A copolymer at a linear selective interface: Variational characterization of the free energy

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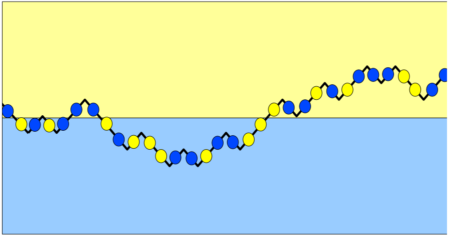
Outline

Copolymer

A copolymer is a polymer consisting of monomers of two or more different types, e.g. hydrophilic and hydrophobic.

Copolymers are used as surfactants, emulsifiers, foaming/ anti-foaming agents.

Case of interest: Copolymer with randomly arranged monomer types located near a linear interface separating two immiscible solvents that have *affinity* for the monomer types.



The model

Polymer configuration is a directed path in $\mathbb{N}_0 \times \mathbb{Z}$

$$\Pi = \big\{\pi = (k, \pi_k)_{k\in\mathbb{N}_0} \colon \; \pi_0 = 0, \, \mathrm{sign}(\pi_k) + \mathrm{sign}(\pi_{k-1}) \neq 0, \; k \in \mathbb{N}\big\}.$$

P^*-probability measure on Π such that excursions below and above the linear interface $\mathbb{N} \times \{0\}$ occur with equal probability and $\rho(k) := P^*(\pi_1, \cdots, \pi_{k-1} \neq 0, \pi_k = 0)$, for $k \in \mathbb{N}$, satisfies

$$\lim_{\substack{k\to\infty \\ \rho(k)>0}} \frac{\log \rho(k)}{\log k} = -\alpha, \quad \text{for some} \quad \alpha \in [1, \infty).$$

Monomer disorder: $\omega = (\omega_n)_{n\in\mathbb{N}}$ is an $\mathbb{R}$-valued i.i.d. sequence with law $\mathbb{P} = \nu^{\otimes\mathbb{N}}$ such that $\mathbb{E}(\omega_1) = 0$, $\mathbb{E}(\omega_1^2) = 1$ and

$$M(\lambda) = \log \int_{\mathbb{R}} e^{-\lambda\omega_1} \, \nu(d\omega_1) < \infty \qquad \forall \, \lambda \in \mathbb{R}.$$

The model

Quenched copolymer model is the path measure

$$P_n^{\beta,h,\omega}(\pi) = \frac{1}{\widetilde{Z}_n^{\beta,h,\omega}} e^{\beta \sum_{k=1}^{n} (\omega_k + h)\Delta_k} P^*(\pi), \qquad \pi \in \Pi, \quad n \in \mathbb{N}$$

where $\Delta_k = \pm 1$ if the kth edge of π is above or below the interface, $\omega \in \mathbb{R}^{\mathbb{N}}$, $\beta \geq 0$ and $h \geq 0$ are respectively the interaction strength (inverse temperature) and the disorder bias and $\widetilde{Z}_n^{\beta,h,\omega}$ is the normalizing partition sum.

Example: P^* = simple random walk ($\alpha = \frac{3}{2}$) and $\nu = \frac{1}{2}(\delta_- + \delta_+)$ models copolymer with hydrophilic ($\omega_i = -1$) and hydrophobic ($\omega_i = +1$) monomers near a linear interface separating oil and water [Garel, Huse, Leibler and Orland (1986)].

Localization-Delocalization Transition: Quenched version

localized **delocalized**

The quenched free energy per monomer

$$f^{\text{que}}(\beta,h)=\lim_{n\to\infty}\frac{1}{n}\log\widetilde{Z}_n^{\beta,h,\omega}=\lim_{n\to\infty}\frac{1}{n}\log\left(\sum_{\pi\in\Pi}e^{\beta\sum_{k=1}^{n}(\omega_k+h)\Delta_k}\,P^*(\pi)\right)$$

exists and is constant ω-a.s., and satisfies

$$f^{\text{que}}(\beta,h)\geq\beta h.$$

Localization-Delocalization Transition: Quenched version

The quenched excess free energy

$$g^{\mathrm{que}}(\beta,h) = f^{\mathrm{que}}(\beta,h) - \beta h$$

is the free energy per monomer for the model with partition sum

$$Z_{n,0}^{\beta,h,\omega} = \sum_{\pi\in\Pi;\pi_n=0} P(\pi)\,\exp\left[\beta\sum_{k=1}^{n}(\omega_k+h)[\Delta_k-1]\right].$$

and it exhibits a *localization-delocalization transition* with

$$\mathcal{D}^{\mathrm{que}} = \{(\beta,h)\colon\ g^{\mathrm{que}}(\beta,h)=0\},$$
$$\mathcal{L}^{\mathrm{que}} = \{(\beta,h)\colon\ g^{\mathrm{que}}(\beta,h)>0\}.$$

