Interacting partially directed self-avoiding walk (polymer collapse)

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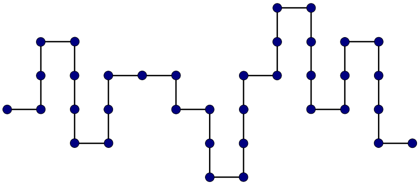
1. A directed model : the IPDSAW

Introduced by Zwanzig and Lauritzen (1968)

1.1) Trajectories.

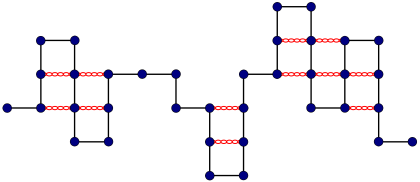
For a polymer of length $L \in \mathbb{N}$ the set of allowed configurations is

$$\Omega_L = \{L - \text{step directed self-avoiding paths starting at the origin and taking steps in } \{\uparrow, \rightarrow, \downarrow\}\}.$$



1.2) Self-interactions.

An energetic reward $\beta \in (0, \infty)$ is associated with each self touching made by the polymer



Self-touching : two non consecutive sites along the path at distance 1 from each other.

1.3) Hamiltonian.

With each $\pi \in \Omega_L$ we associate an energy given by the Hamiltonian

$$H_{L,\beta}(\pi) := \beta \sum_{\substack{i,j=0 \\ i<j-1}}^{L} \mathbf{1}_{\{\|\pi_i - \pi_j\|=1\}}$$

$\beta \in (0, \infty)$: intensité de l'attraction (self-touching).

1.4) Polymer measure.

For every $\pi \in \Omega_L$;

$$P_{L,\beta}(\pi) = \frac{e^{H_{L,\beta}(\pi)}}{Z_{L,\beta}}$$

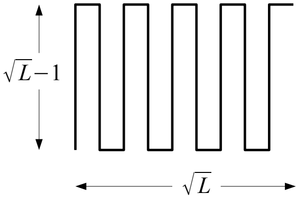
with the partition function

$$Z_{L,\beta} = \sum_{\pi \in \Omega_L} e^{H_{L,\beta}(\pi)}$$

1.5) Phase transition.

Free energy : for $\beta \in (0,\infty)$, set $f(\beta) := \lim_{L\to\infty} \frac{1}{L} \log Z_{L,\beta}$.

For all $\beta \in (0,\infty)$, $f(\beta) \geq \beta$ because (for $L \in \mathbb{N}^2$)

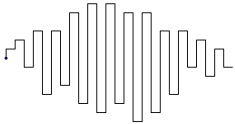


$$H_{L,\beta}(\tilde{\pi}) = \beta(\sqrt{L}-1)^2$$

$$\beta_c := \inf\{\beta \geq 0 : f(\beta) = \beta\}$$

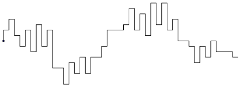
Partition $[0, \infty)$ into a collapsed ($\mathcal{C}$) and an extended ($\mathcal{E}$) phase

$$\mathcal{C} := \{\beta : f(\beta) = \beta\} = \{\beta : \beta \geq \beta_c\}$$



and

$$\mathcal{E} := \{\beta : f(\beta) > \beta\} = \{\beta : \beta < \beta_c\}.$$



1.6) What do we want to show ?

- **Assymptotics of the free energy close to β_c :** spot β_c and find $\gamma > 0$ and $\alpha > 0$ s.t.

$$\tilde{f}(\beta_c - \epsilon) - \tilde{f}(\beta_c) = \gamma \epsilon^{\alpha}$$

- **Path results :** in each regimes (i.e., extended, critical and collapsed), describe the geometric conformation adopted by the path π under $P_{L,\beta}$, when L is large but finite. Give the infinite volume limit.
- **Simulate long polymers :** sample path π under $P_{L,\beta}$ with large L.

