

On the phase diagram of random copolymers at selective interfaces

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Università degli Studi di Padova

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References

- ▶ [CGG] C., Giacomini and Gubinelli, *A numerical approach to copolymers at selective interfaces*, J. Stat. Phys. (2006)
- ▶ [CG] C. and Giacomini, *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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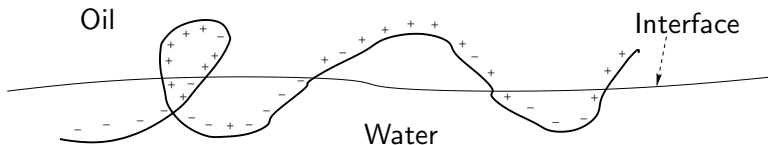
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Qualitative introduction

Copolymer (= inhomogeneous polymer) near a selective interface

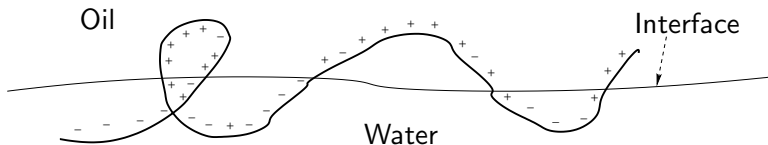
Monomers: $(+)$ \rightarrow hydrophobic $(-)$ \rightarrow hydrophilic



Qualitative introduction

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}

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

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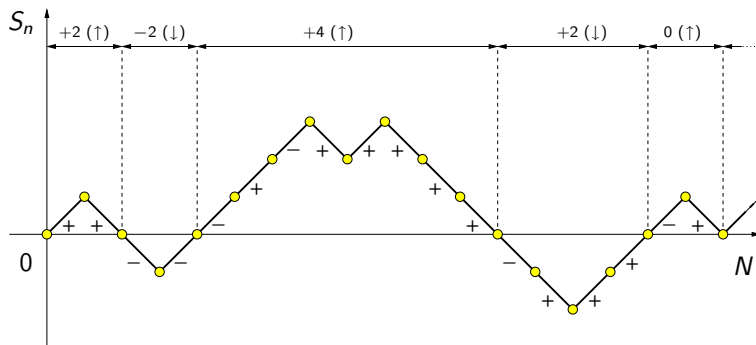
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Polymer measure $\mathbf{P}_{N,\omega}^{\lambda,h}$ [Bolthausen and den Hollander 97]

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

A sample path



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

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

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}):

$$\begin{aligned}\mathbb{E}[\omega_1] &= 0 & \mathbb{E}[\omega_1^2] &= 1 \\ M(\alpha) &:= \mathbb{E}[\exp(\alpha\omega_1)] < \infty & \forall \alpha \in \mathbb{R}\end{aligned}$$

(generalization: $\omega_n \in \{-1, +1\} \rightarrow \omega_n \in \mathbb{R}$)

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Typical examples:

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

The free energy

Interested in the asymptotic properties of the model as $N \rightarrow \infty$
(localization-delocalization)

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(**localization-delocalization**)

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

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. ω

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

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

- ▶ Localized region $\mathcal{L} = \{(\lambda, h) : f(\lambda, h) > \lambda h\}$
- ▶ Delocalized region $\mathcal{D} = \{(\lambda, h) : f(\lambda, h) = \lambda h\}$

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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

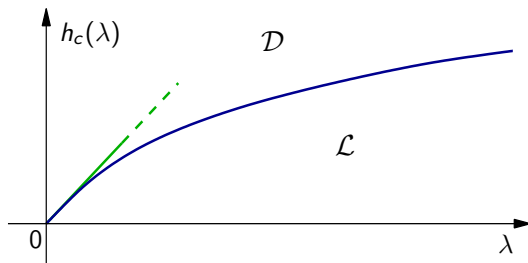
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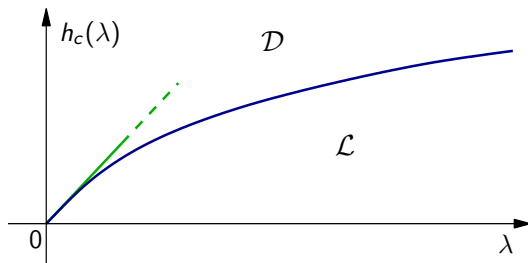


