What is the order of $2d$ escape transition?

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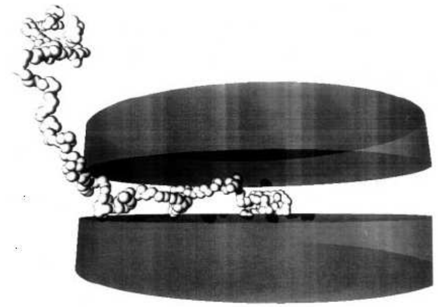
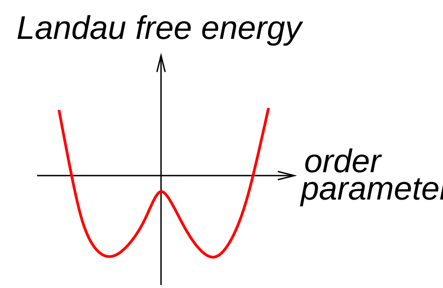
Motivations

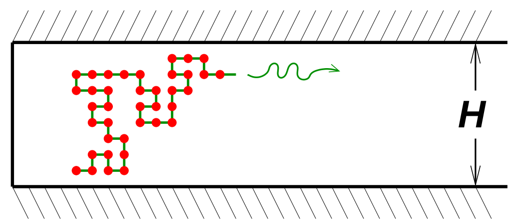
- $3d$ escape transition of a compressed end-grafted chain
  - Polymer chain: first-order
    Milchev et. al., MC simulation
    Europhys. Lett. 47, 675 (1999)



  - Gaussian chain: first-order
    Skvortsov et. al., Landau theory
    Europhys. Lett. 58, 292 (2002)

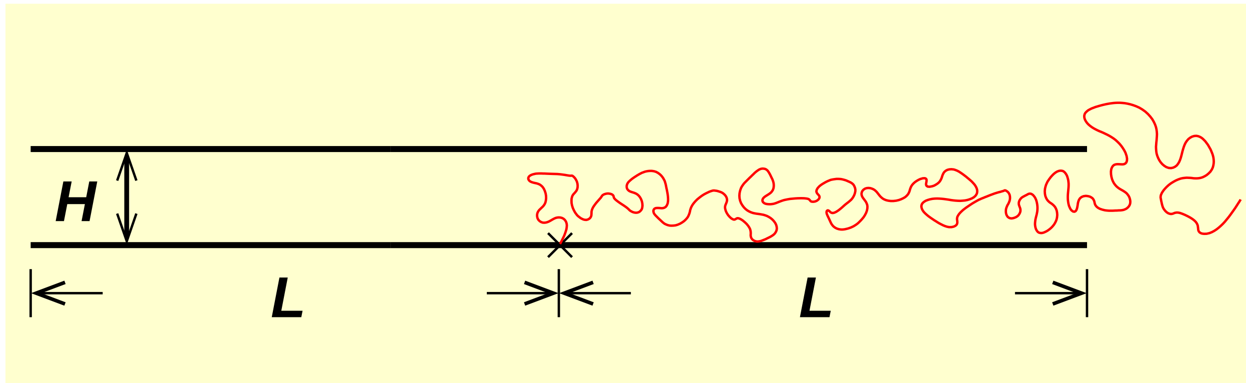


- $2d$ long polymer chains confined in a strip
  Hsu & Grassberger, PERM
  Eur. Phys. J. B36, 209 (2003)



- What is the order of escape transition in $2d$???

Outline



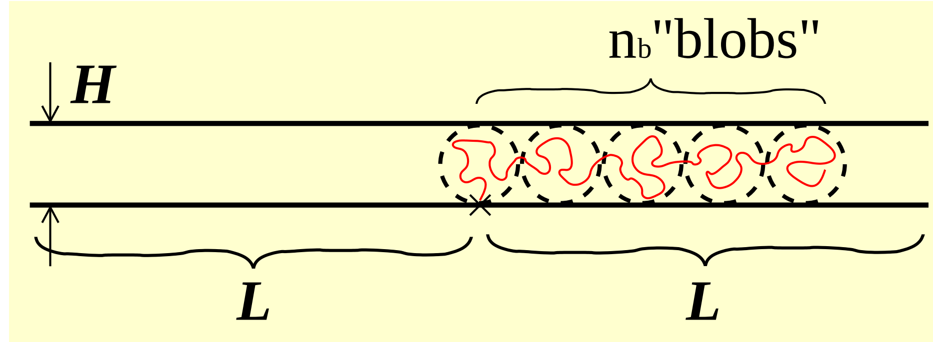
- Theoretical predictions
  - Blob picture
  - Landau theory
- Monte Carlo simulation:

  Algorithm: Pruned-enriched Rosenbluth method PERM
- Conclusions

Blob picture

- Imprisoned chains
  - End-to-end distance:

