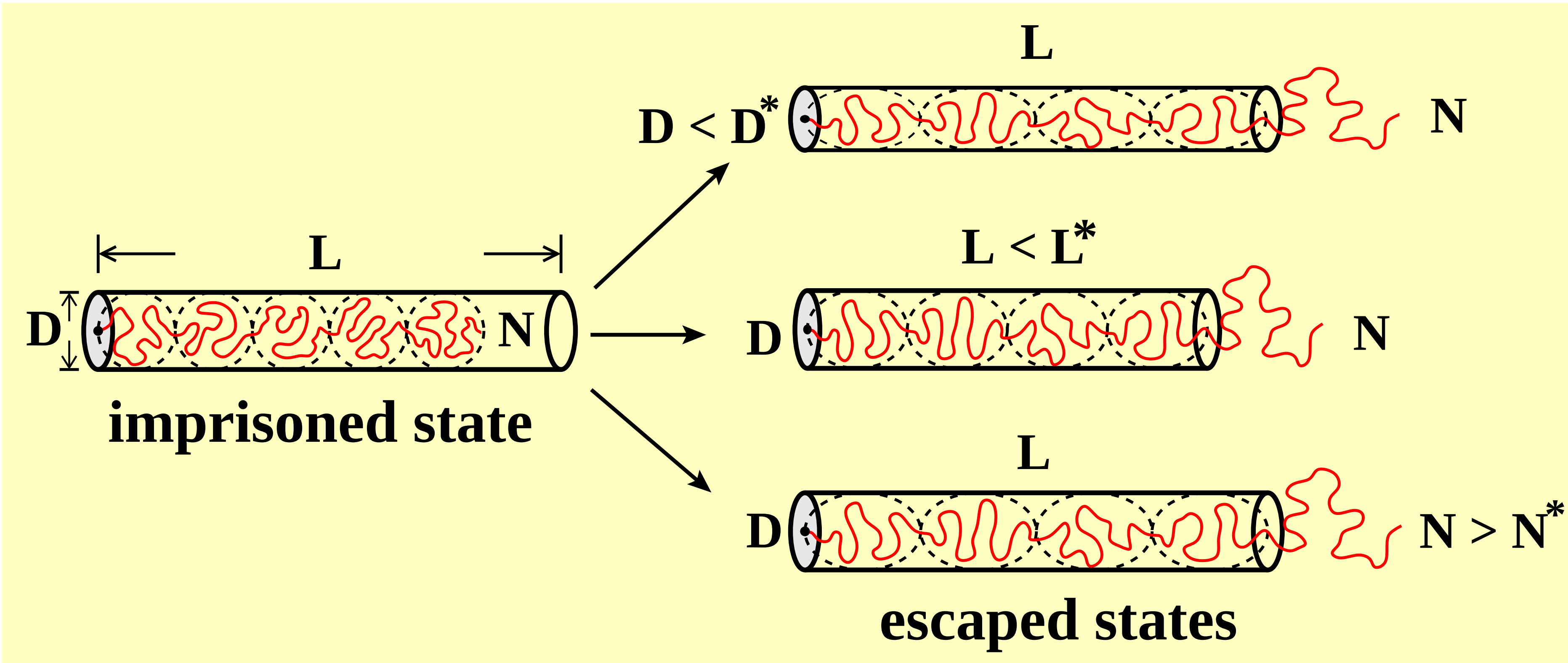
$n_b = N(D/a)^{-1/\nu}$: # of blobs, $N_{\rm max} = 44000$

- End-to-end distance: $R_{\rm imp} = A_{\rm imp} D n_b$, $A_{\rm imp} = 0.92 \pm 0.03$
- Free energy: $F_{\rm imp} = B_{\rm imp} n_b$, $B_{\rm imp} = 5.33 \pm 0.08$



Escape transition

- Polymer chains of N monomers with one end grafted to the inner wall of a finite cylindrical nanotube



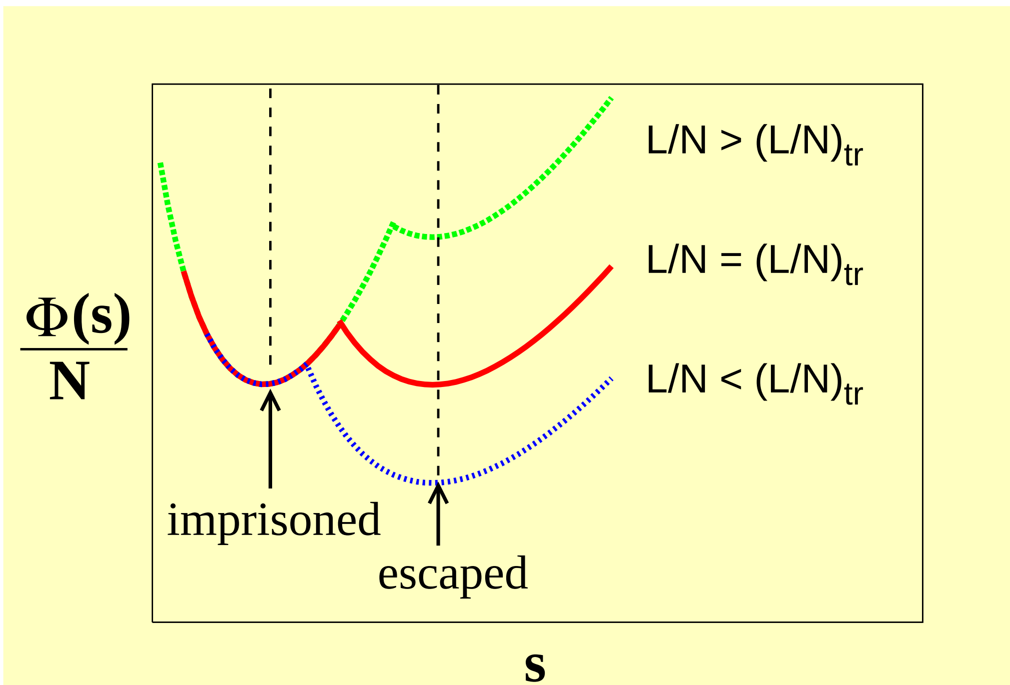
First-Order Phase Transition !

