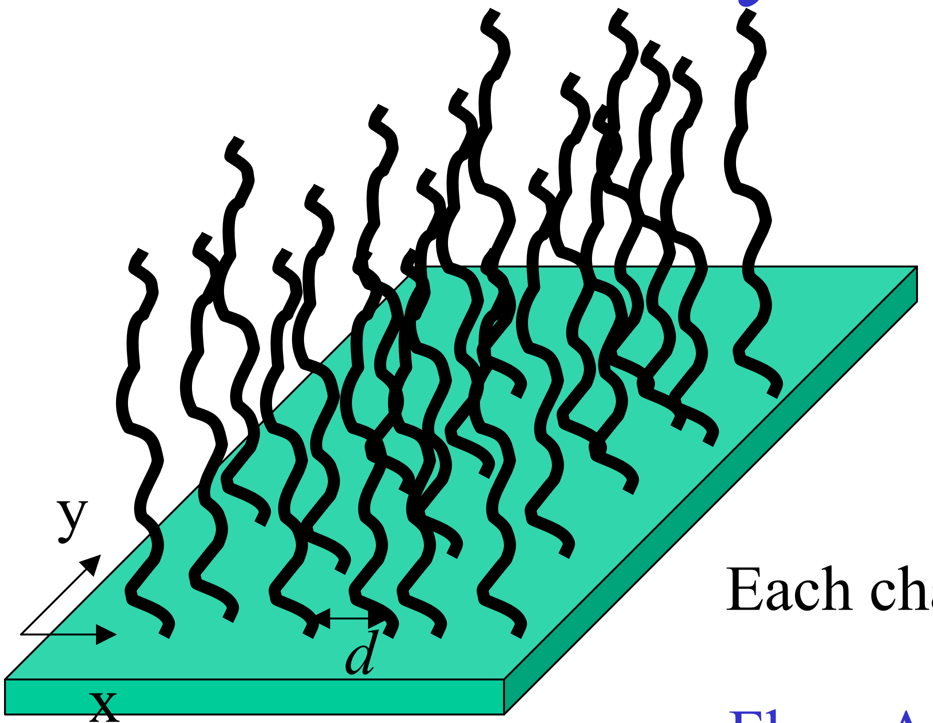
Lecture 19

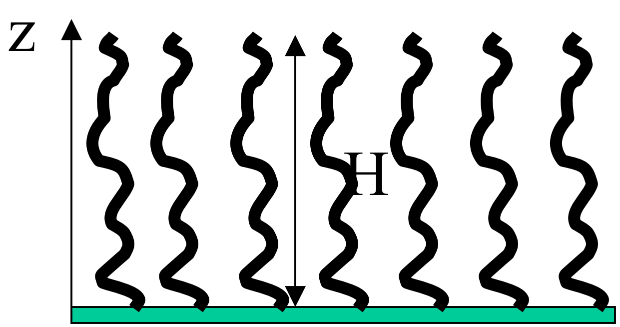
Polymer Brushes

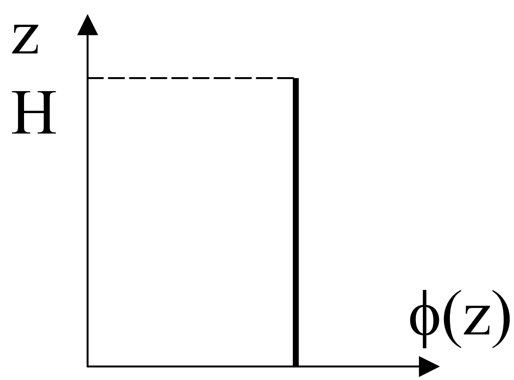


Consider a polymeric chains grafted to a surface by one end. The chains are separated by distance *d* from each other along x and y axes.

Each chain has a degree of polymerization *N*.

Flory Approach





All free ends of grafted chains are located at the same distance *H* from the surface resulting in uniform density distribution.

Polymer Brushes

Flory Approach in θ-solvent

There are two contributions to the chain's free energy.

Elastic energy – associated with chain's conformational degrees of freedom

$$F_{elast} \approx \frac{S}{d^2} kT \frac{H^2}{b^2 N}$$

Total number of chains in the layer

Deformation of each chain.

