Free Energy of a Copolymer in an Emulsion

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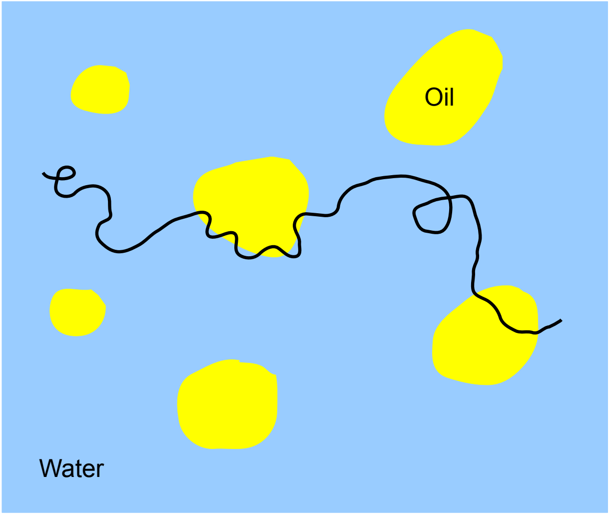
1 Physical motivation

1.1) Copolymer.
2 types of monomers : type A (hydrophobic), type B (hydrophilic).

1.2) Emulsion.
Droplets of type A (oil) in a medium of type B (water).

1.3) Interactions.
The $A - A$ matches get a reward (energy $-\alpha$) and the $B - B$ matches get a reward (energy $-\beta$). The $A - B$ and $B - A$ matches do not get penalties.

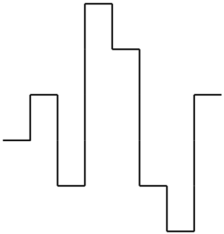

Oil
Water

2 The Model

2.1) Copolymer.

For $n \in \mathbb{N}$ the set of allowed configurations for the copolymer of length n is

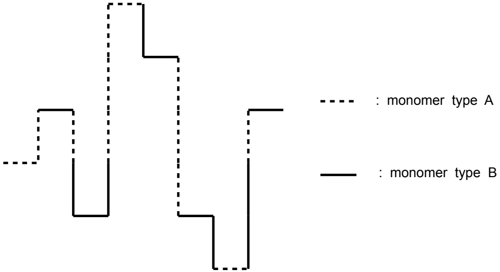
$$\mathcal{W}_n = \Big\{ n - \text{step directed self-avoiding paths starting at the} \\ \text{origin and taking steps in } \{\uparrow, \rightarrow, \downarrow\} \Big\}.$$



Microscopic disorder :

Let $(\omega_i)_{i\in\mathbb{N}}$ be an i.i.d. sequence of $\mathcal{B}er(1/2)$. The variable ω_i gives the type of the i-th monomer :

- $\omega_i = A$: the i-th monomer is of type A
- $\omega_i = B$: the i-th monomer is of type B.



2.2) Emulsion.

Partition $\mathbb{R}^2$ into large squared blocks

$$\mathbb{R}^2 = \cup_{x \in \mathbb{Z}^2} \Lambda_{L_n}(x) \quad \text{with} \quad \Lambda_{L_n}(x) = xL_n + (0, L_n]^2.$$

Mesoscopic Disorder : Fix $p \in (0,1)$ and let $\{\Omega(x), x \in \mathbb{Z}^2\}$ be an i.i.d. field satisfying

$$\mathbb{P}(\Omega(0) = A) = p \quad \text{and} \quad \mathbb{P}(\Omega(0) = B) = 1 - p.$$

A	B	A	A
B	A	B	B
B	A	A	A
B	B	A	B

L_n

$\Omega(x) = A$: block x is of type A

$\Omega(x) = B$: block x is of type B

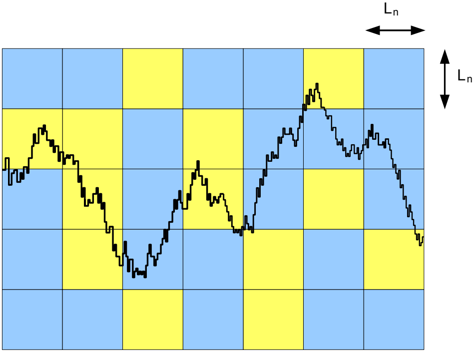


FIGURE: Example of $\pi \in \mathcal{W}_n$

2.3) Parameters.