    $R = n_b(2r_b) = n_b H$



within a blob, SAW

$H = an^{\nu} = 2r_b\ ,\ \ \nu = 3/4$

$\Rightarrow n = (H/a)^{4/3}$ and $n = N/n_b$

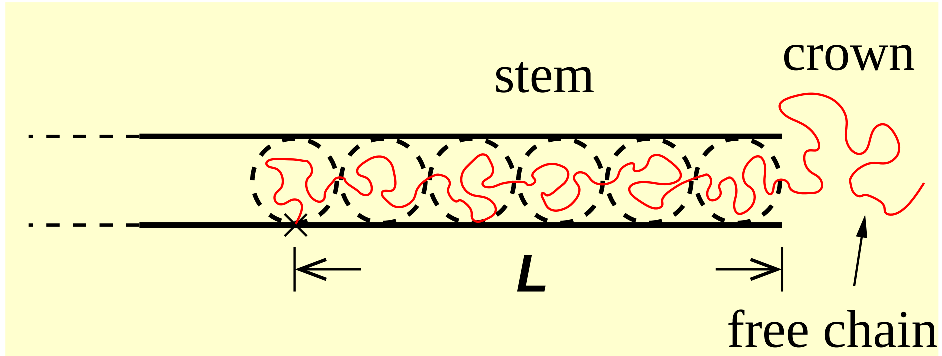
$R/a = N(H/a)^{-1/3}$

$H \sim R_{\text{free}} = aN^{\nu} \Rightarrow R/a = N^{\nu}$ (mushroom)

  - Free energy: each blob contributes $k_B T$

    $F_{\text{impr}} = n_b[k_B T] = N(H/a)^{-4/3}$

- Escape transition at $N = N^*$, $R = L$
- Escaped chains



  - End-to-end distance:
    $R_{\text{esc}} = L + a(N - N^*)^{3/4}$

    stem: N^* monomers

    crown: $N - N^*$ monomers
  - Free energy: $F_{\text{impr}} = N^*(H/a)^{-4/3}$
- Landau order parameter for the stretching, s

$$s = \begin{cases} R/Na & , \text{ imprisoned chain } (N < N^*) \\ L/N^*a & , \text{ escaped chain } (N > N^*) \end{cases}$$

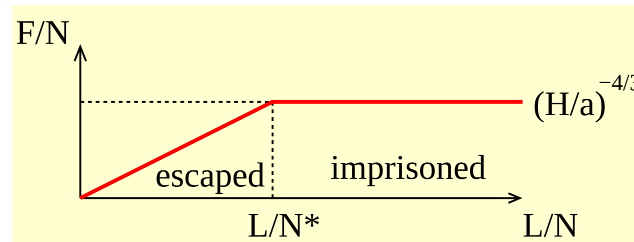
Skvortsov et. al., Europhys. Lett. 58, 292 (2002)

In the thermodynamic limit

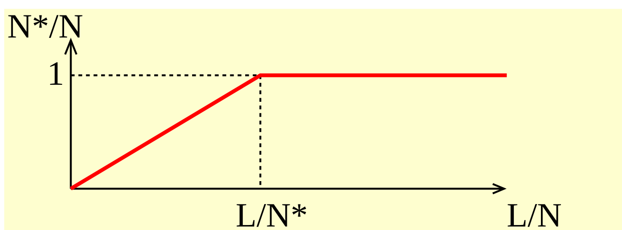
$L \to \infty$, $N \to \infty$,

L/N finite

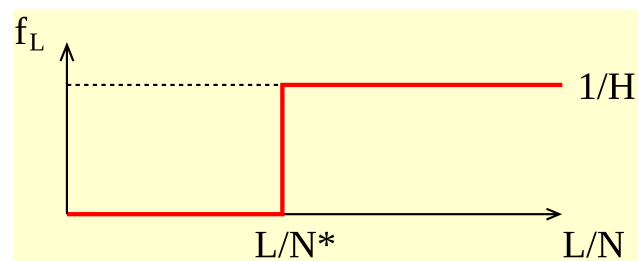
- Free energy F



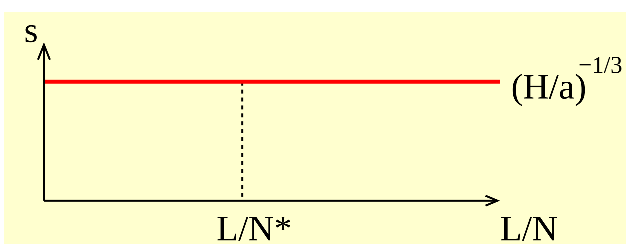
- Imprisoned monomers N^*



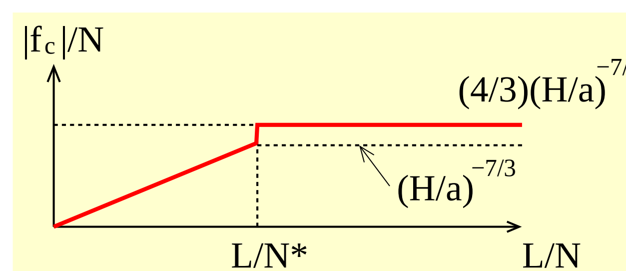
- Lateral force $f_L = \left(\frac{\partial F}{\partial L}\right)_H$



- Landau order parameter s



- Compression force $f_c = \left(\frac{\partial F}{\partial H}\right)_L$



Landau theory

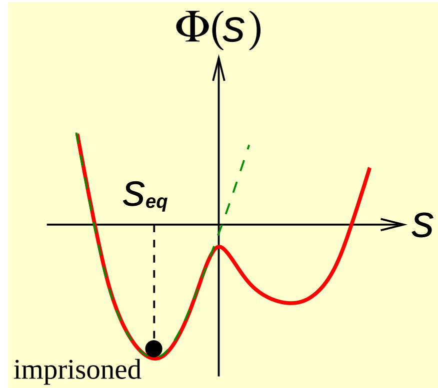
- Partition sum: $Z = \exp(-F) = \int ds \exp(-\Phi(s))$