Theoretical predictions

Landau theory approach

- Partition sum: $Z = \exp(-F) = \int ds \exp(-\Phi(s))$

  F: free energy, $\Phi(s)$: Landau free energy function

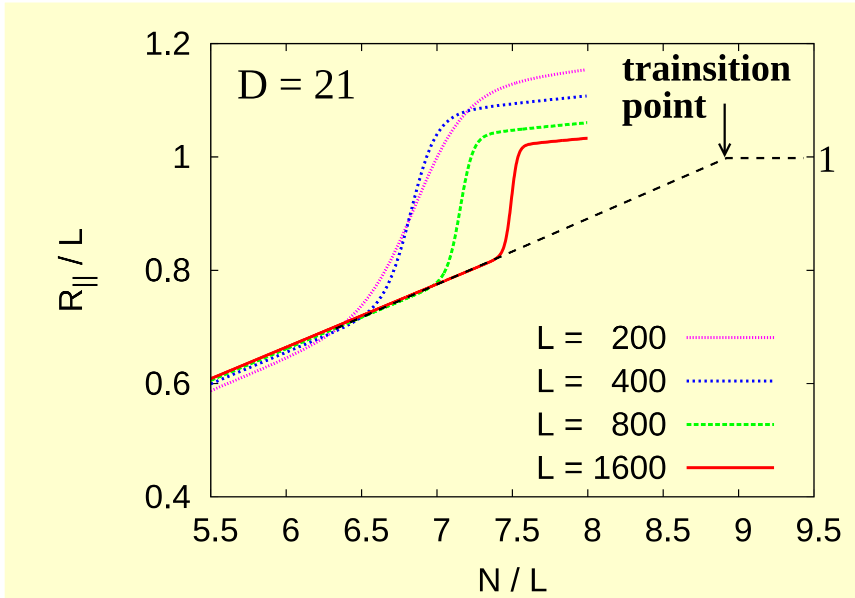


s: order parameter

$$s = \begin{cases} R/N_{\text{imp}}, \text{ imprisoned} \\ L/N_{\text{imp}}, \text{ escaped} \end{cases}$$

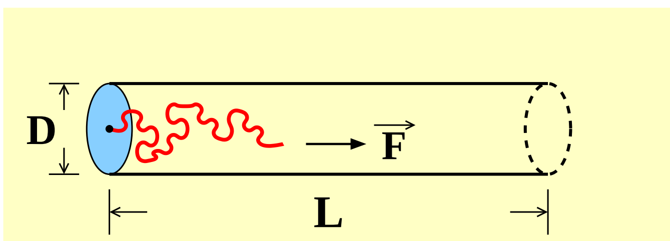
End-to-end distance $R_{||}$

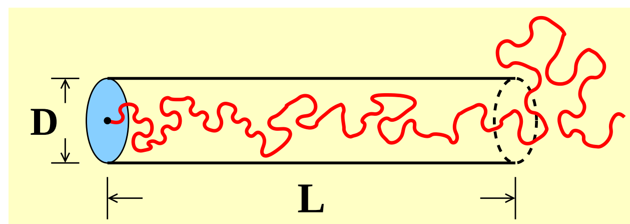
- Algorithm: PERM with k-step Markovian anticipation



Poor samplings of configurations in the escaped state !

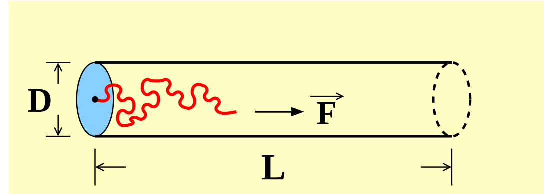
- New strategy:





Biased & unbiased SAWs

- Partition sum: $Z_b(N, L, D) = \sum_{walks} b^{\Delta x}$



$$(= \frac{1}{M_b} \sum W_b(N, L, D))$$

$$b = \begin{cases} \geq 1 & , 0 < x \leq L \; , \; y^2 + z^2 \leq D^2/4 \\ 1 & , \text{otherwise} \end{cases}$$

$b = \exp(\beta a F)$: stretching factor, $\beta = 1/k_B T$, $\beta = a = 1$
$\vec{F}$: stretching force, $\Delta x = (x_{N+1} - x_1) \; || \; \vec{F}$

- Each BSAW of N steps contributes a weight

$$W(N, L, D) = \begin{cases} W_b(N, L, D)/b^{x_{N+1} - x_1} & , \text{ imprisoned} \\ W_b(N, L, D)/b^L & , \text{ escaped} \end{cases}$$

- For any observable $\mathcal{O}$:

