

# On the phase diagram of random copolymers at selective interfaces

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# References

- ▶ [CGG] C., Giacomin and Gubinelli, *A numerical approach to copolymers at selective interfaces*, J. Stat. Phys. (2006)
- ▶ [CG] C. and Giacomin, *On constrained annealed bounds for linear chain pinning models*, Electron. Comm. in Probab. (2005),

# Outline of the talk

## 1. Introduction

Motivations

Definition of the model

The phase diagram: UB and LB on the critical line

## 2. Numerical investigation

The transfer matrix approach

Beating the LB: a statistical test

Beating the UB: numerical observations

A conjecture (?) on the critical line

## 3. Theoretical analysis

Improving the UB: the constrained annealing technique

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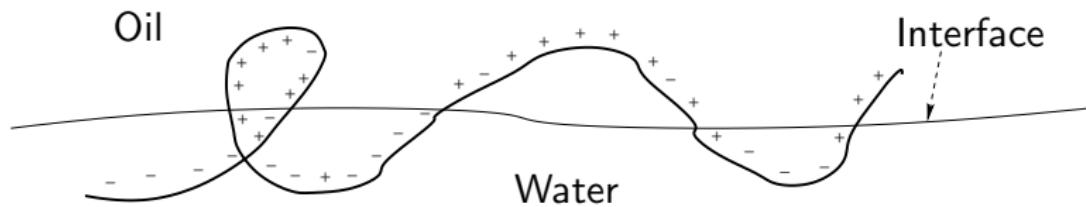
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# Qualitative introduction

Copolymer (= inhomogeneous polymer) near a selective interface

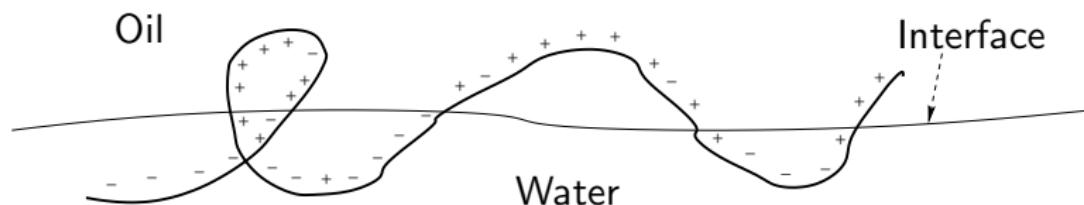
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Copolymer (= inhomogeneous polymer) near a selective interface

Monomers:  $(+)$   $\rightarrow$  hydrophobic       $(-)$   $\rightarrow$  hydrophilic



Phenomenon:

localization at the interface      vs.      delocalization in one solvent

Energy–entropy competition

# Definition of the model

Free process: Simple Symmetric Random Walk  $\{S_n\}_n$  on  $\mathbb{Z}$

$$S_0 = 0 \quad S_n = \sum_{i=1}^n X_i$$

where  $\{X_i\}_i$  are i.i.d. with  $\mathbf{P}(X_1 = \pm 1) = 1/2$ .

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Parameters:

- ▶  $N$  (system size)     $\lambda, h \geq 0$  (inverse temperature, asymmetry)
- ▶  $\omega = \{\omega_n\}_n \in \{-1, +1\}^{\mathbb{N}}$  (**charges**: hydrophobicity-hydrophilicity)

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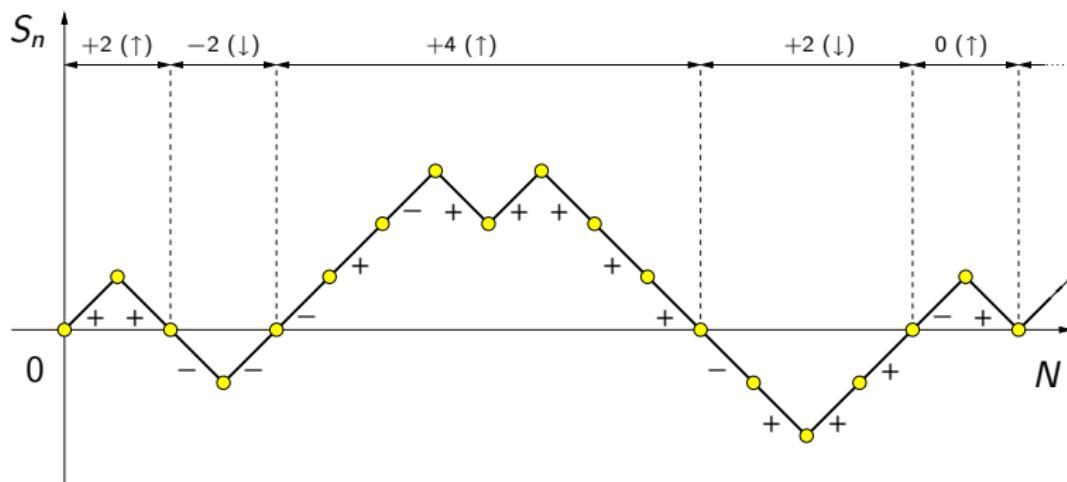
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Polymer measure  $\mathbf{P}_{N,\omega}^{\lambda,h}$  [Bolthausen and den Hollander 97]

$$\frac{d\mathbf{P}_{N,\omega}^{\lambda,h}}{d\mathbf{P}}(S) := \frac{1}{Z_{N,\omega}^{\lambda,h}} \cdot \exp \left( \lambda \sum_{n=1}^N (\omega_n + h) \operatorname{sign}(S_n) \right)$$

