Introduction to Biomaterials and Biomolecular Self Assembly

Monica Olvera de la Cruz

Northwestern University

Department of Materials Science and Engineering

2220 Campus Drive

Evanston, IL 60202

Outline

- Introduction to Statistical Mechanics
    - Magnetic system with two states (up and down)
    - Entropy
    - Boltzman factor
- Diffusion
- Polymers
    - Polymer Conformation
- Copolymers
    - Melts (SCMF)
    - Micelles (Simulations)

Introduction to Statistical Mechanics

- Relationship of number of accessible states to entropy

$$\boxed{\sigma = \log g}^{*} \quad (1)$$

- Transfer of energy between two systems, increases entropy and achieves the same temperature

$$\boxed{\frac{1}{\tau} \equiv \left(\frac{\partial \sigma}{\partial U}\right)_{N,V}} \quad (2)$$

- Probability of finding a system at energy ε over 0

$$\boxed{\frac{P(\varepsilon)}{P(0)} = \frac{g(U_0 - \varepsilon)}{g(U_0)} = \frac{\exp[\sigma(U_0 - \varepsilon)]}{\exp[\sigma(U_0)]}} \quad (3)$$

- Thermal average energy at temperature τ

$$\boxed{< \varepsilon >= \sum_i \varepsilon_i P(\varepsilon_i)} \quad (4)$$

- Helmholtz free enegy $\boxed{F \equiv U - \tau\sigma}$ (5)

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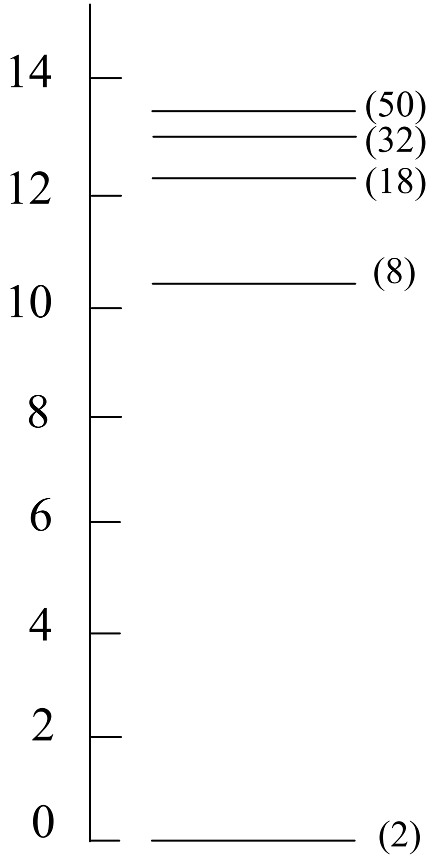
*All log are base e.

Quantum States

- Fundamental assumption: equally likely to be found in any of the quantum states accessible to it
- Each quantum state has a definite energy
- Multiplicity or degeneracy: quantum states that have nearly the same energy
- Important: number of quantum states, not number of energy levels



Atomic hydrogen

Binary Model System

- Magnetic system: N non-interacting spins
- Spin value: +m (↑) or –m (↓)
- 2^N equally accessible arrangements
- Each arrangement specifies the configuration of the 1st, 2nd,…Nth spin:

…↑↑↓↓↓↑↑↓↓↓↓↑↓…

- Total magnetization M: Nm, (N-2)m, (N-4)m,… -Nm
  - The same value of M can occur with multiple arrangements

Enumeration of States

- Spin excess with s being an integer having $N_\uparrow$ spins up and $N_\downarrow$ spins down:

$$\boxed{N_\uparrow - N_\downarrow = 2s}$$

- The multiplicity factor or the number of arrangements [$g(N,s)$] for a system of N magnets that have the same value of s:

$$\boxed{g(N,s) = \frac{N!}{\left(\frac{1}{2}N+s\right)!\left(\frac{1}{2}N-s\right)!} = \frac{N!}{N_\uparrow!N_\downarrow!}}$$