Interaction energy which is due excluded volume interaction between monomers.

$$F_{\text{int}} \approx kT \frac{SH}{b^3} \phi^3$$

Three body interactions

Where polymer volume fraction ϕ is equal to $\phi \approx \frac{S}{d^2} \frac{Nb^3}{SH} \approx \frac{Nb^3}{d^2 H}$

Polymer Brushes

Flory Approach in θ-solvent

The total free energy is

$$\frac{F}{kT} \approx \frac{S}{d^2}\left[\frac{H^2}{b^2 N} + \frac{N^3 b^6}{H^2 d^4}\right]$$

The equilibrium thickness of the brush is obtained by minimizing the free energy with respect to brush height *H*

$$\frac{\partial}{\partial H}\frac{F}{kT} \approx \frac{S}{d^2}\left[2\frac{H}{b^2 N} - 2\frac{N^3 b^6}{H^3 d^4}\right] = 0$$

$$H \approx \frac{b^2}{d} N$$

The chains in a brush are strongly stretched $H \sim N$, and thickness increases when the distance *d* between chains decreases.

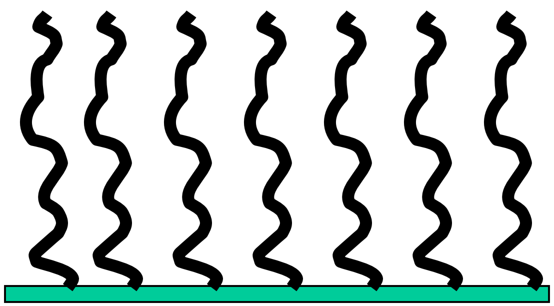
Polymer Brushes

Flory Approach in θ-solvent

Crossover to unperturbed chain regime occurs when the thickness of the layer is equal to ideal chain size $bN^{1/2}$.

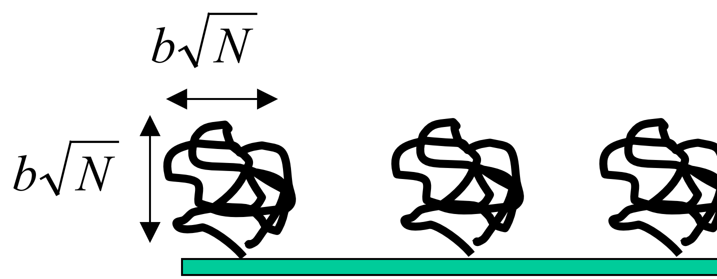
$$b\sqrt{N} \approx H \approx \frac{b^2}{d} N \Rightarrow d \approx b\sqrt{N}$$

$d < b\sqrt{N}$



Stretched chains

$d > b\sqrt{N}$

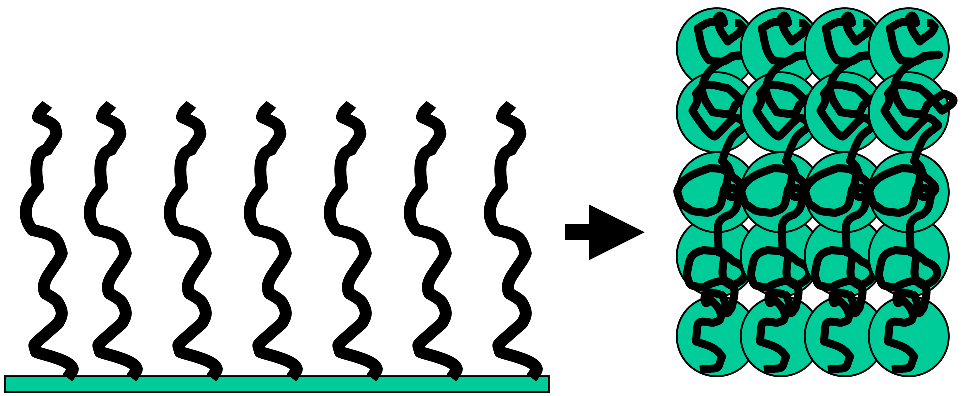


Ideal chains

Polymer Brushes

Scaling Approach in θ-solvent

In the scaling approach each chain is considered to be constraint within a tube of diameter *d* formed by surrounding chains



Chain of blobs

Number of monomers in a blob

$$d \approx b g^{1/2} \Rightarrow g \approx d^2 / b^2$$

Brush thickness

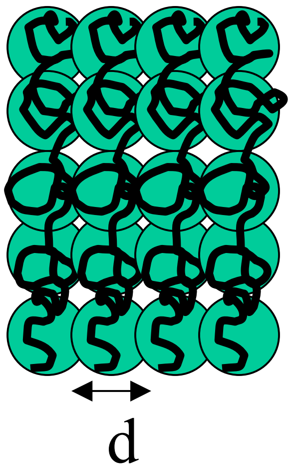
$$H \approx \frac{N}{g} d \approx \frac{N b^2}{d}$$