  $\Phi(s)$: free energy function, $\frac{d\Phi(s)}{ds} = 0 \Rightarrow s_{\mathrm{eq}}$

  - Imprisoned chains $(s = \frac{R}{Na} < \frac{L}{Na})$

    $$\Phi_{\mathrm{impr}}(s) = N\left[A\left(\frac{a}{sH}\right)^2 + Bs^4\right]$$

    A and B: coefficients

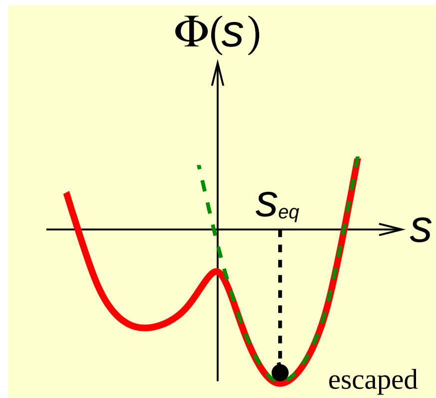


  - Escaped chains $(s = \frac{L}{N^*} > \frac{L}{Na})$

    $$\Phi_{\mathrm{esc}}(s) = N^*\left[A\left(\frac{a}{sH}\right)^2 + Bs^4\right]$$

    $$= \frac{L}{a}\left[A\left(\frac{a}{H}\right)^2 s^{-3} + Bs^3\right]$$

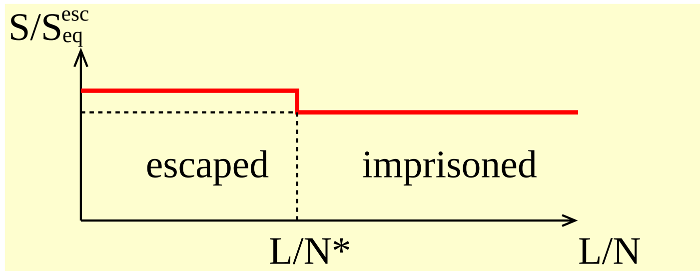
    N^*: imprisoned monomers



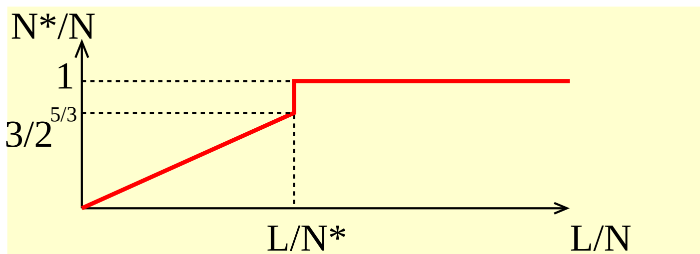
$L \to \infty, N \to \infty, L/N$ finite

- Landau order parameter $s = s_{eq}$:

$$s = \begin{cases} R/N = (A/2B)^{1/6}(a/H)^{1/3} & \text{, imprisoned chain} \\ L/N* = (A/B)^{1/6}(a/H)^{1/3} & \text{, escaped chain} \end{cases}$$

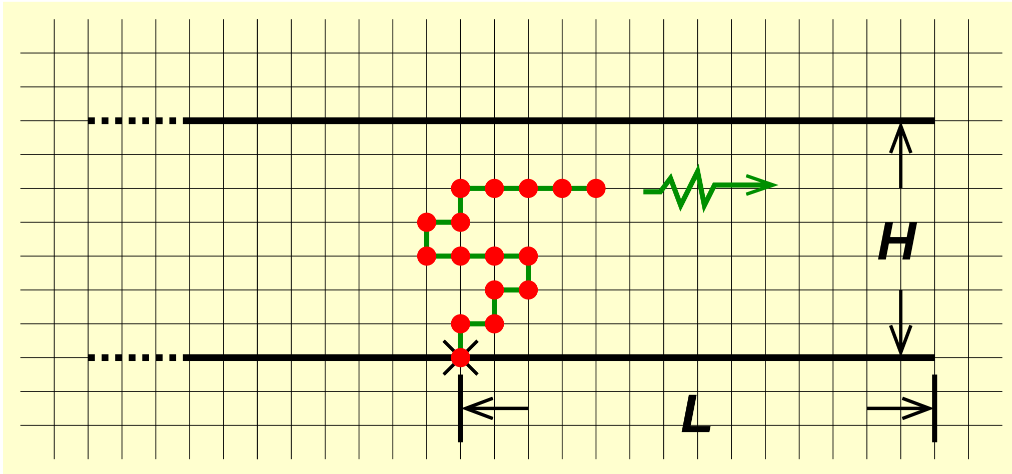


- Imprisoned monomers $N*$:



Simulations

- Model:

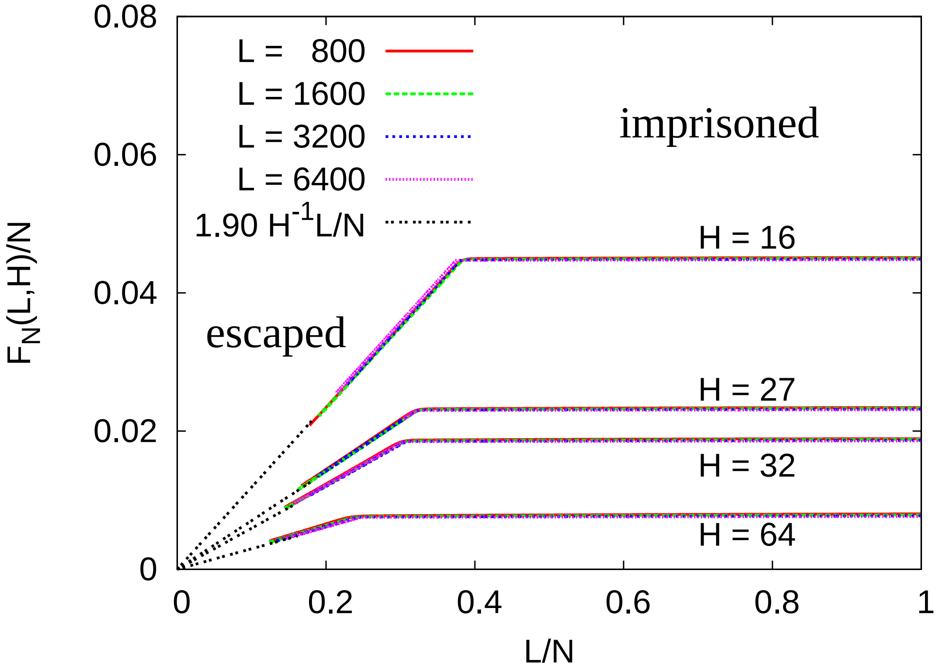


- Algorithm: PERM with $k-$step Markovian anticipation
  Hsu & Grassberger, Eur. Phys. J. B36, 209 (2003)
- Physical quantities:
  - Free energy F, end-to-end distance x, Landau order parameter s (Blob picture)
  - Landau order parameter s, Landau free energy $\Phi(s)$ (Landau theory)

Free energy $F_N(L, H)$

- $F_N(L, H)/N$ vs. L/N

$$\frac{F_N(L,H)}{N} = \begin{cases} 1.93(2) H^{-4/3}\,, & \text{imprisoned chain} \\ 1.90(5) \frac{L}{N} H^{-1}\,, & \text{escaped chain} \end{cases}$$



Blob picture ✓

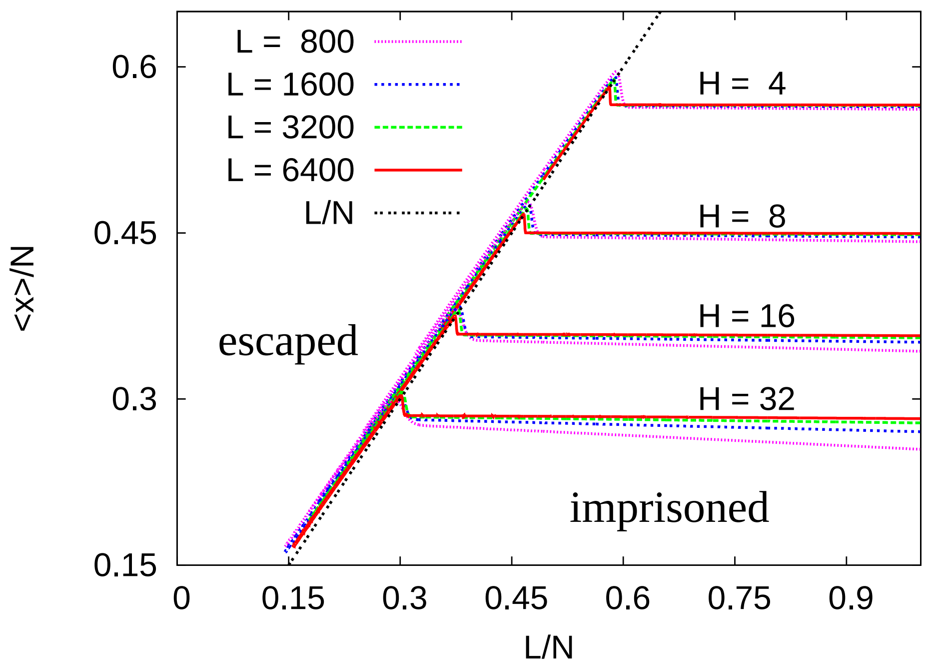
Transition point:

$$F_N^{\mathrm{esc}}(L, H) = F_N^{\mathrm{impr}}(L, H)$$

End-to-end distance $< x >$

- $< x > /N$ vs. L/N

$$\frac{< x >}{N} = \begin{cases} 0.915 H^{-1/3} & \text{, imprisoned chain} \\ \frac{L}{N} + \frac{a(N-N^*)}{N} H^{3/4} & \text{, escaped chain} \end{cases}$$