- Application of magnetic field leads to a different energy for states with a different s
- Total number of arrangements:

$$\boxed{\sum_{s=-\frac{1}{2}N}^{s=\frac{1}{2}N} g(N,s) = 2^N}$$

Sharpness of the Multiplicity Function

- N! prevents calculation of multiplicity for large values of N
- Gaussian distribution (using the Stirling approximation) allows for the approximation of multiplicity when $N >> 1$ and $|s| << N$
  - Sharp peak at s = 0
  - System contains stable physical properties

$$\boxed{g(N,s) \cong g(N,0)\exp\left(\frac{-2s^2}{N}\right)} \quad \text{when} \quad g(N,0) \cong 2^N\left(\frac{2}{\pi N}\right)^{1/2}$$

- Average values are necessary – macroscopic measurements of a constantly changing system

Closed Systems

- Constant: energy, number of particles, volume, and external parameters affecting the system
- Probability (P) of a system being in an accessible state (s)

$$\boxed{P(s) = \frac{1}{g}}$$

- Two systems in thermal contact
  - Energy (only) is transferred freely between the two
  - Total energy is constant
  - Number of accessible states in the combined system:

$$\boxed{g(N, s) = \sum_{s_2} g_1(N_1, s_1) g_2(N_2, s - s_1)}$$

    - N_1, N_2, and s are constant
  - Most probably conformation – when $g_1 g_2$ is at a maximum; dictates most of the properties of the system

Entropy

- Using (1), relate entropy of two systems in thermal contact

$$\boxed{\left(\frac{\partial \sigma_1}{\partial U_1}\right)_{N_1} = \left(\frac{\partial \sigma_2}{\partial U_2}\right)_{N_2}}$$

- (2) comes from: the equation above, the thermal contact of the two systems, and:

$$\boxed{\tau = k_B T}$$

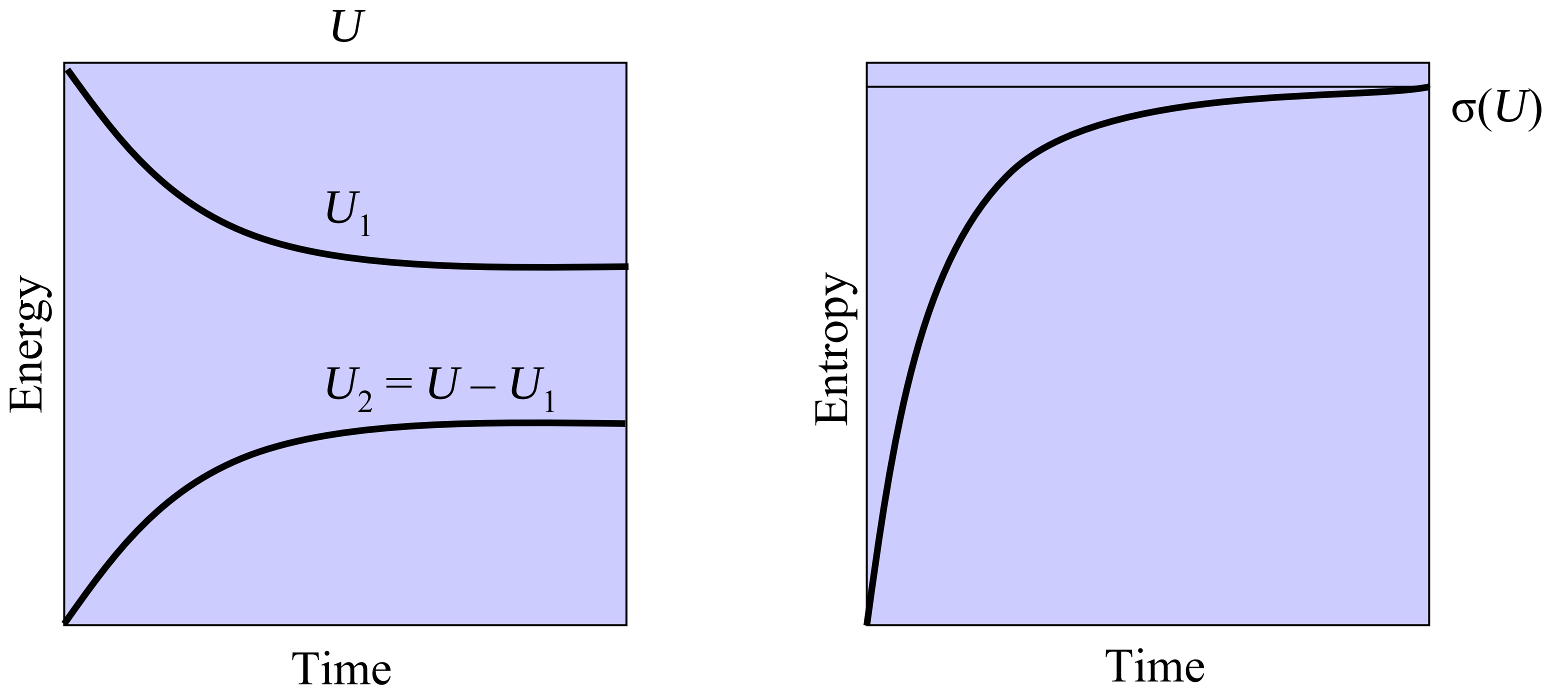
  - Boltzman constant: $k_B = 1.381 \times 10^{-23}$ joules/Kelvin

