Free Energy of a Copolymer in an Emulsion

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January 2013

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1. Physical motivation

1.1) Copolymer.

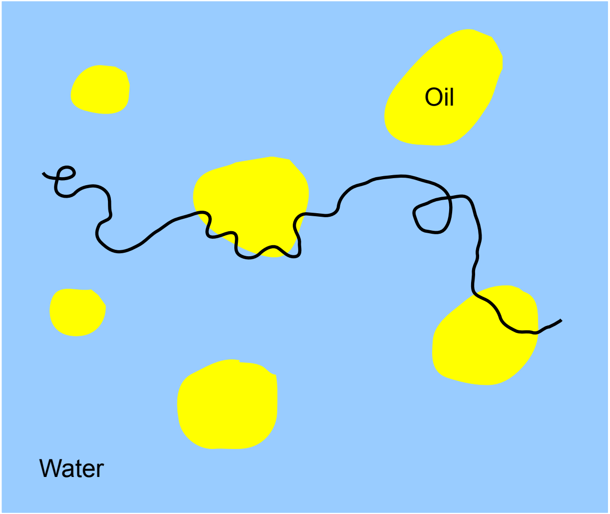
2 types of monomers : type A (hydrophobic), type B (hydrophilic).

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.

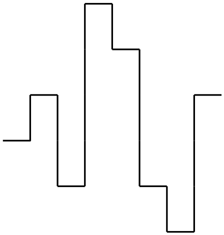

Oil
Water

2 The Model

2.1) Copolymer.

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

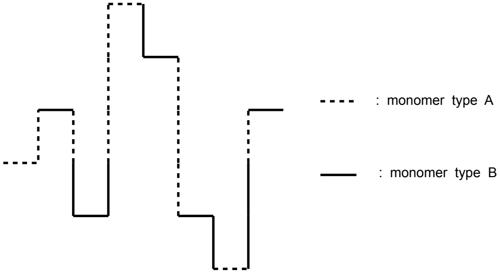
$$\mathcal{W}_n = \{n - \text{step directed self-avoiding paths starting at the origin and taking steps in } \{\uparrow, \rightarrow, \downarrow\}\}.$$



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.



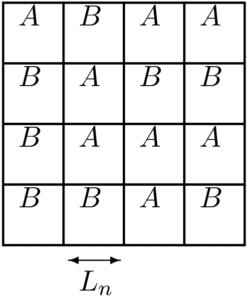
2.2) Emulsion.

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

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



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

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

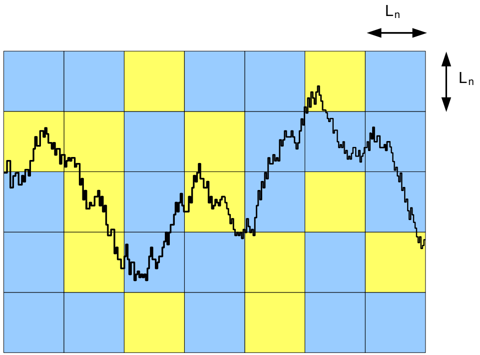


FIGURE: Example of $\pi \in \mathcal{W}_n$

2.3) Parameters.

- $p \in (0,1)$ is fixed and $(L_n)_{n\geq 1}$ satisfies $L_n \to \infty$ and $L_n/n \to 0$.
- CONE $= \{(\alpha,\beta) \in \mathbb{R}^2 \colon |\beta| \leq \alpha \in \mathbb{R}_+\}$ (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 $\pi \in \mathcal{W}_n$;

$$P_{n,L_n}^{\omega,\Omega}(\pi) = \frac{\exp\left(H_{n,L_n}^{\omega,\Omega}(\pi)\right)}{Z_{n,L_n}^{\omega,\Omega}}$$

2.6) Free energy per monomer.

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

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

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

3 Ingredients of the variational formula

Idea.

1)Decompose each trajectory into pieces that are either

- traveling in solvant $k \in \{A, B\}$ at slope $l \in [0, \infty)$ (type (k, l)).
- traveling along an AB interface (type $\mathcal{I}$).

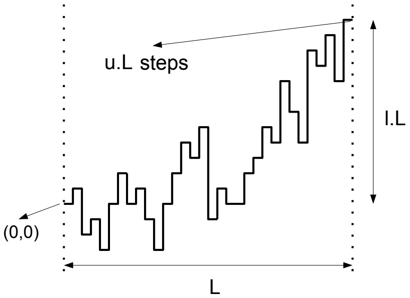
2) Define the free energy per steps of trajectories of type (k, l) and $\mathcal{I}$.

3) Optimize over the possible frequencies with which the copolymer can follow trajectories of type (k, l) and $\mathcal{I}$.

3.1) Entropic function.