The two phases are separated by a quenched critical curve

$$h_c^{\mathrm{que}}(\beta) = \inf\{h\geq 0\colon\ g^{\mathrm{que}}(\beta,h)=0\}, \qquad \beta\geq 0.$$

The phase transition is the result of a competition between entropy and energy.

Localization-Delocalization Transition: Annealed version

The annealed version of the model has excess free energy

$$g^{\mathrm{ann}}(\beta, h) = \lim_{n\to\infty} \frac{1}{n} \log \mathbb{E}(Z_{n,0}^{\beta,h,\omega}),$$

which also exhibits a localization-delocalization transition with

$$\mathcal{D}^{\mathrm{ann}} = \{(\beta, h)\colon\ g^{\mathrm{ann}}(\beta, h) = 0\}\,,$$
$$\mathcal{L}^{\mathrm{ann}} = \{(\beta, h)\colon\ g^{\mathrm{ann}}(\beta, h) > 0\}\,.$$

The two phases are separated by an annealed critical curve

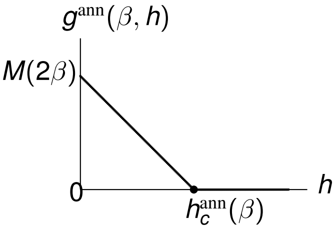
$$h_c^{\mathrm{ann}}(\beta) = \inf\{h \geq 0\colon\ g^{\mathrm{ann}}(\beta, h) = 0\}, \qquad \beta \geq 0.$$

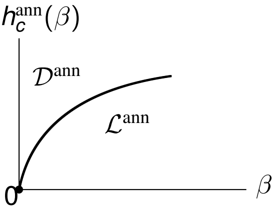
Basic facts

1. Closed form expressions are known for h_c^{ann} and g^{ann}:

$$h_c^{\mathrm{ann}}(\beta) = (2\beta)^{-1} M(2\beta), \qquad \beta > 0,$$

$$g^{\mathrm{ann}}(\beta, h) = 0 \vee [M(2\beta) - 2\beta h], \qquad \beta, h \geq 0.$$



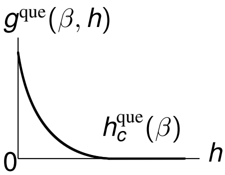


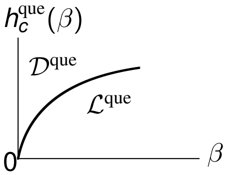
Basic facts

2. No closed form expressions are known for h_c^{que} and g^{que}. They satisfy the bounds

$$h_c^{\text{ann}}(\beta/\alpha) \le h_c^{\text{que}}(\beta) \le h_c^{\text{ann}}(\beta)\,, \qquad \beta > 0,$$

$$g^{\text{que}}(\beta,h) \le g^{\text{ann}}(\beta,h), \qquad \beta, h \ge 0.$$





Many interesting related results have been obtained in the past 10 years by: Biskup, Bodineau, Caravenna, Giacomin, Lacoin, Pétrélis, Rechnitzer, Soteros, Toninelli, Whittington,. . .

Main results:

Theorem

For every $\beta, h > 0$, there are lower semi-continuous, convex and non-increasing functions

$$g \mapsto S^{\mathrm{que}}(\beta, h; g),$$
$$g \mapsto S^{\mathrm{ann}}(\beta, h; g),$$

given by explicit variational formulas, such that

$$g^{\mathrm{que}}(\beta, h) = \inf\{g \in \mathbb{R} \colon \; S^{\mathrm{que}}(\beta, h; g) < 0\},$$
$$g^{\mathrm{ann}}(\beta, h) = \inf\{g \in \mathbb{R} \colon \; S^{\mathrm{ann}}(\beta, h; g) < 0\}.$$

Main results:

Theorem

For every $\beta > 0$ and $g = 0$, the maps

$$h \mapsto S^{\text{que}}(\beta, h; 0),$$
$$h \mapsto S^{\text{ann}}(\beta, h; 0)$$

are lower semi-continuous, convex and non-increasing functions.