- Positive change in entropy when the two systems come into contact:

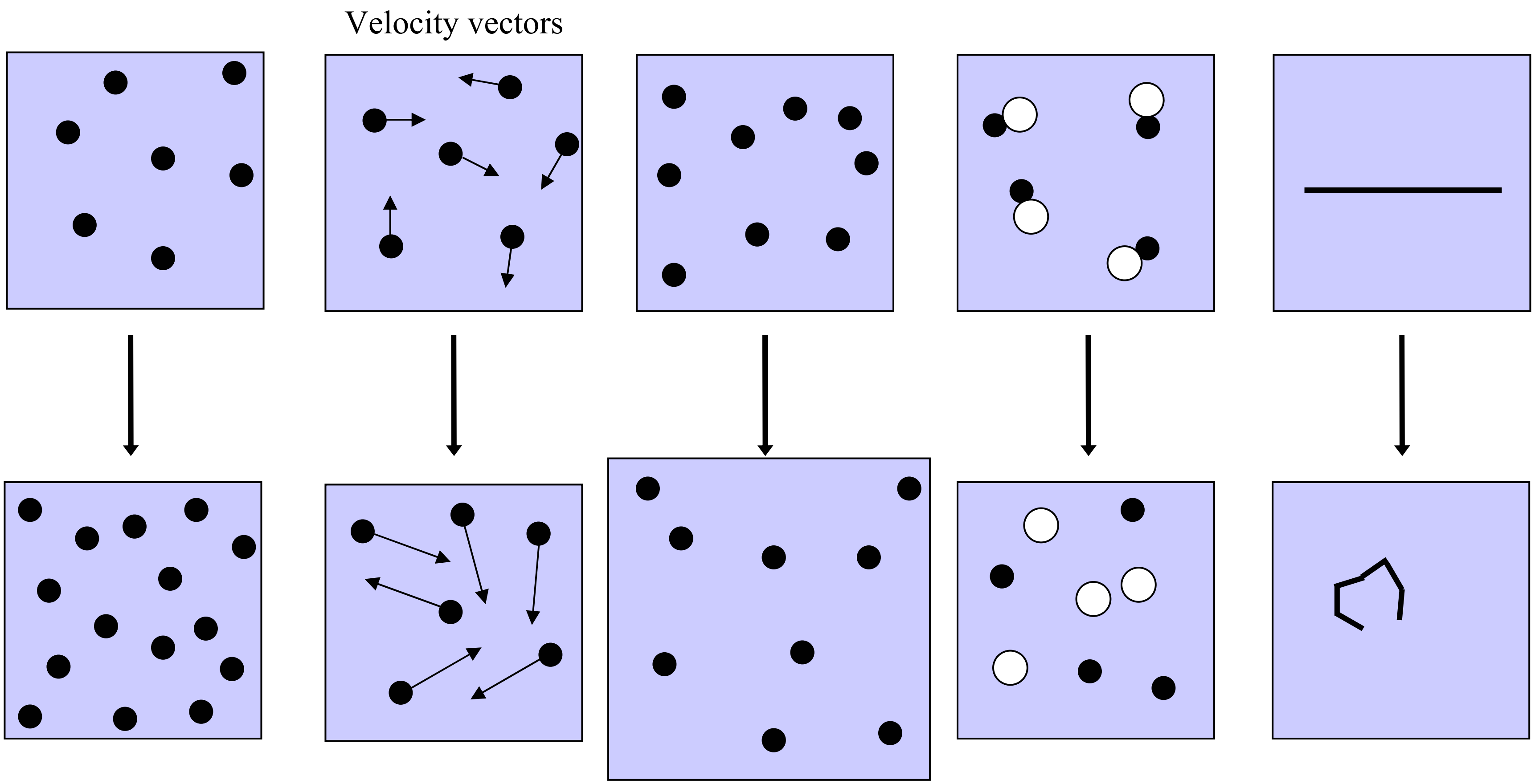
$$\boxed{\Delta\sigma = \left(\frac{\partial \sigma_1}{\partial U_1}\right)_{N_1}(-\Delta U) + \left(\frac{\partial \sigma_2}{\partial U_2}\right)_{N_2}(\Delta U) = \left(-\frac{1}{\tau_1} + \frac{1}{\tau_2}\right)\Delta U}$$