For all $l \in \mathbb{R}$ and $u \geq 1 + |l|$ set

$$\kappa(u,l) = \lim_{L\to\infty} \frac{1}{uL} \log |\{\pi \in \mathcal{W}_{uL} \colon \ \pi_{uL} = (L, lL)\}|.$$



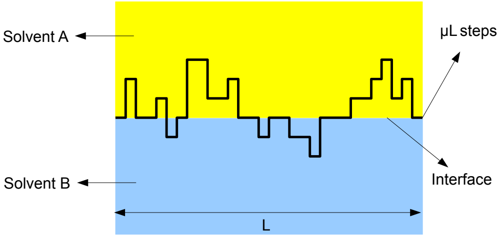
3.2) Free energy along a linear interface.

For all $(\alpha, \beta) \in \mathbb{R}^2$ and $\mu \in [1, \infty)$ set

$$\phi_{\mathcal{I}}(\mu; \alpha, \beta) = \lim_{L \to \infty} \frac{1}{\mu L} \log Z^{\omega, \mathcal{I}}_{L,\mu} \qquad \text{for } \mathcal{P}\text{-a.e. } \omega.$$

with

$$Z^{\omega,\mathcal{I}}_{L,\mu} = \sum_{\pi:\, \pi_{uL}=(L,0)} e^{\sum_{i=1}^{\mu L} \left(\beta\, 1\{\omega_i = B\} - \alpha\, 1\{\omega_i = A\}\right)\, 1\{(\pi_{i-1}, \pi_i) < 0\}}.$$

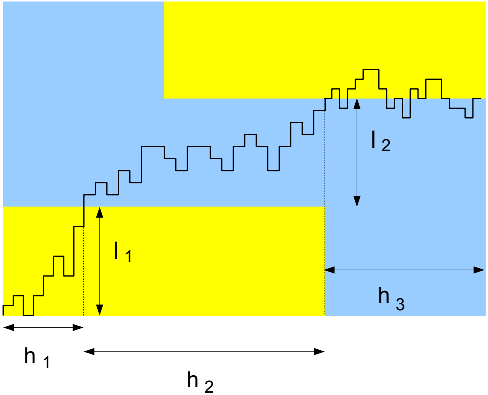


3.3) Frequencies of visits in each solvent.

When moving in the emulsion, the polymer can adopt different strategies corresponding to probability measures.

$$\rho = (\rho_A, \rho_B, \rho_{\mathcal{I}}) \in \mathcal{R}^{\Omega}_{p,M} \subset \mathcal{M}^1(\mathbb{R}^+ \times \mathbb{R}^+ \times \{\mathcal{I}\})$$

- For $k \in \{A, B\}$ and $l \in \mathbb{R}^+$, $\rho_k([l, l + dl])$ is the fraction of horizontal steps made by the copolymer when moving in solvent k with slope $\in [l, l + dl]$.
- Similarly $\rho_{\mathcal{I}}$ is the fraction of horizontal steps made by the copolymer when moving along an AB interface.



$$\rho = \frac{1}{h_1 + h_2 + h_3}\left[h_1\, \delta_{A,\frac{l_1}{h_1}} + h_2\, \delta_{B,\frac{l_2}{h_2}} + h_3\, \delta_{\mathcal{I}}\right]$$

By Kolmogorov $0-1$ Law

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

Examples of elements in $\mathcal{R}_{p,M}$.

- For $p \in (0,1)$,

$$p^2\delta_{A,0} + (1-p)^2\delta_{B,0} + 2p(1-p)\delta_{\mathcal{I}} \in \mathcal{R}_{p,M},$$

- For $p > p_c$, $\exists \rho \in \mathcal{R}_{p,M}$ such that

$$\rho_B([0,\infty)) = 0,$$

- For $p < p_c$, $\nexists \rho \in \mathcal{R}_{p,M}$ such that

$$\rho_B([0,\infty)) = 0.$$

3.4) Time spent in each solvent at each slope.

- For $k \in \{A, B\}$ and $l \in [0, \infty)$ set $u_{k,l}$: number of steps per horizontal step made by the copolymer when moving in solvent k with slove l.

$$u_{k,l} \geq 1 + l$$

- $u_{\mathcal{I}}$: number of steps per horizontal step when moving along an AB interface.

$$u_{\mathcal{I}} \geq 1.$$

We set

$$(u) = (u_A, u_B, u_{\mathcal{I}})$$

and

$$\begin{aligned} \mathcal{B} = \{(u) \colon & u_{\mathcal{I}} \in [1, \infty) \\ & u_A \in \mathcal{C}_{[0,\infty)}, u_{A,l} \geq 1 + l \\ & u_B \in \mathcal{C}_{[0,\infty)}, u_{B,l} \geq 1 + l\} \end{aligned}$$