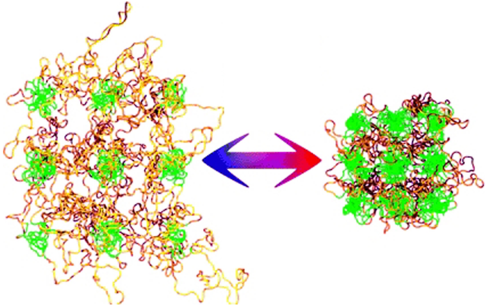
2 Physical motivation

1.1) homopolymer. A long chain of monomers of the same type (ex : polystyrene).

1.2) Medium. A pure phase of a particular solvent (ex : cyclohexane).

1.3) Interactions.
Weak chemical affinity between the monomers and the solvent : repulsion.

Collapse transition :



Random coil *Compact ball*

3. Background and new approach

3.1) Combinatoric techniques.

$$G(\beta, z) = \sum_{L=1}^{\infty} Z_{L,\beta}\, z^L$$

Use some smart concatenations of path to provide an explicit formula for $G(\beta, z)$. Study $G(\beta, z)$ and obtain :

- results on the free energy
- weak results on the path
- no results on the disordered version of the model

3.2) New probabilistic approach.

Let $\mathbf{P}_\beta$ be the law of the random walk V with geometric increment, i.e., $V_0 = 0$ and $(V_{i+1} - V_i)_{i\in\mathbb{N}}$ is i.i.d. and

$$\mathbf{P}_\beta(V_1 = k) = \frac{e^{-\frac{\beta}{2}|k|}}{c_\beta}, \quad k \in \mathbb{N}.$$

We get

$$Z_{L,\beta} = e^{\beta L} \sum_{N=1}^{L} (\Gamma_\beta)^N \, \mathbf{P}_\beta(\mathcal{V}_{N+1,L-N}).$$

with $\Gamma_\beta = \frac{c_\beta}{e^\beta}$, and also for $N \in \{1, \dots, L\}$:

$$P_{L,\beta}\big(\pi \in \cdot \mid N_\pi = N\big) = \mathbf{P}_\beta\big(T_N(V) \in \cdot \mid V \in \mathcal{V}_{N+1,L-N}\big).$$

4 Phase transition asymptotics

Theorem (Phase transition asymptotics)

The phase transition occurs at β_c the unique solution of $e^{\beta} = c_{\beta}$. It is second order with critical exponent $3/2$, i.e.,

$$\lim_{\epsilon \to 0^+} \frac{\tilde{f}(\beta_c - \epsilon)}{\epsilon^{3/2}} = \left(\frac{b}{d}\right)^{3/2}$$

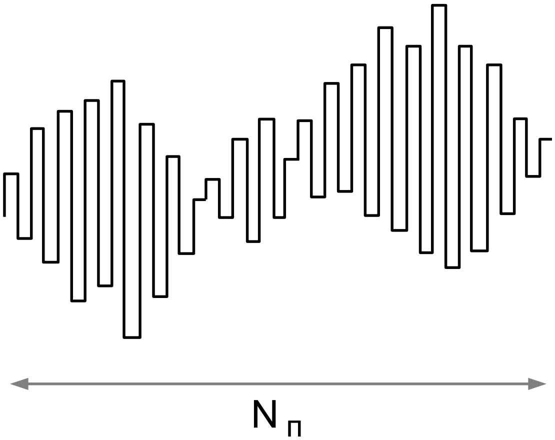
where

- $b = 1 + \frac{e^{-\beta_c/2}}{1 - e^{-\beta_c}}$
- $d = -\lim_{T \to \infty} \frac{1}{T} \log \mathbf{E}\big(e^{-\sigma_{\beta_c} \int_0^T |B(t)| dt}\big) = 2^{-1/3} |a_1'| \sigma_{\beta_c}^{2/3}$
- $\sigma_{\beta}^2 = \mathbf{E}_{\beta}(V_1^2)$
- a_1' *: smallest zero (in modulus) of the first derivative of the Airy function.*