Entropy Flow Between Systems

- Energy flow: from the system with higher temperature (U_1) to system with lower temperature (U_2)
- The entropy increases until the system reaches the most probable configuration



Ways to Increase the Entropy of a System



Add particles

Add energy

Increase the volume

Decompose molecules

Let a linear polymer curl up

Laws of Thermodynamics

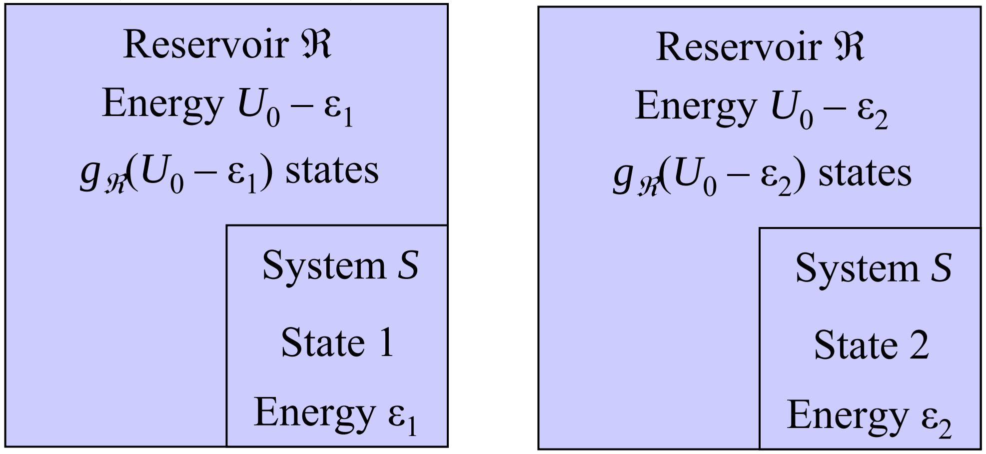
- Zeroth law: if two systems are in thermal equilibrium with a third system, they must be in thermal equilibrium with each other
- First law: heat is a form of energy (conservation of energy)
- Second law: if a closed system is in a configuration that is not the equilibrium configuration, the most probably consequence will be that the entropy of the system will increase (law of increase of entropy)

$$\boxed{\sigma_{final} \cong \log(g_1 g_2)_{\max} \geq \sigma_{initial} = \log(g_1 g_2)_0}$$

- Third law: the entropy of a system approaches a constant value as the temperature approaches zero

Boltzmann Factor

- Closed system: small system in thermal contact with a very large system (reservoir)