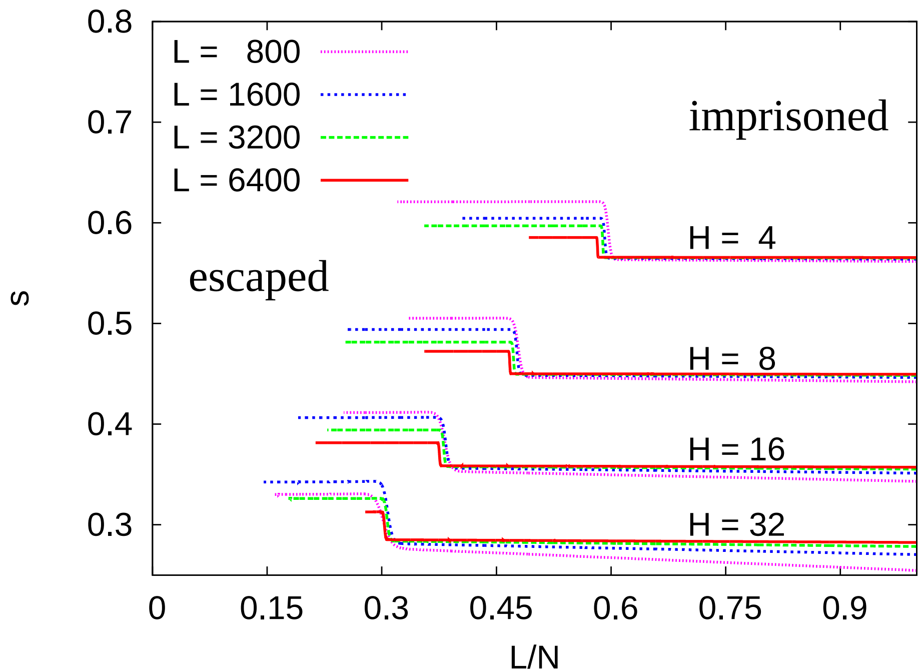
Blob picture ×

N^*: imprisoned monomers

Landau order parameter s

- $< s >$ vs. L/N

$$s = \begin{cases} R/N & , \text{imprisoned chain} \\ L/N^* & , \text{escaped chain} \end{cases}$$