The critical curves $h_c^{\text{que}}(\beta)$ and $h_c^{\text{ann}}(\beta)$ are respectively the unique h-values that solve the equations

$$S^{\text{que}}(\beta, h; 0) = 0,$$
$$S^{\text{ann}}(\beta, h; 0) = 0.$$

Quenched variational formulas

Suppose that up to time n, the path $\pi \in \Pi$ makes $N \leq n$ visits to the interface $\mathbb{N}_0 \times \{0\}$. Then w.r.t. π

$$\beta \sum_{k=1}^{n} (\omega_k + h)[\Delta_k - 1] = -2\beta \sum_{i=1}^{N} 1_{A_i} \sum_{k \in I_i} (\omega_k + h)$$

where I_i is the ith excursion interval and A_i is the event that the ith excursion is below the interface.

The contribution of the ith excursion to the partition sum $Z_{n,0}^{\beta,h,\omega}$ is

$$\phi_{\beta,h}(\omega_{I_i}) = \frac{1}{2}\left(1 + e^{-2\beta \sum_{k \in I_i}(\omega_k + h)}\right),$$

where ω_{I_i} is the word cut out from ω by the ith excursion interval.

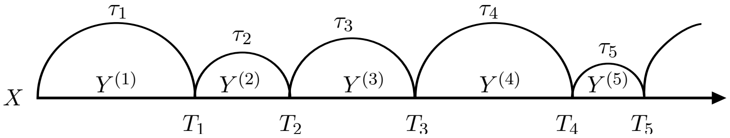
Quenched variational formulas

Hence
$$Z_{n,0}^{\beta,h,\omega} = \sum_{N=1}^{n} \sum_{0=k_0<k_1<\cdots<k_N=n} \left(\prod_{i=1}^{N} \rho(k_i - k_{i-1}) \right) \times e^{\sum_{i=1}^{N} \log \phi_{\beta,h}(\omega_{I_i})}.$$

A key tool is the generating function of $Z_{n,0}^{\beta,h,\omega}$:
$$\sum_{n\in\mathbb{N}} e^{-gn} Z_{n,0}^{\beta,h,\omega} = \sum_{N\in\mathbb{N}} F_N^{\beta,h,\omega}(g), \quad g \in [0,\infty), \quad \text{with}$$
$$F_N^{\beta,h,\omega}(g) = \mathcal{N}(g)^N \sum_{0=k_0<k_1<\cdots<k_N<\infty} \left(\prod_{i=1}^{N} \rho_g(k_i - k_{i-1}) \right) \times e^{\sum_{i=1}^{N} \log \phi_{\beta,h}(\omega_{I_i})}$$
$$\rho_g(n) = \frac{e^{-ng}}{\mathcal{N}(g)} \rho(n), \quad \mathcal{N}(g) = \sum_{n\in\mathbb{N}} \rho(n) e^{-gn}, \quad g \ge 0.$$

Quenched variational formulas

Let $\widetilde{\mathbb{R}} = \cup_{n\in\mathbb{N}}\mathbb{R}^n$ (finite word space).



The random word sequence $Y = (Y^{(i)})_{i\in\mathbb{N}}$, with $Y^{(i)} = \omega_{I_i}$, under the law $\mathbb{P}\otimes P_g^*$ is an i.i.d. $\widetilde{\mathbb{R}}$-valued sequence of random variables with marginal law $q_{\rho_g,\nu}$ given by

$$q_{\rho_g,\nu}(d\omega_1,\dots,d\omega_n) = \rho_g(n)\,\nu(d\omega_1)\times\cdots\times\nu(d\omega_n),$$
$$n\in\mathbb{N},\quad \omega_1,\dots,\omega_n\in\mathbb{R}.$$

Let $\mathcal{P}^{\mathrm{inv}}(\widetilde{\mathbb{R}}^{\mathbb{N}})$ be the set of probability measures on the sentence space $\widetilde{\mathbb{R}}^{\mathbb{N}}$, invariant under the left shift $\widetilde{\theta}$ acting on $\widetilde{\mathbb{R}}^{\mathbb{N}}$.

