HOW DOES A CHARGED POLYMER COLLAPSE?

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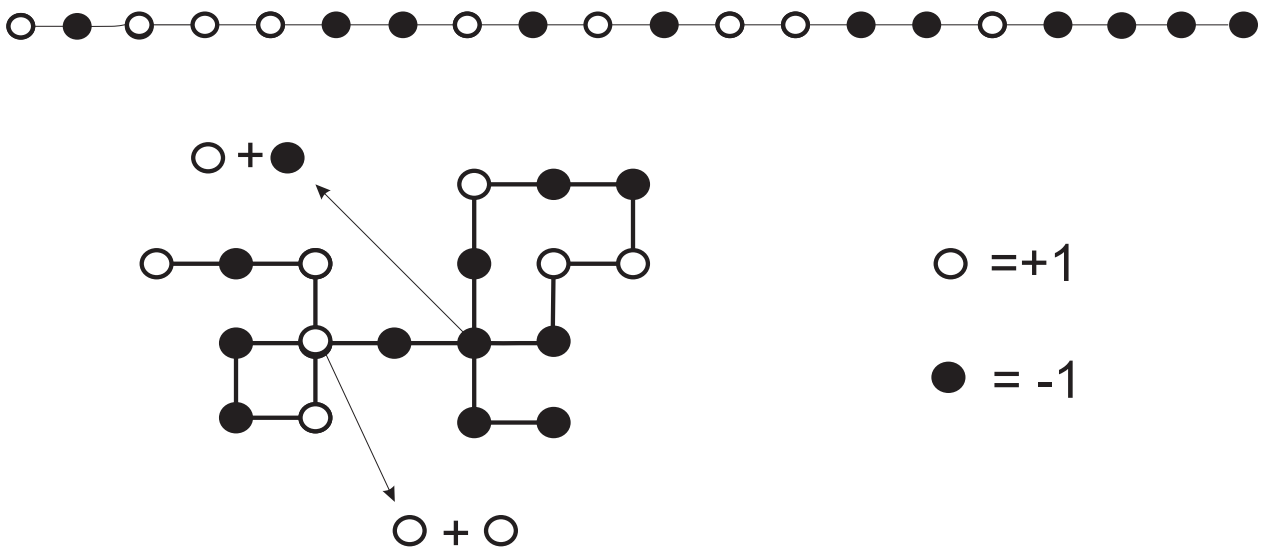
§ MOTIVATION

DNA and proteins are polyelectrolytes whose monomers are in a charged state that depends on the pH of the solution in which they are immersed. The charges may fluctuate in space and in time.

In this talk we consider a model of a charged polymer chain introduced by Kantor & Kardar in 1991.

We focus on the annealed version of the model, which turns out to exhibit a very rich scaling behavior.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§ MODEL

1. Let $S = (S_i)_{i \in \mathbb{N}_0}$ be simple random walk on $\mathbb{Z}^d$ starting at 0. The path S models the configuration of the polymer chain, i.e., S_i is the location of monomer i. We use the letter P for probability with respect to S.

2. Let $\omega = (\omega_i)_{i \in \mathbb{N}}$ be i.i.d. random variables taking values in $\mathbb{R}$. The sequence ω models the electric charges along the polymer chain, i.e., ω_i is the charge of monomer i. We use the letter $\mathbb{P}$ for probability with respect to ω, and assume that

$$\mathbb{E}(\omega_1) = 0, \qquad \mathbb{V}\mathrm{ar}(\omega_1) = 1.$$

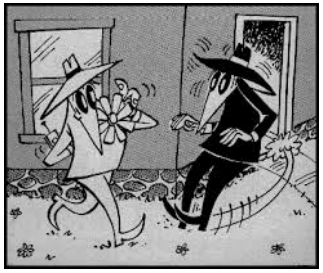
To allow for biased charges, we use a tilting parameter $\delta \in \mathbb{R}$ and write $\mathbb{P}^\delta$ for the i.i.d. law of ω with marginal

$$\mathbb{P}^\delta(\mathrm{d}\omega_1) = \frac{e^{\delta\omega_1}\,\mathbb{P}(\mathrm{d}\omega_1)}{M(\delta)}, \qquad M(\delta) = \mathbb{E}(e^{\delta\omega_1}).$$

W.l.o.g. we may take $\delta \in [0,\infty)$. Throughout the sequel we assume that $M(\delta) < \infty$ for all $\delta \in [0,\infty)$.

