

Adsorption and localization of random copolymers

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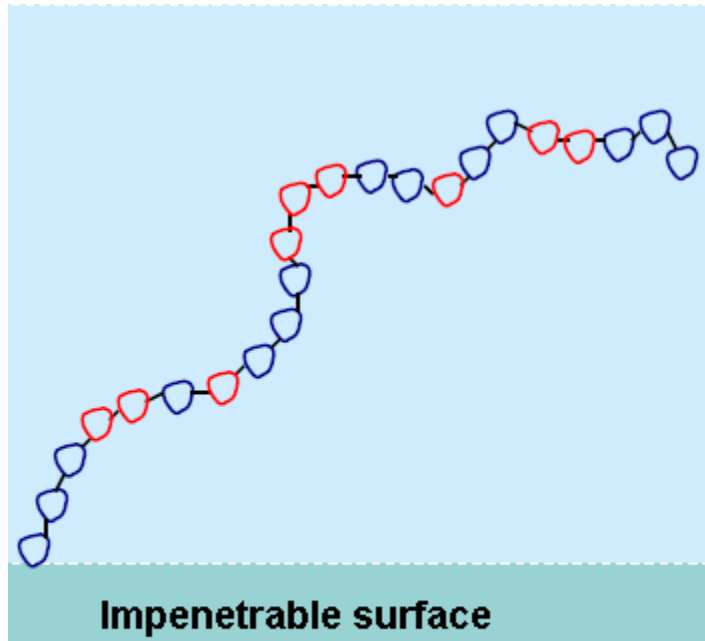
Outline

- Brief introduction to random copolymers
- Adsorption of random copolymers
- Localization of random copolymers

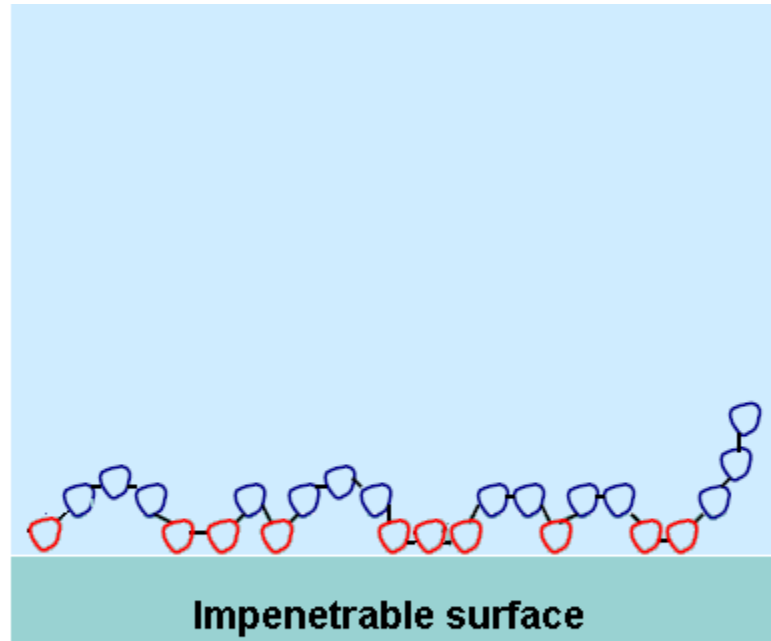
Brief introduction to random copolymers

- **Monomer**: a molecule that can react with other molecules to form large molecules (**polymers**)
- **Homopolymer**: a polymer that is composed of only one type of monomer.
- **Copolymer**: a polymer that is composed of at least two different types of monomers.
- **Random copolymer**: a copolymer whose monomer sequence is determined by a random process.

Adsorption of random copolymers



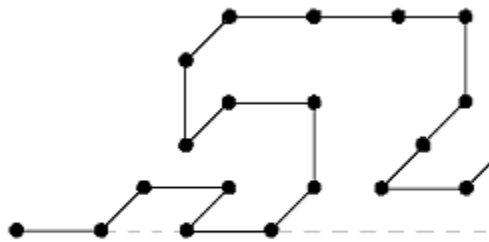
**Desorbed phase
(High T)**



**Adsorbed phase
(Low T)**

Assumptions

- Dilute solution so polymer-polymer interactions can be ignored.
- Polymer's conformation is represented by a self-avoiding walk on a lattice (take the first quadrant of Z^2 for simplicity), a Motzkin path or a Dyck path.



