COPOLYMERS IN EMULSIONS

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§ BACKGROUND

The physical situation we want to describe is that of a copolymer, consisting of hydrophobic and hydrophilic monomers, in an emulsion, consisting of droplets of oil floating in water.



The mathematical model described in this talk is introduced and analyzed in:

- F. den Hollander and S.G. Whittington, Localization transition for a copolymer in an emulsion, Theor. Prob. Appl. 51 (2006) 193–240.*
 - * Festschrift for Ya. Sinai's 70th birthday.

Refinements are obtained in (2 preprints):

• F. den Hollander and N. Pétrélis, On the localized phase of a copolymer in an emulsion: I. Supercritical percolation regime & II. Subcritical percolation regime.

§ MODEL

I. The randomness along the copolymer is labelled by $\omega = (\omega_i)_{i \in \mathbb{N}} \in \{A, B\}^{\mathbb{N}}$, i.i.d. w.p. $(\frac{1}{2}, \frac{1}{2})$, A = hydrophobic monomer, B = hydrophilic monomer.

II. Fix $p \in (0, 1)$ and $L_n \in \mathbb{N}$. Partition \mathbb{R}^2 into square blocks of size L_n . The randomness of the emulsion is labelled by

$$\Omega = (\Omega_x)_{x \in \mathbb{Z}^2} \in \{A, B\}^{\mathbb{Z}^2}, \text{ i.i.d. w.p. } (p, 1 - p),$$

 $A = \text{oil block}, B = \text{water block}.$

III. Let \mathcal{W}_n denote the set of *n*-step directed self-avoiding paths starting at 0 and drawing their steps from $\{\uparrow, \downarrow, \rightarrow\}$. Let

• W_{n,L_n} = the subset of those paths in W_n that enter and exit blocks at diagonally opposite corners, and in between stay confined to the two neighboring blocks seen upon entrance.



The corner restriction is unphysical, but is put in to make the model mathematically tractable.

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

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

where $\alpha, \beta \in \mathbb{R}$ and $\Omega_{(\pi_{i-1},\pi_i)}^{L_n}$ denotes the label of the block that the edge (π_{i-1},π_i) lies in.

W.I.o.g. the interaction parameters may be restricted to the cone

CONE = {
$$(\alpha, \beta) \in \mathbb{R}^2$$
: $\alpha \ge |\beta|$ }.

\S THE FREE ENERGY

Given ω, Ω and n, define the quenched free energy per step as

$$f_{n,L_n}^{\omega,\Omega} = \frac{1}{n} \log Z_{n,L_n}^{\omega,\Omega},$$

$$Z_{n,L_n}^{\omega,\Omega} = \sum_{\pi \in \mathcal{W}_{n,L_n}} \exp\left[-H_{n,L_n}^{\omega,\Omega}(\pi)\right].$$

We are interested in the limit $n \to \infty$ subject to the restriction

$$L_n \to \infty$$
 and $\frac{1}{n}L_n \to 0.$

This is a coarse-graining limit where the path spends a long time in each single block yet visits many blocks. In this limit, there is a separation between a polymer scale and an emulsion scale.

Let

- \mathcal{A} is the set of all 2 × 2-matrices whose elements are \geq 2.
- R(p) is the set of all 2×2-matrices whose elements are the possible limiting frequencies at which the four types of pairs of blocks are visited along a coarse-grained path.
- $\psi(\alpha, \beta; a)$ is the 2×2-matrix of free energies per step of the copolymer in a pair of blocks of size $L \times L$ when the total number is aL, in the limit as $L \to \infty$.

A	В	A	A
В	A	B	В
B	A	A	A
В	В	A	В

THEOREM: For all $(\alpha, \beta) \in \mathbb{R}^2$ and $p \in (0, 1)$, $\lim_{n \to \infty} f_{n,L_n}^{\omega,\Omega} = f = f(\alpha, \beta; p)$

exists ω , Ω -a.s., is finite and non-random, and is given by the variational formula

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

CONCLUSION:

In order to get the phase diagram, we need to analyze the two key ingredients of the variational formula: ψ_{kl} , $kl \in \{A, B\}^2$, and $\mathcal{R}(p)$.

