Adsorption of random and periodic copolymers: a theoretical study using simple model

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Introduction

What is adsorption ?

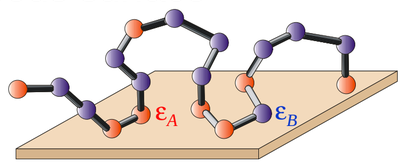
- **Adsorption** is an increase in the concentration of a dissolved substance at the interface of a condensed and a liquid phase due to the operation of surface forces. *(IUPAC Compendium of Chemical Terminology - the Gold Book)*.

Application of polymer adsorption

- Surface modification
- Stabilization of colloidal dispersions
- Polymer-nanofiller interactions in polymer nanocomposites
- Adsorption chromatography

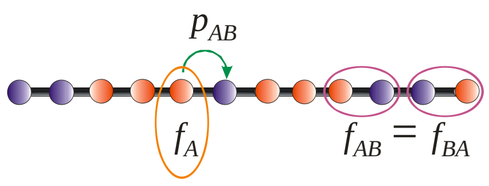
The system we study

- A single *random* or *regular (periodic)* AB-copolymer chain adsorbing onto a homogeneous surface



Theory

Random copolymer



- Monomer sequence – first order Markov chain
- Transition (nearest-neighbour) probabilities form the stochastic matrix

$$\mathbf{P} = \begin{pmatrix} p_{AA} & p_{AB} \\ p_{BA} & p_{BB} \end{pmatrix}$$

- Correlation parameter $c = 1 - p_{AB} - p_{BA}$
  - $c > 0$ – quasi-blocky
  - $c < 0$ – quasi-alternating
  - $c = 0$ – Bernoullian (uncorrelated)

Generating functions (GFs) approach and annealed approximation

- Partition function $Z_n(\beta) = \sum_{\omega} \exp[-\beta E(\omega,\chi)]$, where $\beta = 1/k_B T$ is the inverse temperature, E – energy, ω stands for chain conformation.
- Annealed free energy $F_a = -k_B T \log\langle Z \rangle_\chi$
- Calculate the GF: $\Xi(z) = \sum_{n=1}^{\infty} \langle Z_n(\beta) \rangle_\chi x^n$
- Then $\langle Z_n(\beta) \rangle_\chi = x_c^{-n}$, where x_c is the smallest singularity of $\Xi(x)$ (radius of convergence)

- The GF smallest singularity can be found as the smallest root of the equation:

$$\det[\mathbf{E} - \mathbf{\Xi}_L(x)\mathbf{\Xi}_S(x)] = 0$$

where $\mathbf{\Xi}_S(x)$ и $\mathbf{\Xi}_L(x)$ are matrix GFs of adsorbed segments (trains) and loops

$$\mathbf{\Xi}_S(x) = \sum_{n=1}^{\infty} \Omega_S(n) x^n (\mathbf{PW})^n$$

$$\mathbf{\Xi}_L(x) = \sum_{n=1}^{\infty} \Omega_L(n) x^n \mathbf{P}^n$$

$\Omega_{S,L}(n)$ is the number of trains or loops of length n, respectively

- Matrix GFs are calculated by using scalar GFs (GFs for homopolymer adsorption).
- $\mathbf{W}$ is the diagonal matrix of statistical weights of adsorbed units

$$\mathbf{W} = \begin{pmatrix} e^{-\beta\varepsilon_A} & 0 \\ 0 & e^{-\beta\varepsilon_B} \end{pmatrix}$$

Second order Morita approximation

- Introduce constraints on the monomer distribution in the sequence:

$$\sum_{i=1}^{n} \chi_i = n f_A \qquad \sum_{i=2}^{n} \chi_{i-1}\chi_i = (n-1) f_{AA}$$

- This modifies the stochastic matrix

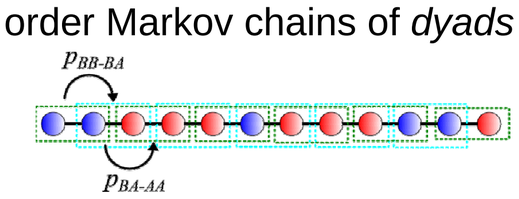
$$\mathbf{P} = \begin{pmatrix} p_{AA} & p_{AB} \\ p_{BA} & p_{BB} \end{pmatrix} \rightarrow \mathbf{P} = \begin{pmatrix} p_{AA}L_1L_2 & p_{AB} \\ p_{BA}L_1 & p_{BB} \end{pmatrix}$$

and $x \rightarrow x L_1^{-f_A} L_2^{-f_{AA}}$

$L_i = e^{\lambda_i}$, where λ_i is the Lagrange multiplier coupled to the i-th constraint

Third order Morita approximation

- First order Markov chains of *dyads*



- Additional constraints on monomer *triads*:

$$\sum_{i=3}^{n} \chi_{i-2}\chi_{i-1}\chi_i = (n-2) f_{AAA} = (n-2) f_A p_{AA} p_{AA}$$

$$\sum_{i=3}^{n} (1-\chi_{i-2})(1-\chi_{i-1})(1-\chi_i) = (n-2) f_{BBB} = (n-2) f_B p_{BB} p_{BB}$$