Self avoiding walk



Motzkin path



Dyck path

- System in equilibrium.
- Conformations with same energy are equally likely.
- Degree of polymerization (number of monomers) in copolymer is n .

- Two types of monomers: A and B .
- Coloring of i th monomer is χ_i
 $\chi_i = 0 \Rightarrow$ type B . Occurs with probability $1 - p$.
 $\chi_i = 1 \Rightarrow$ type A . Occurs with probability p .
- $\chi_1, \chi_2, \chi_3, \dots, \chi_n$ i.i.d. r.v.'s
- System state: (χ, ω)
 - ω - particular n -step self-avoiding walk (or Motkzin path, or Dyck path)
 - χ - a particular colouring (sequence of monomers).
- Sequence of monomers is determined by a random process but, once determined, it is then fixed (**quenched randomness**).
 Monomer sequence is determined by the polymerization process and it can't then change without some chemical reaction occurring.

Probability of a particular state (ω, χ) :

$$\rho(\omega, \chi) = \frac{\pi(\chi)e^{-E(\omega|\chi)/kT}}{Z_n(T|\chi)}$$

where

- $\pi(\chi)$: probability of coloring χ .
- $E(\omega|\chi)$: energy of conformation ω at fixed χ .
- k : Boltzmann's constant.
- T : temperature
- $Z_n(T|\chi)$: partition function at temperature T for fixed χ .

$$Z_n(T|\chi) = \sum_{\omega} e^{-E(\omega|\chi)/kT}$$

- We are interested in the **limiting quenched average free energy**:

$$\bar{\kappa}(T) = \lim_{n \rightarrow \infty} \left\langle \frac{\log Z_n(T|\chi)}{n} \right\rangle$$

where $\langle \cdot \rangle$ denotes expectation over χ .

- This will tell us the preferred phase of the system:
 - Desorbed
 - Adsorbed
- There is a phase transition at some value of T .
It corresponds to a point of non-analyticity of $\bar{\kappa}(T)$.
- Hard problem

- Better consider **limiting annealed average free energy**:

$$\bar{\kappa}^a(T) = \lim_{n \rightarrow \infty} \frac{\log \langle Z_n(T|\chi) \rangle}{n} \geq \bar{\kappa}(T)$$

- Good bound for high T .
- Bad bound for low T .

- Even better consider **limiting constrained annealed average free energy** (also known as the Morita approximation to the limiting quenched average free energy):

$$\bar{\kappa}^m(T) = \lim_{n \rightarrow \infty} \frac{\log \langle Z_n(T|\chi, \lambda_1, \lambda_2, \dots) \rangle}{n} \geq \bar{\kappa}(T)$$

where $\lambda_1, \lambda_2, \dots$ are the Lagrange multipliers corresponding to constraints on the distribution of χ (e.g. having the correct number of type **A** vertices, having the correct number of pairs of type **A** vertices, etc.)

- Good bound for high T .
- For low T ????

- What happens to the phase transition point?

A model for random copolymer adsorption

- Energy at fixed χ is such that:

$$-E(\omega|\chi)/kT = \alpha v_A$$

where

- v_A is the number of type A vertices at the surface.
 - α is the contribution from each of these vertices to the energy.
- The partition function becomes

$$Z_n(\alpha|\chi) = \sum_{v_A} c_n(v_A|\chi) e^{\alpha v_A}$$

where $c_n(v_A|\chi)$ is the number of walks (or paths) with v_A type A vertices at the surface given the coloring χ .