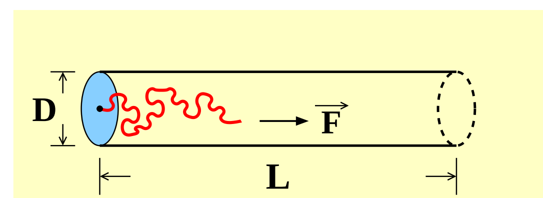
$$\langle \mathcal{O} \rangle = \frac{\sum_k \sum_{\mathrm{config} \in C_{b_k}} \mathcal{O}(C_{b_k}) W^{(k)}(N,L,D)}{\sum_k \sum_{\mathrm{config} \in C_{b_K}} W^{(K)}(N,L,D)}$$

- Partition sum:

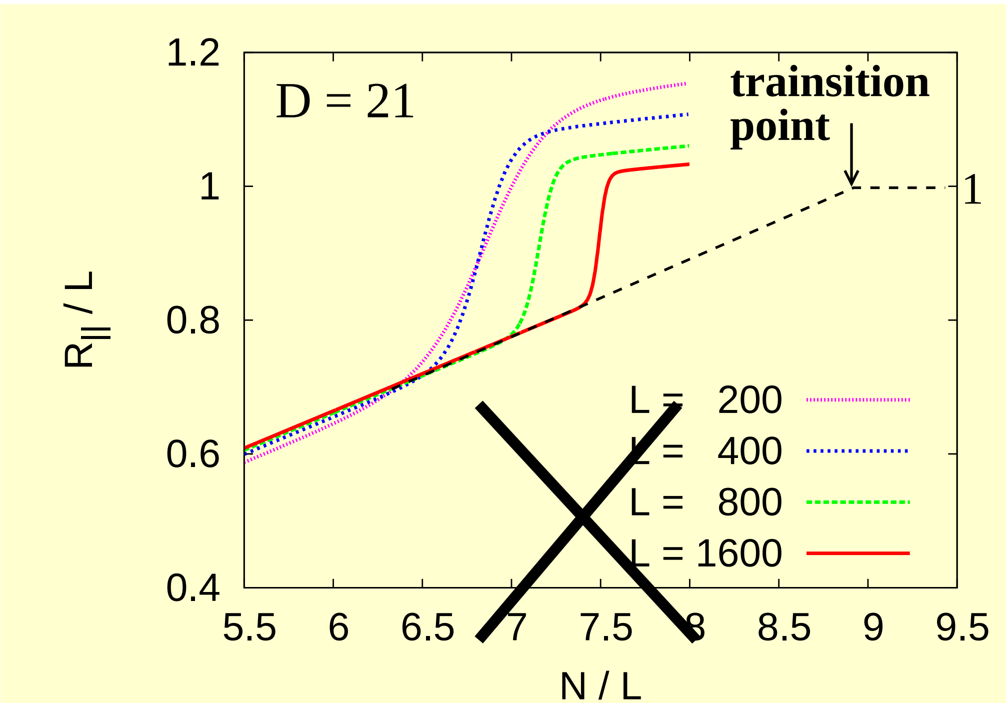
$$Z(N,L,D) = \frac{1}{M} \sum_k \sum_{\mathrm{config} \in C_{b_k}} W^{(k)}(N,L,D)$$

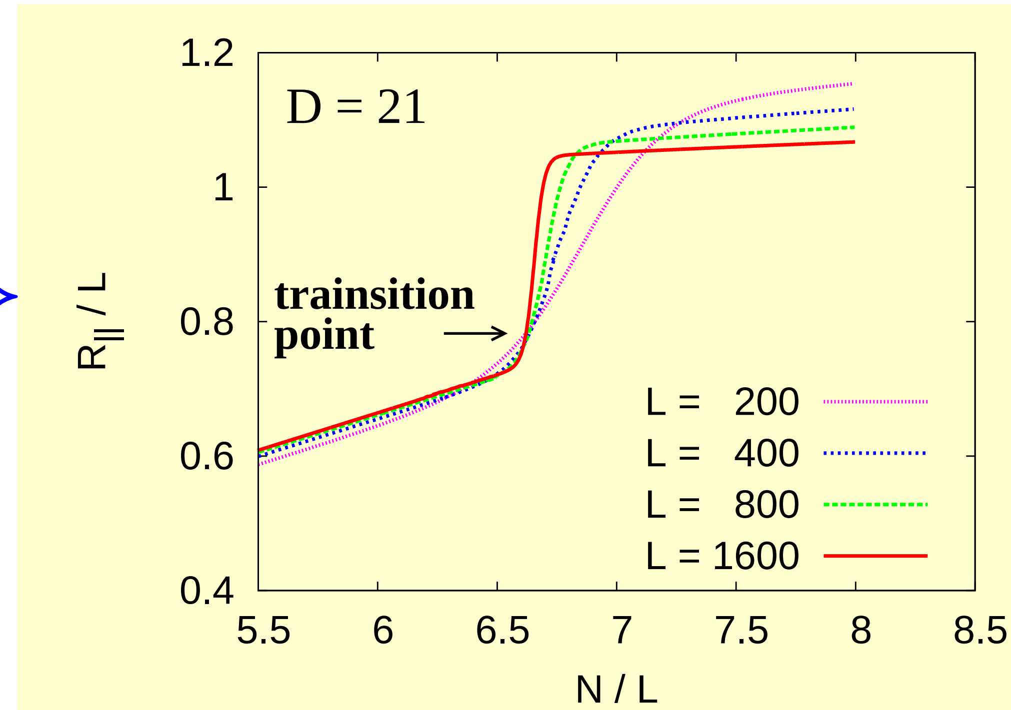
$$W^{(k)}(N,L,D) = \begin{cases} W_{b_k}(N,L,D)/b_k^{x_{N+1}-x_1} & , \ x_N \leq L \\ W_{b_k}(N,L,D)/b_k^{L} & , \ x_N > L \end{cases}$$