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Slope at the origin:

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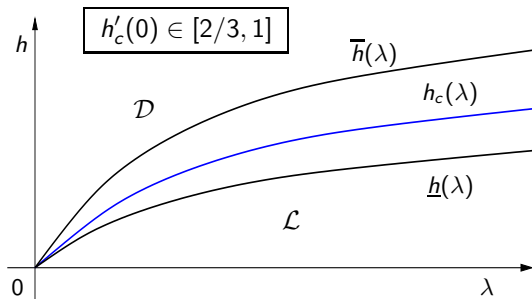
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Theorem ([BdH 97], [Bodineau and Giacomin 04])

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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 (λ, h) and typical ω , **compute** numerically $\mathcal{Z}_{N,\omega}^{\lambda,h}$ 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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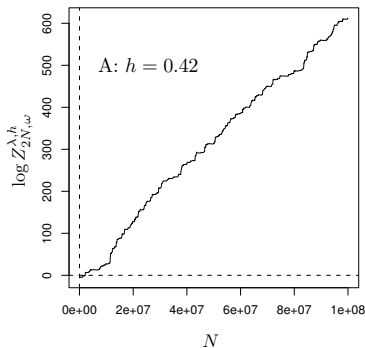
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Computations in the case $\omega_n \in \{-1, +1\}$ (tried also Gaussian, . . .)

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

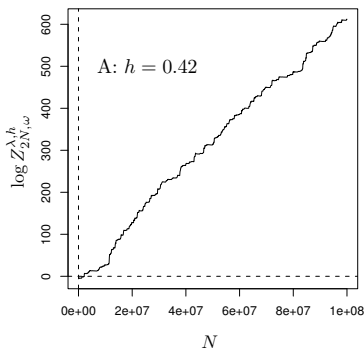
Dichotomy for the asymptotics of $\{Z_{N,\omega}^{\lambda,h}\}_N$:



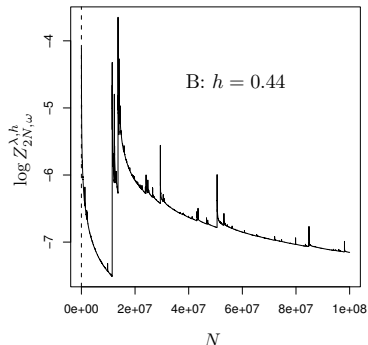
it diverges exponentially...

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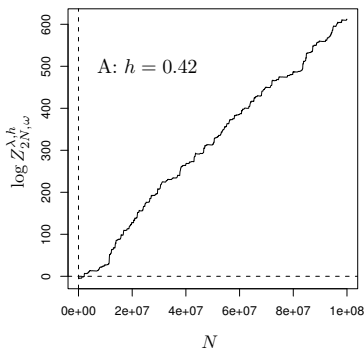
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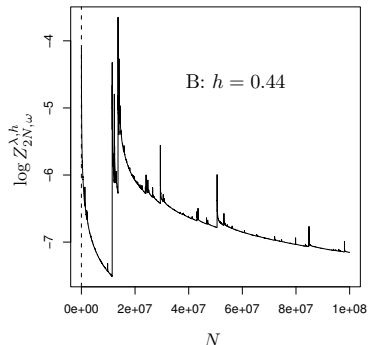
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(outside of the “critical” region... come back after)

Qualitative results

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 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 $N, M \in 2\mathbb{N}$

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

\Rightarrow the sequence $N \mapsto \mathbb{E}[\log \mathcal{Z}_{N,\omega}(0)]$ is superadditive

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Since $\mathcal{Z}_N(0) \asymp \mathcal{Z}_N$ we have the basic formula:

$$F(\lambda, h) = \sup_{N \in \mathbb{N}} \frac{1}{N} \mathbb{E}[\log \mathcal{Z}_{N,\omega}(0)]$$

In a suggestive way:

$$(\lambda, h) \in \mathcal{L} \quad \Longleftrightarrow \quad \exists N \in \mathbb{N} : \mathbb{E}[\log \mathcal{Z}_{N,\omega}(0)] > 0$$