- Remember we're interested in the asymptotic behavior of $\langle Z_n(\alpha|\chi) \rangle$.
- It'll help to consider the homopolymer case first.
- Assume all monomers are type A , then

$$\langle Z_n(\alpha|\chi) \rangle = Z_n(\alpha) = \sum_{v_A} c_n(v_A) e^{\alpha v_A}$$

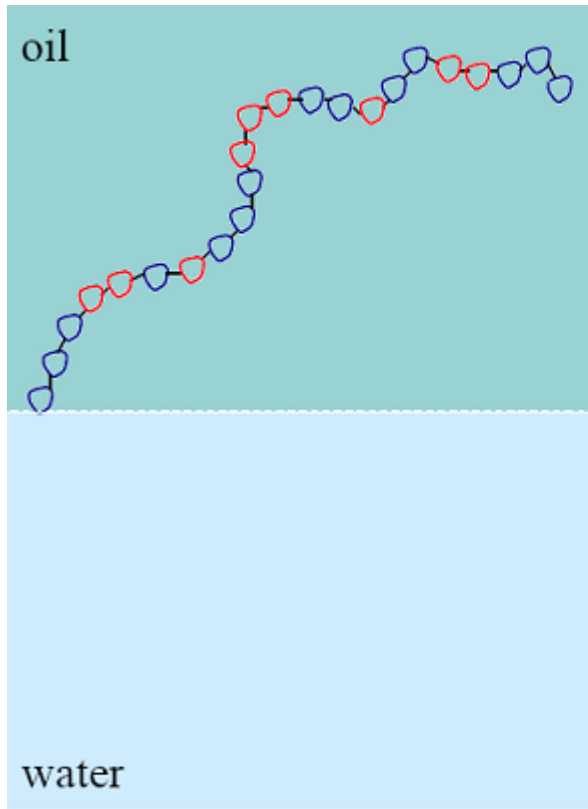
- For large n , the asymptotic behavior of $\langle Z_n(\alpha|\chi) \rangle$ is determined by the dominant singularity of the generating function

$$D_H(z, \alpha) = \sum_{n, v_A} c_n(v_A) e^{\alpha v_A} z^n$$

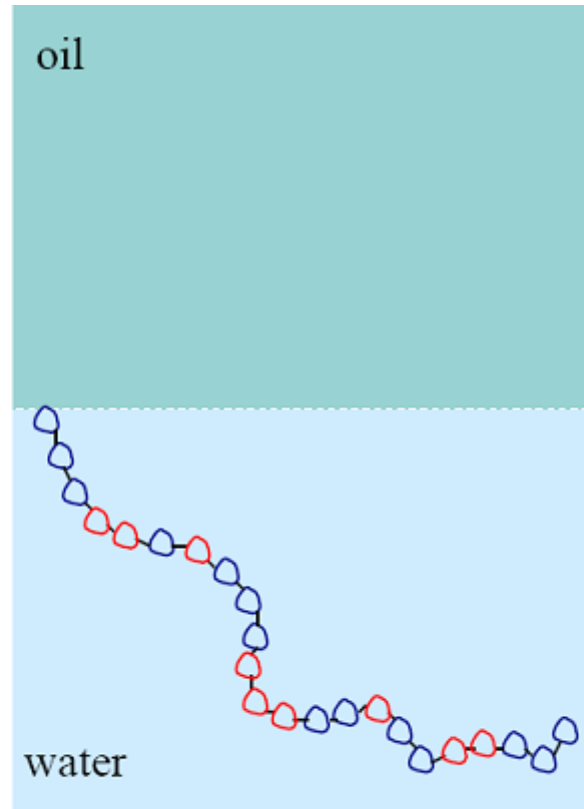
- The limiting quenched (and the annealed) average free energy exists for all $\alpha < \infty$.
- There exists a phase transition for some value of α .

- We can look at the annealed copolymer model by a simple transformation of variables in the generating function.
 - For large n , the asymptotic behavior of $\langle Z_n(\alpha|\chi) \rangle$ is determined by the dominant singularity of the transformed generating function
 - The limiting quenched (and the annealed) average free energy exists for all $\alpha < \infty$.
 - There exists a phase transition for some value of α .
- In some cases, we can also look at the constrained annealed copolymer model by a transformation of variables in the generating function.
 - For large n , the asymptotic behavior of $\langle Z_n(\alpha|\chi, \lambda_1, \lambda_2, \dots) \rangle$ is determined by the dominant singularity of the transformed generating function
 - The limiting constrained annealed average free energy exists for all $\alpha < \infty$.
 - There exists a phase transition for some value of α (so far, it is the same as the annealed phase transition point).