- New modified stochastic matrix

$$\begin{array}{c} \\ AA \\ AB \\ BA \\ BB \end{array} \begin{array}{c} \begin{array}{cccc} AA & AB & BA & BB \end{array} \\ \begin{pmatrix} p_{AA}L_1L_2L_3 & p_{AB} & 0 & 0 \\ 0 & 0 & p_{BA}L_1 & p_{BB} \\ p_{AA}L_1L_2 & p_{AB} & 0 & 0 \\ 0 & 0 & p_{BA}L_1 & p_{BB}L_4 \end{pmatrix} \end{array} = \mathbf{P}$$

Periodic copolymer

- Represent the period of a periodic copolymer (surface) as a sequence of *different* monomers:

$$\mathbf{AAABBB} \rightarrow \mathbf{M_1\,M_2\,M_3\,M_4\,M_5\,M_6}$$

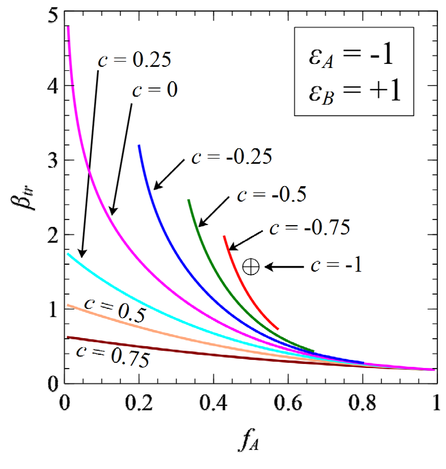
Periodic copolymer can be viewed as a first order Markov chain with *circulant* transition probability matrix

$$\mathbf{P} = \begin{pmatrix} p_{M_1M_1} & p_{M_1M_2} & p_{M_1M_3} & \cdot & p_{M_1M_{mp}} \\ p_{M_2M_2} & p_{M_2M_2} & p_{M_2M_3} & \cdot & p_{M_2M_{mp}} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ p_{M_{mp-1}M_1} & p_{M_{mp-1}M_2} & p_{M_{mp-1}M_3} & \cdot & p_{M_{mp-1}M_{mp}} \\ p_{M_{mp}M_1} & p_{M_{mp}M_2} & p_{M_{mp}M_3} & \cdot & p_{M_{mp}M_{mp}} \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 & . & 0 \\ 0 & 0 & 1 & . & 0 \\ . & . & . & . & . \\ 0 & 0 & 0 & . & 1 \\ 1 & 0 & 0 & . & 0 \end{pmatrix}$$

Results

Annealed approximation

- Adsorption transition point (polymer is modeled as a simple random walk on the cubic lattice)

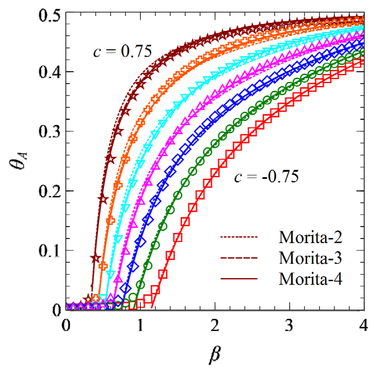


- For the Morita approximation the adsorption transition point is the same

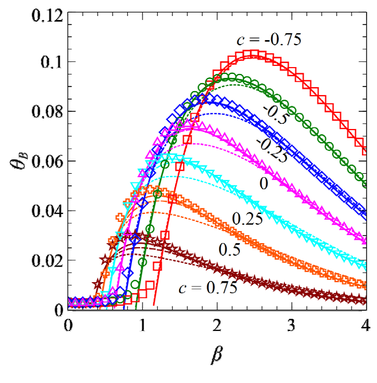
Morita approximation

- Comparison of the results for the Morita approximation with direct numerical simulations for "quenched" chains (N=1000 units, 100 random sequences). ε_A=-1, ε_B=+1

Fraction of adsorbed A units



Fraction of adsorbed B units

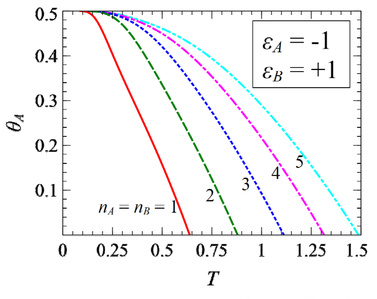


- Good quantitative agreement for higher order Morita approximations

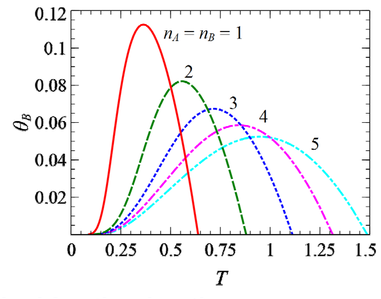
Periodic multiblock copolymer

- Copolymer with symmetric compostion: $[A_{nA}B_{nB}]_m$

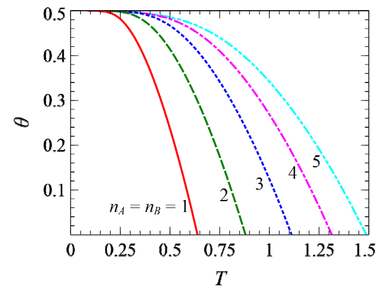
Fraction of adsorbed A units



Fraction of adsorbed B units



Overall adsorbed fraction (A+B)



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