- When S is in a specific state the total number of accessible states = $g_{\Re}$
- A Taylor series expansion on (3) altered for the two states above gives:

$$\boxed{\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = \frac{\exp(-\varepsilon_1/\tau)}{\exp(-\varepsilon_2/\tau)}}$$

  - Boltzmann factor: term in the form of $\exp(-\varepsilon/\tau)$
  - Probability of finding the system in quantum state 1 versus 2

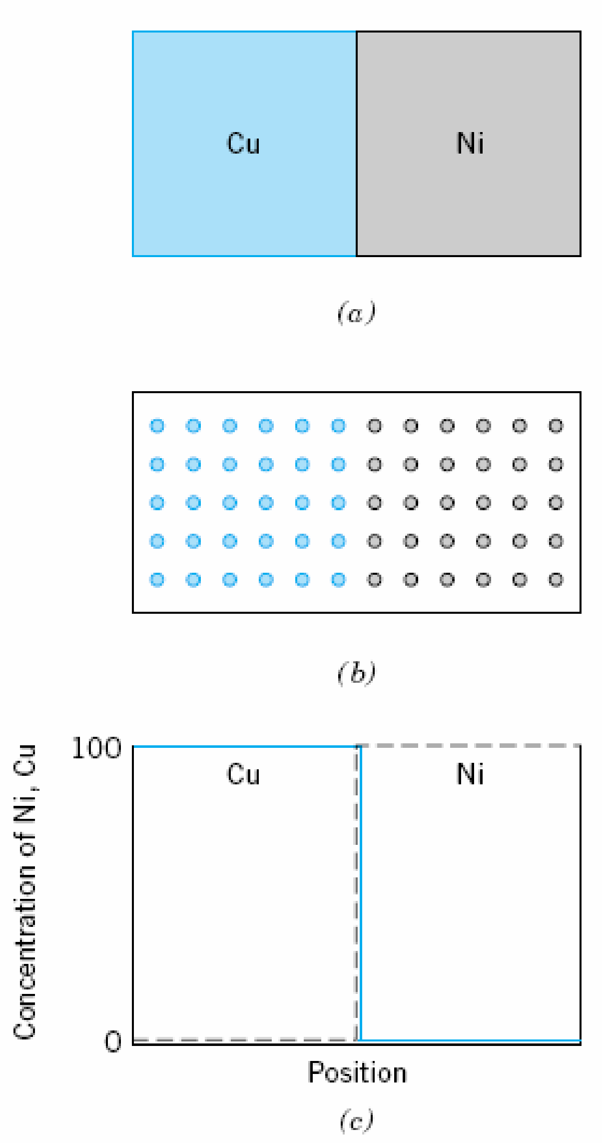
Partition Function and Helmholtz Free Energy