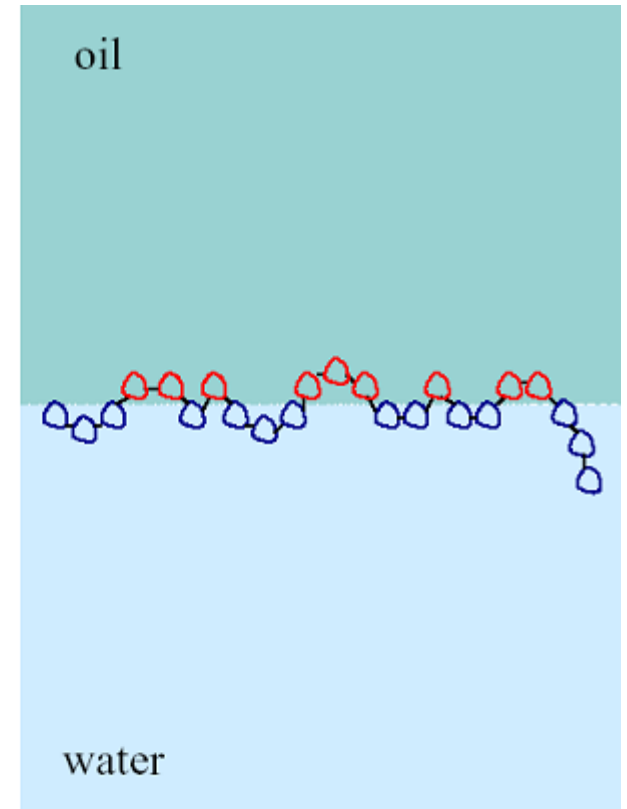
Localization of random copolymers



Delocalized



Delocalized



Localized

Assumptions

- Same as for adsorption.
- Polymer's conformation is represented by a self-avoiding walk on a lattice (take right half of Z^2 for simplicity), a bilateral Motzkin path or a bilateral Dyck path.



Bilateral Motzkin path



Bilateral Dyck path

- We are interested in the **limiting quenched average free energy**.
- This will tell us the preferred phase of the system:
 - Delocalized into the water phase
 - Delocalized into the oil phase
 - Localized
- Again:
 - Hard problem
 - Consider **limiting annealed average free energy**.
 - Consider **limiting constrained annealed average free energy**.

A model for random copolymer localization

- Energy at fixed χ is such that:

$$-E(\omega|\chi)/kT = \alpha v_A + \beta v_B + \gamma w$$

where

- v_A is the number of type A vertices above the interface.
- α is the contribution from each of these vertices to the energy.
- v_B is the number of type B vertices below the interface.
- β is the contribution from each of these vertices to the energy.
- w is the number of vertices (A and B) at the interface.
- γ is the contribution from each of these vertices to the energy.

- The partition function becomes

$$Z_n(\alpha|\chi) = \sum_{v_A, v_B, w} c_n(v_A, v_B, w|\chi) e^{\alpha v_A + \beta v_B + \gamma w}$$

where $c_n(v_A, v_B, w|\chi)$ is the number of walks (or paths) with v_A type A vertices above the interface, v_B type B vertices below the interface, and w vertices at the interface, given the coloring χ .

- We're interested in the asymptotic behavior of $\langle Z_n(\alpha, \beta, \gamma|\chi) \rangle$.
- Phase transition corresponds to a point of non-analyticity of the limiting quenched average free energy $\bar{\kappa}(\alpha, \beta, \gamma)$.
- It'll help to consider the homopolymer case first.

