Escape transition of grafted polymer chains from a cylindrical tube

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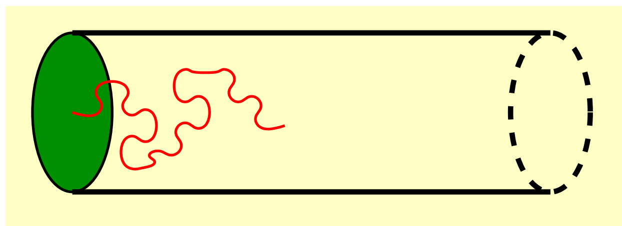
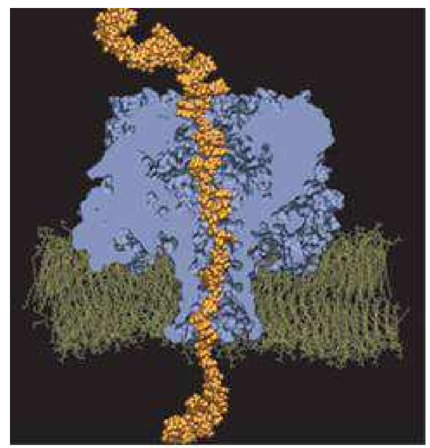
Motivations

- What is the order of the two-dimensional polymer escape transition? *Hsu et. al., Phys. Rev. E 76, 021108 (2007).*
  a weak first-order phase transition !
- The confinement/escape problem of polymer chains in cylindrical tubes of finite length



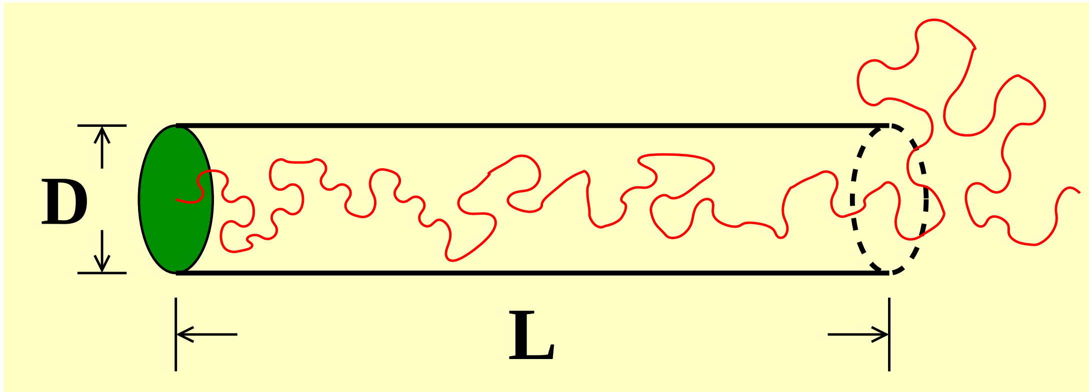
  - Polymer translocation through pores in membrane
  - DNA confined in artificial nanochannels