3. Let Π denote the set of nearest-neighbor paths on $\mathbb{Z}^d$ starting at 0. Given $n \in \mathbb{N}$, we associate with each $(\omega, S) \in \mathbb{R}^{\mathbb{N}} \times \Pi$ an energy given by the Hamiltonian

$$H_n^\omega(S) = \sum_{1 \le i,j \le n} \omega_i \omega_j \, 1_{\{S_i = S_j\}}.$$



4. Let β denote the inverse temperature. Throughout the sequel the relevant space for the pair of parameters (δ, β) is the quadrant

$$\mathcal{Q} = [0, \infty) \times (0, \infty).$$

5. Given $(\delta, \beta) \in \mathcal{Q}$, the annealed polymer measure of length n is the Gibbs measure $\mathbb{P}_n^{\delta,\beta}$ defined as

$$\frac{\mathrm{d}\mathbb{P}_n^{\delta,\beta}}{\mathrm{d}(\mathbb{P}^\delta \times \mathsf{P})}(\omega, S) = \frac{1}{\mathbb{Z}_n^{\delta,\beta}} e^{-\beta H_n^\omega(S)}, \qquad (\omega, S) \in \mathbb{R}^{\mathbb{N}} \times \Pi,$$

where

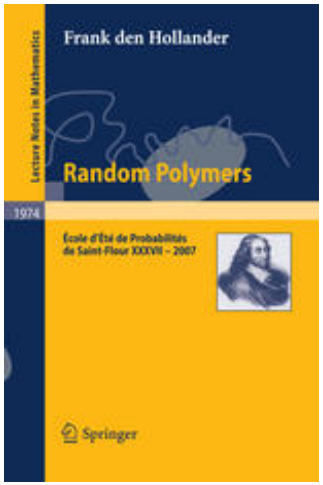
$$\mathbb{Z}_n^{\delta,\beta} = (\mathbb{E}^\delta \times \mathsf{E}) \left[e^{-\beta H_n^\omega(S)} \right]$$

is the annealed partition function of length n.

Literature: The charged polymer with binary disorder interpolates between

simple random walk	$\beta = 0$
self-avoiding walk	$\beta = \delta = \infty$
weakly self-avoiding walk	$\beta \in (0, \infty), \delta = \infty$

Only very little mathematical literature is available on the charged polymer. In what follows we focus on $d = 1$ and later comment on $d \geq 2$.



PART I: general properties

KEY FORMULA:

For every $n \in \mathbb{N}$ and $(\delta, \beta) \in \mathcal{Q}$,

$$\mathbb{Z}_n^{\delta,\beta}\, M(\delta)^n = \mathsf{E}\left(\exp\left[\sum_{x\in\mathbb{Z}^d} G^*_{\delta,\beta}(\ell_n(x))\right]\right)$$

with

$$\ell_n(x) = \sum_{i=1}^{n} 1\{S_i = x\}$$

the local time of simple random walk at site x up to time n, and $G^*_{\delta,\beta}(\ell)$ the free energy at a site that is visited ℓ times (defined below).

§ FREE ENERGY

1. Let $Q(i,j)$ be the probability matrix defined by

$$Q(i,j) = \begin{cases} 1_{\{j=0\}}, & \text{if } i = 0,\ j \in \mathbb{N}_0, \\ \binom{i+j-1}{i-1} \left(\frac{1}{2}\right)^{i+j}, & \text{if } i \in \mathbb{N},\ j \in \mathbb{N}_0, \end{cases}$$

which is the transition kernel of a critical Galton-Watson branching process with a geometric offspring distribution.

2. For $(\delta, \beta) \in \mathcal{Q}$, let $G^*_{\delta,\beta}$ be the function defined by

$$G^*_{\delta,\beta}(\ell) = \log \mathbb{E}\left[e^{\delta\Omega_\ell - \beta\Omega_\ell^2}\right], \quad \Omega_\ell = \sum_{k=1}^{\ell} \omega_k, \quad \ell \in \mathbb{N}_0.$$