$b_k = \exp(\beta a F_k)$: stretching factor



End-to-end distance $R_{||}$





old

new

Performance of algorithms

$P(N, L, D, s)$ near the transition point imprisoned $\leftrightarrow$ escaped

- Partition sum (in the Landau theory approach):

$$Z(N, L, D) = \sum_s H(N, L, D, s)$$

with

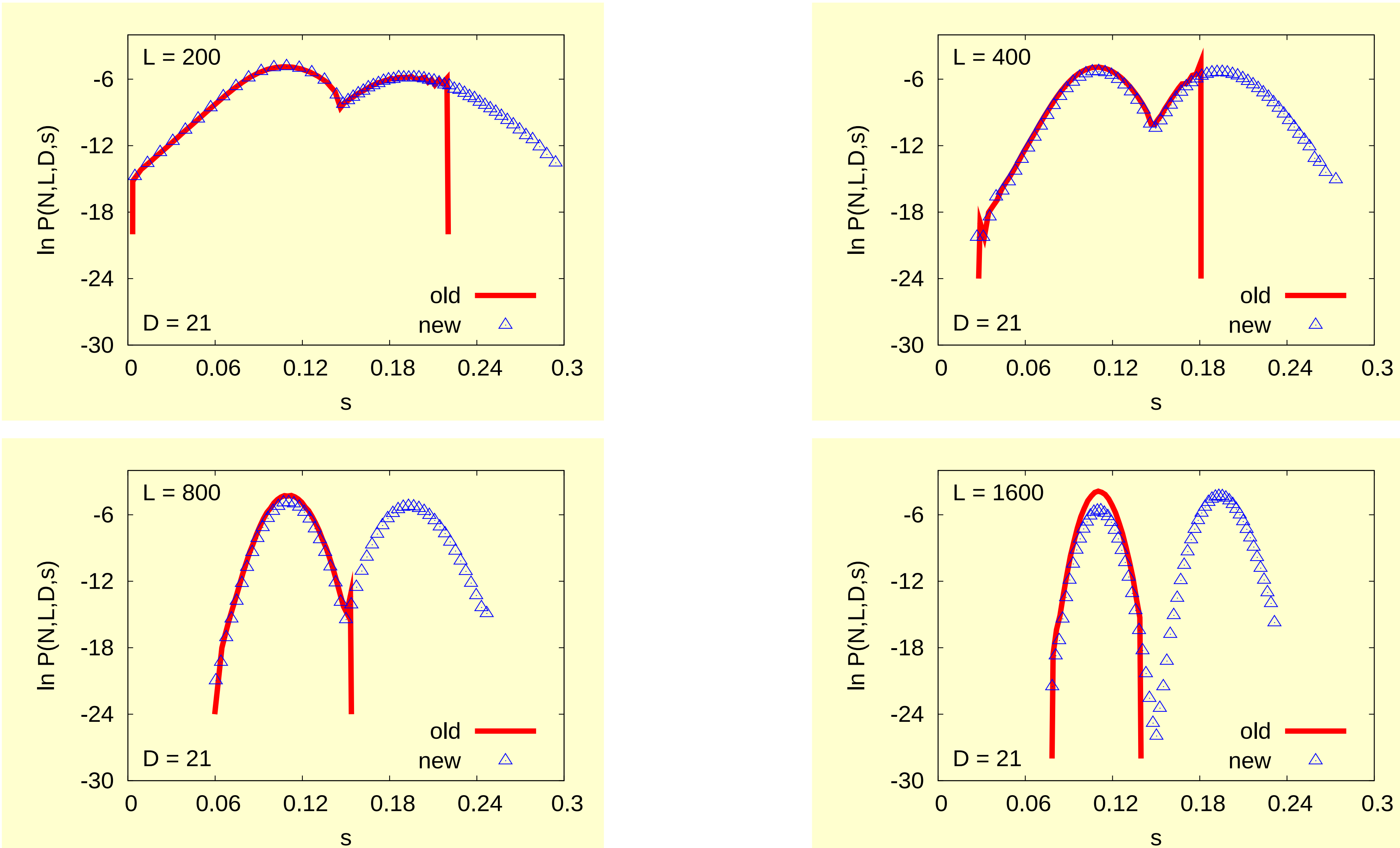
$$H(N, L, D, s) = \frac{1}{M} \sum_k \sum_{configs. \in C_{b_k}} W^k(N, L, D, s') \delta_{s,s'}$$