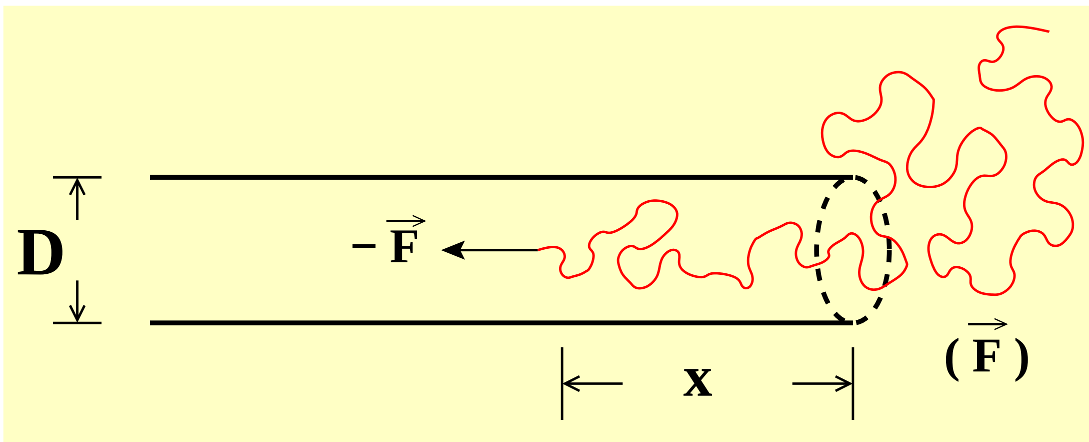
http://www.ks.uiuc.edu/ ale/

Two equivalent problems

- Polymer chains escape from a tube



- Dragging polymer chains into a tube



x "=" L

Theoretical predictions

Landau free energy approach

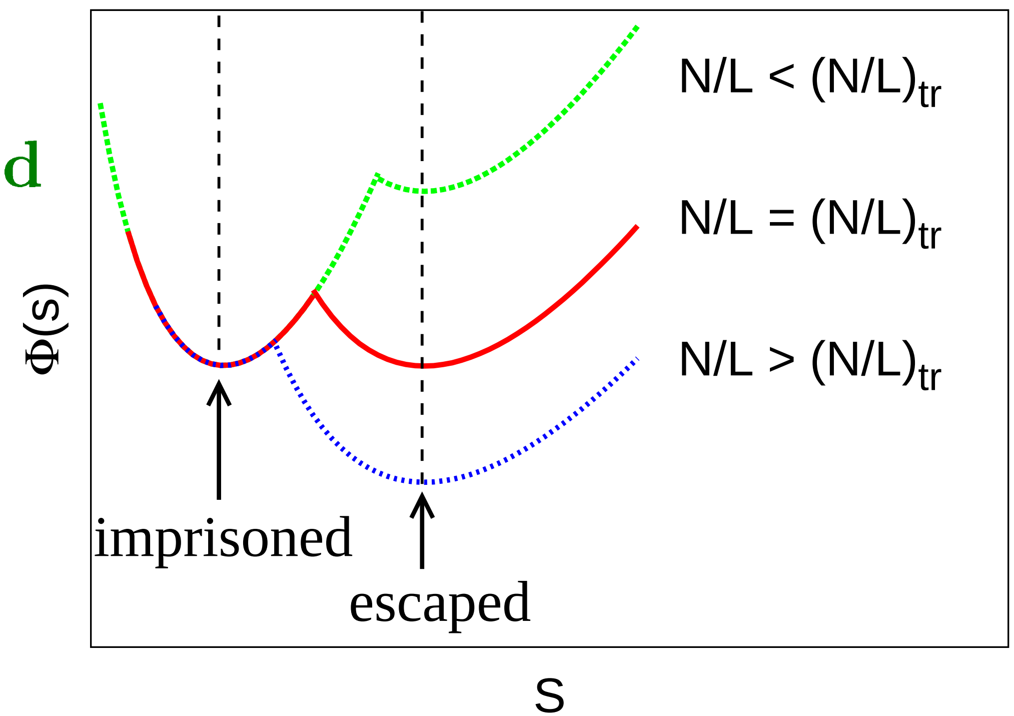
- Partition sum: $Z = \exp(-F) = \int dS \exp(-N\Phi(S))$

  F: free energy

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

  S: order parameter

$$S = \begin{cases} R_{||}/N & \text{, imprisoned} \\ L/N_{\text{imp}} & \text{, escaped} \end{cases}$$



$L \to \infty, N \to \infty, L/N$ finite

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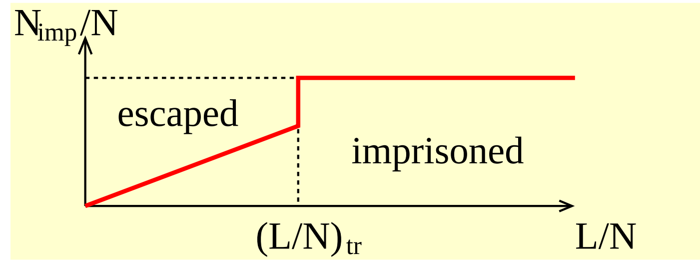
- Imprisoned monomers N_{imp}:

$$\Delta_N = \frac{N - N_{\mathrm{imp}}}{N} \approx 0.22$$

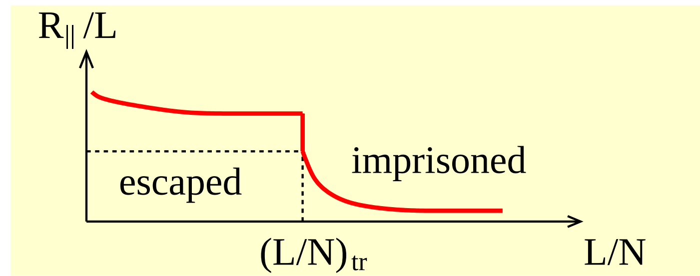
$$\Delta_N = 0.055 \ \ (2D)$$



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

$$\Delta_{R_{||}} = \frac{L - R_{||}}{L} \approx 0.247$$

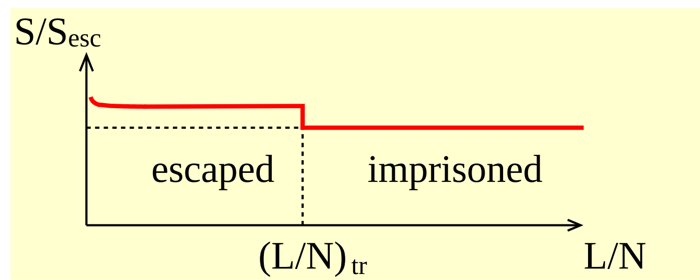
$$\Delta_{R_{||}} = 0.0572 \ \ (2D)$$



- Landau order parameter $S = S_{eq}$:

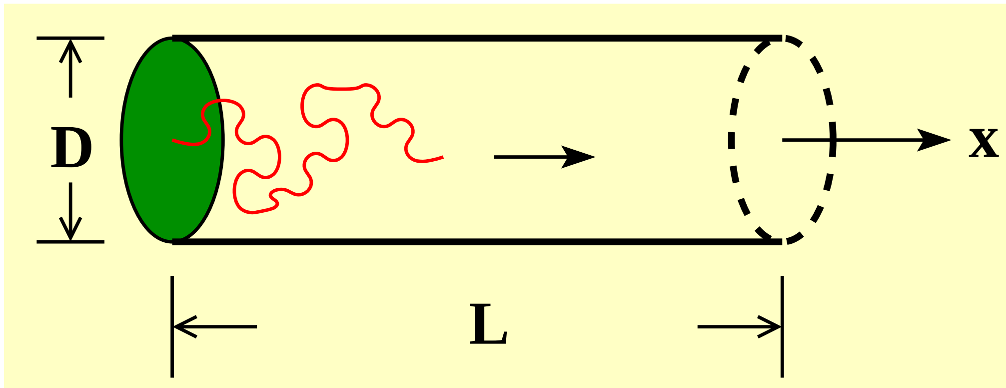
$$\Delta_S = \frac{S_{\mathrm{esc}} - S_{\mathrm{imp}}}{S_{\mathrm{esc}}} \approx 0.41$$

$$\Delta_S = 0.1091 \ \ (2D)$$



Simulations

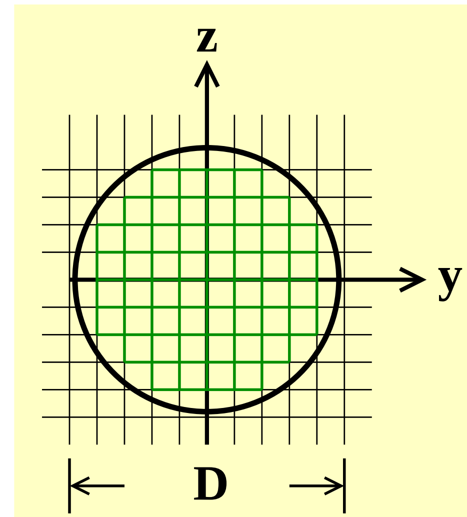
- Model: Self-avoiding random walks on a simple cubic lattice



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

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

  Hsu & Grassberger, Eur. Phys. J. B 36, 209 (2003))

Polymers confined in a "∞"-tube

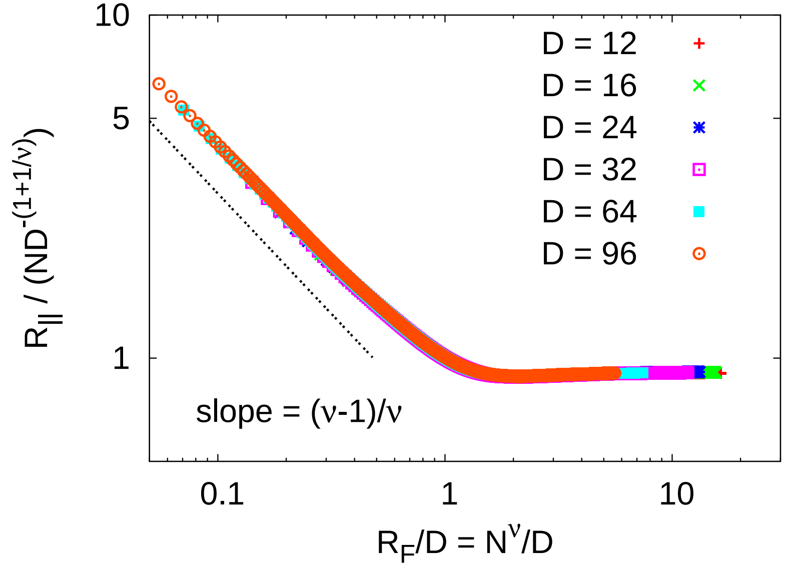
- End-to-end distance $R_{||}(N, D)$:

  $R_{||}(N, D) = R_F \Psi_R(R_F/D)$,

  $R_F \sim N^{\nu}$: Flory radius

  - For $1 \ll D \ll R_F$

    $R_{||} \sim 0.9 N D^{-1+1/\nu}$



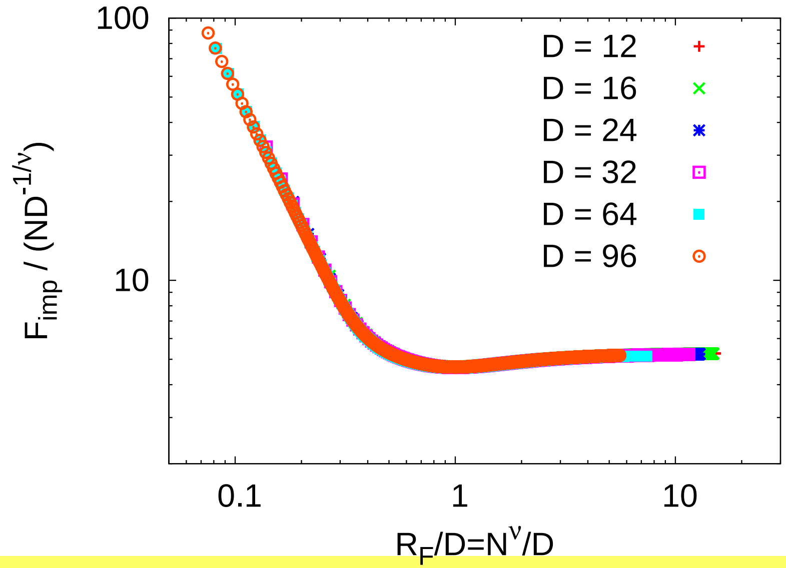
- Free energy $F_{\text{imp}}(N, L, D)$:

  $Z(N, D) = Z_1(N) \Psi_z(R_F/D)$,

  $F_{\text{imp}} = -\ln\left(\frac{Z(N,D)}{Z_1(N)}\right)$

  - For $1 \ll D \ll R_F$

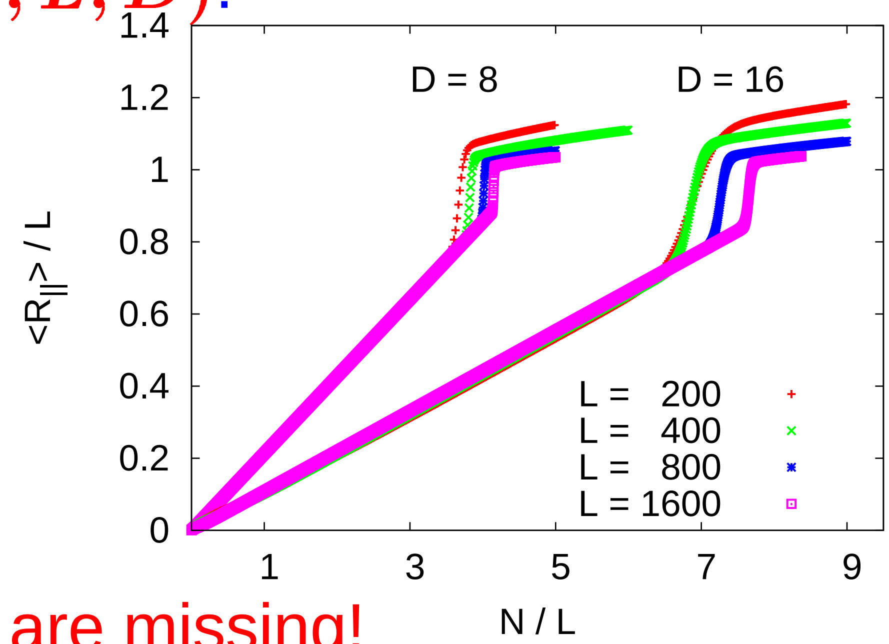
    $F_{\text{imp}} \sim 4.83 N D^{-1/\nu}$