3. For $(\mu, \delta, \beta) \in [0, \infty) \times \mathcal{Q}$, define the $\mathbb{N}_0 \times \mathbb{N}_0$ matrix

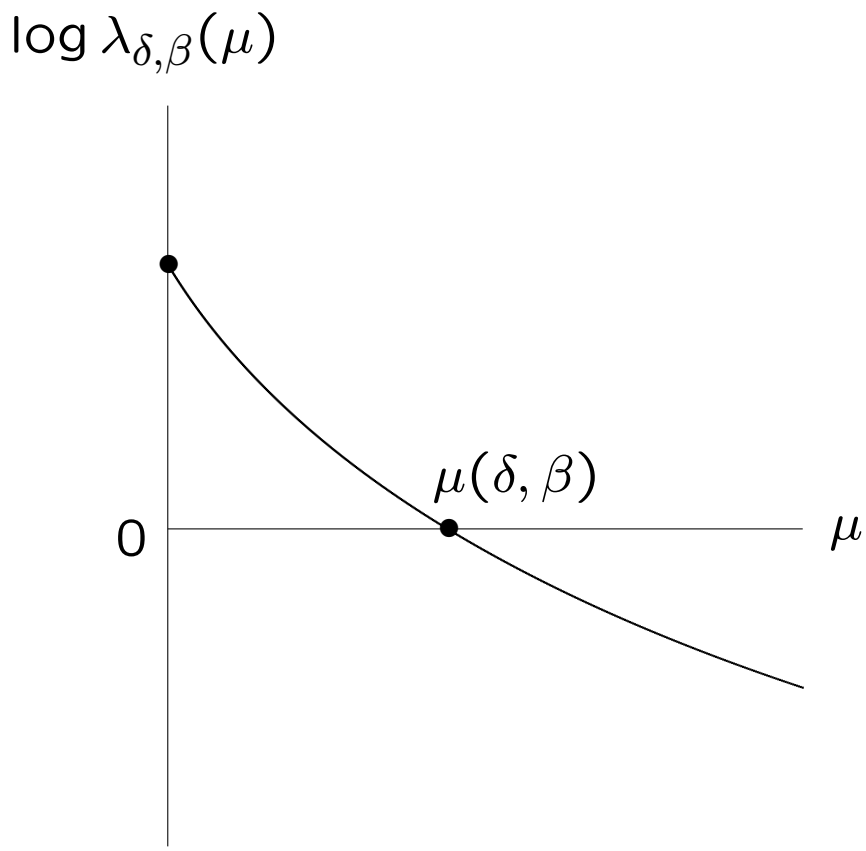
$$A_{\mu,\delta,\beta}(i,j) = e^{-\mu(i+j+1)+G^*_{\delta,\beta}(i+j+1)}\, Q(i+1,j), \quad i,j \in \mathbb{N}_0.$$

4. Let $\lambda_{\delta,\beta}(\mu)$ be the spectral radius of $A_{\mu,\delta,\beta}$. For every $(\delta, \beta) \in \mathcal{Q}$, $\mu \mapsto \lambda_{\delta,\beta}(\mu)$ is continuous, strictly decreasing and log-convex on $[0, \infty)$, and is analytic on $(0, \infty)$, with a finite strictly negative right-slope at 0.

5. For $(\delta, \beta) \in \mathcal{Q}$, let $\mu(\delta, \beta)$ be the unique solution of the equation

$$\lambda_{\delta,\beta}(\mu) = 1$$

when it exists and $\mu(\delta, \beta) = 0$ otherwise.


$\log \lambda_{\delta,\beta}(\mu)$
$\mu(\delta, \beta)$
0
μ

THEOREM 1

FREE ENERGY

(1) *For every* $(\delta, \beta) \in \mathcal{Q}$, *the annealed free energy per monomer*

$$F(\delta, \beta) = \lim_{n \to \infty} \frac{1}{n} \log \mathbb{Z}_n^{\delta, \beta}$$

exists, takes values in $(-\infty, 0]$, *and satisfies the inequality*

$$F(\delta, \beta) \geq f(\delta) = -\log M(\delta) \in (-\infty, 0].$$

(2) *The excess free energy*

$$F^*(\delta, \beta) = F(\delta, \beta) - f(\delta)$$

is convex in (δ, β) *and has the spectral representation*

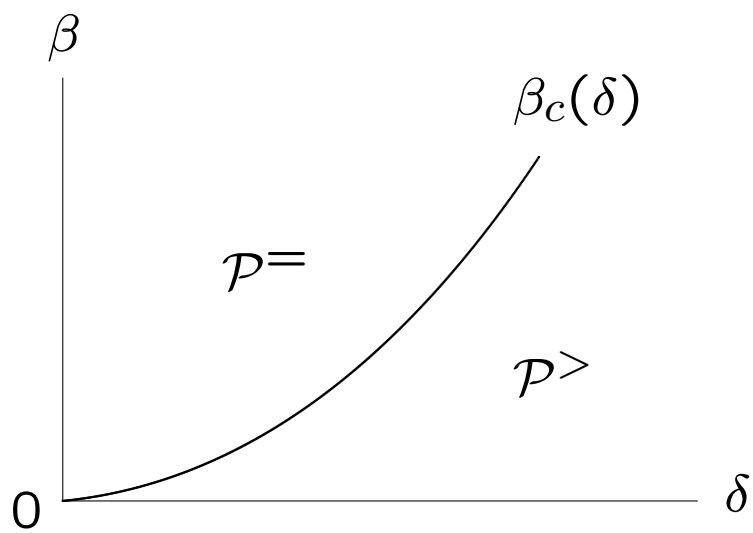
$$F^*(\delta, \beta) = \mu(\delta, \beta).$$