# A sample path



$$\text{Energy: } \mathcal{H}_{N,\omega}^{\lambda,h}(S) := \lambda \sum_{n=1}^N (\omega_n + h) \operatorname{sign}(S_n) = \lambda(6 + 6h)$$

( if  $S_n = 0 \rightarrow \operatorname{sign}(S_n) := \operatorname{sign}(S_{n-1})$  )

# The choice of the charges

Quenched randomness:  $\omega = \{\omega_n\}_n$  is a typical sample from a centered i.i.d. sequence (law  $\mathbb{P}$ ):

$$\mathbb{E}[\omega_1] = 0 \quad \mathbb{E}[\omega_1^2] = 1$$

$$M(\alpha) := \mathbb{E}[\exp(\alpha\omega_1)] < \infty \quad \forall \alpha \in \mathbb{R}$$

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Typical examples:

- ▶ **Binary:**  $\mathbb{P}(\omega_1 = \pm 1) = \frac{1}{2} \rightarrow \log M(\alpha) = \log \cosh(\alpha)$
- ▶ **Gaussian:**  $\omega_1 \sim N(0, 1) \rightarrow \log M(\alpha) = \frac{1}{2}\alpha^2$

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**Partition function:**  $Z_{N,\omega}^{\lambda,h} := \mathbf{E}\left(\exp(\mathcal{H}_{N,\omega}^{\lambda,h})\right)$

**Free energy:** rate of exponential growth of  $Z_N$ :

$$f_\omega(\lambda, h) := \lim_{N \rightarrow \infty} \frac{1}{N} \log Z_{N,\omega}^{\lambda,h}$$

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- ▶ The limit exists  $\mathbb{P}$ -a.s. (and in  $L_1(d\mathbb{P})$ ) by superadditivity
- ▶ Self-averaging property:  $f_\omega(\lambda, h) = f(\lambda, h)$  for  $\mathbb{P}$ -a.e.  $\omega$

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Proof: restrict  $Z_N$  on positive trajectories

$$Z_{N,\omega}^{\lambda,h} \geq \mathbf{E} \left[ \exp \left( \lambda \sum_{n=1}^N (\omega_n + h) \operatorname{sign}(S_n) \right) ; S_1 > 0, \dots, S_N > 0 \right]$$

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Therefore we split the phase diagram  $\{(\lambda, h) : \lambda, h \geq 0\}$  into

- ▶ Localized region  $\mathcal{L} = \{(\lambda, h) : f(\lambda, h) > \lambda h\}$
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Two main questions:

1. Study of the phase diagram
2. Free energy definition of  $\mathcal{L}$  and  $\mathcal{D} \rightarrow$  path properties?
  - ▶  $\mathcal{L}$ : strong path localization [Sinai 93] [Biskup and den Hollander 99]
  - ▶  $\mathcal{D}$ : many open questions [Giacomin and Toninelli 05]

# The critical line

## Theorem ([BdH 97])

*There exists a continuous, increasing curve  $h_c : [0, \infty) \rightarrow [0, \infty)$ , with  $h_c(0) = 0$  and  $0 < h'_c(0) < \infty$ , such that*

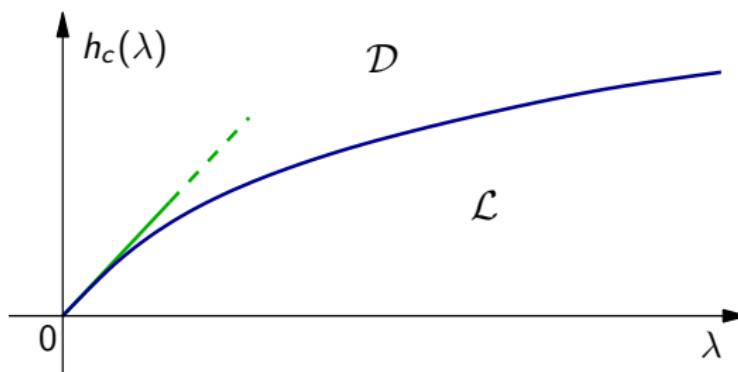
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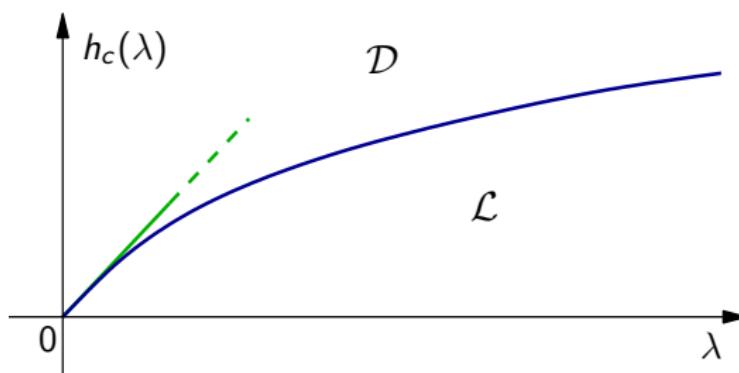