- Assume all monomers are type A , then

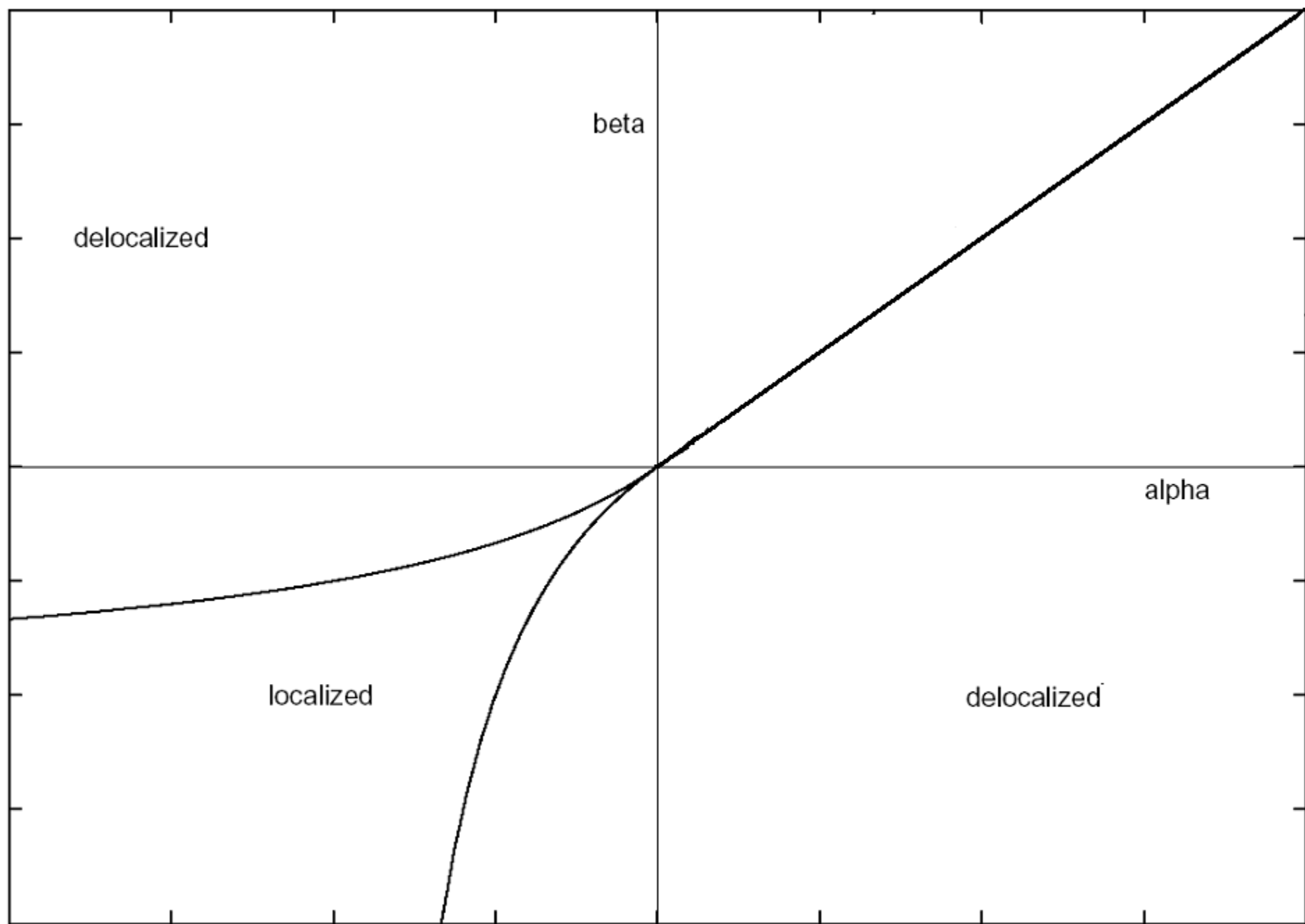
$$\langle Z_n(\alpha, \beta, \gamma | \chi) \rangle = Z_n(\alpha, \beta, \gamma) = \sum_{v_A, v_B, w} c_n(v_A, v_B, w) e^{\alpha v_A + \beta v_B + \gamma w}$$

- For large n , the asymptotic behavior of $\langle Z_n(\alpha, \beta, \gamma | \chi) \rangle$ is determined by the dominant singularity of the generating function