§ PHASE TRANSITION

The inequality $F^*(\delta,\beta) \geq 0$ leads us to define two phases:

$$\mathcal{P}^{>} = \Big\{(\delta,\beta) \in \mathcal{Q}\colon\ F^*(\delta,\beta) > 0\Big\},$$

$$\mathcal{P}^{=} = \{(\delta,\beta) \in \mathcal{Q}\colon\ F^*(\delta,\beta) = 0\Big\}.$$



THEOREM 2

(1) *There exists a critical curve* $\delta \mapsto \beta_c(\delta)$ *such that*

$$\mathcal{P}^{>} = \Big\{(\delta,\beta) \in \mathcal{Q}\colon\ 0 < \beta < \beta_c(\delta)\Big\},$$
$$\mathcal{P}^{=} = \Big\{(\delta,\beta) \in \mathcal{Q}\colon\ \beta \geq \beta_c(\delta)\Big\}.$$

(2) *For every* $\delta \in [0,\infty)$, $\beta_c(\delta)$ *is the unique solution of the equation* $\lambda_{\delta,\beta}(0) = 1$.

(3) $\delta \mapsto \beta_c(\delta)$ *is continuous, strictly increasing and convex on* $[0,\infty)$, *is analytic on* $(0,\infty)$, *and satisfies* $\beta_c(0) = 0$.

(4) $(\delta,\beta) \mapsto F^*(\delta,\beta)$ *is analytic on* $\mathcal{P}^{>}$.

§ LAWS OF LARGE NUMBERS

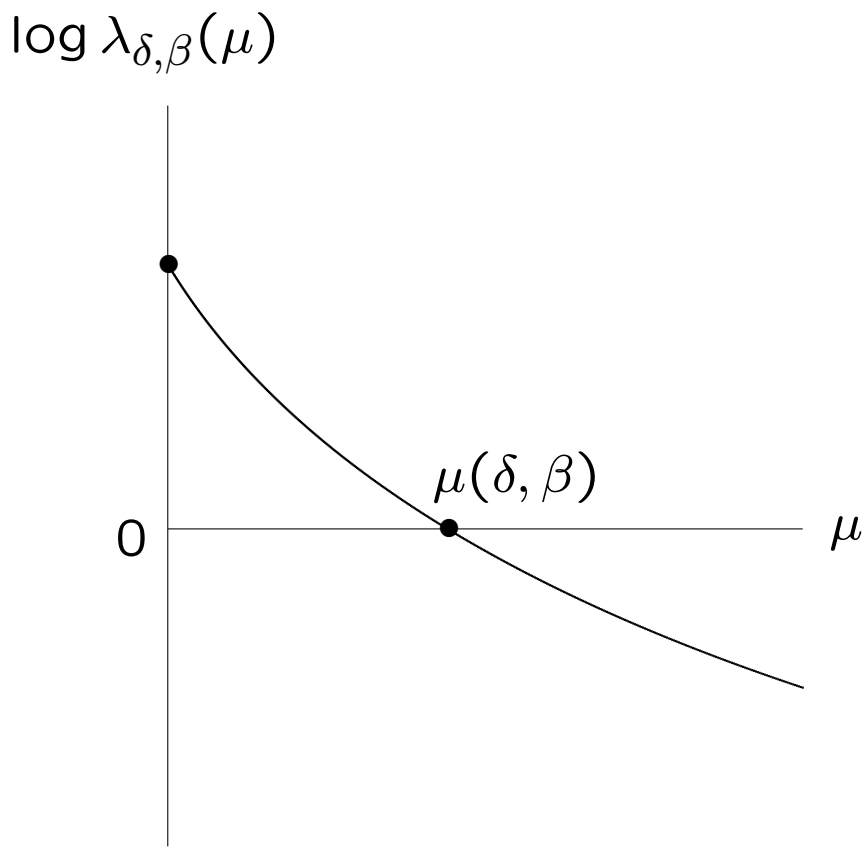
We proceed by stating a LLN for the empirical speed $n^{-1}S_n$ and the empirical charge $n^{-1}\Omega_n$, where

$$S_n = \sum_{i=1}^{n} X_i, \qquad \Omega_n = \sum_{i=1}^{n} \omega_i.$$

Let

$$\mathcal{B} = \Big\{(\delta, \beta) \in \mathcal{Q} \colon\ 0 < \beta \leq \beta_c(\delta)\Big\}, \qquad \mathcal{S} = \mathcal{Q} \backslash \mathcal{B}.$$

The set $\mathcal{B}$ will be referred to as the ballistic phase, the set $\mathcal{S}$ as the subballistic phase, for reasons that become apparent in the next theorem.