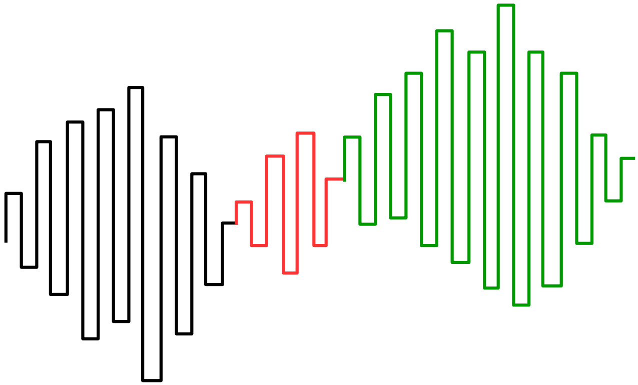
5 Geometry of the path

5.1) Three features of interest

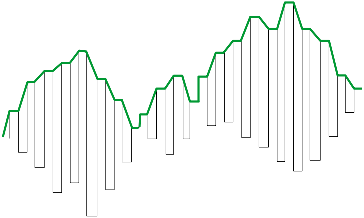
- The horizontal expansion N_π of $\pi \in \Omega_L$



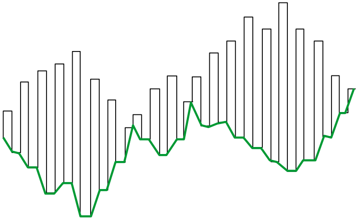
- The decomposition into beads

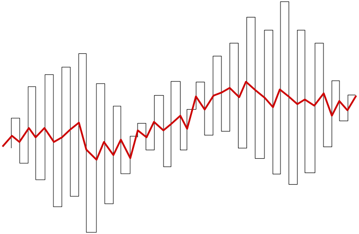


Upper envelope : $\mathcal{E}_\pi^+ = (\mathcal{E}_{\pi,i}^+)_{i=0}^{N_\pi}$

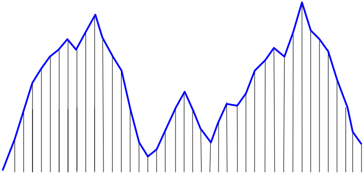


Lower envelope : $\mathcal{E}_\pi^-$





Center of mass walk : $\mathcal{M}_\pi$



Profile : $\mathcal{T}_\pi$

5.2) Horizontal expansion

N_π : number of horizontal step of π (sampled from $P_{L,\beta}$).

Theorem

(1) *Extended : there exists* $e_\beta \in (0,1)$ *so that*

$$\lim_{L\to\infty} P_{L,\beta}\Big(\Big|\frac{N_\pi}{L} - e_\beta\Big| \geq \epsilon\Big) = 0.$$

(2) *Critical :*

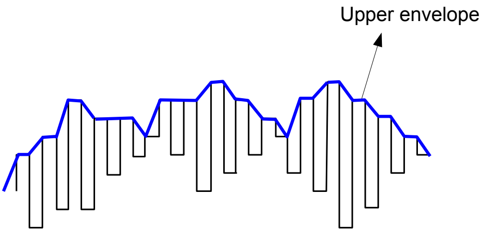
$$\lim_{L\to\infty} \frac{N_\pi}{L^{2/3}} =_{law} \sum_{i=1}^{\infty} Y_i\, U_i^{2/3}$$

(3) *Collapsed : there exists* $a_\beta \in (0,\infty)$ *so that*

$$\lim_{L\to\infty} P_{L,\beta}\Big(\Big|\frac{N_\pi}{\sqrt{L}} - a_\beta\Big| \geq \epsilon\Big) = 0.$$

5.3) Vertical expansion

For $\pi \in \Omega_L$ let $\mathcal{E}_\pi^+ = (\mathcal{E}_{\pi,i}^+)_{i=0}^{N_\pi}$ and $\mathcal{E}_\pi^- = (\mathcal{E}_{\pi,i}^-)_{i=0}^{N_\pi}$ be the upper and lower envelops of the path π.



Let $\widetilde{\mathcal{E}}_\pi^+$ and $\widetilde{\mathcal{E}}_\pi^- : [0,1] \to \mathbb{R}$ be the time-space rescaled cadlag process defined as

$$\tilde{\mathcal{E}}_\pi^a(t) = \frac{1}{N_\pi + 1}\, \mathcal{E}^a_{\pi, \lfloor t\,(N_\pi+1) \rfloor}, \quad a \in \{\pm\},\ t \in [0,1].$$

5.3.1) Extended phase

When $\beta < \beta_c$ and under $P_{L,\beta}$, We let also $(B_s)_{s\in[0,1]}$ be a standard Brownian motion.

