HOW DOES A CHARGED POLYMER COLLAPSE?

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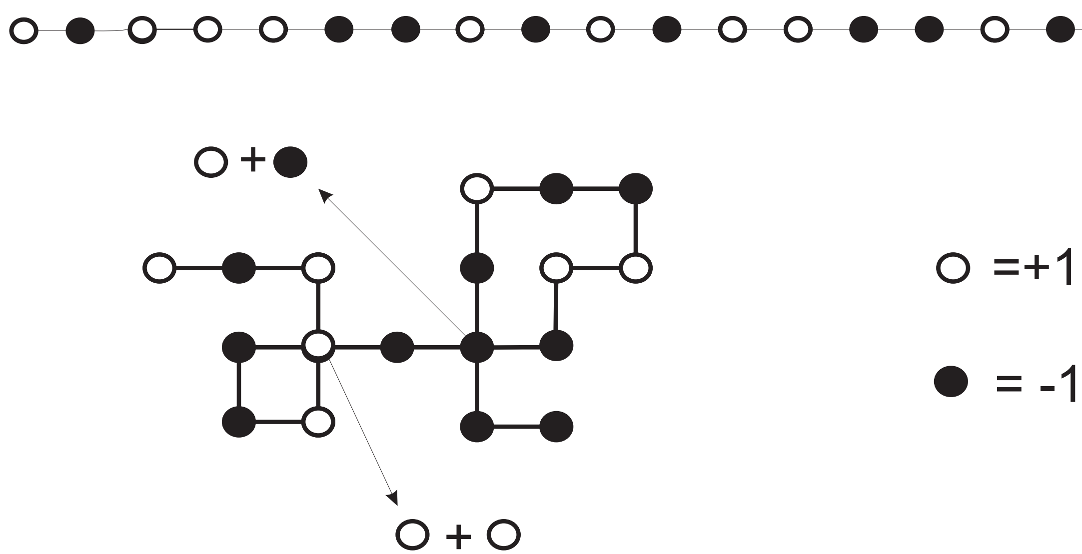
§ MOTIVATION

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.



+
+
=+1
= -1

§ 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

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

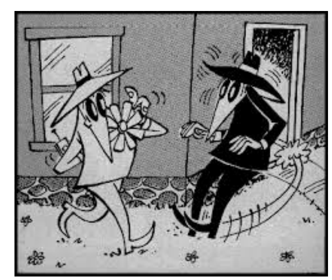
To allow for biased charges, we use a tilting parameter $\delta \in \mathbb{R}$ and write $\mathbb{P}^\delta$ for the i.i.d. law of ω with marginal

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

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

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

where

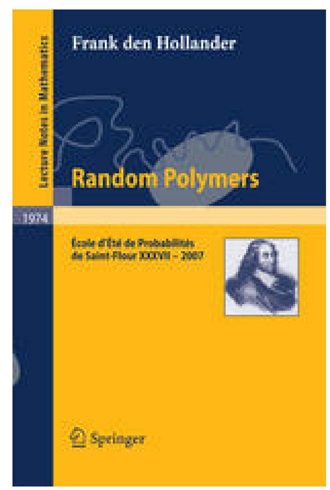
$$\mathbb{Z}_n^{\delta,\beta} = (\mathbb{E}^\delta \times \mathrm{E}) \left[e^{-\beta H_n^\omega(S)} \right]$$

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 first consider $d = 1$ and afterwards $d \geq 2$.



§ KEY FORMULA:

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

$$\mathbb{Z}_n^{\delta,\beta} = \frac{1}{M(\delta)^n} \mathsf{E}\left(\exp\left[\sum_{x \in \mathbb{Z}^d} G^*_{\delta,\beta}(\ell_n(x))\right]\right)$$

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 under the biased charge law at a site that is visited ℓ times.