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Slope at the origin:

- ▶ Brownian scaling
- ▶ Universality

# Upper and Lower Bound on the critical line

Family of increasing curves indexed by  $m > 0$ :

$$h^{(m)}(\lambda) := \frac{1}{2m\lambda} \log M(-2m\lambda) \quad \left( \frac{dh^{(m)}}{d\lambda}(0) = m \right)$$

Binary:  $h^{(m)}(\lambda) = \frac{\log \cosh(2m\lambda)}{2m\lambda}$       Gaussian:  $h^{(m)}(\lambda) = m\lambda$

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## Physical literature:

- ▶  $h_c(\cdot) = h^{(1)}(\cdot)$  [Garel et al. '89, Maritan and Trovato '99]
- ▶  $h_c(\cdot) = h^{(2/3)}(\cdot)$  [Monthus '00, Stepanov et al. '98]

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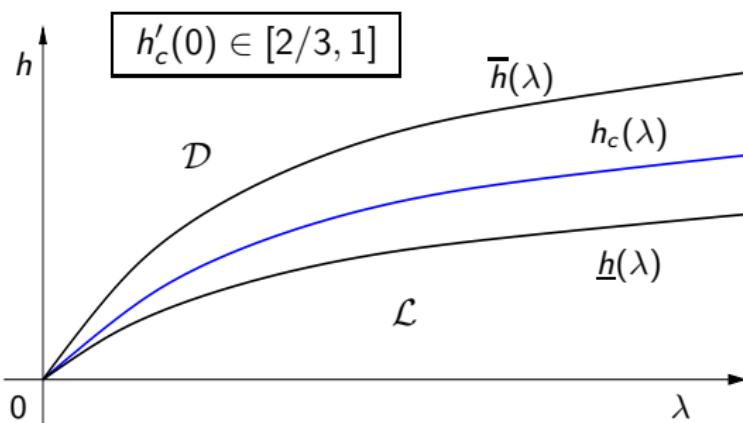
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## Theorem ([BdH 97], [Bodineau and Giacomin 04])

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# A preliminary transformation

Reduced free energy:  $F(\lambda, h) := f(\lambda, h) - \lambda h$

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$(\lambda, h) \in \mathcal{L}$  iff  $\mathcal{Z}_{N,\omega}^{\lambda,h}$  grows exponentially in  $N$ .

# The transfer matrix approach

Naïve idea: for fixed  $(\lambda, h)$  and typical  $\omega$ , **compute** numerically  $Z_{N,\omega}^{\lambda,h}$  as a function of  $N$ , to decide between  $\mathcal{L}$  and  $\mathcal{D}$

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$$\mathcal{Z}_N(x) := \{\mathcal{Z}_N \text{ restricted to path ending at } x \in \mathbb{Z}\}$$

Markov property + Additivity of the Hamiltonian give:

$$\mathcal{Z}_{M+2}(y) = \begin{cases} \frac{1}{4}\mathcal{Z}_M(y+2) + \frac{1}{2}\mathcal{Z}_M(y) + \frac{1}{4}\mathcal{Z}_M(y-2) & y > 0 \\ \frac{1}{4}[\mathcal{Z}_M(2) + \mathcal{Z}_M(0)] + \frac{1}{4}\alpha_M [\mathcal{Z}_M(0) + \mathcal{Z}_M(-2)] & y = 0 \\ \alpha_M \left[ \frac{1}{4}\mathcal{Z}_M(y+2) + \frac{1}{2}\mathcal{Z}_M(y) + \frac{1}{4}\mathcal{Z}_M(y-2) \right] & y < 0 \end{cases}$$

where  $\alpha_M := \exp(-2\lambda(\omega_{2M+1} + \omega_{2M+2} + 2h))$ .