- $p \in (0,1)$ is fixed and $(L_n)_{n\geq 1}$ satisfies $L_n \to \infty$ and $L_n/n \to 0$.
- $|\beta| \leq \alpha \in \mathbb{R}_+$ (without loss of generality).

2.4) Hamiltonian.

Given ω, Ω and n, with each path $\pi \in \mathcal{W}_n$ we associate an energy given by the Hamiltonian

$$H_{n,L_n}^{\omega,\Omega}(\pi) = -\sum_{i=1}^{n} \Big(\alpha 1\{\omega_i = \Omega_{\pi_i}^{L_n} = A\} + \beta 1\{\omega_i = \Omega_{\pi_i}^{L_n} = B\}\Big).$$

2.5) Polymer measure.

For every $\pi \in \mathcal{W}_n$;

$$P^{\omega,\Omega}_{n,L_n}(\pi) = \frac{\exp\Big(- H^{\omega,\Omega}_{n,L_n}(\pi)\Big)}{Z^{\omega,\Omega}_{n,L_n}}$$

2.6) Free energy per monomer.

For $(\alpha, \beta) \in \mathbb{R}^2$ and $p \in (0,1)$,

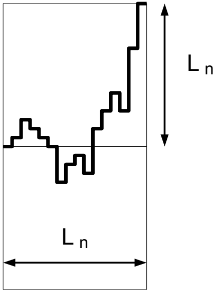
$$\lim_{n\to\infty} \frac{1}{n} \log Z^{\omega,\Omega}_{n,L_n} = f(\alpha, \beta; p)$$

exists ω, Ω-a.s., is finite and non-random.

3 Results with additional path restrictions

In [dHW06], [dHP09a], [dHP09b], a version of this model was studied with additional path restrictions, i.e.,

$\mathcal{W}_{n,L_n} = \{\pi \in \mathcal{W}_n : \pi$ enter blocks at a corner, exit blocks at one of the two corners *diagonally opposite* the one where it entered, and in between *stay confined* to the two blocks that are seen upon entering$\}$.



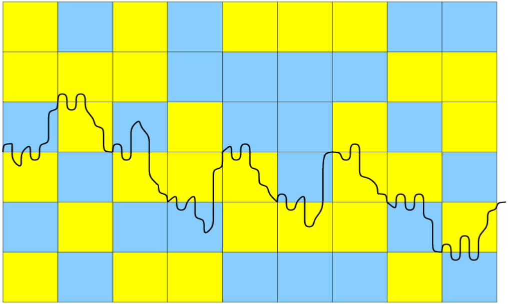
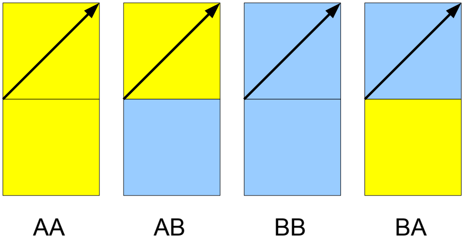


Figure: Example of $\pi \in \mathcal{W}_{n,L_n}$

The polymer can cross 4 types of pairs of blocks



$\mathcal{R}(p)$ is the set of 2×2 matrices $(\rho_{kl})_{k,l \in \{A,B\}}$ giving the possible frequencies at which each type of pair of blocks is visited.

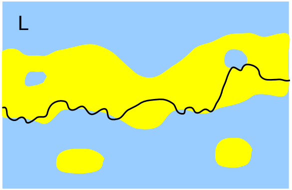
$\mathcal{A}$ is the set of 2×2 matrices $(a_{kl})_{k,l \in \{A,B\}}$ such that $a_{kl} \geq 2$ $\forall (k,l) \in \{A,B\}$.