PART I: $d = 1$

§ 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

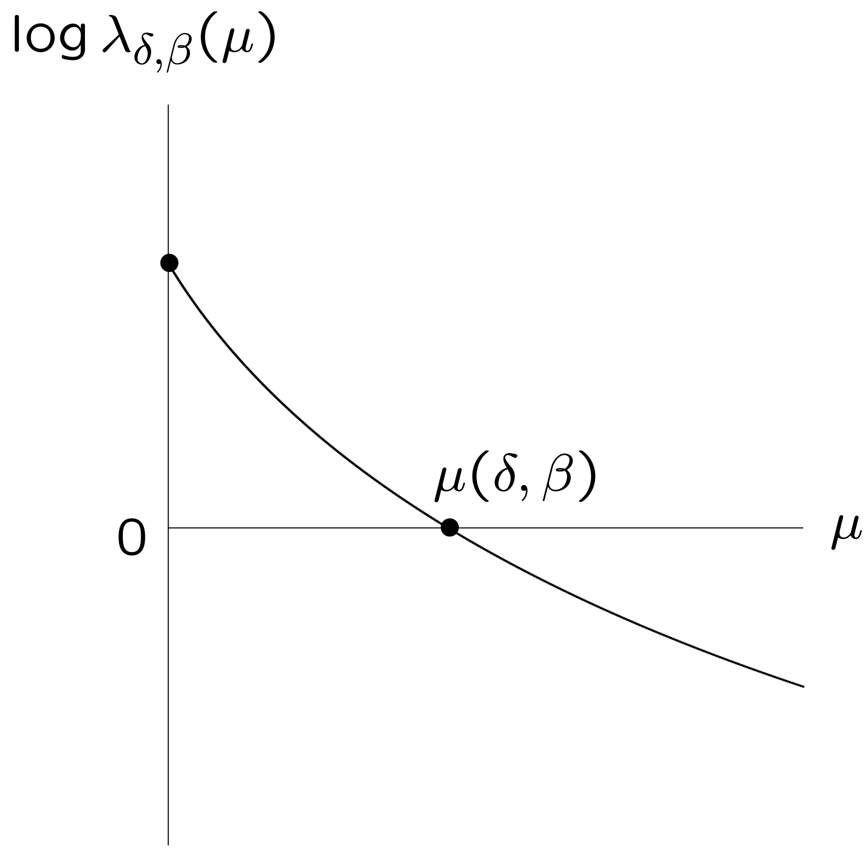
$$A_{\mu,\delta,\beta}(i,j) = e^{-\mu(i+j+1)+G^*_{\delta,\beta}(i+j+1)}\, Q(i+1,j), \quad i,j \in \mathbb{N}_0.$$

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*

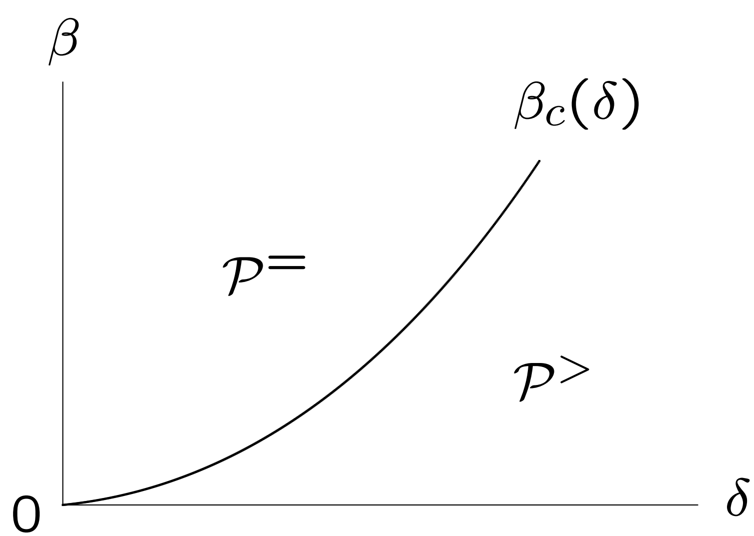
$$F^*(\delta,\beta) = \mu(\delta,\beta).$$

§ PHASE DIAGRAM

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

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

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.