Polymers confined in a tube of L

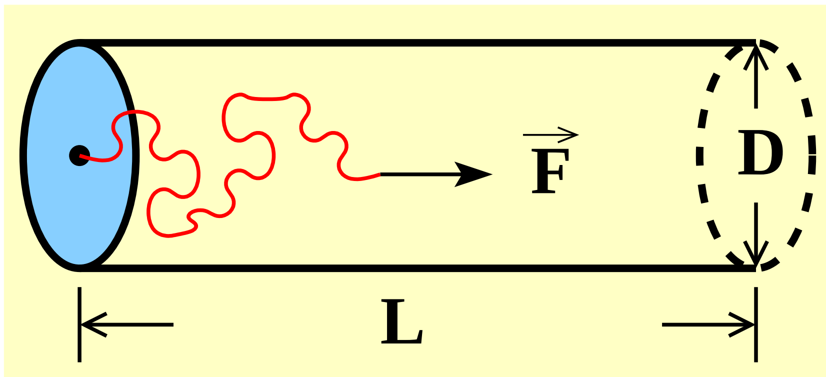
- End-to-end distance $R_{||}(N, L, D)$:

  $R_{||}/L$ vs. N/L



  Some of the escape states are missing!

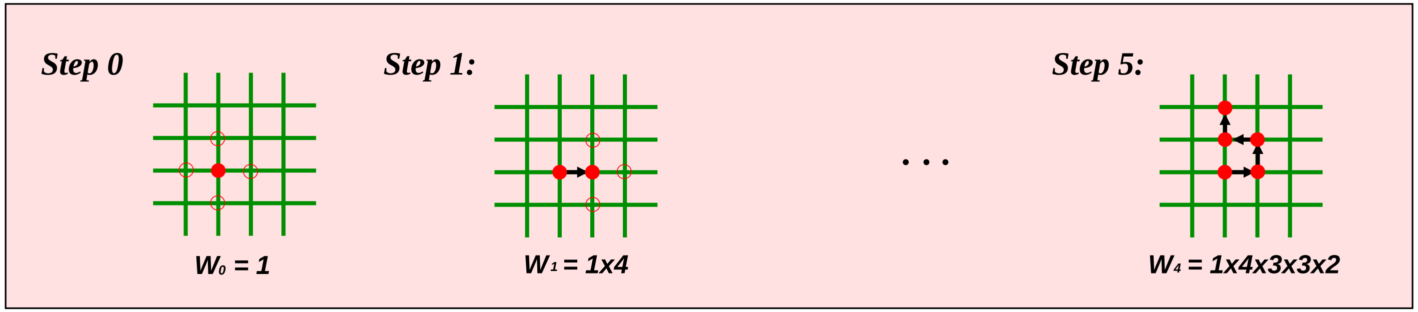
- New strategy:



Algorithm: PERM

PERM=Pruned-enriched Rosenbluth method

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



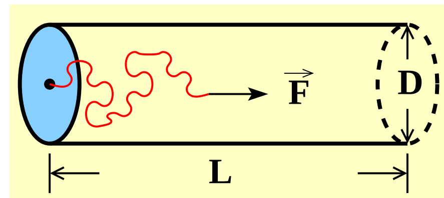
($P_{n,i}$: the selection probability for the ith direction)

- Each sample configuration carries its own weight
  $W_n = \Pi_{j=1}^{n} w_j = W_{n-1} w_n$, $w_j \rightarrow w_j / P_{j,i}$
- Partition sum of a chain of length N:
  $\hat{Z}(N) = M^{-1} \sum_{\alpha=1}^{M} W_N(\alpha)$, M: total trial # of config.

Biased SAW

- Partition sum: $Z_b(N,L,D) = \sum_{walks} b^x$
  $$(= \frac{1}{M_b} \sum W_b(N,L,D))$$
  $b = \exp(\beta a F_s)$: stretching factor, F_s:stretching force,
  $\beta = 1/k_B T$, x: end-to-end distance $|| \vec{F}_s$