Theorem

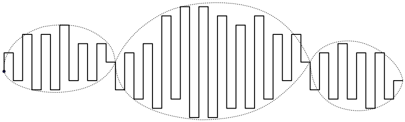
For $\beta < \beta_c$, and with π sampled from $P_{L,\beta}$, there exists a $\sigma_\beta > 0$ such that

$$\lim_{L\to\infty} \sqrt{N_\pi}(\tilde{\mathcal{E}}_\pi^+, \tilde{\mathcal{E}}_\pi^-) =_{Law} \sigma_\beta \big(B_s, B_s\big)_{s\in[0,1]},$$

and σ_β is explicit.

5.3.2) Path results : inside the collapsed phase ($\beta > \beta_c$)

Divide the path into beads :



Let $I_{\max}(\pi)$ be the number of steps made by the path $\pi \in \mathcal{W}_L$ inside its largest bead.

Theorem (One bead Theorem)

For $\beta > \beta_c$ there exists $c > 0$ such that

$$\lim_{L\to\infty} P_{L,\beta}\big(I_{max}(\pi) \geq L - c\,(\log L)^4\big) = 1.$$

Theorem (Convergence to Wulff shapes)

For $\beta > \beta_c$ *and* $\epsilon > 0$,

$$\lim_{L\to\infty} P_{L,\beta}\Big(\|\widetilde{\mathcal{E}}_\pi^+ - \frac{\gamma_\beta^*}{2}\|_\infty > \epsilon\Big) = 0,$$

$$\lim_{L\to\infty} P_{L,\beta}\Big(\|\widetilde{\mathcal{E}}_\pi^- + \frac{\gamma_\beta^*}{2}\|_\infty > \epsilon\Big) = 0.$$

where γ_β^* is the Wulff shape given by

$$\gamma_\beta^*(s) = \int_0^s L'\Big[(\tfrac{1}{2} - x)\tilde{h}_\beta\Big] dx, \quad s \in [0,1]$$

and

- $L(x) = \log \mathbf{E}_\beta[\exp(xV_1)]$ for $x \in (-\frac{\beta}{2}, \frac{\beta}{2})$
- $\tilde{h}_\beta$ is the unique sol. of $\quad h \int_0^1 L'(h(x - \frac{1}{2}))dx = \frac{1}{a_\beta^2}$.

Theorem (Fluctuation around Wulff Shape)

For $\beta > \beta_c$ and π sampled from $\widetilde{P}_{L,\beta}$,

$$\lim_{L\to\infty} \sqrt{N_\pi}\left(\tilde{\mathcal{E}}_\pi^{+} - \frac{\gamma_\beta^*}{2}, \tilde{\mathcal{E}}_\pi^{-} + \frac{\gamma_\beta^*}{2}\right) =_{Law} \left(\xi_\beta - \xi_\beta^c, \xi_\beta + \xi_\beta^c\right),$$

with

- W *a standard BM,*
- ξ_β *defined as*

$$\xi_\beta(t) := \int_0^t \sqrt{L''((\tfrac{1}{2} - x)\tilde{h}_\beta)}\, dW_x, \quad t \in [0,1]$$

- ξ_β^c *independent of* ξ_β *with the same law but conditioned on* $\xi_\beta^c(1) = \int_0^1 \xi_\beta^c(s)ds = 0$