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*

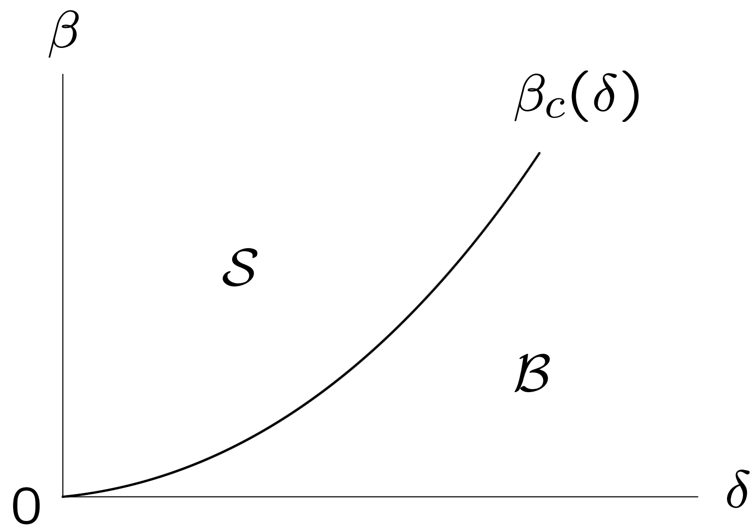
$$\lim_{n\to\infty} \mathbb{P}_n^{\delta,\beta}\left(\left|n^{-1}\Omega_n - \rho(\delta,\beta)\right| > \epsilon\right) = 0 \qquad \forall\,\epsilon > 0,$$

where

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

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

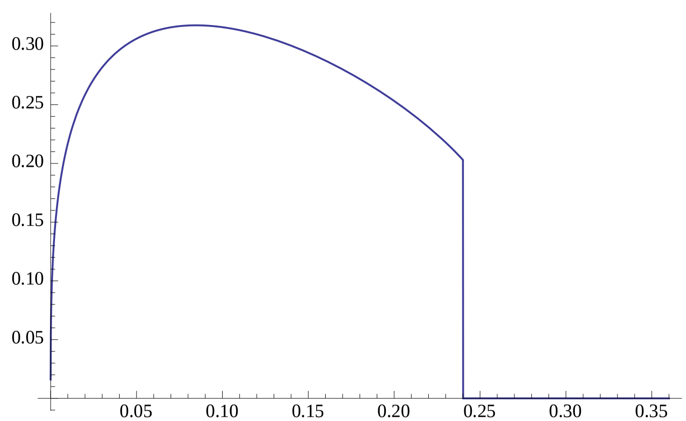
$$\rho(\delta,\beta) = \frac{\partial}{\partial\delta}\,\mu(\delta,\beta).$$

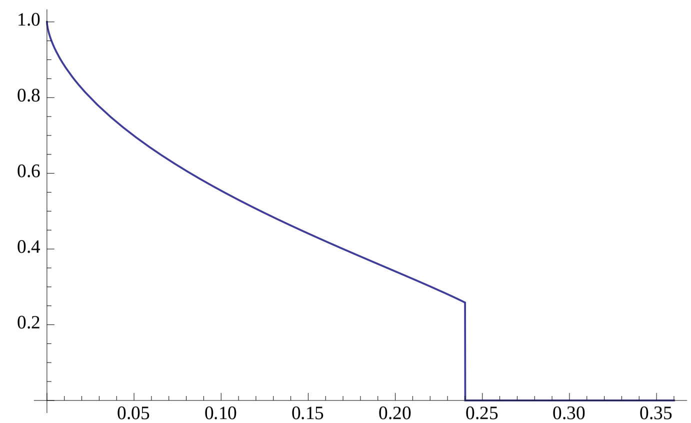


Plot of the ballistic phase $\mathcal{B}$ and the subballistic phase $\mathcal{S}$.

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 $\delta = 1$:





Besides LLN, also CLT and LDP have been derived.

The rate functions exhibit linear pieces: inhomogeneous optimal strategies to realise large deviations.