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

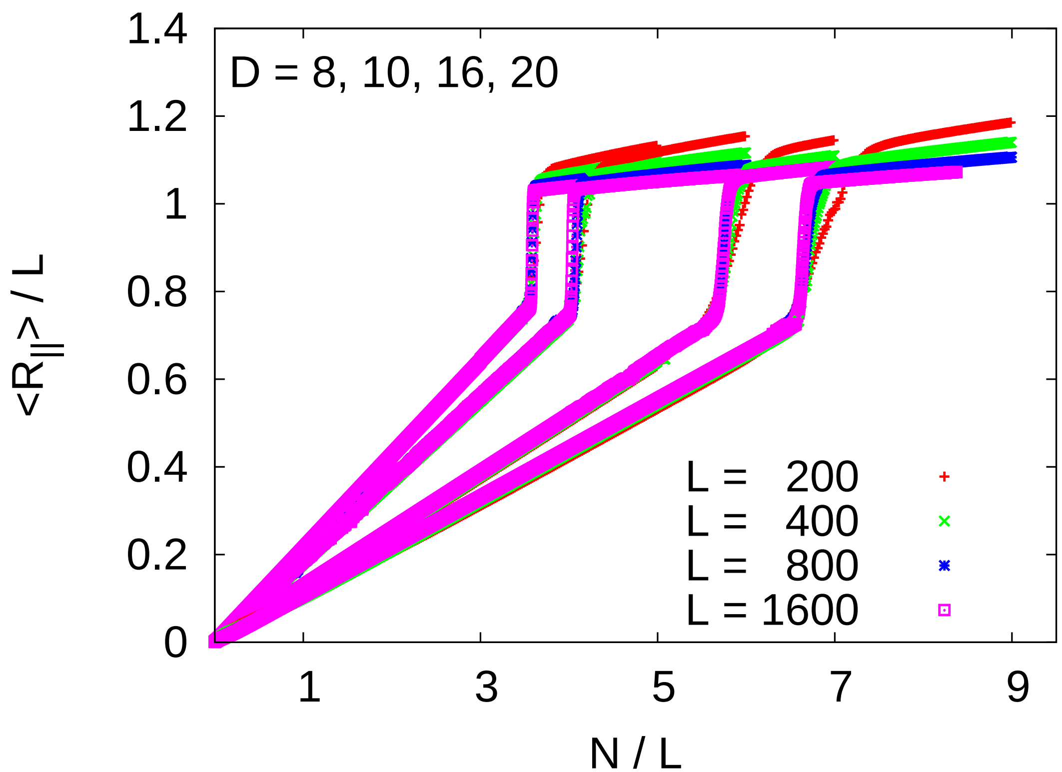


- For a biased SAW of N steps, the unbiased weight

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

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

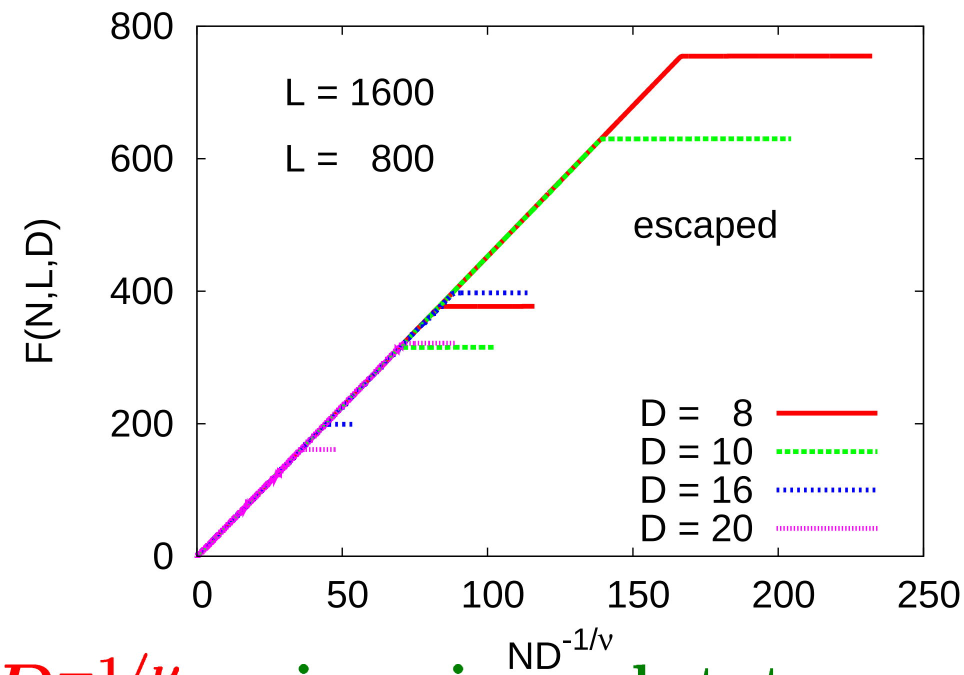
- $< R_{||} > /L$ vs. N/L



- $\Delta_{R_{||}} \approx 0.247$ (prediction)