$\Rightarrow$ the distribution of the order parameter s

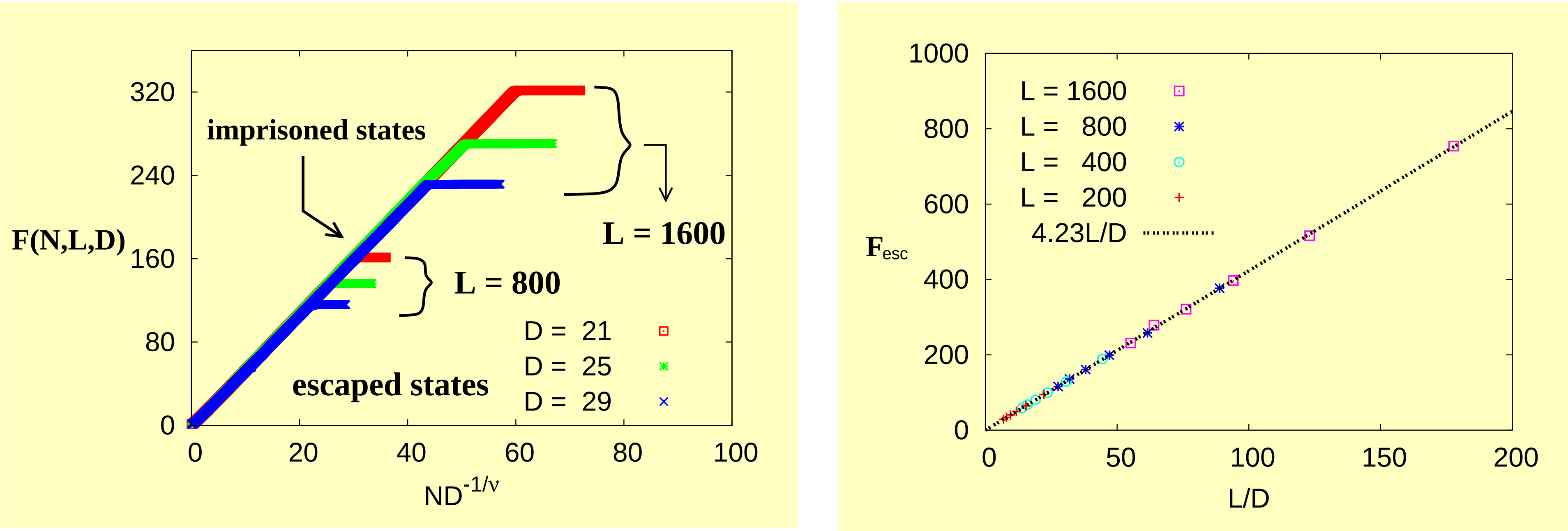
$P(N, L, D, s) \propto H(N, L, D, s)$ and $\sum_s P(N, L, D, s) = 1$

Performance of algorithms

$P(N, L, D, s)$ near the transition point imprisoned $\leftrightarrow$ escaped



Free energy $F(N, L, D)$



- Scaling:

$$F(N,L,D) = \begin{cases} F_{\mathrm{imp}} = 5.33(8) N D^{-1/\nu} , & \text{imprisoned state} \\ F_{\mathrm{esc}} = 4.23(6) L/D , & \text{escaped state} \end{cases}$$

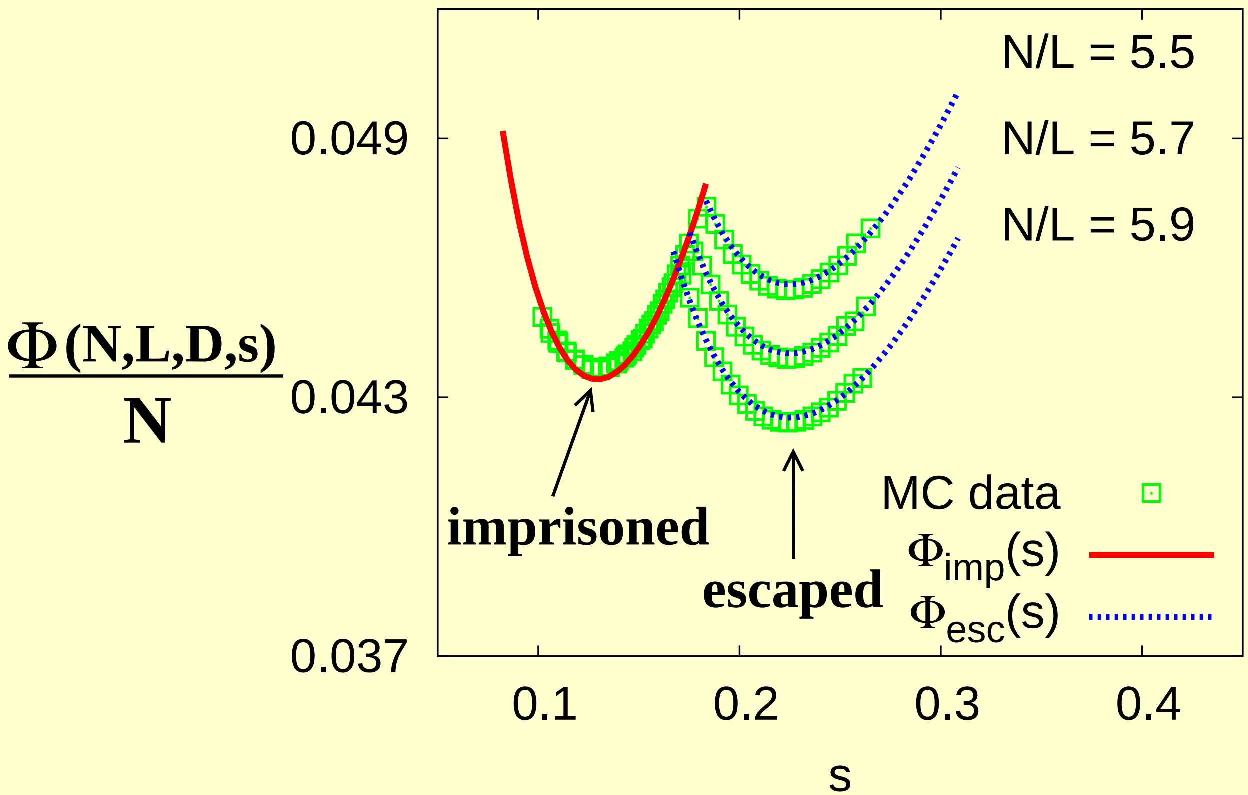
- Transition point:

$$F_{\mathrm{imp}} = F_{\mathrm{esc}} \Rightarrow \left(\frac{L}{N}\right)_{\mathrm{tr}} \sim 1.26(4) D^{1-1/\nu}$$