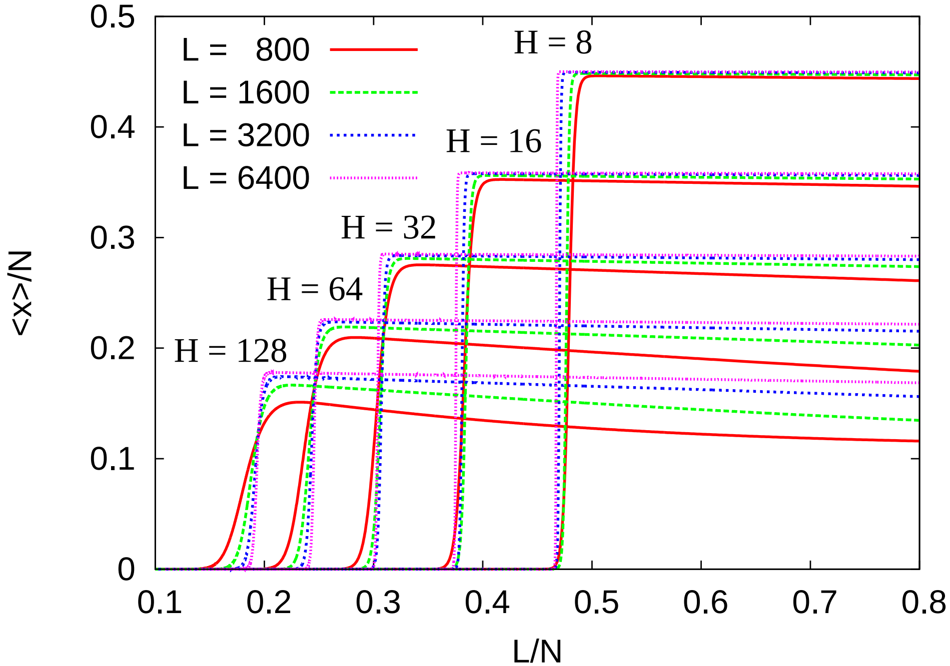


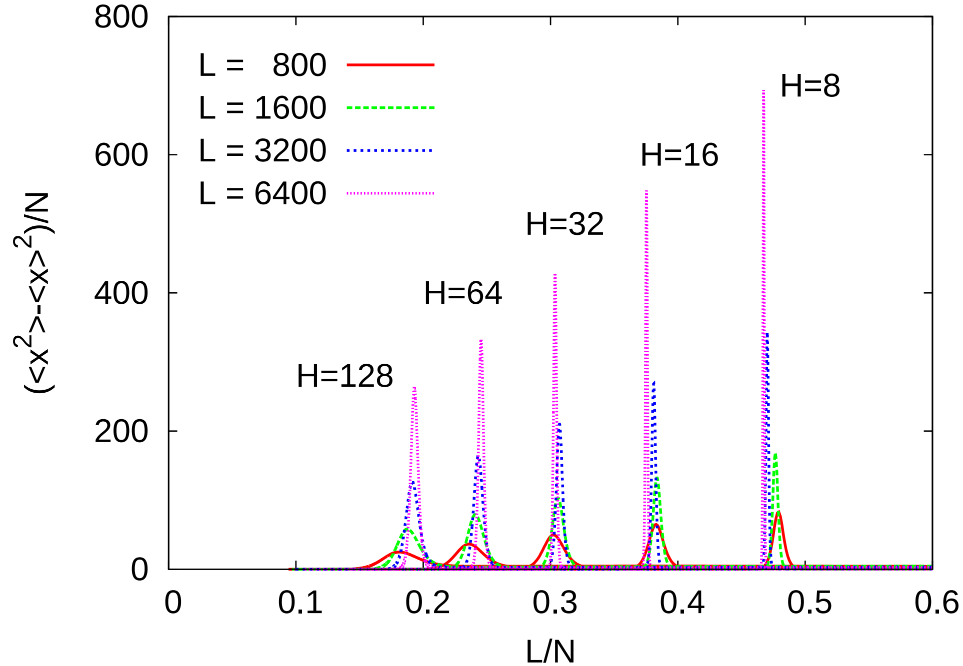
Blob picture ×

Landau theory ✓

Escape transition points

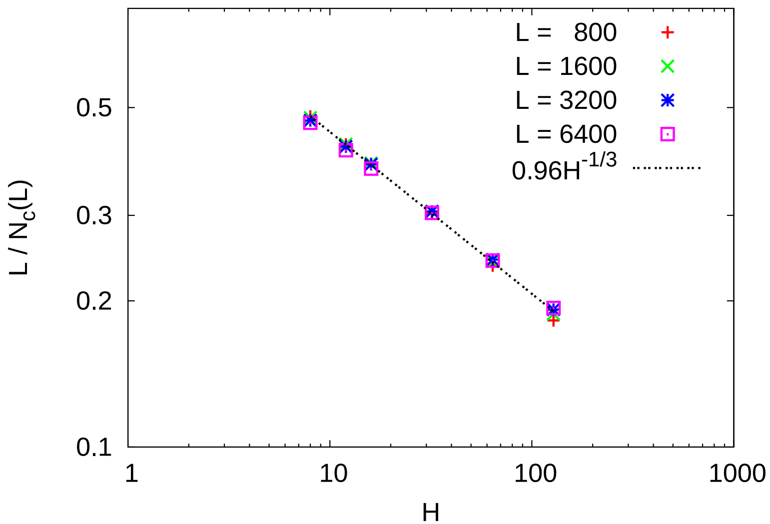
- End-to-end distance of imprisoned chains, x
  - $< x > /N$ vs. L/N, $< x > /N \sim H^{-1/3}$
  - $(< x^2 > - < x >^2)/N$ vs. L/N





Escape transition points

- Transition points:
  - Peaks of variances of x



$$\Rightarrow L/N \sim 0.96(3)H^{-1/3}$$

  - Free energy:

$$F_N^{\text{impr}}(L,H) = F_N^{\text{esc}}(L,H) \Rightarrow L/N \sim 1.02(4)H^{-1/3}$$

WHAT IS THE ORDER?

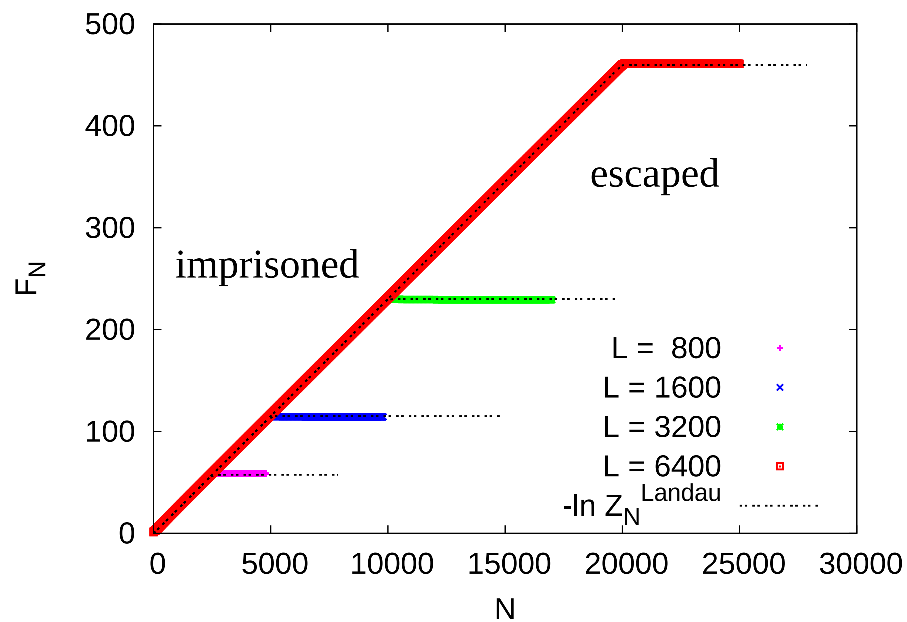
Landau free energy $\Phi(s)$

- Theoretical prediction of the partition sum: $Z = \int ds \exp(-\Phi(s))$

$$Z_N^{Landau}(L,H) = \exp(-\Phi_N^{\rm impr}(s_{\rm eq}^{\rm impr})) + \exp(-\Phi_N^{\rm esc}(s_{\rm eq}^{\rm esc}))$$

$$= \exp\left[-3\left(\frac{A^2B}{4}\right)^{1/3} N\left(\frac{a}{H}\right)^{4/3}\right] + \exp\left[-2(AB)^{1/2}\frac{L}{H}\right]$$