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Approximate computation (LB) in  $O(N^{3/2})$  steps  $\Rightarrow N \sim 10^8$

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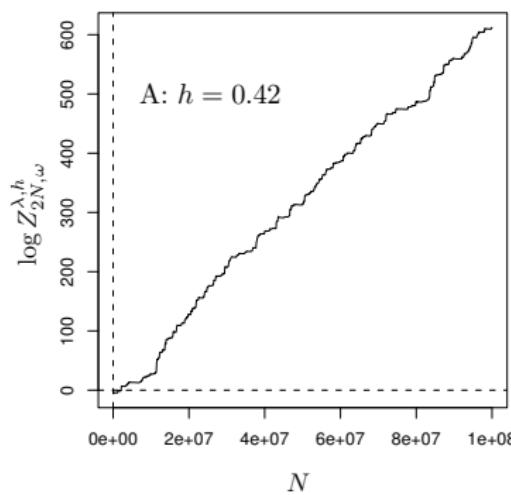
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Computations in the case  $\omega_n \in \{-1, +1\}$  (tried also Gaussian, ...)

# Qualitative results ( $\lambda = 0.6$ , $\underline{h} = 0.36$ , $\overline{h} = 0.49$ )

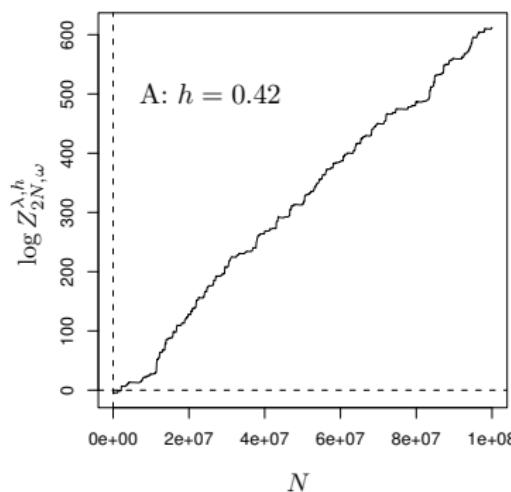
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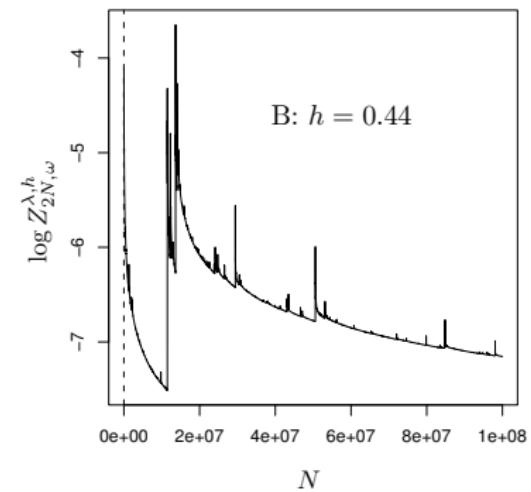
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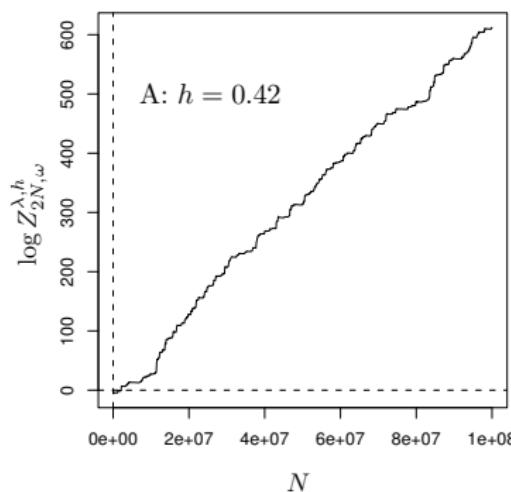
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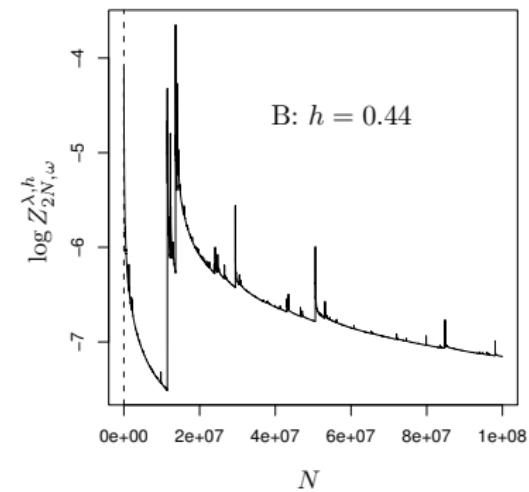
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(outside of the “critical” region... come back after)

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It is numerically rather evident that the true critical line  $h_c(\lambda)$  lies strictly in between  $\underline{h}(\lambda)$  and  $\overline{h}(\lambda)$ , i.e.:

- ▶ for some  $h > \underline{h}(\lambda)$  we see an exponential growth of  $\mathcal{Z}_N$
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Beating the LB:  $h_c(\lambda) > \underline{h}(\lambda)$