§ BLOCK PAIR FREE ENERGIES

Trivially,

$$\psi_{AA}(\alpha,\beta;a) = \frac{1}{2}\alpha + \kappa(a,1),$$

$$\psi_{BB}(\alpha,\beta;a) = \frac{1}{2}\beta + \kappa(a,1),$$

where $\kappa(a, 1)$ is the entropy per step of walks that diagonally cross a block of size $L \times L$ in aL steps, in the limit as $L \rightarrow \infty$ (which can be computed).

PROPOSITION:

$$a\psi_{AB}(\alpha,\beta;a) = \sup_{\substack{0 \le b \le 1, c \ge b \\ a-c \ge 2-b}} \left\{ c\phi^{\mathcal{I}}(\alpha,\beta;c/b) + (a-c) \left[\frac{1}{2}\alpha + \kappa(a-c,1-b) \right] \right\},\$$

where for $L \to \infty$

- $\phi^{\mathcal{I}}(\alpha,\beta;c/b)$ is the free energy per step associated with walks running along a linear interface over a distance cL in bL steps;
- $\kappa(a c, 1 b)$ is the entropy per step of walks that diagonally cross a block of size $(1 b)L \times L$ in (a c)L steps (which can be computed).



CRUCIAL:

The link with the single interface free energy constitutes a major simplification, in view of the methods and techniques available for linear interfaces. \S percolation set

Let $p_c \approx 0.64$ be the critical threshold for directed bond percolation on the square lattice. Let

$$\rho^{*}(p) = \sup_{\substack{(\rho_{kl}) \in \mathcal{R}(p)}} [\rho_{AA} + \rho_{AB}],$$

= the maximal frequency at which
the copolymer crosses *A*-blocks.



\S PHASE DIAGRAM FOR $p \ge p_c$

The phase diagram is relatively simple in the supercritical regime. This is because the oil percolates, and so the copolymer can choose between moving inside the oil or running along the interface between the oil and the water.



PROPOSITION:

Let $p \ge p_c$. Then $(\alpha, \beta) \in \mathcal{L}$ if and only if $\sup_{\mu \ge 1} \mu \Big[\phi^{\mathcal{I}}(\alpha, \beta; \mu) - \frac{1}{2}\alpha - \frac{1}{2}\log 5 \Big] > \frac{1}{2}\log \frac{9}{5}.$

HEURISTICS:

Localization occurs if and only if it is advantageous enough to run along the interface in order to compensate for the loss of entropy due to the steeper crossing angle.



The two phases are characterized by

$$\mathcal{D} = \{ (\alpha, \beta) \in \text{CONE} \colon f(\alpha, \beta; p) = \frac{1}{2}\alpha + \frac{1}{2}\log 5 \}, \\ \mathcal{L} = \{ (\alpha, \beta) \in \text{CONE} \colon f(\alpha, \beta; p) > \frac{1}{2}\alpha + \frac{1}{2}\log 5 \}, \end{cases}$$

and are separated by a single critical curve $\alpha \mapsto \beta_c(\alpha)$.

\S REFINEMENTS

THEOREM:

Let $p \geq p_c$.

(i) $\alpha \mapsto \beta_c(\alpha)$ is strictly increasing on $[0,\infty)$.

(ii) For every $\alpha \in (\alpha^*, \infty)$ there exist $0 < C_1 < C_2 < \infty$ and $\delta_0 > 0$ such that for all $\delta \in (0, \delta_0]$,

 $C_1 \,\delta^2 \leq f(\alpha, \beta_c(\alpha) + \delta; p) - f(\alpha, \beta_c(\alpha); p) \leq C_2 \,\delta^2.$

(iii) $(\alpha, \beta) \mapsto f(\alpha, \beta; p)$ is infinitely differentiable throughout \mathcal{L} .

\S PHASE DIAGRAM FOR $p < p_c$

In the subcritical regime the phase diagram is much more complex. The reason is that the oil does not percolate, and so the copolymer no longer has the option to run along the interface.

It turns out that there are three critical curves, all of which depend on p. There are two tricritical points.









QUOTE FROM STU:

Damn, this model is so hard: our phase diagram depends on time!