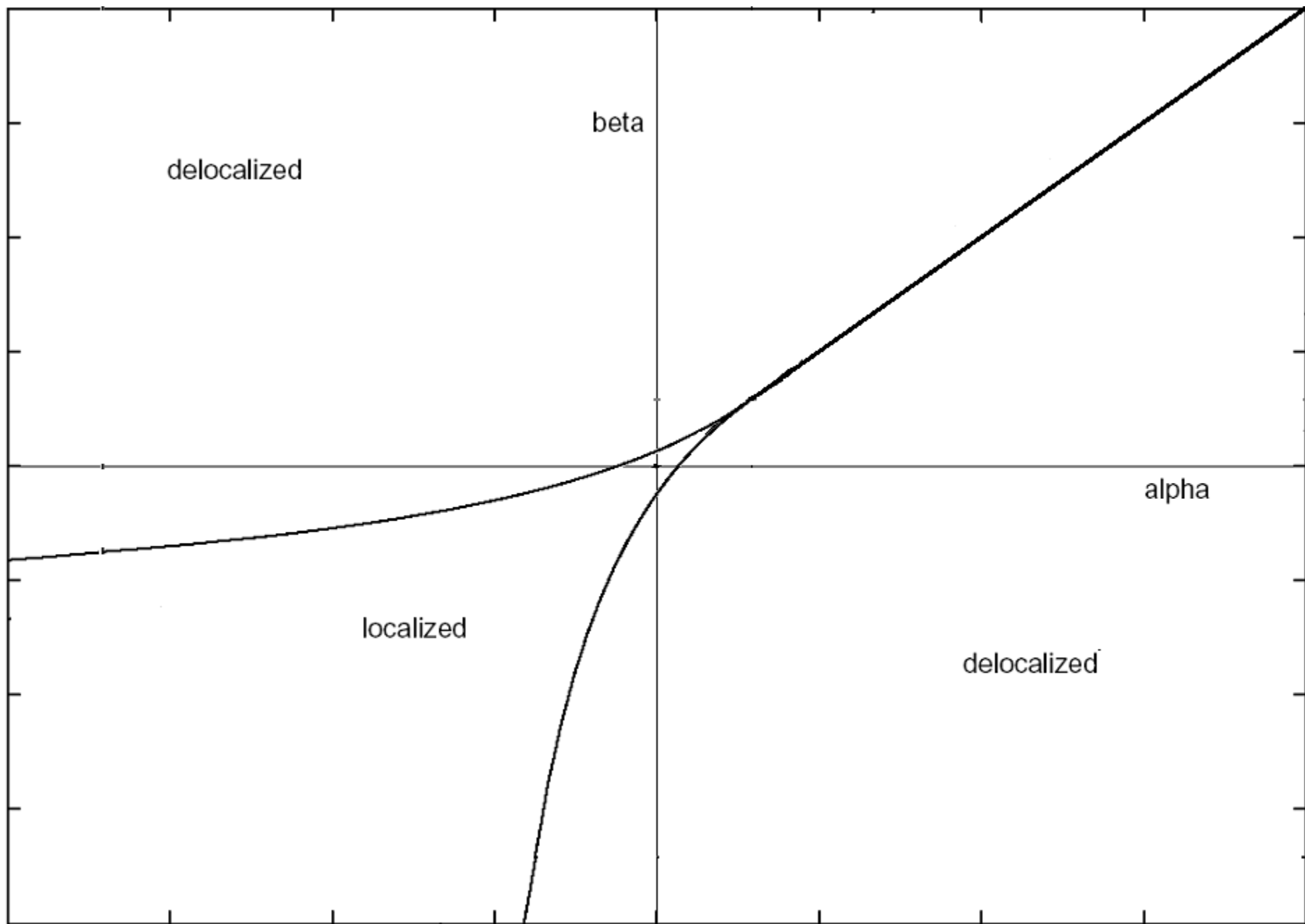
$$D_H(z, \alpha, \beta, \gamma) = \sum_{n, v_A, v_B, w} c_n(v_A, v_B, w) e^{\alpha v_A + \beta v_B + \gamma w} z^n$$

- The limiting quenched (and the annealed) average free energy exists for all $\alpha, \beta, \gamma < \infty$.
- Let's consider the phase transitions.