Rigorous statistical test for Localization with explicit error bound  
(superadditivity + concentration of measure)

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Beating the LB:  $h_c(\lambda) > \underline{h}(\lambda)$

Rigorous statistical test for Localization with explicit error bound  
(superadditivity + concentration of measure)

Beating the UB:  $h_c(\lambda) < \overline{h}(\lambda)$

Quantitative criterion to measure the convergence under diffusive rescaling to the Brownian meander

# Localization in a finite volume

Markov property of  $S \Rightarrow$  for  $N, M \in 2\mathbb{N}$

$$\mathcal{Z}_{N+M,\omega}(0) \geq \mathcal{Z}_{N,\omega}(0) \cdot \mathcal{Z}_{M,\theta^N\omega}(0) \quad [(\theta^N\omega)_n := \omega_{N+n}]$$

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Localization can be proven by looking at *finite systems*

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Lipschitz function  $G : \{-1, +1\}^N \rightarrow \mathbb{R}$  with Lipschitz constant  $C_{Lip}$ :

$$\mathbb{P}[G > \mathbb{E}(G) + u] \leq \exp\left(-\frac{u^2}{4C_{Lip}^2}\right)$$

More generally for an i.i.d. family  $\{G_i\}_i$ :

$$\mathbb{P}\left[\frac{\sum_{i=1}^n G_i}{n} > \mathbb{E}(G_1) + u\right] \leq \exp\left(-\frac{n u^2}{4 C_{Lip}^2}\right)$$

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- ▶ If  $\hat{u}_n > 0$  then we refuse  $H_0$  (that is  $(\lambda, h) \in \mathcal{L}!$ ) with a level of error not larger than

$$p := \exp\left(-\frac{\hat{u}_n^2 n}{16\lambda^2 N}\right)$$

# Statistical test for Localization

Numerical results: the LB is strict

$\lambda$	0.3	0.6	1
$h$	0.22	0.41	0.58
$\underline{h}(\lambda)$	0.195	0.363	0.530
$\bar{h}(\lambda)$	0.286	0.495	0.662
$p$ -value	$1.5 \times 10^{-6}$	$9.5 \times 10^{-3}$	$1.6 \times 10^{-5}$
$N$	300000	500000	160000
$n$	225000	330000	970000

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# Computer-assisted proof?

Back to naïve idea: can we hope that

$$\mathbb{E}[\log Z_{N,\omega}^{\lambda,h}] > 0 \quad \text{for small values of } N \quad (\text{up to } N \approx 20)$$

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NO!

$\lambda$	0.05(*)	0.1	0.2	0.4	0.6	1	2(★)	4(★★)
$N_+$	750000	190000	40000	9500	4250	1800	900	800
$N_-$	600000	130000	33000	7500	3650	1550	750	700

$$p = 10^{-5} \sim 10^{-6} \quad (*) \quad p = 10^{-2} \sim 10^{-3} \quad (**) \quad \text{limit model } (\lambda \rightarrow \infty)$$

With the stated  $p$ -value and for  $h = h^{(2/3)}(\lambda)$ , both

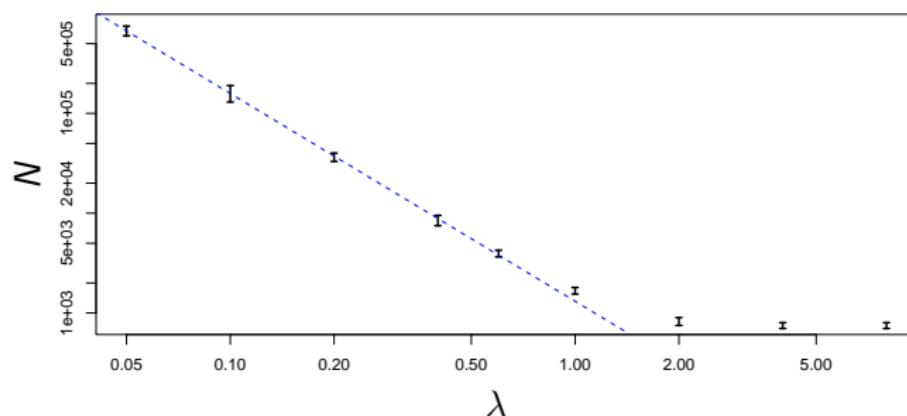
$$\mathbb{E}[\log Z_{N_+,\omega}^{\lambda,h}] > 0 \quad \mathbb{E}[\log Z_{N_-,\omega}^{\lambda,h}] < 0$$