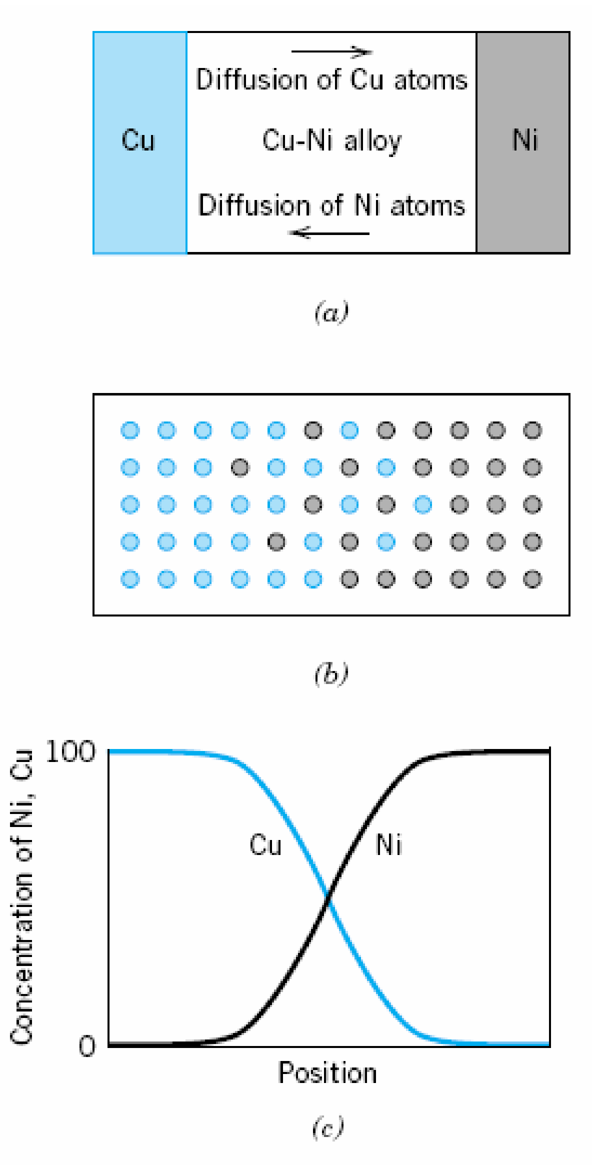
- Partition function: $$\boxed{Z(\tau)=\sum_s \exp(-\varepsilon_s/\tau)}$$
- Proportionality between the probability and the Boltzmann factor $$\boxed{P(\varepsilon_s)=\frac{\exp(-\varepsilon_s/\tau)}{Z}}$$
- The average energy for *S* given in (4) is *U* or <ε>
- Helmholtz free energy (5) shows the balance of a system with minimum energy and maximum entropy
- Relation of the Helmhotlz and the partition function: $$\boxed{Z=\exp\left(-\frac{F}{\tau}\right)}$$
- Relation of probability to the Helmholtz and the energy $$\boxed{P(\varepsilon_s)=\frac{\exp(-\varepsilon_s/\tau)}{\exp(-F/\tau)}=\exp\frac{F-\varepsilon_s}{\tau}}$$

Introduction to Diffusion

- The movement of atoms or molecules from an area of higher concentration to an area of lower concentration
- Time dependent process
- Break present bonds and form new bonds
- Surrounding atoms may need to be pushed out of the way
- Energy of vibration and movement comes from surrounding heat
- Self-diffusion – within same material; no macroscopic change
- Inter / impurity diffusion – between two different materials; change in concentration

Example of Diffusion





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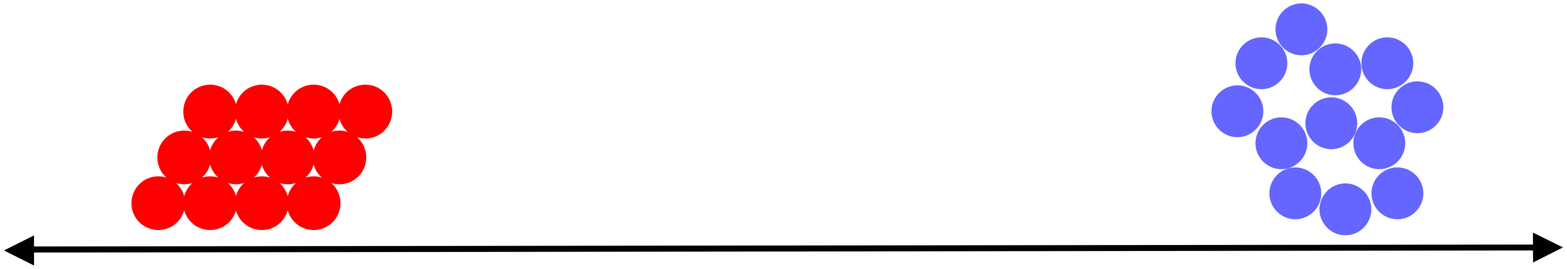
Range of Structure in the Solid State