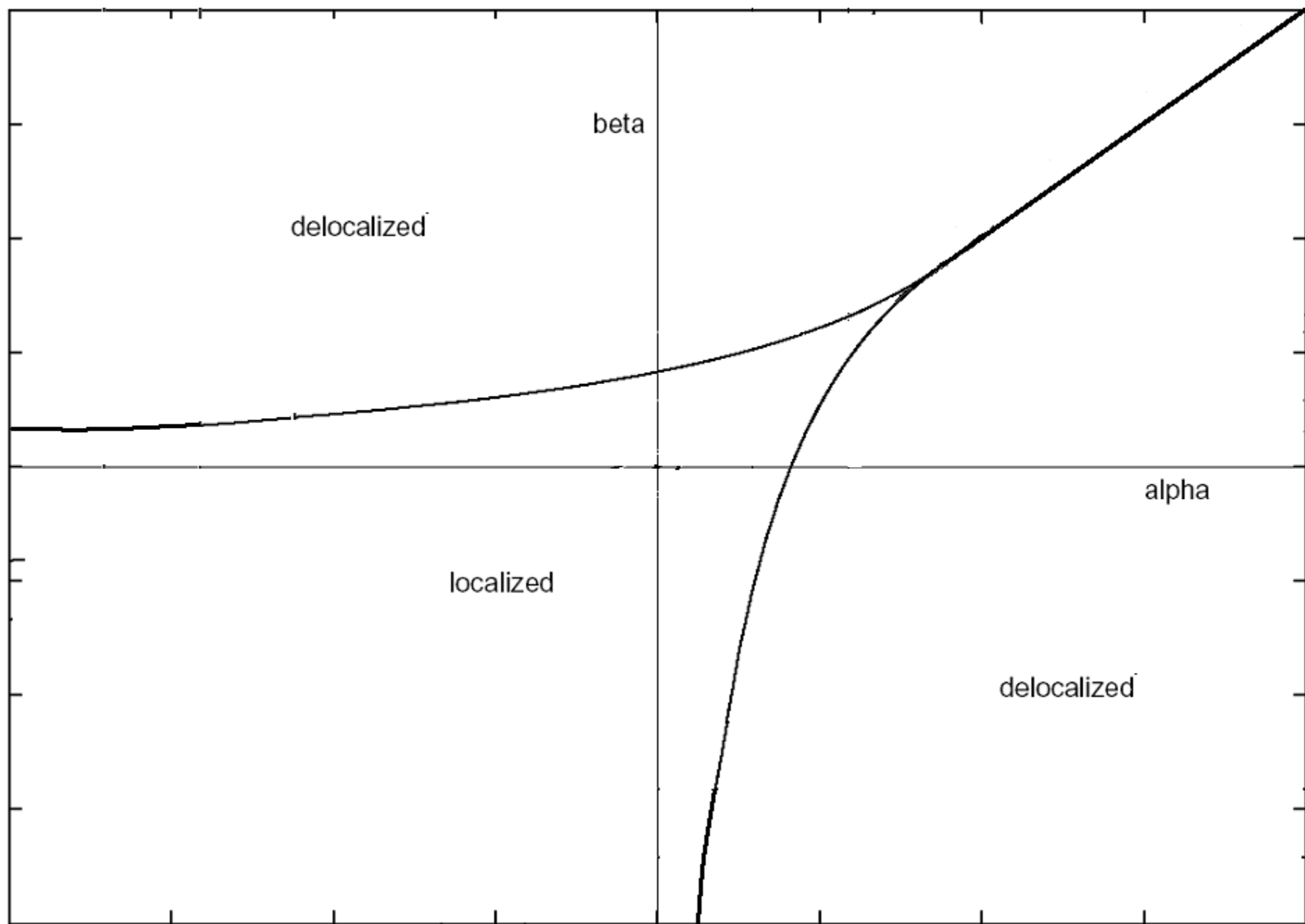
$$\gamma \leq 0$$



$$0 < \gamma < \gamma^*$$

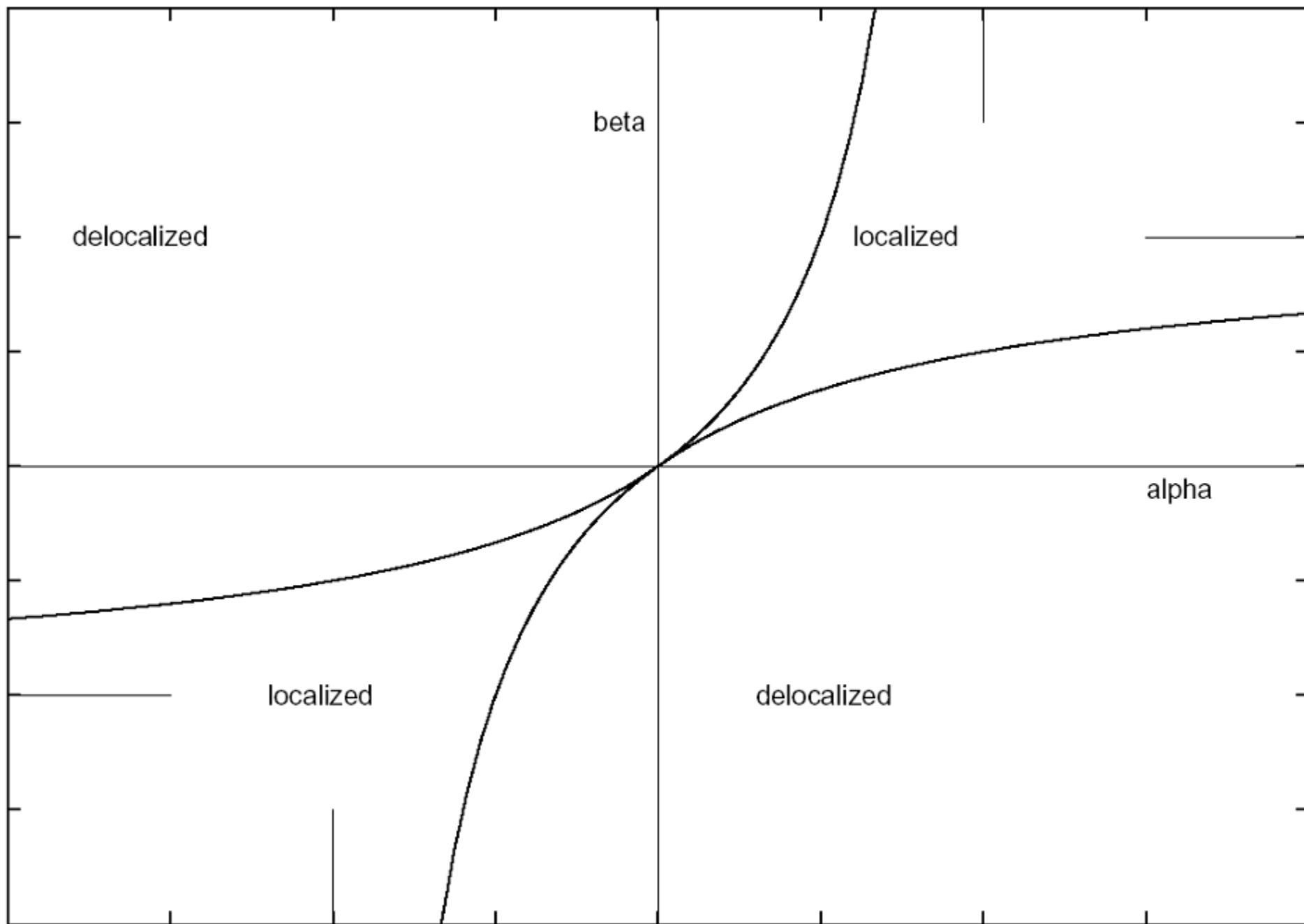


$$\gamma^* \geq \gamma$$



- We can look at the annealed copolymer model by a simple transformation of variables in the generating function.
 - For large n , the asymptotic behavior of $\langle Z_n(\alpha, \beta, \gamma | \chi) \rangle$ is determined by the dominant singularity of the transformed generating function
 - The limiting quenched (and the annealed) average free energy exists for all $\alpha, \beta, \gamma < \infty$.
 - The phase transitions are very similar to the homopolymer model.
- In some cases, we can also look at the constrained annealed copolymer model by a transformation of variables in the generating function.
 - For large n , the asymptotic behavior of $\langle Z_n(\alpha, \beta, \gamma | \chi, \lambda_1, \lambda_2, \dots) \rangle$ is determined by the dominant singularity of the transformed generating function
 - The limiting constrained annealed average free energy exists for all $\alpha, \beta, \gamma < \infty$.
 - Let's look at the phase transitions.

$$\gamma \leq 0$$



$$0 < \gamma_1 < \gamma < \gamma_2$$