§ SCALING OF THE CRITICAL CURVE

THEOREM 5

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

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

where a^* *is the principal eigenvalue of a certain Sturm-Liouville operator.*

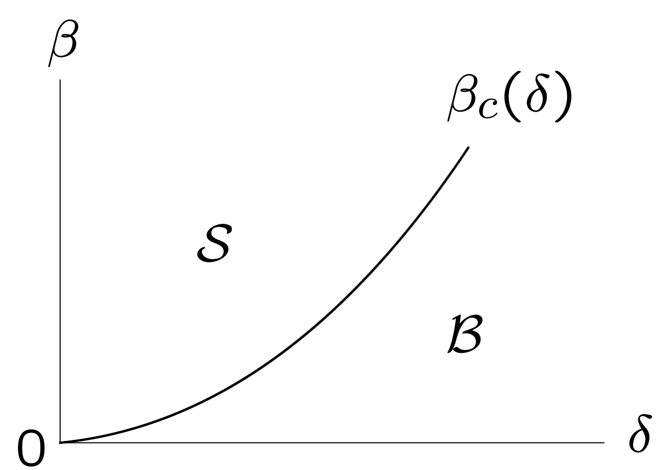
§ WEAK INTERACTION LIMIT

THEOREM 6

For any $\delta \in (0, \infty)$, *as* $\beta \downarrow 0$,

$$F(\delta, \beta) \sim -C_\delta \beta^{2/3}.$$

The weak interaction limit is anomalous.

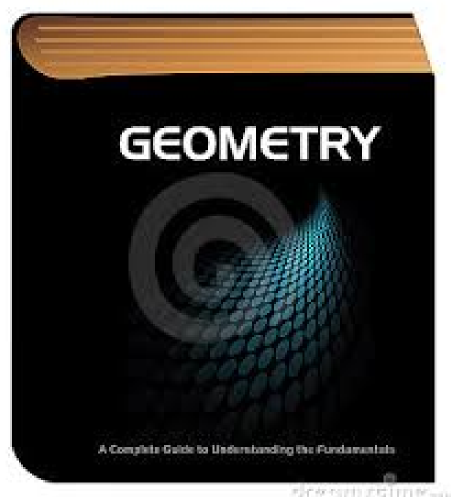


PART II: $d \geq 2$

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

Quentin Berger, dH, Julien Poisat, work in progress

Dima Ioffe, dH, work in progress



DISCLAIMER:

The proof of the existence of the annealed free energy is still open and seems highly non-trivial.

§ SCALING OF THE CRITICAL CURVE

Let $Q_n = \sum_{x \in \mathbb{Z}^d} \ell_n(x)^2$ denote the self-intersection local time at time n of SRW. A standard computation gives, as $n \to \infty$,

$$E[Q_n] = \sum_{1 \leq i,j \leq n} P(S_i = S_j) \sim \begin{cases} \lambda_1 n^{3/2}, & \text{if } d = 1, \\ \lambda_2 n \log n, & \text{if } d = 2, \\ \lambda_d n, & \text{if } d \geq 3, \end{cases}$$

with

$$\lambda_1 = \sqrt{8/\pi}, \qquad \lambda_2 = 2/\pi, \qquad \lambda_d = 2G_d - 1, \quad d \geq 3,$$

where $G_d = \sum_{n \in \mathbb{N}_0} P(S_n = 0)$ is the Green function at the origin of SRW.

Abbreviate $m_k = \mathbb{E}[\omega_1^k]$, $k \in \mathbb{N}$, and recall that $m_1 = 0$, $m_2 = 1$.

THEOREM 7

As $\delta \downarrow 0$,

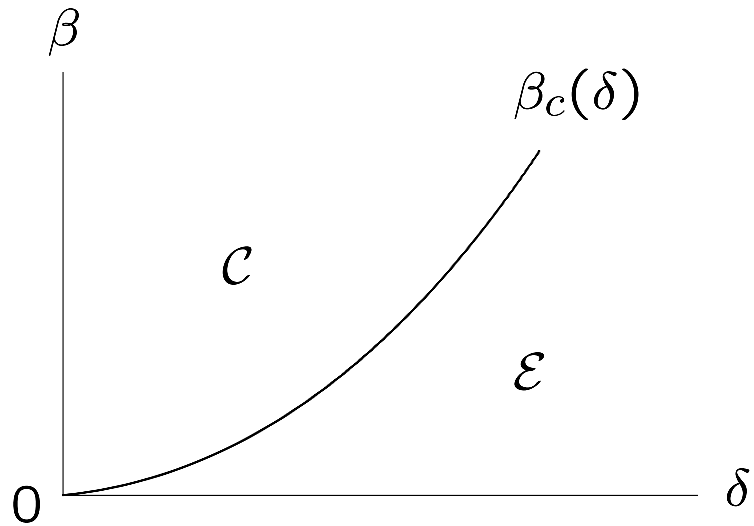
$$\beta_c(\delta) = \frac{1}{2}\delta^2 - \frac{1}{3}m_3\delta^3 - [1 + o(1)]\,\chi_d$$