Quenched variational formulas

Let $(\omega_{I_1}, \ldots, \omega_{I_N})$ be the N-tupple of words cut out from ω by the first N-excursions and define the empirical process of N-tupple of words as

$$R_N^\omega = \frac{1}{N} \sum_{i=0}^{N-1} \delta_{\widetilde{\theta}^i (\omega_{I_1}, \ldots, \omega_{I_N})^{\mathrm{per}}} \in \mathcal{P}^{\mathrm{inv}}\big(\widetilde{\mathbb{R}}^{\mathbb{N}}\big).$$

This implies that

$$F_N^{\beta,h,\omega}(g) = \mathcal{N}(g)^N E_g^* \left(e^{N\,\Phi_{\beta,h}(R_N^\omega)} \right)$$

where

$$\Phi_{\beta,h}(Q) \quad = \quad \int_{\widetilde{\mathbb{R}}} (\pi_1 Q)(dy) \log \phi_{\beta,h}(y),$$

and $\pi_1 Q$ is the single-word marginal of $Q \in \mathcal{P}^{\mathrm{inv}}\big(\widetilde{\mathbb{R}}^{\mathbb{N}}\big)$.

Quenched variational formulas

The radius of convergence of the power series

$$\sum_{n\in\mathbb{N}} e^{-gn}\, Z_{n,0}^{\beta,h,\omega}$$

equals $g^{\text{que}}(\beta, h)$, and is the unique value of g where

$$\begin{aligned} S^{\text{que}}(\beta, h; g) &= \limsup_{N\to\infty} \frac{1}{N} \log\, F_N^{\beta,h,\omega}(g) \\ &= \log \mathcal{N}(g) + \limsup_{N\to\infty} \frac{1}{N} \log E_g^* \left(e^{N\,\Phi_{\beta,h}(R_N^{\omega})} \right) \qquad \omega - \text{a.s.} \end{aligned}$$

changes sign.

Annealed large deviation principle (LDP)

[Birkner (2008) and Birkner, Greven and den Hollander (2010)]

For $Q \in \mathcal{P}^{\mathrm{inv}}(\widetilde{\mathbb{R}}^{\mathbb{N}})$, the specific relative entropy of Q w.r.t. $q_{\rho_g,\nu}^{\otimes\mathbb{N}}$ is defined as

$$H(Q|q_{\rho_g,\nu}^{\otimes\mathbb{N}}) = \lim_{n\to\infty} \frac{1}{n} h(\pi_n Q|q_{\rho_g,\nu}^{\otimes n}).$$

Theorem

For every $g \in [0,\infty)$, the family $\mathbb{P} \otimes P_g^*(R_N^\omega \in \cdot\,)$, $N \in \mathbb{N}$, satisfies the LDP on $\mathcal{P}^{\mathrm{inv}}(\widetilde{\mathbb{R}}^{\mathbb{N}})$ with rate N and with rate function I_g^{ann} given by $I_g^{\mathrm{ann}}(Q) = H\big(Q \mid q_{\rho_g,\nu}^{\otimes\mathbb{N}}\big), \quad Q \in \mathcal{P}^{\mathrm{inv}}(\widetilde{\mathbb{R}}^{\mathbb{N}}).$
In particular,

$$I_g^{\mathrm{ann}}(Q) = I^{\mathrm{ann}}(Q) + g\mathbb{E}_Q(\tau_1) + \log \mathcal{N}(g).$$

Quenched LDP

1. The concatenation map $\kappa : \widetilde{\mathbb{R}}^{\mathbb{N}} \to \mathbb{R}^{\mathbb{N}}$ glues a word sequence together into letter sequence.

2. For $Q \in \mathcal{P}^{\mathrm{inv}}(\widetilde{\mathbb{R}}^{\mathbb{N}})$ such that $m_Q = E_Q(\tau_1) < \infty$, define

$$\Psi_Q = \frac{1}{m_Q} E_Q\left(\sum_{k=0}^{\tau_1 - 1} \delta_{\theta^k \kappa(Y)} \right) \in \mathcal{P}^{\mathrm{inv}}(\mathbb{R}^{\mathbb{N}}),$$

where θ is the left-shift acting on $\mathbb{R}^{\mathbb{N}}$ and τ_1 is the length of the first word.