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# Delocalized observations

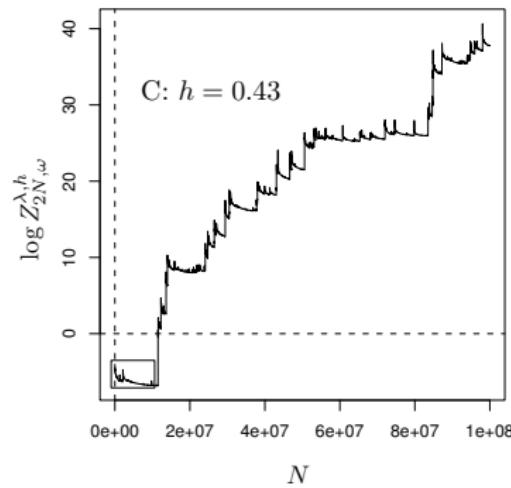
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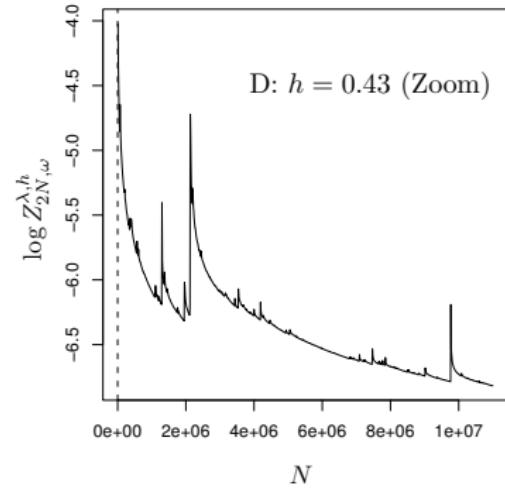
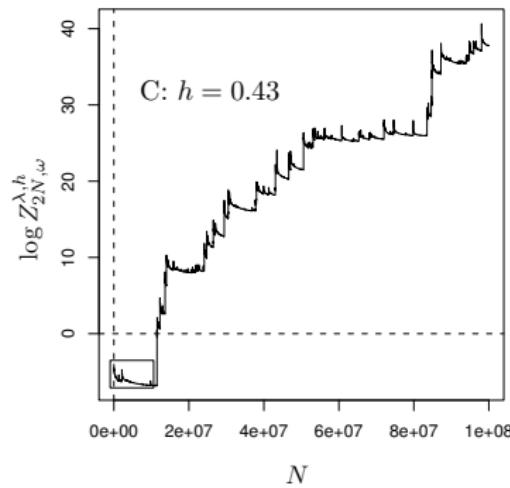
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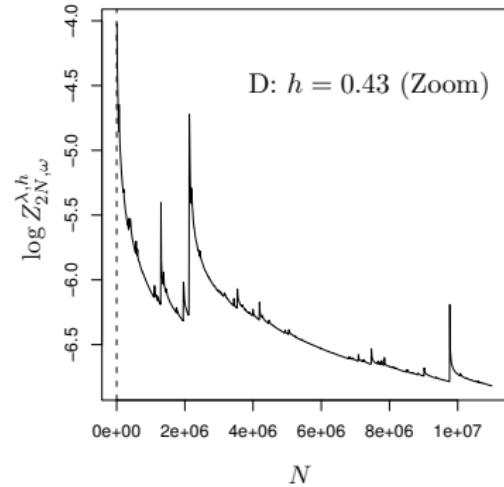
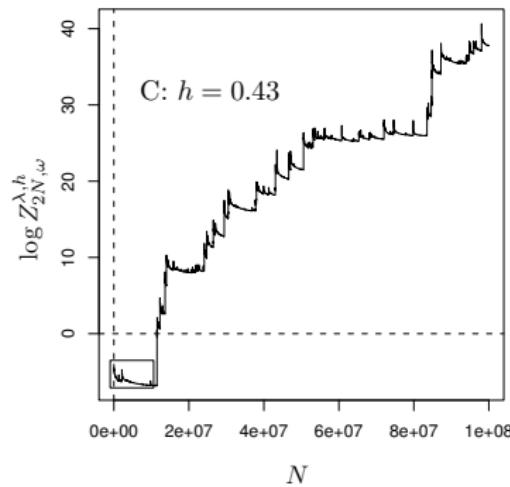
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# Delocalized observations

Difficult to make rigorous numerical claims on  $\mathcal{D}$ :

Delocalization is not a finite-volume issue



Jumps correspond to atypical stretches in the environment  $\omega$

# Delocalized path analysis

Assume the convergence to Brownian meander in  $\overset{\circ}{\mathcal{D}}$ :

under  $\mathbf{P}_{N,\omega}$       
$$\frac{S_N}{\sqrt{N}} \implies x e^{-x^2/2} dx =: \varphi^+(x) dx$$

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## Quantitative measure of Delocalization ( $\ell_1$ distance)

$$\Delta_N^{\lambda,h}(\omega) := \sum_{x \in \mathbb{Z}} \left| \mathbf{P}_{N,\omega}^{\lambda,h}[S_N = x] - \frac{1}{\sqrt{N}} \varphi^+ \left( \frac{x}{\sqrt{N}} \right) \right|$$