Free energy of a chain in a brush

$$F_{ch} \approx kT \frac{N}{g} \approx kTN \frac{b^2}{d^2}$$

Polymer Brushes

Scaling Approach in Arbitrary Solvent



Number of monomers in a blob

$$d \approx bg^{\nu} \Rightarrow g \approx \left(\frac{d}{b}\right)^{1/\nu}$$

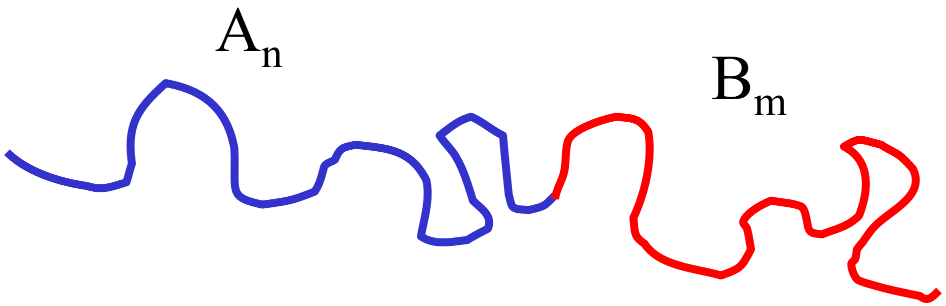
Brush thickness

$$H \approx \frac{N}{g} d \approx N \frac{b^{1/\nu}}{d^{1/\nu - 1}}$$

Free energy of a chain in a brush

$$F_{ch} \approx kT \frac{N}{g} \approx kTN \left(\frac{b}{d}\right)^{1/\nu}$$

Block Copolymers



Chain degree of polymerization $N=m+n$

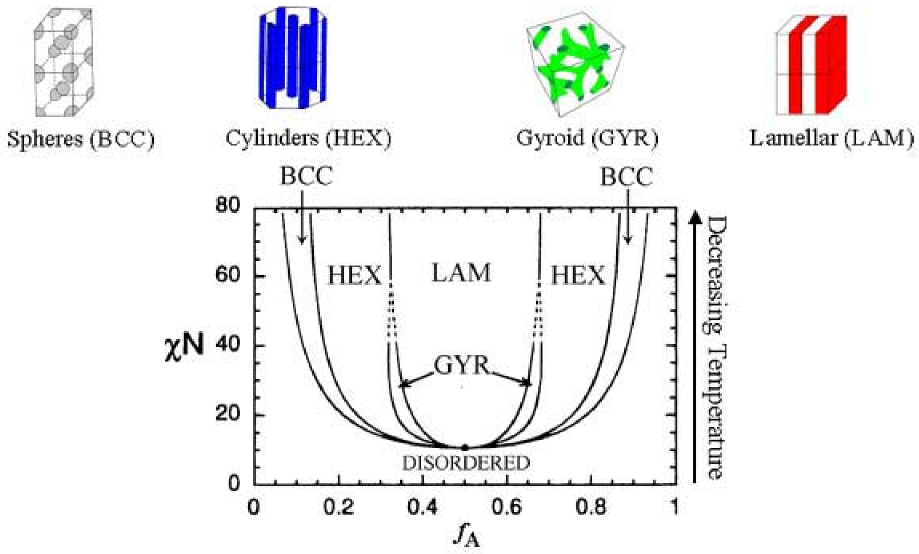
Chain composition $f_A=n/(n+m)$

What will happen with melt of this polymers if the Flory-Huggins parameter χ is large?

MICROPHASE SEPARATION

Optimization of interaction between A and B blocks is achieved by redistributing monomers locally – forming domains rich with one component.