3. Let

$$\mathcal{R} = \left\{ Q \in \mathcal{P}^{\mathrm{inv}}(\widetilde{\mathbb{R}}^{\mathbb{N}}) : \ \Psi_Q = \nu^{\otimes \mathbb{N}} \right\}.$$

Quenched LDP

Theorem

For $\mathbb{P}$–almost all ω and all $g \in [0,\infty)$, the family $P_g^*(R_N^\omega \in \cdot \mid \omega)$, $N \in \mathbb{N}$, satisfies the LDP on $\mathcal{P}^{\mathrm{inv}}(\widetilde{\mathbb{R}}^{\mathbb{N}})$ with rate N and with deterministic rate function I_g^{que} given for $g > 0$ by

$$I_g^{\mathrm{que}}(Q) = \begin{cases} I_g^{\mathrm{ann}}(Q), & \text{if } Q \in \mathcal{R}, \\ \infty, & \text{otherwise}, \end{cases}$$

and for $g = 0$ by

$$I^{\mathrm{que}}(Q) = H(Q \mid q_{\rho,\nu}^{\otimes\mathbb{N}}) + (\alpha - 1)\, m_Q\, H\big(\Psi_Q \mid \nu^{\otimes\mathbb{N}}\big),$$

when $m_Q < \infty$, and by its truncation approximation when $m_Q = \infty$.

Quenched variational formulas

Let $\mathcal{C}^{\mathrm{fin}} = \Big\{ Q \in \mathcal{P}^{\mathrm{inv}}(\widetilde{\mathbb{R}}^{\mathbb{N}}) : \; I^{\mathrm{ann}}(Q) < \infty, \; m_Q < \infty \Big\}$.

Theorem

1. *For every* $\beta, h > 0$ *and* ω*-a.s*

$$g^{\mathrm{que}}(\beta, h) = \inf \Big\{ g \in \mathbb{R} : S^{\mathrm{que}}(\beta, h; g) < 0 \Big\}, \quad \textit{where}$$

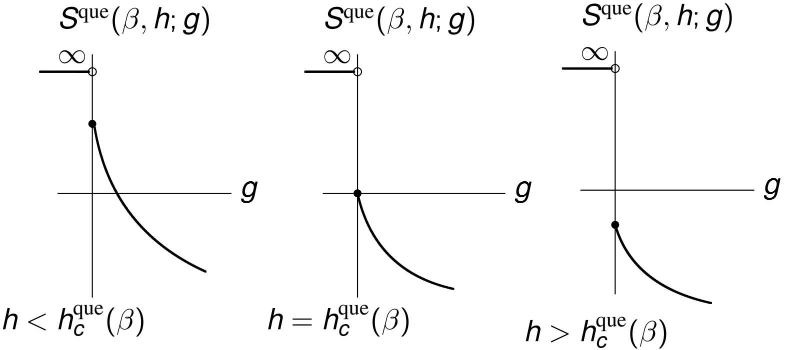
$$S^{\mathrm{que}}(\beta, h; g) = \sup_{Q \in \mathcal{C}^{\mathrm{fin}} \cap \mathcal{R}} \left[\Phi_{\beta,h}(Q) - g m_Q - I^{\mathrm{ann}}(Q) \right].$$

2. *Alternatively, for* $g = 0$

$$S^{\mathrm{que}}(\beta, h; 0) = S_*^{\mathrm{que}}(\beta, h) := \sup_{Q \in \mathcal{C}^{\mathrm{fin}}} \left[\Phi_{\beta,h}(Q) - I^{\mathrm{que}}(Q) \right].$$

3. *For every* $\beta, h > 0$, $S^{\mathrm{que}}(\beta, h; g) < \infty$, *for* $g > 0$.

Quenched variational formulas

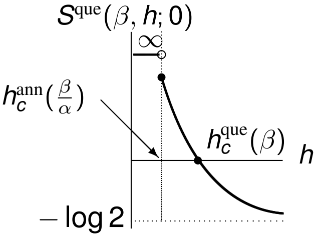


Corollary

For $\beta > 0$ and $h \leq h_c^{\text{que}}(\beta)$, $g^{\text{que}}(\beta, h)$ is the unique g-value that solves the equation

$$S^{\text{que}}(\beta, h; g) = 0.$$

Quenched variational formulas



Corollary

For every $\beta > 0$ *and* $g = 0$,

$$S^{\text{que}}(\beta, h; 0) \begin{cases} = \infty & \text{for } h < h_c^{\text{ann}}(\beta/\alpha), \\ > 0 & \text{for } h = h_c^{\text{ann}}(\beta/\alpha), \\ < \infty & \text{for } h > h_c^{\text{ann}}(\beta/\alpha). \end{cases}$$

$h_c^{\text{que}}(\beta)$ *is the unique* $h-$*value that solves the equation* $S^{\text{que}}(\beta, h; 0) = 0$.