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We work at  $\lambda = 0.6$     [ $\underline{h} = 0.36$ ,     $h_{test} = 0.41$ ,     $\overline{h} = 0.49$ ]

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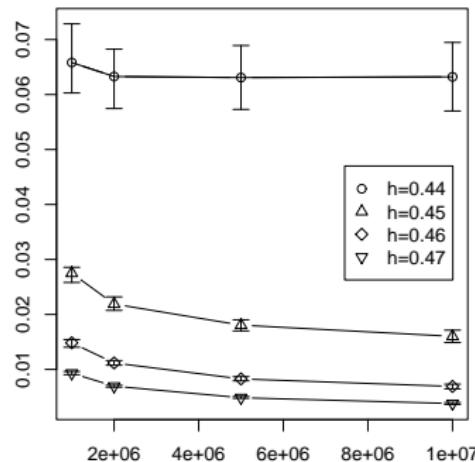
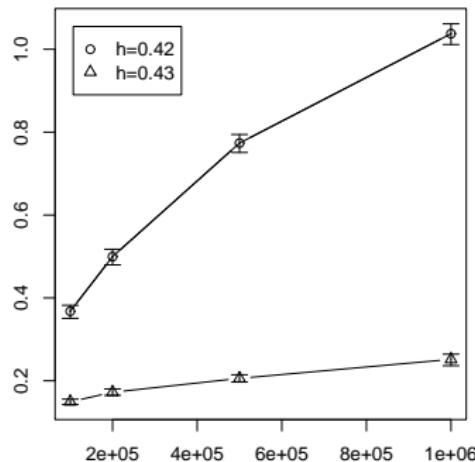
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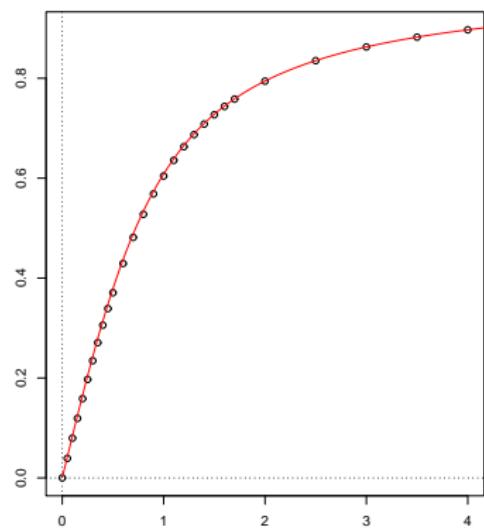
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Numerical computations show that

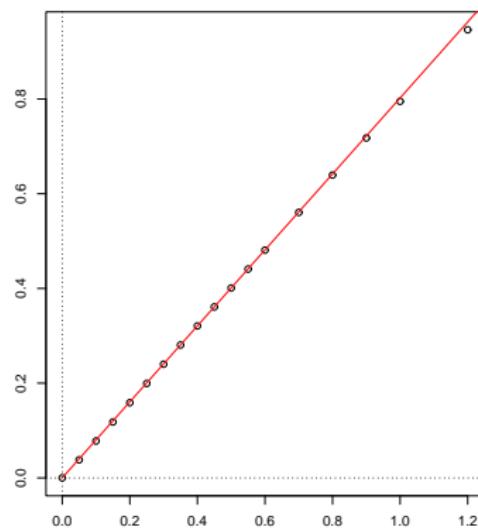
$$h_c(\cdot) \simeq h^{(m)}(\cdot) \quad m = 0.82 - 0.83$$

with [remarkable precision](#) (value of  $m$  somewhat criterion dependent)