- Free energy $F_N(L,H) = -\ln(\frac{Z_N(L,H)}{Z_N})$ vs. $N \Rightarrow A\ ,B$



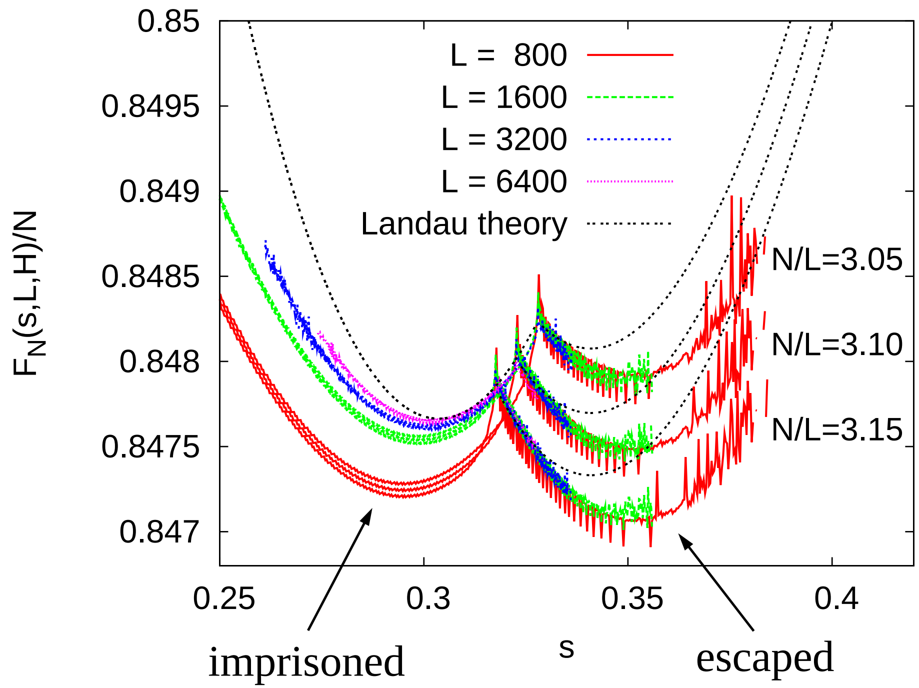
$H = 27$

- Theoretical prediction:

$$\Phi_N(s) = \begin{cases} N\left[A\left(\frac{a}{sH}\right)^2 + Bs^4\right] & \text{, imprisoned chain} \\ \frac{L}{a}\left[A\left(\frac{a}{H}\right)^2 s^{-3} + Bs^3\right] & \text{, escaped chain} \end{cases}$$

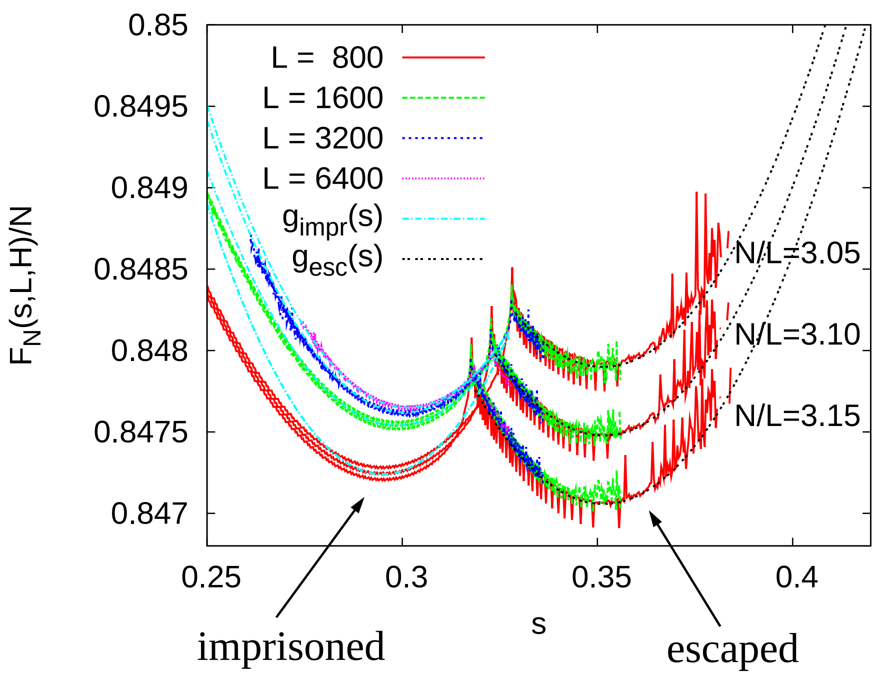
- MC simulations:

  $F_N(s, L, H)/N$ vs. s



$F_N(s, L, H = 27)$ vs. s

- Min. of F_N is determined by fitting a parabola
  - $g_{\mathrm{impr}}(s) = a_{1,L}(s - s_{\mathrm{eq}}^{\mathrm{impr}}(L))^2 + c_{1,L}$
  - $g_{\mathrm{esc}}(s) = a_2(s - s_{\mathrm{eq}}^{\mathrm{esc}}(L))^2 + c_2 + d_2 \frac{N}{L}$
- Transition points: $g_{\mathrm{impr}}(s = s_{\mathrm{eq}}^{\mathrm{impr}}(L)) = g_{\mathrm{esc}}(s = s_{\mathrm{eq}}^{\mathrm{esc}}(L))$