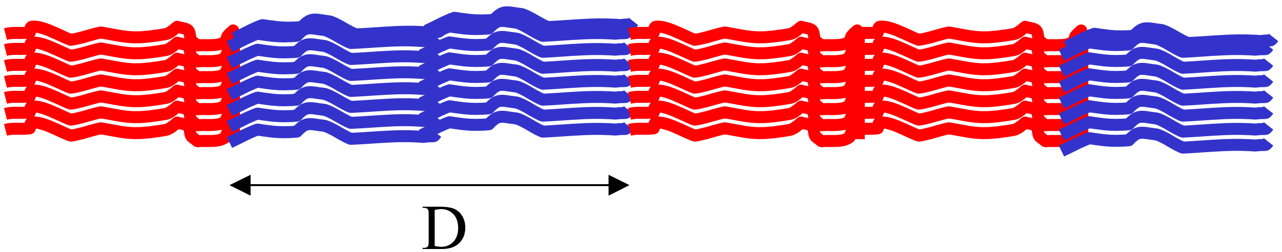
Phase Diagram of Block Copolymers



Phase diagram of diblock copolymers: f_A polymer composition, χ – Flory-Huggins interaction parameter, N - diblock degree of polymerization. Known equilibrium mesophases are S(pheres), C(ylinders), G(yroid), and L(amellae), as well as the disordered (DIS, homogeneous) at small interblock segregation strength (χN). Diagram adapted from Matsen and Bates (1996).

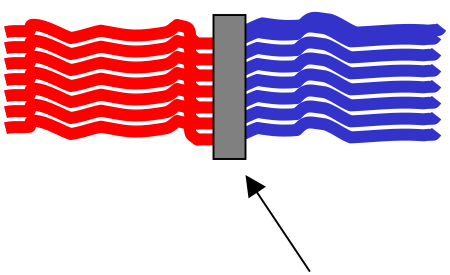
Block Copolymers

Equilibrium size of the domains



Consider domains as brush-like layers of thickness D which grafting density should be optimized to minimize the chain free energy

Free energy of a chain in the domain



Interphase between A-rich and B-rich regions

γ-surface energy

$$F \approx kT\frac{D^2}{b^2 n} + kT\frac{D^2}{b^2 m} + \gamma d^2$$

Elastic Energy   Interfacial Energy

In a melt polymer volume fraction is equal to 1.

$$1 = \phi = \frac{Nb^3}{Dd^2} \Rightarrow d^2 = \frac{Nb^3}{D}$$

Block Copolymers

Using relation between distance between chains *d* and domain thickness *D* we can write

$$F \approx kT\frac{D^2}{b^2 n} + kT\frac{D^2}{b^2 m} + \gamma\frac{Nb^3}{D} \approx kT\frac{D^2}{b^2 N} + \gamma\frac{Nb^3}{D}$$

Minimizing the chain's free energy with respect to domain size *D* one has

$$\frac{\partial F}{\partial D} \approx 2kT\frac{D}{b^2 N} - \gamma\frac{Nb^3}{D^2} \qquad D \approx bN^{2/3}\left(\frac{\gamma b^2}{kT}\right)^{1/3}$$

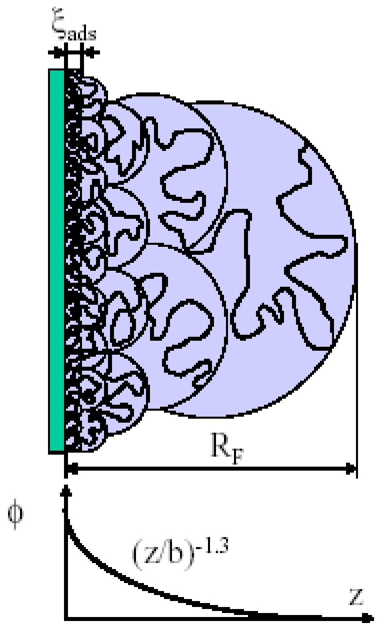
As in the case of polymeric brush chains are strongly stretched.

The interfacial energy γ is related to the Flory-Huggins parameter χ

$$\gamma \approx \frac{kT}{b^2}\chi^{1/2}$$

Polymer Adsorption

Correlation length in semidilute solution



$$\xi \approx b\phi^{-\nu/(3\nu-1)}$$

de Gennes assumption: $\xi = z$

de Gennes self-similar carpet

Polymer density profile inside adsorbed layer

$$\phi(z) \approx \left(\xi(z)/b\right)^{-(3\nu-1)/\nu} \approx \left(z/b\right)^{-(3\nu-1)/\nu}$$

Polymer surface coverage

$$\Gamma \approx \int \frac{\phi(z)}{b^3} dz \approx b^{-3} \int_{\xi_{ads}}^{R_F} \left(z/b\right)^{-(3\nu-1)/\nu} dz \approx b^{-2}\left(\frac{b}{\xi_{ads}}\right)^{(2\nu-1)/\nu}$$

Adsorption blob: $\xi_{ads} \approx b\delta^{-\nu/(1-\nu)}$

Summary of Polymer Solutions