$\Phi(N, L = 1600, D = 17, s)$

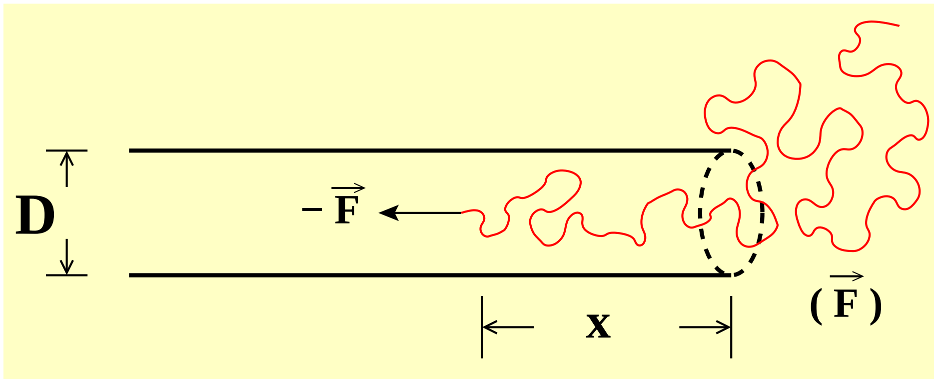
- Landau free energy: $\Phi(N, L, D, s) = -\ln\left(\frac{P(N,L,D,s)}{Z_1(N)}\right)$