# A conjecture (?) on the true critical line

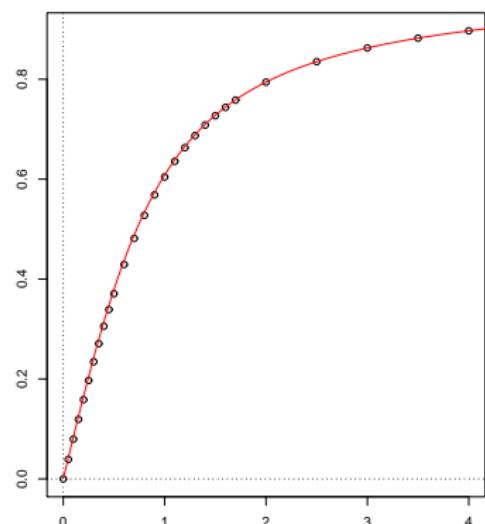


Binary case

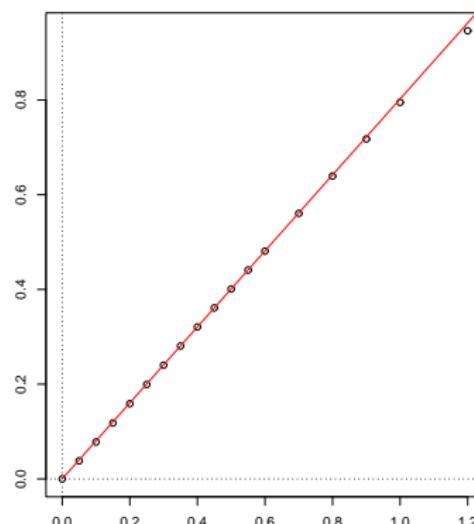


Gaussian case

# A conjecture (?) on the true critical line



Binary case



Gaussian case

Plotted points are obtained for one fixed realization of  $\omega$

# Outline of the talk

## 1. Introduction

Motivations

Definition of the model

The phase diagram: UB and LB on the critical line

## 2. Numerical investigation

The transfer matrix approach

Beating the LB: a statistical test

Beating the UB: numerical observations

A conjecture (?) on the critical line

## 3. Theoretical analysis

Improving the UB: the constrained annealing technique

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Annealed bound on  $Z_{N,\omega}$  (old partition function):

$$f(\lambda, h) = \lim_{N \rightarrow \infty} \frac{1}{N} \mathbb{E} \log Z_{N,\omega}^{\lambda, h} \leq \lim_{N \rightarrow \infty} \frac{1}{N} \log \mathbb{E} Z_{N,\omega}^{\lambda, h} =: f_a(\lambda, h)$$

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Therefore  $f(\lambda, h) \leq f'_a(\lambda, h)$

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## Theorem ([C. and Giacomin])

For every local function  $B(\cdot)$  and for every  $h < \bar{h}(\lambda)$  we have

$$F'_a(\lambda, h) > 0$$

# The proof

$$F'_a = \lim_{N \rightarrow \infty} \frac{1}{N} \log \mathbb{E} \left\{ Z_{N,\omega} \exp \left( \sum_{n=1}^N B(\theta^n \omega) \right) \right\} \quad (1)$$

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hence

$$F'_a \geq \lim_{N \rightarrow \infty} \frac{1}{N} \log \mathbb{E} \exp \left( \sum_{n=1}^N B(\theta^n \omega) \right) =: \gamma$$

- ▶ if  $\gamma > 0$  then  $F'_a > 0$  and we are done

# The proof

$$F'_a = \lim_{N \rightarrow \infty} \frac{1}{N} \log \mathbb{E} \left\{ Z_{N,\omega} \exp \left( \sum_{n=1}^N B(\theta^n \omega) \right) \right\} \quad (1)$$

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- ▶ if  $\gamma = 0$  then  $B(\cdot)$  is trivial, i.e.  $\sup_{\omega} \sum_{n=1}^N B(\theta^n \omega) = o(N)$ .

# The proof

$$F'_a = \lim_{N \rightarrow \infty} \frac{1}{N} \log \mathbb{E} \left\{ \mathcal{Z}_{N,\omega} \exp \left( \sum_{n=1}^N B(\theta^n \omega) \right) \right\} \quad (1)$$

By the basic Delocalization bound

$$\mathcal{Z}_{N,\omega} \geq P(S_n > 0, 1 \leq n \leq N) \approx N^{-1/2}$$

hence

$$F'_a \geq \lim_{N \rightarrow \infty} \frac{1}{N} \log \mathbb{E} \exp \left( \sum_{n=1}^N B(\theta^n \omega) \right) =: \gamma$$

- ▶ if  $\gamma > 0$  then  $F'_a > 0$  and we are done
- ▶ if  $\gamma = 0$  then  $B(\cdot)$  is trivial, i.e.  $\sup_\omega \sum_{n=1}^N B(\theta^n \omega) = o(N)$ . Hence by (1)

$$F'_a = \lim_{N \rightarrow \infty} \frac{1}{N} \log \mathbb{E} \mathcal{Z}_{N,\omega} = F_a > 0$$

# A general statement

## Theorem

Let  $\mathcal{Z}_{N,\omega}$  be the partition function of a system of size  $N$  and with i.i.d. disorder  $\omega$ . Assume that

- ▶ for every  $\mathcal{Z}_{N,\omega} \geq c_N > 0$  with  $\frac{1}{N} \log c_N \rightarrow 0$
- ▶ the annealed free energy is positive:  $F_a > 0$

Then, for any choice of the local function  $B(\omega)$  with

$$\mathbb{E}(B(\omega)) = 0 \quad \mathbb{E}(\exp(\alpha B(\omega))) < \infty \quad \forall \alpha \in \mathbb{R}$$

the constrained annealed free energy with  $A_N(\omega) = \sum_{n=1}^N B(\theta^n \omega)$  is positive:  $F'_a > 0$ .