Localization in a finite volume

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

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

\Rightarrow the sequence $N \mapsto \mathbb{E}[\log \mathcal{Z}_{N,\omega}(0)]$ is superadditive

Since $\mathcal{Z}_N(0) \asymp \mathcal{Z}_N$ we have the basic formula:

$$F(\lambda, h) = \sup_{N \in \mathbb{N}} \frac{1}{N} \mathbb{E}[\log \mathcal{Z}_{N,\omega}(0)]$$

In a suggestive way:

$$(\lambda, h) \in \mathcal{L} \quad \Longleftrightarrow \quad \exists N \in \mathbb{N} : \mathbb{E}[\log \mathcal{Z}_{N,\omega}(0)] > 0$$

Localization can be proven by looking at *finite systems*

Statistical test for \mathcal{L} ocalization

To prove $(\lambda, h) \in \mathcal{L}$ it suffices to find N s.t. $\mathbb{E}[\log \mathcal{Z}_{N,\omega}^{\lambda,h}(0)] > 0$

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

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

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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- ▶ $\hat{u}_n :=$ average of a sample of n independent realizations of $\log \mathcal{Z}_{N,\omega}^{\lambda,h}$.
- ▶ 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 \mathcal{L} ocalization

Numerical results: the LB is strict

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

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Computer-assisted proof?

Back to naïve idea: can we hope that

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

for $h > \underline{h}(\lambda)$, to perform an explicit computation?

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NO!

| λ | 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 |

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

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

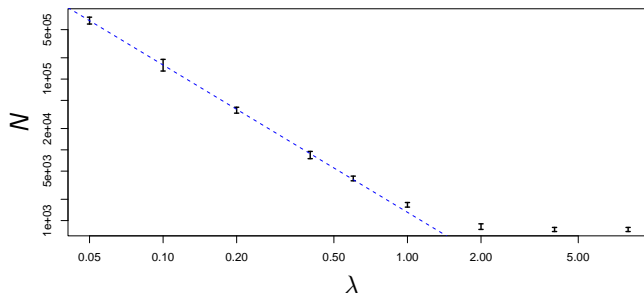
$$\mathbb{E}[\log Z_{N_+,\omega}^{\lambda,h}] > 0 \quad \mathbb{E}[\log Z_{N_-,\omega}^{\lambda,h}] < 0$$

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Delocalized observations

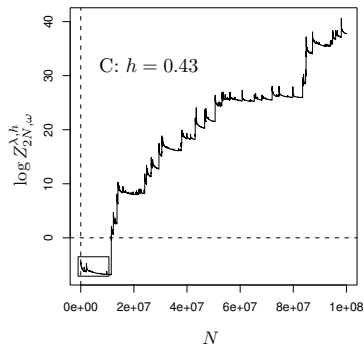
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Delocalization is not a finite-volume issue

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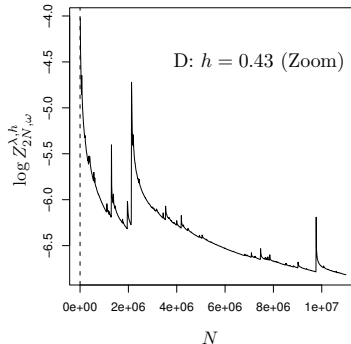
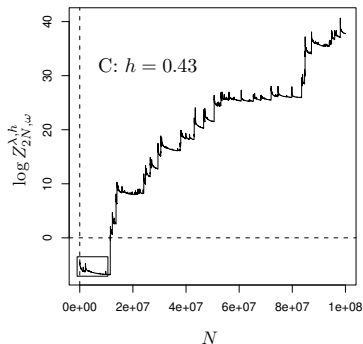
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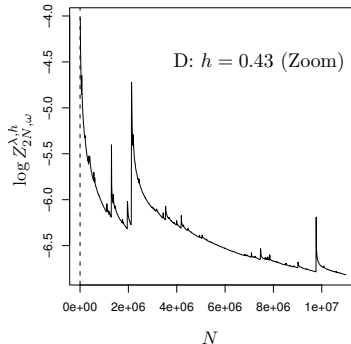
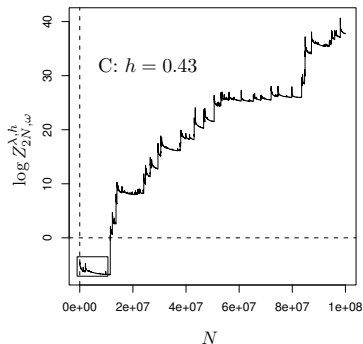
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Jumps correspond to **atypical stretches in the environment ω**