$\log \lambda_{\delta,\beta}(\mu)$
$\mu(\delta, \beta)$
0
μ

THEOREM 3

(1) *For every* $(\delta,\beta)\in\mathcal{Q}$ *there exists a* $v(\delta,\beta)\in[0,1]$ *such that*

$$\lim_{n\to\infty}\mathbb{P}_n^{\delta,\beta}\Big(\Big|n^{-1}S_n-v(\delta,\beta)\Big|>\varepsilon\,\Big|\,S_n>0\Big)=0\qquad\forall\,\varepsilon>0,$$

where

$$v(\delta,\beta)\begin{cases}>0, & (\delta,\beta)\in\mathcal{B},\\ =0, & (\delta,\beta)\in\mathcal{S}.\end{cases}$$

(2) *For every* $(\delta,\beta)\in\mathcal{B}$,

$$\frac{1}{v(\delta,\beta)}=\Big[-\frac{\partial}{\partial\mu}\log\lambda_{\delta,\beta}(\mu)\Big]_{\mu=\mu(\delta,\beta)}.$$

THEOREM 4

(1) *For every* $(\delta, \beta) \in \mathcal{Q}$, *there exists a* $\rho(\delta, \beta) \in [0, \infty)$ *such that*

$$\lim_{n \to \infty} \mathbb{P}_n^{\delta,\beta} \left(\left| n^{-1} \Omega_n - \rho(\delta, \beta) \right| > \epsilon \right) = 0 \qquad \forall \, \epsilon > 0,$$

where

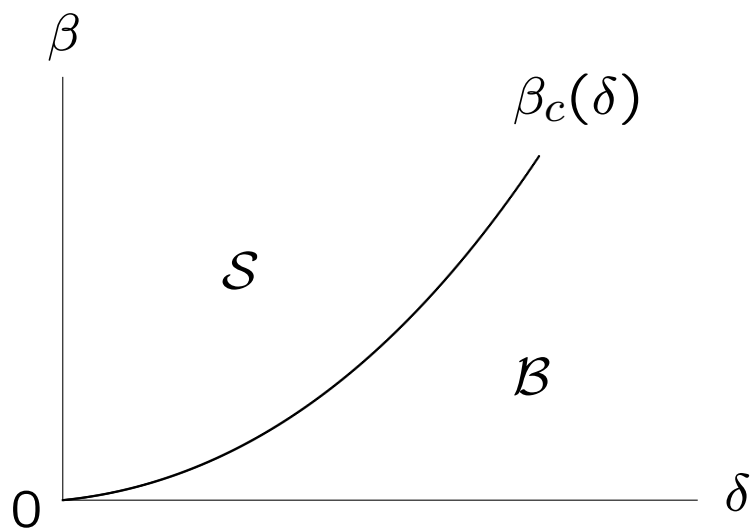
$$\rho(\delta, \beta) \begin{cases} > 0, & (\delta, \beta) \in \mathcal{B}, \\ = 0, & (\delta, \beta) \in \mathcal{S}. \end{cases}$$

(2) *For every* $(\delta, \beta) \in \mathcal{B}$,

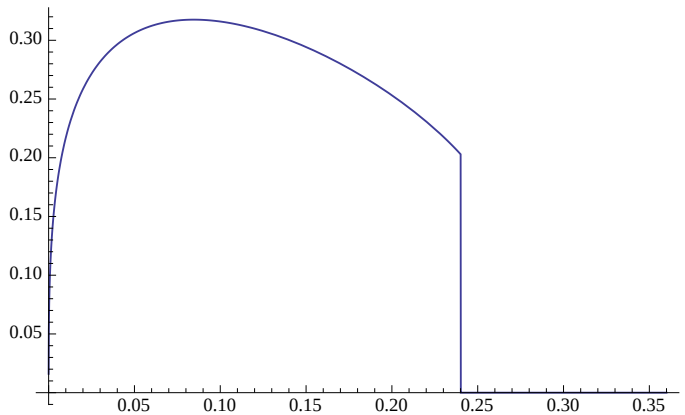
$$\rho(\delta, \beta) = \frac{\partial}{\partial \delta} \mu(\delta, \beta).$$

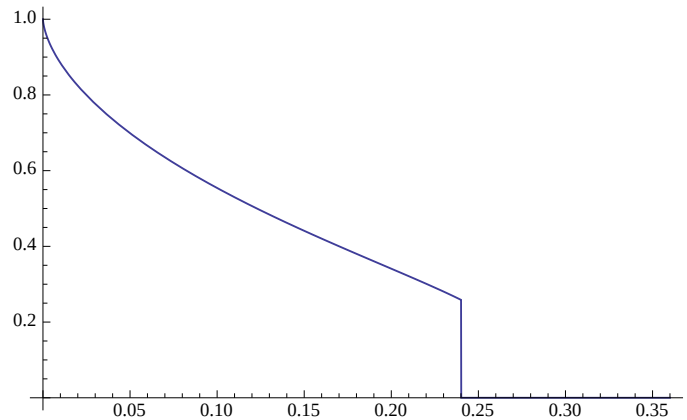
§ PHASE DIAGRAM

Picture of the ballistic phase $\mathcal{B}$ and the subballistic phase $\mathcal{S}$. The critical curve is part of $\mathcal{B}$, which implies that the phase transition is first order.