4 Variational formula for the free energy

4.1) Variational formula

Theorem

For $p \in (0,1)$ *and* $(\alpha,\beta) \in \mathrm{CONE}$

$$f(\alpha,\beta;p) = \sup_{\rho \in R_{p,M}} \sup_{(u)\in\mathcal{B}} \frac{N(\rho,u)}{D(\rho,u)}$$

with

$$N(\rho,u) = \int_0^\infty u_{A,l}\,\kappa(u_{A,l},l)\,\rho_A(dl) + \int_0^\infty u_{B,l}\left[\kappa(u_{B,l},l) + \tfrac{\beta-\alpha}{2}\right]\rho_B(dl) + \rho_{\mathcal{I}}\,u_{\mathcal{I}}\,\phi(u_{\mathcal{I}}).$$

and

$$D(\rho,u) = \int_0^\infty u_{A,l}\,\rho_A(dl) + \int_0^\infty u_{B,l}\,\rho_B(dl) + \rho_{\mathcal{I}}\,u_{\mathcal{I}}$$

For $p \in (0,1)$ and $(\alpha, \beta) \in \text{CONE}$ set

$$\mathcal{O}_{\alpha,\beta,p} = \left\{ \rho \in \mathcal{R}_{p,M} : \sup_{(u)\in\mathcal{B}} \frac{N(\rho,u)}{D(\rho,u)} = f(\alpha,\beta;p) \right\}$$

Theorem

For all $p \in (0,1)$ *and* $(\alpha,\beta) \in \text{CONE}$,

- $\mathcal{O}_{\alpha,\beta,p} \neq \emptyset$
- *there exists a unique* $(\bar{u}) \in \mathcal{B}$ *such that*

$$f(\alpha,\beta;p) = \frac{N(\rho,\bar{u})}{D(\rho,\bar{u})}, \quad \forall \rho \in \mathcal{O}_{\alpha,\beta,p}.$$

5. Phase diagram : general structure

5.1) Delocalized free energy

$$f_{\mathcal{D}}(\alpha,\beta;p) = \sup_{\rho\in R_{p,M}} \sup_{(u)\in\mathcal{B}} \frac{N_{\mathcal{D}}(\rho,u)}{D_{\mathcal{D}}(\rho,u)}$$

with

$$N_{\mathcal{D}}(\rho,u) = \int_0^\infty u_{A,l}\,\kappa(u_{A,l},l)\,(\rho_A+\rho_{\mathcal{I}}\,\delta_{A,0})(dl) + \int_0^\infty u_{B,l}\left[\kappa(u_{B,l},l)+\tfrac{\beta-\alpha}{2}\right]\rho_B(dl).$$

and

$$D_{\mathcal{D}}(\rho,u) = \int_0^\infty u_{A,l}\,(\rho_A+\rho_{\mathcal{I}}\,\delta_{A,0})(dl) + \int_0^\infty u_{B,l}\,\rho_B(dl)$$

$$\mathcal{D} = \{(\alpha, \beta) \in \text{CONE}\colon\ f(\alpha, \beta) = f_{\mathcal{D}}(\alpha, \beta)\}$$
$$\mathcal{L} = \{(\alpha, \beta) \in \text{CONE}\colon\ f(\alpha, \beta) > f_{\mathcal{D}}(\alpha, \beta)\}$$

For $\alpha \geq 0$,

$$J_\alpha = \{(\alpha + \beta, \beta)\colon\ \beta \in [-\tfrac{\alpha}{2}, \infty)\}.$$

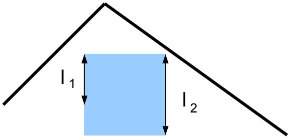
Proposition

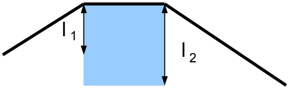
For every $p \in (0, 1)$ and $\alpha \in (0, \infty)$ there exists a $\beta_c(\alpha) \in (0, \infty)$ such that

$$\mathcal{L} \cap J_\alpha = \{(\alpha + \beta, \beta)\colon\ \beta \in (\beta_c(\alpha), \infty)\},$$
$$\mathcal{D} \cap J_\alpha = \left\{(\alpha + \beta, \beta)\colon\ \beta \in \left[-\tfrac{\alpha}{2}, \beta_c(\alpha)\right]\right\}.$$

Hypothesis 1) : for all $p \in (0,1)$ and all $\alpha \in (0,\infty)$ there exists $\bar{\rho} \in \mathcal{O}_{\alpha,0,p}$ such that $\bar{\rho}_{\mathcal{I}} > 0$.