  $Z_1(N)$: Partition sum of a grafted random coil



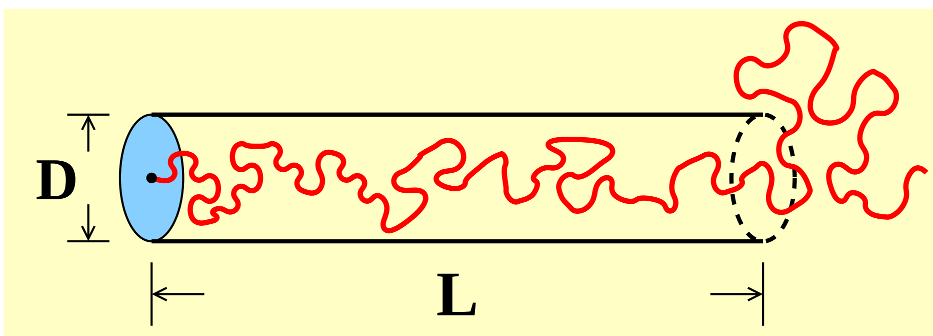
Two equivalent problems

- Dragging polymer chains into a tube



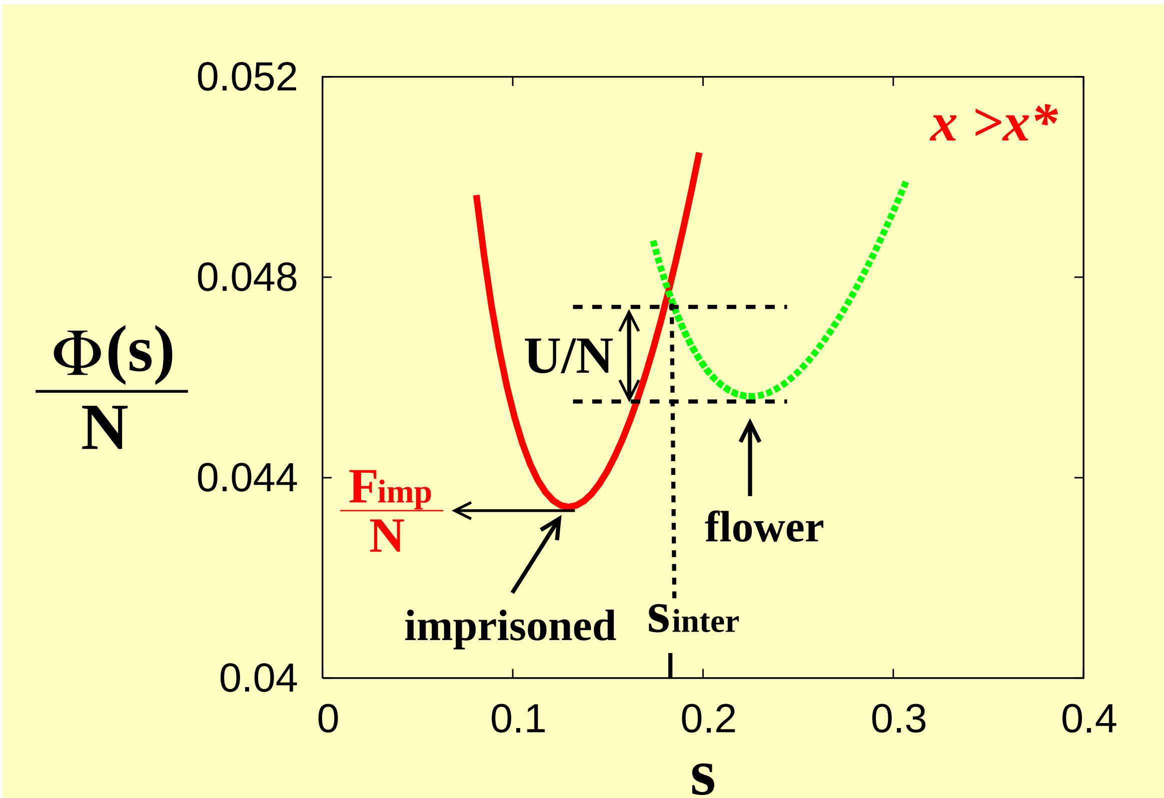
x "=" L

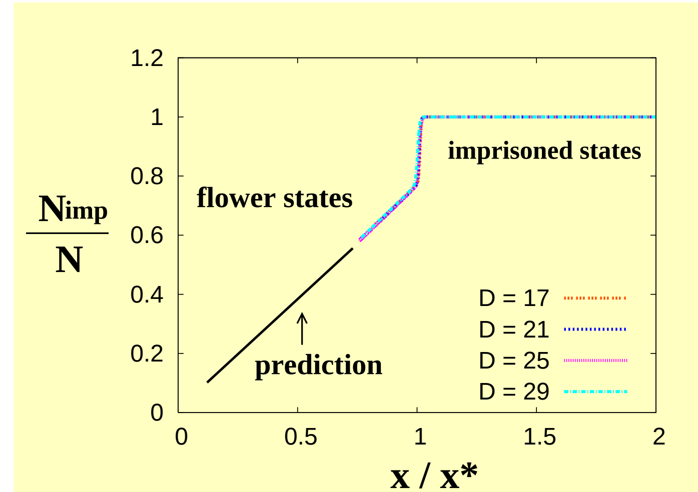
- Polymer chains escape from a tube



Metastable regions

- For $x > x^*$: $x = (L/N)\ , x^* = (L/N)_{\rm tr},\ n_b = N(D/a)^{-1/\nu}$

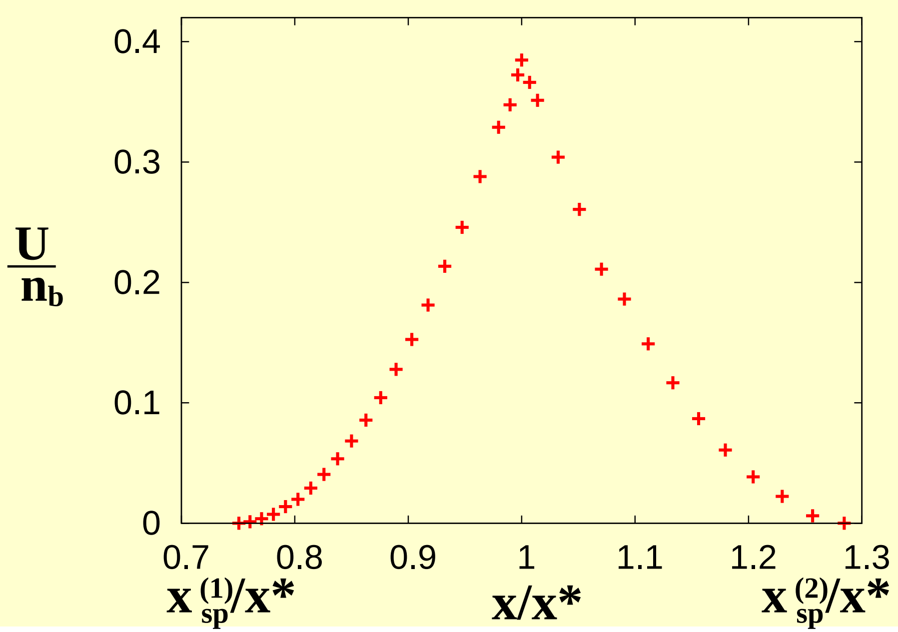


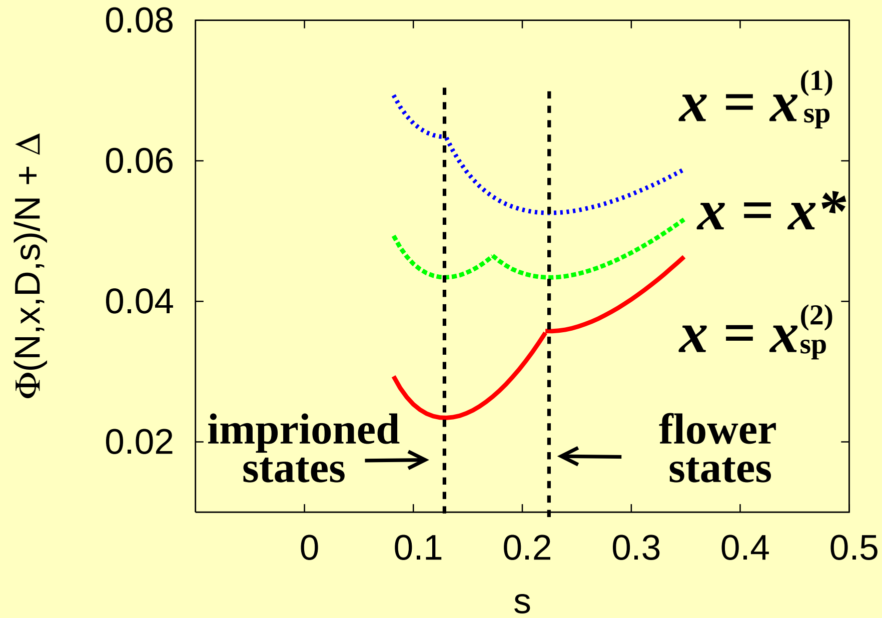


Imprisoned states (stable), flower states (metastable)

Metastable regions

- For $x > x^*$: $x = (L/N)$, $x^* = (L/N)_{\mathrm{tr}}$, $n_b = N(D/a)^{-1/\nu}$
  Imprisoned states (stable), flower states (metastable)
- Barrier height U & spinodal points x_{sp}:
  - $\frac{U}{n_b} - \frac{x}{x^*}$, independent of N and $D \Longrightarrow U_{\max} = 0.38 n_b k_B T$