Numerical plots of $\beta \mapsto v(\delta, \beta)$ and $\beta \mapsto \rho(\delta, \beta)$ for $\delta = 1$:





§ LARGE DEVIATION PRINCIPLES


Varadhan

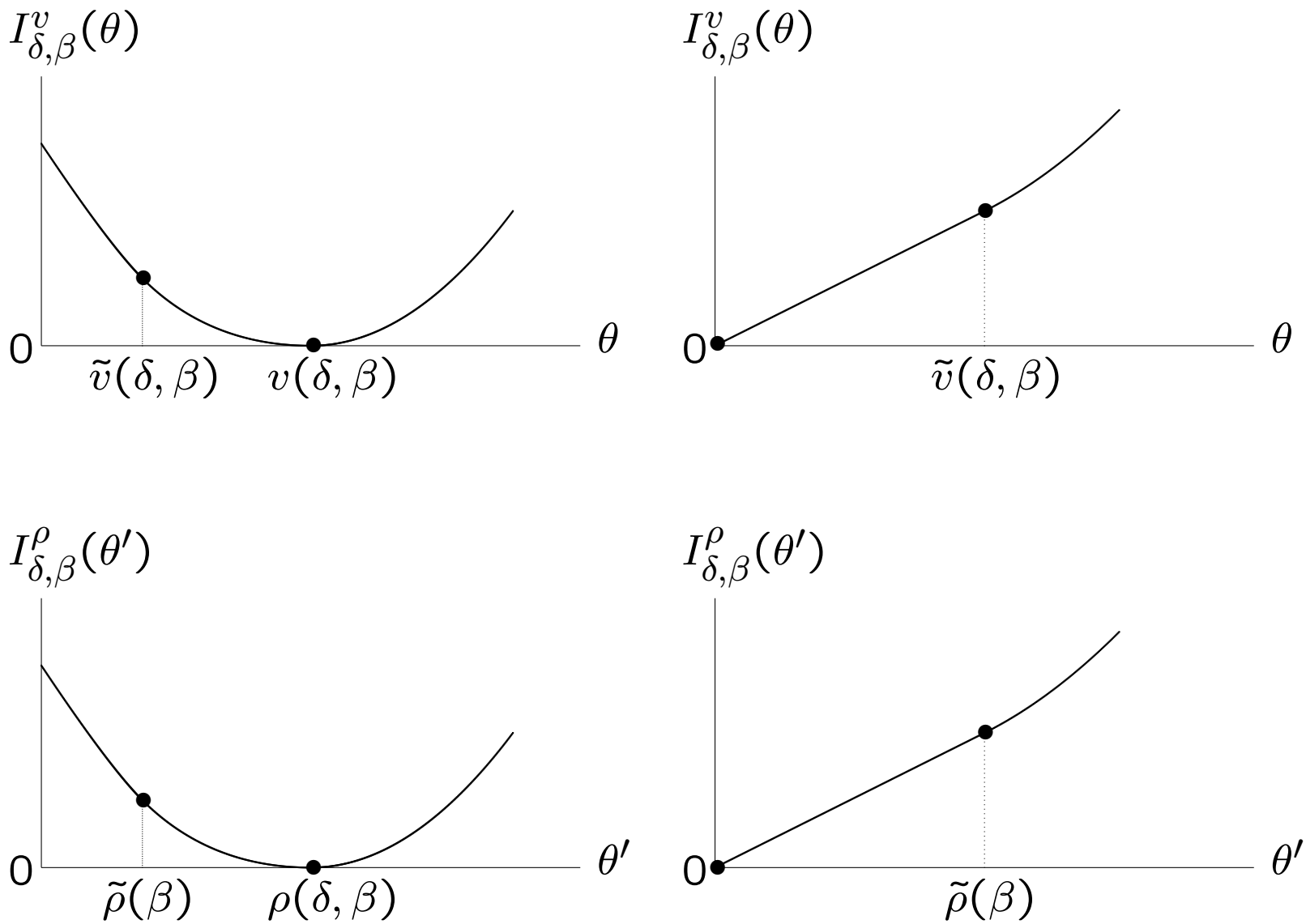
THEOREM 5

For every $(\delta, \beta) \in \mathcal{Q}$*:*

(1) *The sequence* $(n^{-1}S_n)_{n\in\mathbb{N}}$ *conditionally on* $\{S_n > 0\}_{n\in\mathbb{N}}$ *satisfies the LDP on* $[0, \infty)$ *with rate function* $I^v_{\delta,\beta}$*.*