with

$$\chi_\delta = \begin{cases} \kappa_2\delta^4 \log(1/\delta), & \text{if } d = 2, \\ \kappa_d\delta^4, & \text{if } d \geq 3, \end{cases}$$

and

$$\kappa_2 = \frac{1}{4}\lambda_2, \qquad \kappa_d = \frac{1}{4}(\lambda_d - 1) - \frac{1}{3}m_3^2 + \frac{1}{12}m_4, \quad d \geq 3.$$



$\mathcal{E}$ extended phase   SAW-like
$\mathcal{C}$ collapsed phase   coil-like

§ WEAK INTERACTION LIMIT

THEOREM 8

For any $\delta \in (0, \infty)$, *as* $\beta \downarrow 0$,

$$F(\delta, \beta) \sim \begin{cases} -\beta \log(1/\beta)\, \lambda_2 m(\delta)^2, & \text{if } d = 2, \\ -\beta\, [\lambda_d m(\delta)^2 + v(\delta)], & \text{if } d \geq 3, \end{cases}$$

where $m(\delta) = \mathbb{E}^\delta[\omega_1]$ *and* $v(\delta) = \mathbb{V}\text{ar}^\delta[\omega_1]$.

§ SCALING IN THE COLLAPSED PHASE

THEOREM 9

Under the annealed polymer measure,

$$\left(\frac{1}{\alpha_n} S_{\lfloor nt \rfloor}\right)_{0\le t\le 1} \Longrightarrow (U_t)_{0\le t\le 1}, \qquad n \to \infty,$$

where

$$\alpha_n = \left(\frac{n}{\log n}\right)^{1/(d+2)}$$

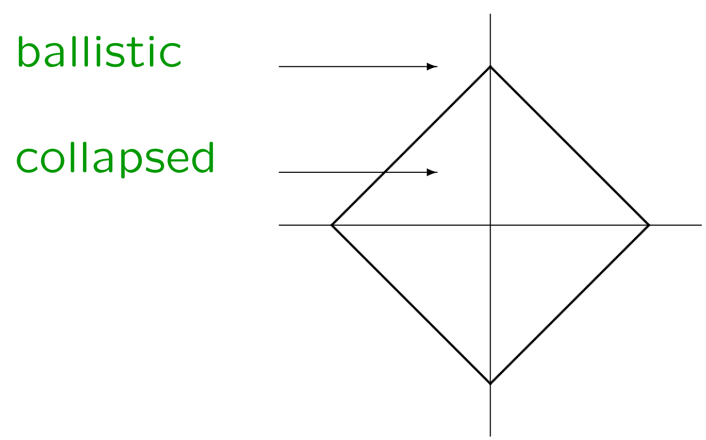
and $(U_t)_{t\ge 0}$ *is a Brownian motion on* $\mathbb{R}^d$ *conditioned not to leave a ball with a deterministic radius and a randomly shifted centre.*

§ APPLICATION OF A FORCE

THEOREM 10

(i) *In the interior of* $\mathcal{E}$ *the polymer becomes ballistic when an arbitrarily small force is applied to its endpoint.*

(ii) *In the interior of* $\mathcal{C}$ *the polymer stays collapsed when a suffciently small force is applied to its endpoint.*



§ CONCLUSIONS

- The annealed charged polymer shows very rich scaling behaviour.
- The limit of weak interaction is anomalous.
- 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 reflecting inhomogeneous strategies.


Thank You