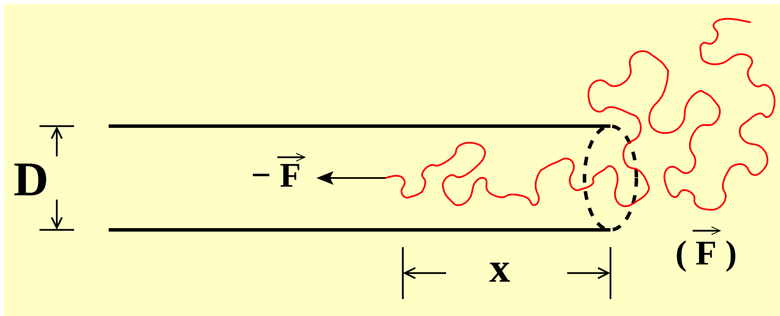




Lifetime of a metastable state

- Lifetime: $\tau_{\mathrm{ms}} = \tau_0 \exp(U/k_B T), \quad U = 0.38 n_b k_B T$

  τ_0: characteristic relaxation time, U: barrier height



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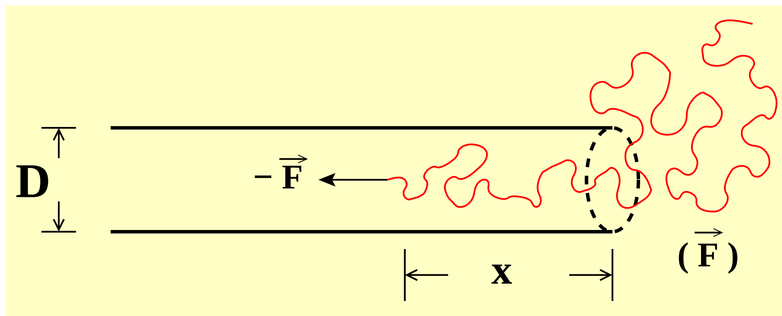

- Contour length $L = 16\mu m$, persistence length $a = 50nm$, tube diameter $D = 150nm$, characteristic relaxation time $\tau_0 \sim 1$ sec

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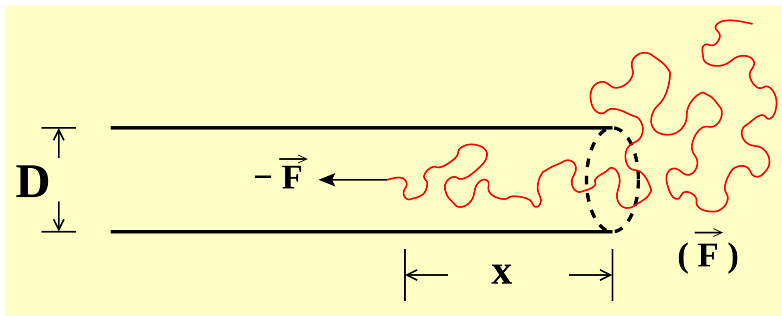

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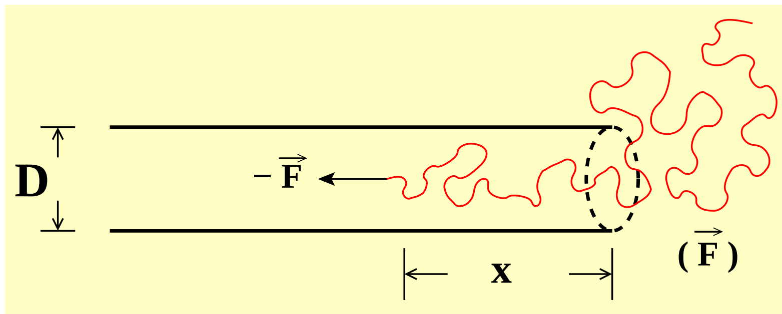

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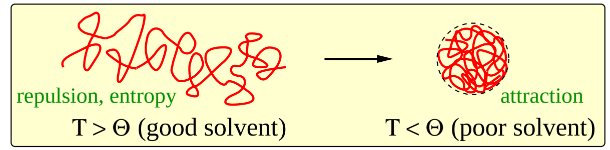
- $D = 300nm \Rightarrow n_b = 15$, $\tau_{\rm ms} \sim 5$ mins.

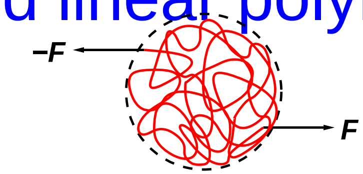
Summary

Polymer simulations with PERM

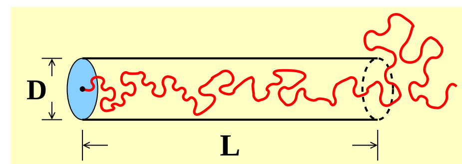
- Linear polymer chains in dilute solution under various solvent conditions



- Conformational change of stretched collapsed linear polymer chains under a poor solvent condition



- Single polymer chains fully/partially confined in a tube



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For low energy dense systems:

New PERM, *Hsu, Mehra, Nadler & Grassberger, J. Chem. Phys. 118, 444 (2003); Phys. Rev. E 68, 021113 (2003).*

"Multicanonical" PERM, *Bachmann & Janke, Phys. Rev. Lett. 91, 208105 (2003)*

"Flat" PERM, *Prellberg & Krawczyk, Phys. Rev. Lett. 92, 120602 (2004)*