Annealed variational formulas

Similarly, $g^{\mathrm{ann}}(\beta, h)$ is the unique value of g where

$$S^{\mathrm{ann}}(\beta, h; g) = \limsup_{N\to\infty} \frac{1}{N} \log \mathbb{E}\left(F_N^{\beta,h,\omega}(g)\right)$$

changes sign.

Theorem

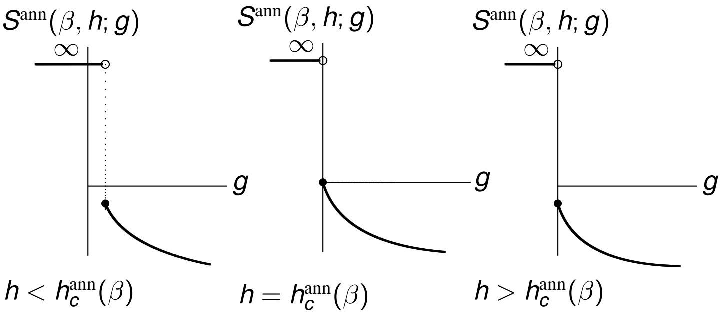
For $\beta, h \geq 0$,

$$g^{\mathrm{ann}}(\beta, h) = \inf\left\{g \geq 0 : S^{\mathrm{ann}}(\beta, h; g) < 0\right\}, \quad \textit{where}$$

$$S^{\mathrm{ann}}(\beta, h; g) = \sup_{Q\in\mathcal{C}^{\mathrm{fin}}} \left[\Phi_{\beta,h}(Q) - g m_Q - I^{\mathrm{ann}}(Q)\right]$$

$$= \log\left[\tfrac{1}{2}\mathcal{N}(g) + \tfrac{1}{2}\mathcal{N}\left(g - [M(2\beta) - 2\beta h]\right)\right].$$

Annealed variational formulas

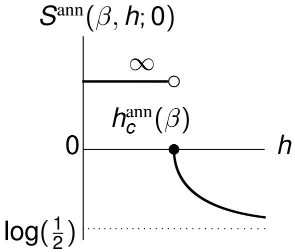


Corollary

For every $\beta \geq 0$ and $h = h_c^{\text{ann}}(\beta)$, $g^{\text{ann}}(\beta, h)$ is the unique g-value that solves the equation

$$S^{\text{ann}}(\beta, h; g) = 0.$$

Annealed variational formulas



Corollary

For every $\beta > 0$, $h_c^{\mathrm{ann}}(\beta)$ is the unique h-value that solves the equation

$$S^{\mathrm{ann}}(\beta, h; 0) = 0.$$

Consequences of variational formulas

Corollary

1. *For any* $\beta > 0$ *and* $\alpha \in (1, \infty)$,

$$h_c^{\mathrm{ann}}\left(\frac{\beta}{\alpha}\right) < h_c^{\mathrm{que}}(\beta) < h_c^{\mathrm{ann}}(\beta).$$

2.

$$\liminf_{\beta \downarrow 0} \frac{h_c^{\mathrm{que}}(\beta)}{\beta} \geq \begin{cases} \frac{1}{\alpha} B(\alpha), & \text{for } 1 < \alpha < 2, \\ \frac{1+\alpha}{2\alpha}, & \text{for } \alpha \geq 2, \end{cases}$$

for some $1 < B(\alpha) < \infty$.

3. *For any* $(\beta, h) \in \mathcal{L}^{\mathrm{ann}}$ *and* $\alpha \in [1, \infty)$,

$$g^{\mathrm{que}}(\beta, h) < g^{\mathrm{ann}}(\beta, h).$$

Other applications

The variational approach has been successfully applied to

- Study the phase diagram of copolymer with pinning model [den Hollander, A.O.]
- Settle a conjecture about existence of an intermediate phase in pinning of random walk by random walk [den Hollander, A.O.]
- Random pinning model [D. Cheliotis, F. den Hollander]

Open problems

1. The order of the phase transition.

2. The weak interaction limit

$$\lim_{\beta \downarrow 0} \frac{h_c^{\mathrm{que}}(\beta)}{\beta}, \qquad \alpha \in (1, \infty).$$

3. Analyticity of

$$\beta \mapsto h_c^{\mathrm{que}}(\beta) \qquad \text{on} \qquad (0, \infty),$$

$$(\beta, h) \mapsto g^{\mathrm{que}}(\beta, h) \qquad \text{on} \qquad \mathcal{L}^{\mathrm{que}}.$$

THANK YOU