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

- $F(N,L,D) = -\ln\left(\frac{Z(N,L,D)}{Z_1(N)}\right)$
- F vs. $N/D^{1/\nu}$



- Scaling:

$$F(N,L,D) = \begin{cases} F_{\text{imp}} = 4.83 D^{-1/\nu}\,, & \textbf{imprisoned state} \\ F_{\text{esc}} = 4.05 L/D\,, & \textbf{escaped state} \end{cases}$$

- Transition point:

$$F_{\text{imp}} = F_{\text{esc}} \Rightarrow \left(\frac{N}{L}\right)_{tr} \sim 0.83 D^{-1+1/\nu}$$

Landau free energy $\Phi(S)$

$$(Z = \exp(-F) = \int dS \exp(-N\Phi(S)))$$

- Theoretical prediction:

$$\Phi(S) = \begin{cases} \Phi_{\text{imp}}(S) = D^{-1/\nu} A(u^{-\alpha} + Bu^{\delta} + C) & , S \leq L/N \\ \Phi_{\text{esc}}(S) = \frac{L}{N}\frac{A}{D}\left(\frac{u^{-\alpha}+Bu^{\delta}+C)}{u}\right) & , S \geq L/N \end{cases}$$

$\alpha = \frac{1}{3\nu-1}$, $\delta = \frac{1}{1-\nu}$,

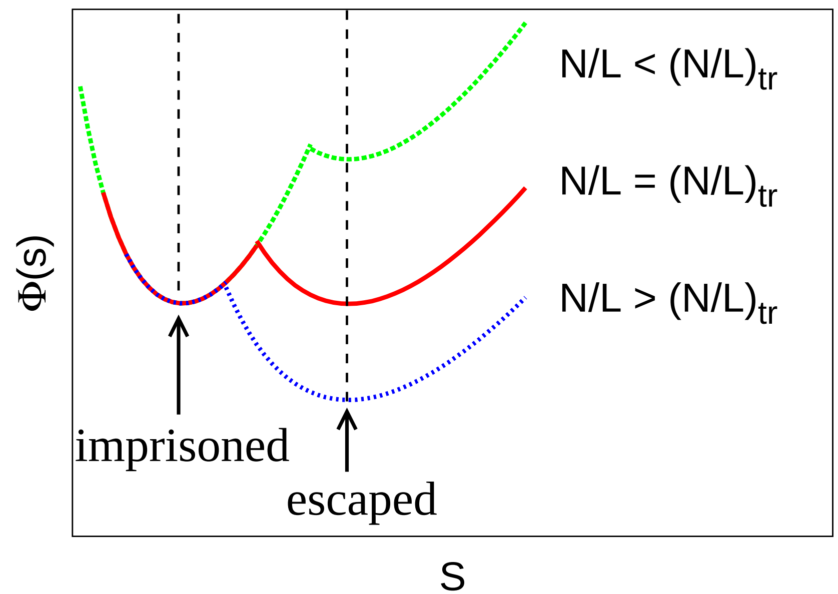
$u = SD^{-1+1/\nu}$, $\nu = 0.588$

A, B, C: coefficients

$A \approx 1.17$

$B \approx 0.80$

$C \approx 2.36$



MC simulations

- Landau free energy $\Phi(N, L, D, S)$

$$\Phi(N, L, H, s) = -\ln \frac{1}{N} \left(\frac{P(N,L,H,S)}{Z_1(N)} \right)$$

$Z_1(N)$: Partition sum of a one-end grafted chain

- Histogram of the order parameter S:

$$P(N, L, H, s) = \sum_{walks} \delta_{S,S'}$$

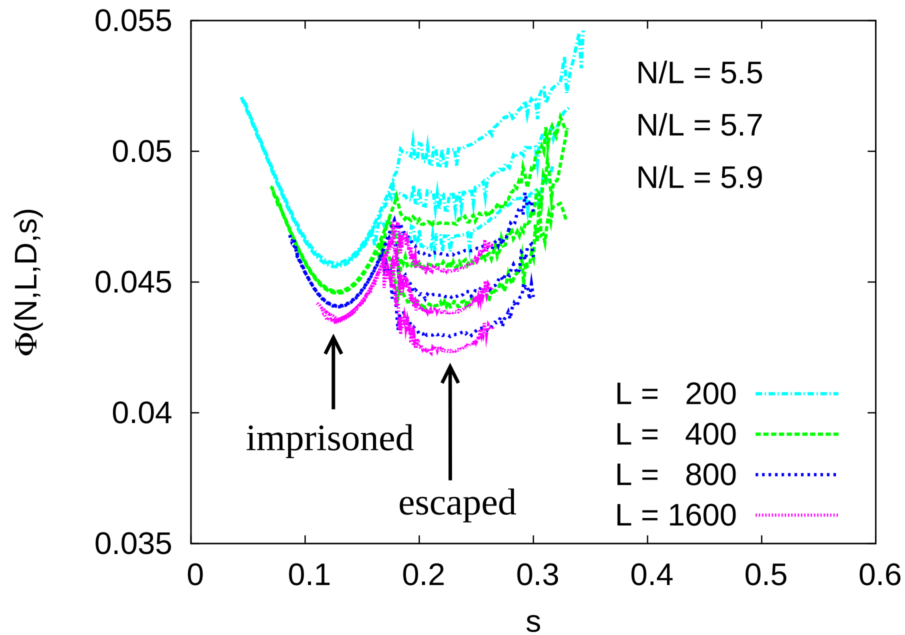
- Partition sum of a partially confined chain: $Z(N, L, H)$

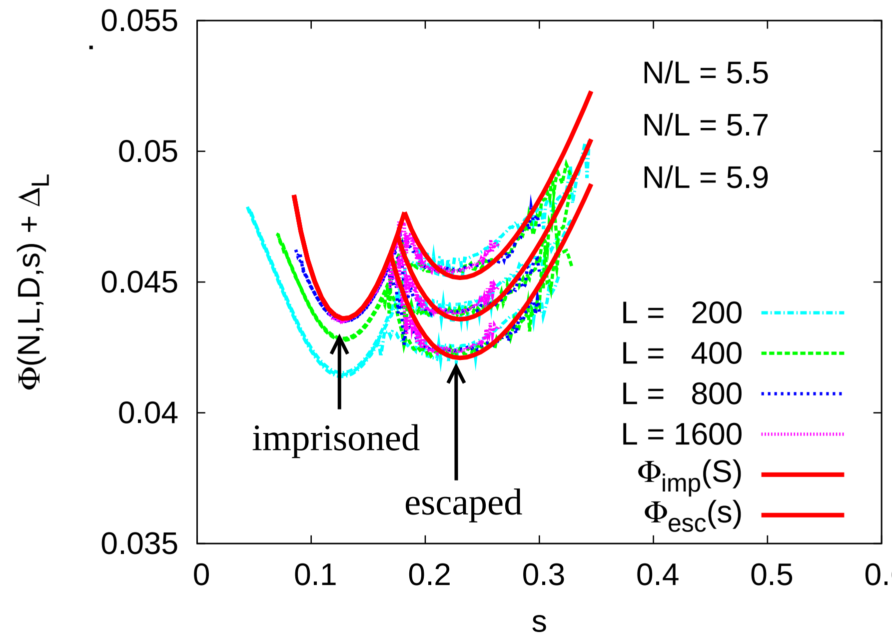
$$Z(N, L, H) = \sum_{s} P(N, L, H, s)$$

Combining data from different runs with bias b

Results $(D = 16)$

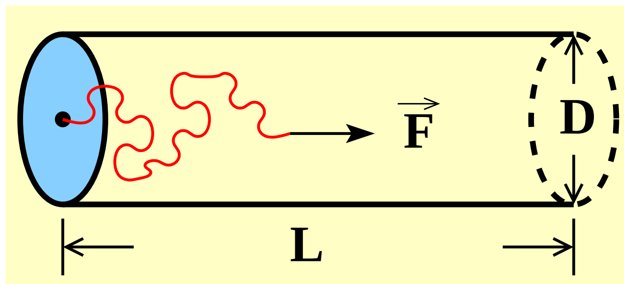
- $\Phi(N, L, D, S)$ vs. S
- $\Phi(N, L, D, S) + \Delta_L$ vs. S
- Theoretical predictions: $\Phi_{\mathrm{imp}}(N, L, D, S)$, $\Phi_{\mathrm{esc}}(N, L, D, S)$





Conclusions

- Theoretical predictions based on the Landau free energy approach are given and verified by MC simulations
- A new strategy is proposed for studying first-order transition



  - Check the scaling laws : free energy F_{imp}, F_{esc}, end-to-end distance R_{imp}
  - Determine the escape transition point: $(N/L)_{tr} \sim 0.83 D^{-1+1/\nu}$
- Further check by experiments