Delocalized path analysis

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

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

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Quantitative measure of \mathcal{D} elocalization (ℓ_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 $\lambda = 0.6$ [$\underline{h} = 0.36$, $h_{test} = 0.41$, $\bar{h} = 0.49$]

- ▶ $(\omega^r)_n := \omega_{N-n}$ environment attached backwards
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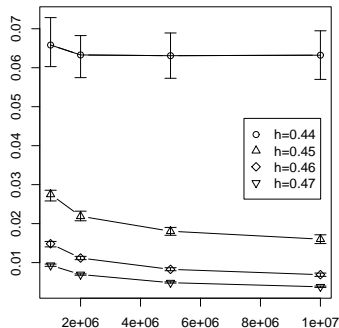
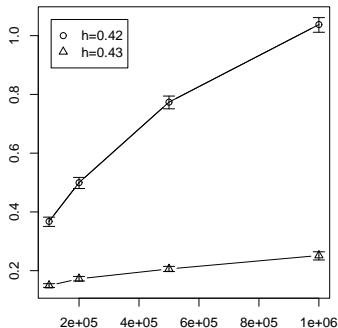
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Possible criteria: for fixed N and λ , take the value of h s.t.

- ▶ $\mathcal{Z}_{N,\omega}^{\lambda,h}(0) = 1$ (monotonicity in h)
- ▶ $\Delta_N^{\lambda,h}(\omega) = 0.1$ (empirical monotonicity in h)

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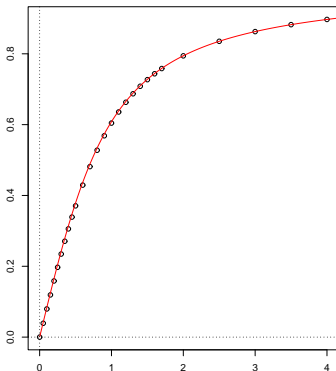
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Numerical computations show that

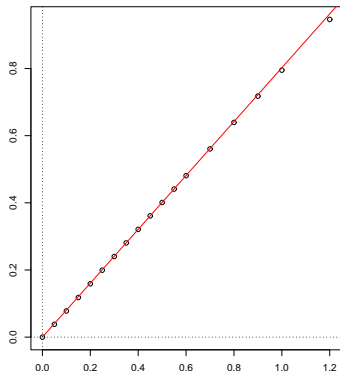
$$h_c(\cdot) \simeq h^{(m)}(\cdot) \quad m = 0.82 - 0.83$$

with **remarkable precision** (value of m somewhat criterion dependent)

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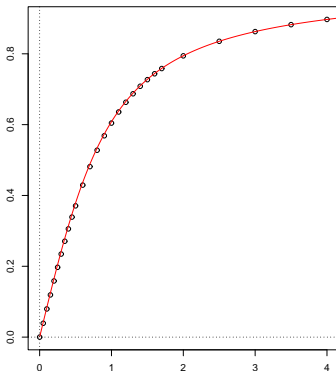


Binary case

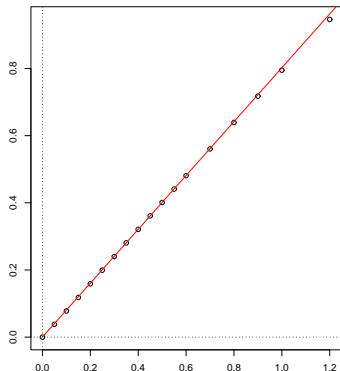


Gaussian case

A conjecture (?) on the true critical line



Binary case



Gaussian case

Plotted points are obtained for **one fixed realization** of ω

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

The constrained annealing technique

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 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 ω . 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: $F'_a > 0$.