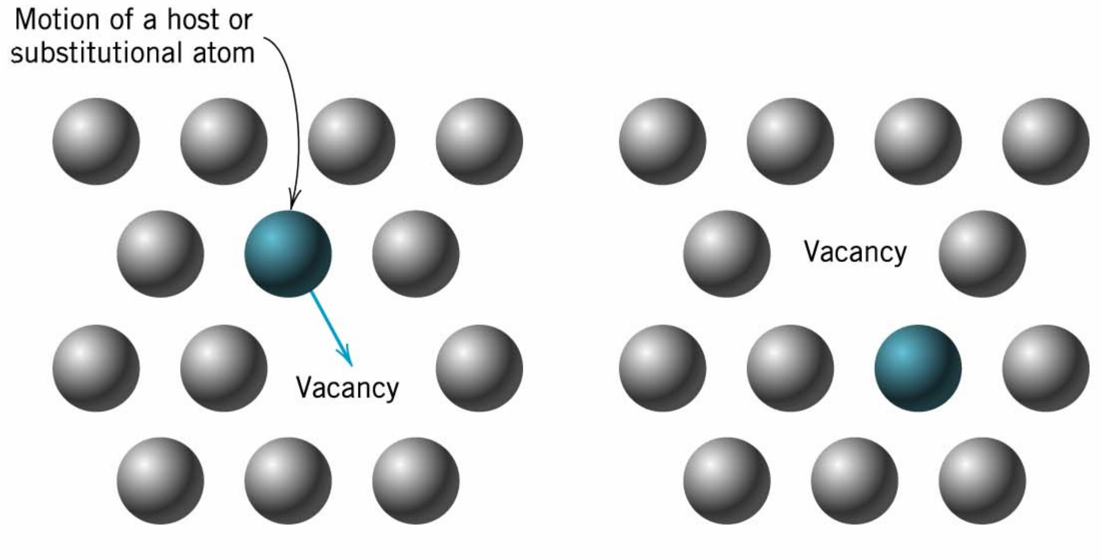


- Crystalline: symmetry, lattice structure
- Amorphous or non-crystalline: no symmetry

- Close-packed structure: densely packed
- Open structure: loosely packed
- Crystallinity does not dictate open or close-packed
- Materials can be crystalline, polycrystalline, or amorphous
- Defects: small as an atom (vacancy) → large enough to see with naked eye (cracks)
- Impurity: interstitial atom

Vacancy Diffusion

- Occurs more often with open structures
- Vacancy must be present in structure
- Atom replaces a vacancy from a similar sized atom
- See with self of interdiffusion



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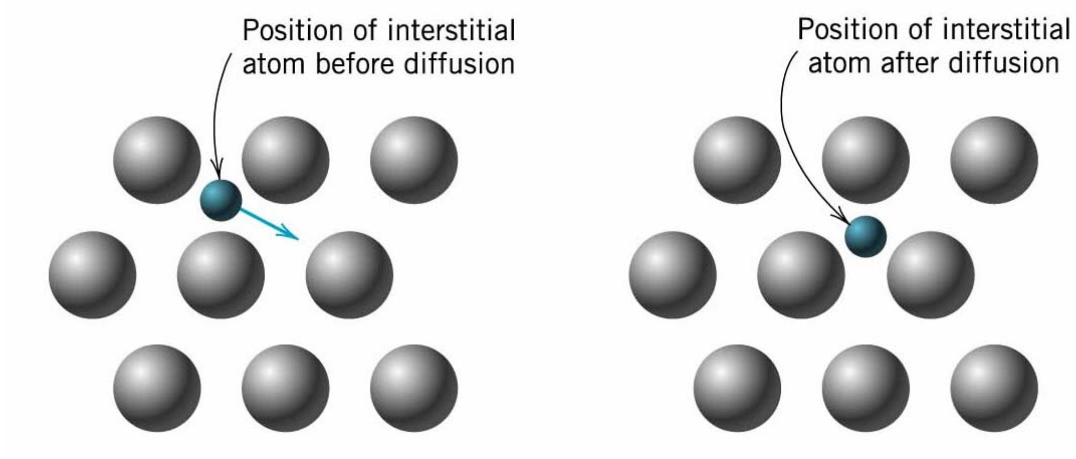
Interstitial Diffusion

- Occurs more often with open structures
- Atom moves between other atoms of the structure
- Atom tends to be smaller in diameter
- More probable to occur versus vacancy diffusion