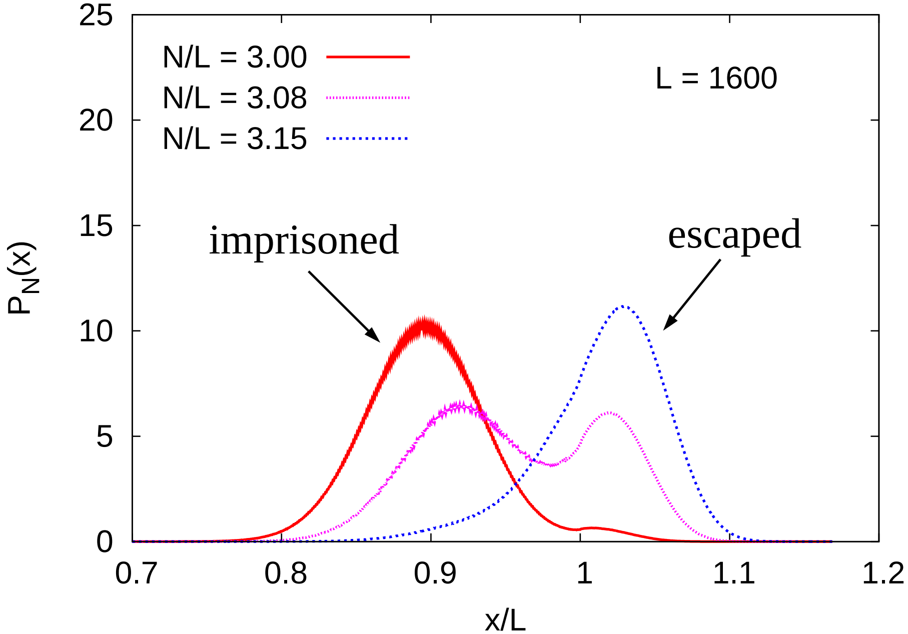


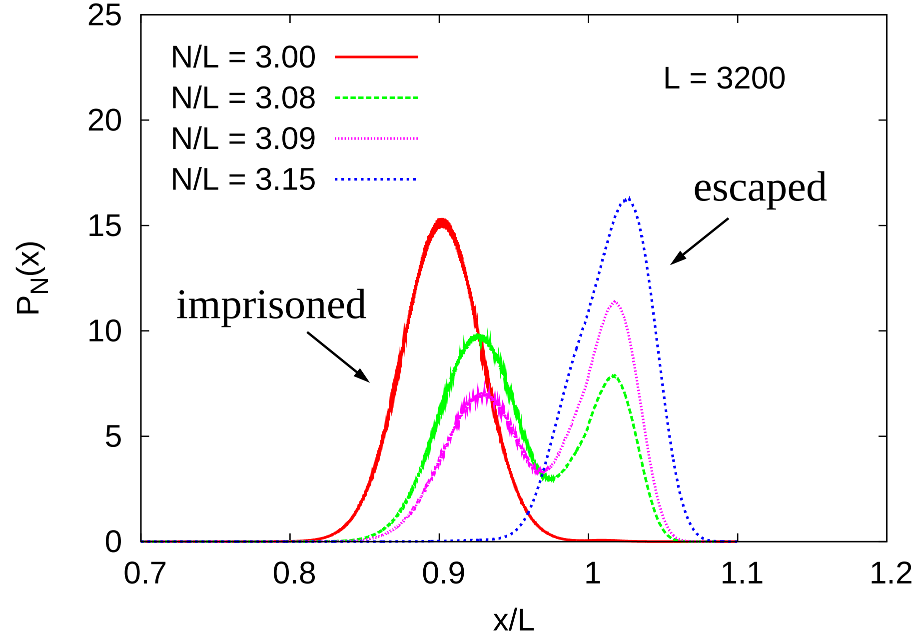
L	N^*/L
800	3.128
1600	3.093
3200	3.083
6400	3.080

$N/L \sim 1.03(5)H^{1/3} \sim 3.09(15)$

Histogram of x, $P_N(x)$

- $P_N(x) = \sum_{walks} \delta_{x',x}$
- $P_N(x)$ vs. x/L $\quad\quad (\sum_x P_N(x) = L)$



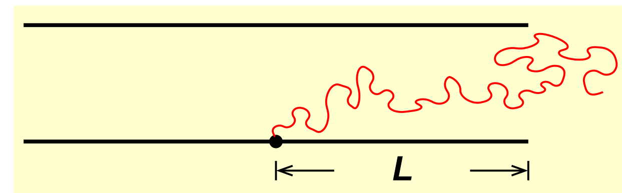


Conclusions

- What is the order of $2d$ escape transition?

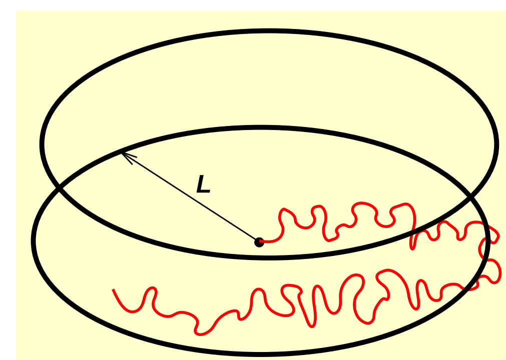
  first-order phase transition

  - Landau theory
  - MC simulations (PERM)



- Transition points: $L/N \sim 1.02(4) H^{-1/3}$
- Does the Landau theory also explain $3d$ escape transition? No!
  - Poor definition of the order parameter

$$s = \begin{cases} R/Na & , N < N^* \\ L/N^*a & , N > N^* \end{cases}$$



R: end-to-end distance