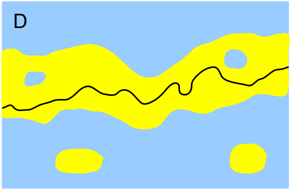
3.4) Variational Formula.

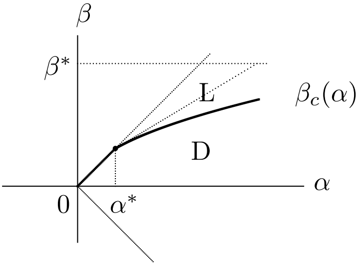
Theorem 1 (F. den Hollander and S. Whittington).
For all $(\alpha, \beta) \in \mathbb{R}^2$ and $p \in (0, 1)$,

$$f(\alpha, \beta; p) = \sup_{(a_{kl}) \in \mathcal{A}} \ \sup_{(\rho_{kl}) \in \mathcal{R}(p)} \frac{\sum_{k,l} \rho_{kl} \, a_{kl} \, \psi_{kl}(a_{kl}, \alpha, \beta)}{\sum_{k,l} \rho_{kl} \, a_{kl}}.$$

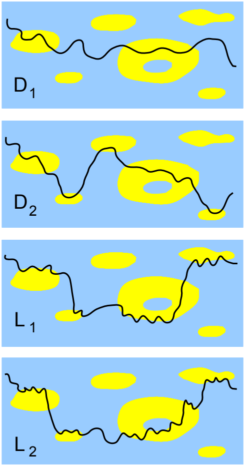
Supercritical regime : $p \geq p_c$ (F.dH., N.P.)

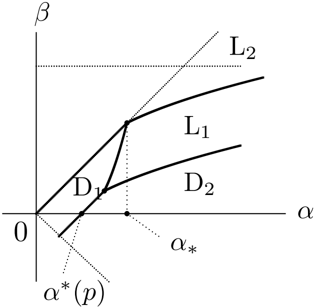






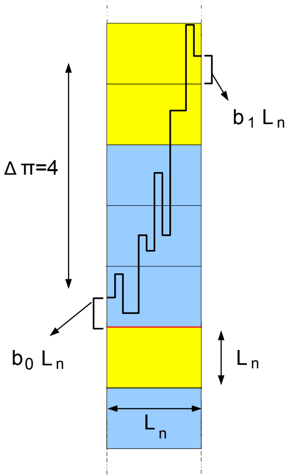
Subcritical regime : $p < p_c$ (F. dH., N.P.)





4 Removal of additional path restrictions

4.1) Type of block column.



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

$$V_M = \{A, B\}^{\mathbb{Z}} \times \{-M, \ldots, M\} \times [0, 1]^2$$

4.2) Free energy per column of blocks

For $\Theta = (\chi, \Delta\Pi, b_0, b_1) \in V_M$, $u \geq t_\Theta$ and $L \in \mathbb{N}$ set

$$W_{\Theta,u,L} = \{uL \text{ steps trajectories from } (0, b_0 L) \text{ to } (L, \Delta\Pi + b_1)\}.$$

There exists a $\psi(\Theta, u) \in \mathbb{R}$ such that

$$\psi(\Theta, u) = \lim_{L\to\infty} \frac{1}{uL} \log \sum_{\pi \in W_{\Theta,u,L}} e^{-H^{\omega,\chi}_{uL,L}(\pi)} \quad \mathbb{P}_\omega - a.s.$$

4.3) Percolation frequencies

Pick $(\Delta\Pi_i)_{i\in\mathbb{N}} \in \{-M,\dots,M\}^{\mathbb{N}}$ and $(b_i)_{i\in\mathbb{N}} \in [0,1]^{\mathbb{N}}$