Heuristic :





Provided hypothesis 1 holds :

$$\beta_c(\alpha) = \inf\left\{\beta > 0\colon\ \phi_{\mathcal{I}}(\bar{u}_{A,0};\alpha+\beta,\beta) > \tilde{\kappa}(\bar{u}_{A,0},0)\right\}$$

where $\bar{u}$ is the unique maximizer of the variational formula on $\mathcal{J}_\alpha$.

6. Phase diagram : the supercritical case

6.1) Delocalized and saturated free energy

$$f_{\mathcal{D}_2}(p) = \sup_{\substack{\rho \in R_{p,M} \\ \rho_B([0,\infty))=0}} \; \sup_{(u)\in\mathcal{B}} \frac{N_{\mathcal{D}_2}(\rho,u)}{D_{\mathcal{D}_2}(\rho,u)}$$

with

$$N_{\mathcal{D}_2}(\rho,u) = \int_0^\infty u_{A,l}\,\kappa(u_{A,l},l)\,(\rho_A + \rho_{\mathcal{I}}\,\delta_{A,0})(dl).$$

and

$$D_{\mathcal{D}_2}(\rho,u) = \int_0^\infty u_{A,l}\,(\rho_A + \rho_{\mathcal{I}}\,\delta_{A,0})(dl)$$

Partition $\mathcal{D}$ into $\mathcal{D}_1 \cup \mathcal{D}_2$ with

$$\mathcal{D}_1 = \left\{(\alpha,\beta) \in \text{CONE}\colon\ f(\alpha,\beta;p) = f_{\mathcal{D}}(\alpha,\beta;p) > f_{\mathcal{D}_2}(p)\right\}$$
$$\mathcal{D}_2 = \left\{(\alpha,\beta) \in \text{CONE}\colon\ f(\alpha,\beta;p) = f_{\mathcal{D}_2}(p)\right\}.$$

Hypothesis 2) : for all $p \in (p_c, 1)$

$$\alpha^* = \max\{\alpha \geq 0 \colon f_{\mathcal{D}}(\alpha, 0; p) > f_{\mathcal{D}_2}(p)\} < \infty.$$

Provided Hypothesis 1 and 2 hold we have

Theorem

(a) For every $\alpha \in [0, \alpha^*)$,

$$J_\alpha \cap \mathcal{D}_1 = J_\alpha \cap \mathcal{D} = \{(\alpha + \beta, \beta) \colon \beta \in [-\tfrac{\alpha}{2}, \beta_c(\alpha)].$$

(b) For every $\alpha \in [\alpha^*, \infty)$,

$$J_\alpha \cap \mathcal{D}_2 = J_\alpha \cap \mathcal{D} = \{(\alpha + \beta, \beta) \colon \beta \in [-\tfrac{\alpha}{2}, \beta_c(\alpha)]\}.$$

(c) For every $\alpha \in [0, \infty)$

$$\beta_c(\alpha) = \inf\left\{\beta > 0 \colon \phi_{\mathcal{I}}(\bar{u}_{A,0}; \alpha + \beta, \beta) > \tilde{\kappa}(\bar{u}_{A,0}, 0)\right\}$$

(d) $\alpha \mapsto \beta_c(\alpha)$ *is concave, continuous, non-decreasing and bounded from above on* $[\alpha^*, \infty)$.

6.2) Localized and saturated free energy

$$f_{\mathcal{L}_2}(\alpha,\beta) = \sup_{\substack{\rho\in R_{p,M} \\ \rho_B([0,\infty))=0}} \; \sup_{(u)\in\mathcal{B}} \frac{N_{\mathcal{L}_2}(\rho,u)}{D_{\mathcal{L}_2}(\rho,u)}$$

with

$$N_{\mathcal{L}_2}(\rho,u) = \int_0^\infty u_{A,l}\,\kappa(u_{A,l},l)\,\rho_A(dl) + \rho_{\mathcal{I}}\,\phi_{\mathcal{I}}(u_{\mathcal{I}}),$$

and

$$D_{\mathcal{L}_2}(\rho,u) = \int_0^\infty u_{A,l}\,\rho_A(dl) + \rho_{\mathcal{I}}\,u_{\mathcal{I}}.$$

We partition $\mathcal{L}$ into $\mathcal{L}_1 \cup \mathcal{L}_2$ with

$$\mathcal{L}_1 = \big\{(\alpha,\beta)\in \text{CONE}\colon\; f(\alpha,\beta;p) > \max\{f_{\mathcal{D}}(\alpha,\beta;p),\, f_{\mathcal{L}_2}(\alpha,\beta;p)\}\big\}$$
$$\mathcal{L}_2 = \big\{(\alpha,\beta)\in \text{CONE}\colon\; f(\alpha,\beta;p) = f_{\mathcal{L}_2}(\alpha,\beta;p) > f_{\mathcal{D}}(\alpha,\beta;\,p)\big\}.$$