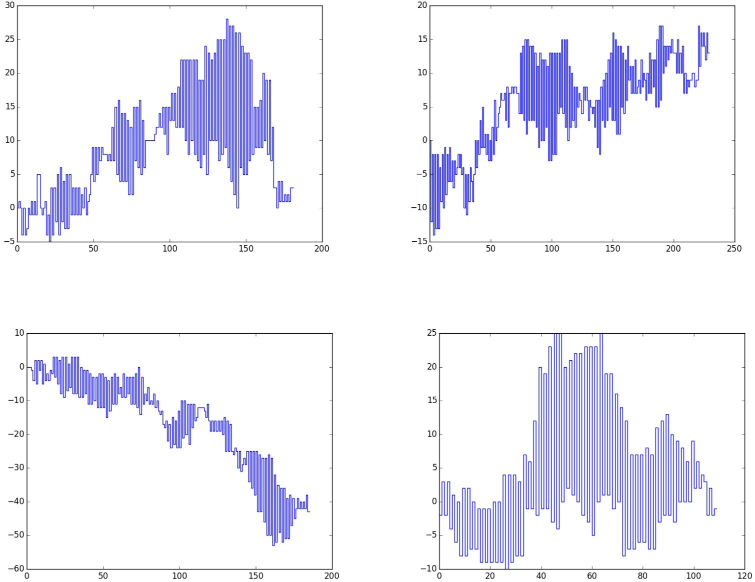
The last result is not obtained under $P_{L,\beta}$ but under $\widetilde{P}_{L,\beta}$ that is

$$\widetilde{P}_{L,\beta}(\pi) = \sum_{L' \in K_L} \frac{\widetilde{Z}_{L',\beta}}{\sum_{k \in K_L} \widetilde{Z}_{k,\beta}} \, P_{L',\beta}(\pi) \; 1_{\{\pi \in \Omega_{L'}\}}, \quad \text{for } \pi \in \widetilde{\Omega}_L.$$

with

- $K_L = \{-(\log L)^5, \dots, (\log L)^5\}$
- $\Omega'_L = \cup_{L' \in K_L} \Omega'_L$

6 Exact simulation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7 random walk representation

7.1) New probabilistic approach.

Let $(V_i)_{i\in\mathbb{N}}$ be an auxiliary random walk on $\mathbb{Z}$ with geometric increments, i.e., $V_0 = 0$, $(V_{i+1} - V_i)_{i\in\mathbb{N}}$ is i.i.d. and

$$\mathbf{P}_\beta(V_1 = k) = \frac{e^{-\frac{\beta}{2}|k|}}{c_\beta}, \quad k \in \mathbb{N}.$$

Build T_N a bijection between $\mathcal{L}_{N,L}$ and

$$\mathcal{V}_{N+1,L-N} = \{V \in \{0\} \times \mathbb{Z}^N : G_N(V) = L - N, \;\; V_{N+1} = 0\}$$

with $G_N(V) = \sum_{i=1}^N |V_i|$ so that T_N transforms the self-touching interaction on $\pi \in \mathcal{L}_{N,L}$ into a probability law on V.

Let $\mathbf{P}_\beta$ be the law of the random walk V with geometric increment, i.e., $V_0 = 0$ and $(V_{i+1} - V_i)_{i \in \mathbb{N}}$ is i.i.d. and

$$\mathbf{P}_\beta(V_1 = k) = \frac{e^{-\frac{\beta}{2}|k|}}{c_\beta}, \quad k \in \mathbb{N}.$$

We obtain (with $\Gamma_\beta = \frac{c_\beta}{e^\beta}$),

$$Z_{L,\beta} = e^{\beta L} \sum_{N=1}^{L} (\Gamma_\beta)^N \, \mathbf{P}_\beta(\mathcal{V}_{N+1,L-N}).$$

and

$$P_{L,\beta}\big(l \in \cdot \mid N_L(l) = N\big) = \mathbf{P}_\beta\big(T_N(V) \in \cdot \mid V_N = 0, = L - N\big).$$

7.2) Analysis of the phase transition.

Theorem (Variational characterizations of $\tilde{f}$)

The excess free energy $\tilde{f}(\beta)$ is given by

$$\tilde{f}(\beta) = \sup_{\alpha \in [0,1]} \left[\alpha \log \Gamma(\beta) + \alpha\, g_\beta \left(\tfrac{1-\alpha}{\alpha}\right)\right],$$

where

$$g_\beta(\alpha) := \lim_{N\to\infty} \frac{1}{N} \log \mathbf{P}_\beta\big(G_N \leq \alpha N,\, V_N = 0\big), \quad \alpha \in [0, \infty).$$

A straightforward consequence is that β_c is the unique positive solution of $\Gamma_\beta = 1$.