(2) *The sequence* $(n^{-1}\Omega_n)_{n\in\mathbb{N}}$ *satisfies the LDP on* $[0, \infty)$ *with rate function* $I^\rho_{\delta,\beta}$*.*

Pictures for $(\delta, \beta) \in \mathrm{int}(\mathcal{B})$ and $(\delta, \beta) \in \mathcal{S}$ are:


$I^v_{\delta,\beta}(\theta)$
0
θ
$\tilde{v}(\delta,\beta)$
$v(\delta,\beta)$
$I^v_{\delta,\beta}(\theta)$
0
θ
$\tilde{v}(\delta,\beta)$
$I^\rho_{\delta,\beta}(\theta')$
0
θ'
$\tilde{\rho}(\beta)$
$\rho(\delta,\beta)$
$I^\rho_{\delta,\beta}(\theta')$
0
θ'
$\tilde{\rho}(\beta)$

§ CENTRAL LIMIT THEOREMS

THEOREM 6

For every $(\delta, \beta) \in \mathrm{int}(\mathcal{B})$ *the scaled quantities*

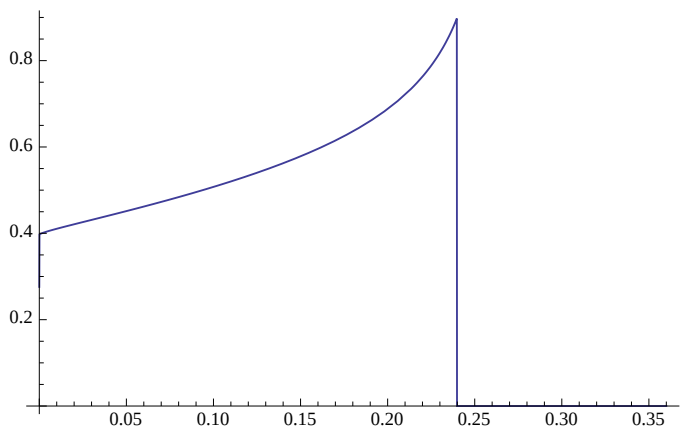
$$\frac{S_n - nv(\delta, \beta)}{\sigma_v(\delta, \beta)\sqrt{n}}, \qquad \frac{\Omega_n - n\rho(\delta, \beta)}{\sigma_\rho(\delta, \beta)\sqrt{n}},$$

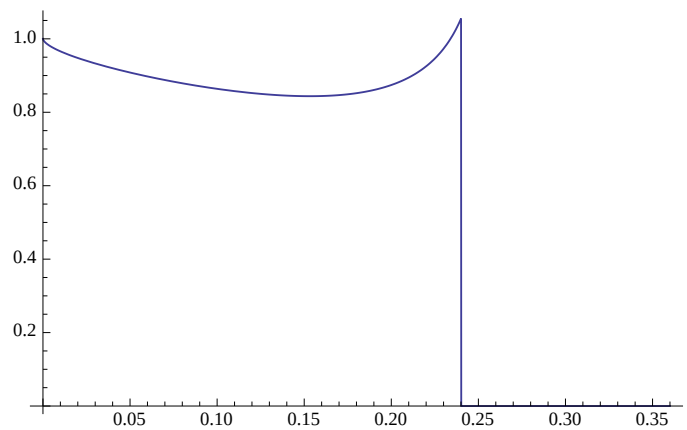
converge in distribution to the standard normal law with

$$\frac{1}{\sigma_v^2(\delta, \beta)} = \left[\frac{\partial^2}{\partial\theta^2} I^v_{\delta,\beta}(\theta)\right]_{\theta = v(\delta,\beta)},$$

$$\frac{1}{\sigma_\rho^2(\delta, \beta)} = \left[\frac{\partial^2}{\partial\theta'^2} I^\rho_{\delta,\beta}(\theta')\right]_{\theta' = \rho(\delta,\beta)}.$$

Numerical plots of $\beta \mapsto \sigma_v^2(\delta, \beta)$ and $\beta \mapsto \sigma_\rho^2(\delta, \beta)$ for $\delta = 1$:





PART II: asymptotic properties

§ SCALING OF THE CRITICAL CURVE

THEOREM 7

(1) *As* $\delta \downarrow 0$,

$$\beta_c(\delta) - \tfrac{1}{2}\delta^2 \sim -a^*(\tfrac{1}{2}\delta^2)^{4/3},$$

where a^* *comes from a certain Sturm-Liouville operator.*

(2) *As* $\delta \to \infty$,

$$\beta_c(\delta) \sim \frac{\delta}{T}$$

with

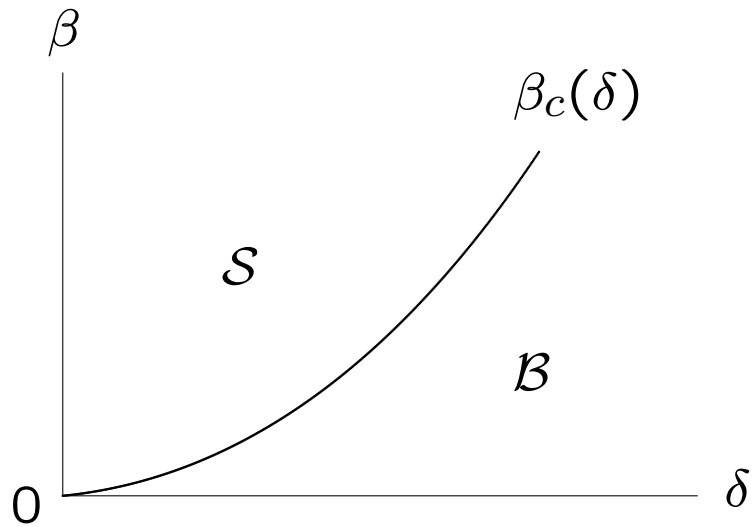
$$T = \sup\left\{t > 0\colon\ \mathbb{P}(\omega_1 \in t\mathbb{Z}) = 1\right\}$$

Either $T > 0$ (lattice case) or $T = 0$ (non-lattice case). If $T = 0$ and ω_1 has a bounded density with respect to the Lebesgue measure, then

$$\beta_c(\delta) \sim \frac{1}{4} \frac{\delta^2}{\log \delta}.$$

Note that the scaling behavior of the critical curve is anomalous for small charge bias. This implies that the critical curve is not analytic at the origin.

Note that the scaling is also delicate for large charge bias.


β
$\beta_c(\delta)$
$\mathcal{S}$
$\mathcal{B}$
0
δ

§ CRITICAL SCALING OF THE EXCESS FREE ENERGY

The scaling behaviour of the excess free energy near the critical curve fits with the phase transition being first order.

THEOREM 8

For every $\delta \in (0, \infty)$*,*

$$F^*(\delta, \beta) \sim K_\delta[\beta_c(\delta) - \beta], \quad \beta \uparrow \beta_c(\delta),$$

for a certain explicit $K_\delta \in (0, \infty)$*.*

§ WEAK INTERACTION SCALING

THEOREM 9

(1) *For every* $\delta \in (0, \infty)$,

$$F(\delta, \beta) \sim -A_\delta \beta^{2/3}, \qquad v(\delta, \beta) \sim B_\delta \beta^{1/3},$$
$$\rho(\delta, \beta) - \rho_\delta \sim C_\delta \beta^{2/3}, \quad \beta \downarrow 0,$$

for certain explicit $A_\delta, B_\delta, C_\delta \in (0, \infty)$, *where* $\rho_\delta = \mathbb{E}^\delta(\omega_1)$.

(2) *For every* $\epsilon > 0$,

$$F(\delta, \beta) \sim \beta_c(\delta) - \beta, \qquad \delta, \beta \downarrow 0,$$

provided $\frac{1}{2}\delta^2 - \beta \asymp \delta^{4/3}$.

§ CONCLUSIONS

- The annealed charged polymer in $d = 1$ exhibits a very rich scaling behaviour.

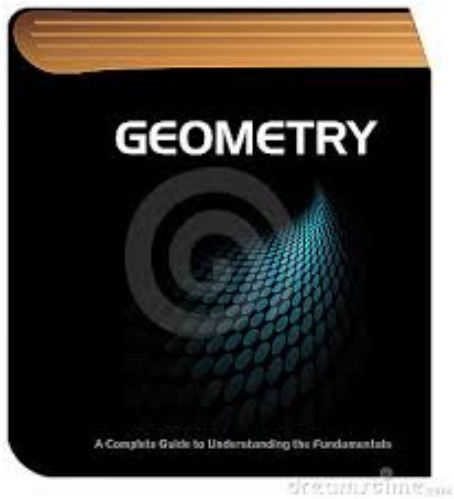
- The phase transition between the ballistic phase and the subballistic phase is first order.

- The large deviation rate functions for the speed and the charge exhibit linear pieces in both phases.

- The limit of weak interaction is anomalous.

For $d \geq 2$ we expect a similar richness:

Quentin Berger, dH, Julien Poisat, work in progress




Thank You