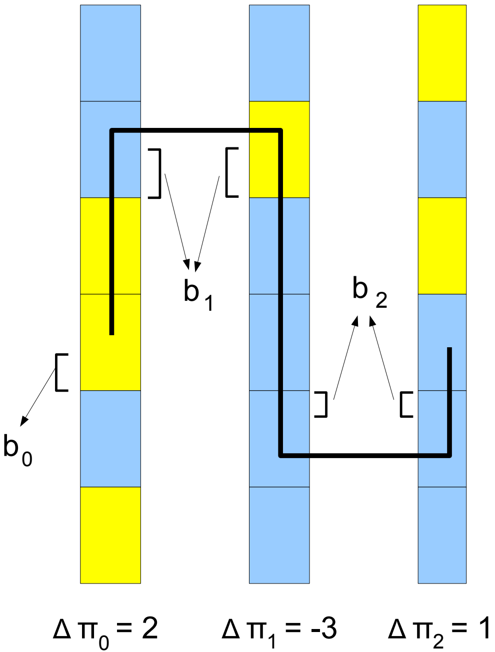
$$\Theta_j = \big(\Omega(j,\Pi_j+\cdot),\Delta\Pi_j,b_j,b_{j+1}\big), \qquad j\in\mathbb{N}_0.$$

Define the empirical distribution

$$\rho_N(\Omega,\Pi,b)(\Theta) = \frac{1}{N}\sum_{j=0}^{N-1} 1_{\{\Theta_j=\Theta\}}, \quad N\in\mathbb{N},\ \Theta\in V_M, \qquad (1)$$

such that

$$\rho_N(\Omega,\Pi,b)\in\mathcal{M}_1(V_M).$$


b_0
b_1
b_2
$\Delta\pi_0 = 2$
$\Delta\pi_1 = -3$
$\Delta\pi_2 = 1$

Set

$$\mathcal{R}_M^{\Omega} = \Big\{\rho \in \mathcal{M}_1(V_M)\colon \rho_{N_k}(\Omega, \Pi, b) \to \rho \text{ as } k \uparrow \infty \\ \text{with } \ \Pi\colon |\Delta \Pi_j| \le M \quad \forall\, j \in \mathbb{N}_0 \\ b \in [0,1]^{\mathbb{N}_0} \text{ and } N_k \uparrow \infty\Big\}.$$

By Kolmogorov $0-1$ Law

$$\mathcal{R}_M^{\Omega} = \mathcal{R}_{p,M} \quad \mathbb{P}_{\Omega} - a.s.$$

4.4) Variational formula for the free energy

Theorem

For every $(\alpha, \beta) \in \mathbb{R}^2$, $M \in \mathbb{N}$ *and* $p \in (0,1)$ *the free energy exists for* P*-a.e.* (ω, Ω) *and in* $L^1(P)$*, and is given by*

$$f(M;\, \alpha, \beta) = \sup_{\rho \in R_{p,M}} \ \sup_{(u_\Theta)_{\Theta \in V_M} \in B_{V_M}} V(\rho, u)$$

with

$$V(\rho, u) = \frac{\int_{V_M} u_\Theta \, \psi(\Theta, u_\Theta; \alpha, \beta) \, \rho(d\Theta)}{\int_{V_M} u_\Theta \, \rho(d\Theta)}.$$

4.4) Another version of the variational formula

$$f(M;\alpha,\beta) = \sup_{\rho\in\widetilde{R}_{p,M}} \;\sup_{(u)_{l\in[0,\infty)}\in\widetilde{B}_{V_M}} V(\rho,u)$$

with

$$V(\rho,u) = \frac{1}{G(u,l)}\Big[\int_0^\infty u_A(l)\,\kappa(u_A(l),l)\,\rho_A(dl) + \int_0^\infty u_B(l)\Big[\kappa(u_B(l),l)+\tfrac{\beta-\alpha}{2}\Big]\rho_B(dl) + \rho_{\mathcal{I}}\,u_{\mathcal{I}}\,\phi(u_{\mathcal{I}})\Big].$$

and

$$G(\rho,u) = \int_0^\infty u_A(l)\rho_A(dl) + \int_0^\infty u_B(l)\,\rho_B(dl) + \rho_{\mathcal{I}}\,u_{\mathcal{I}}$$