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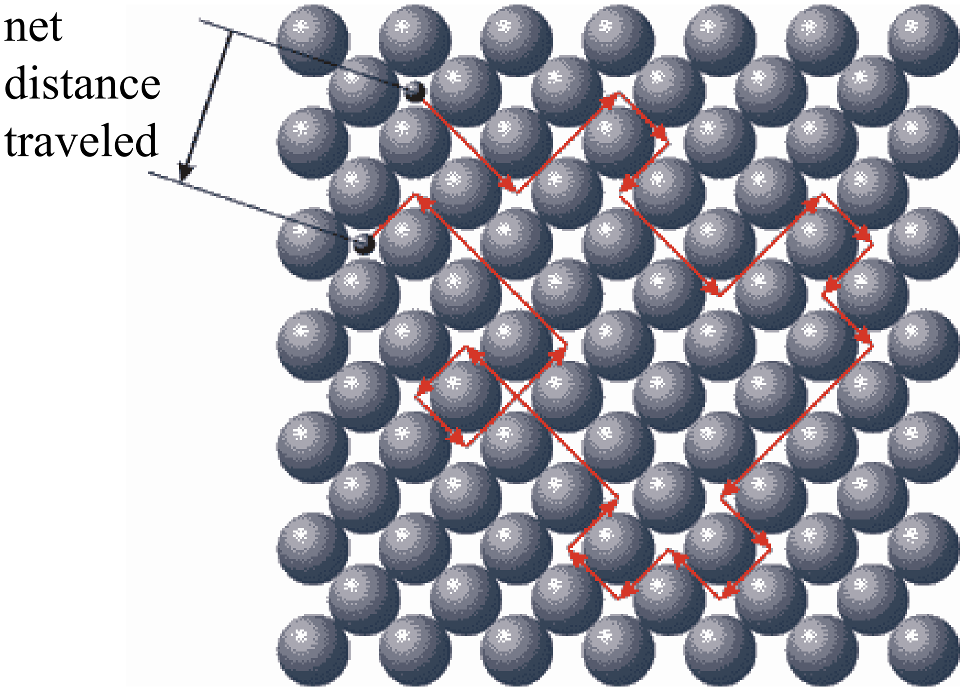
Path of Diffusion

- Diffusing atom follows a random path

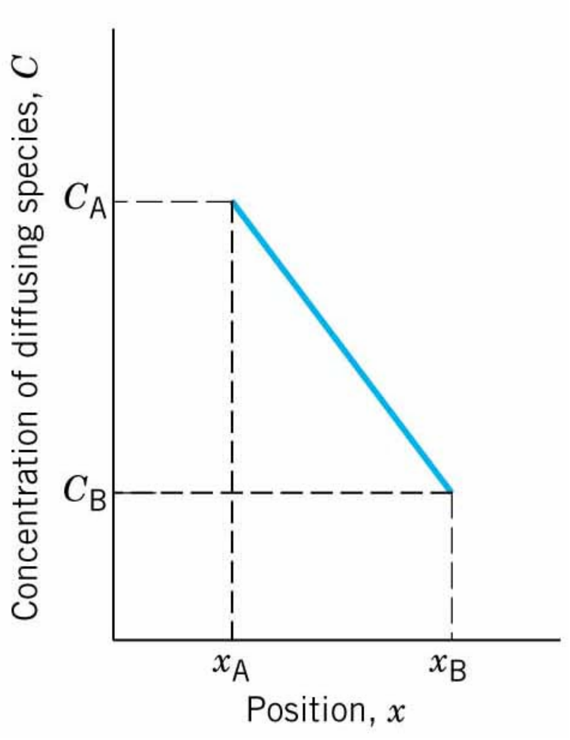


http://butler.cc.tut.fi/~materwww/minustako/minustako.html

Fick’s First Law of Diffusion

- Fickian or Type I diffusion
- Steady-state
- Diffusion flux (*F*) – rate of transfer per unit area of cross section
- Diffusion constant (*D*) –dependent on identity of solute and type of diffusion
- Concentration (*C*)
- Distance (*X*) – coordinate normal to cross section
- Concentration gradient – slope of the line

$$\boxed{F = -D\frac{\partial C}{\partial x}}$$



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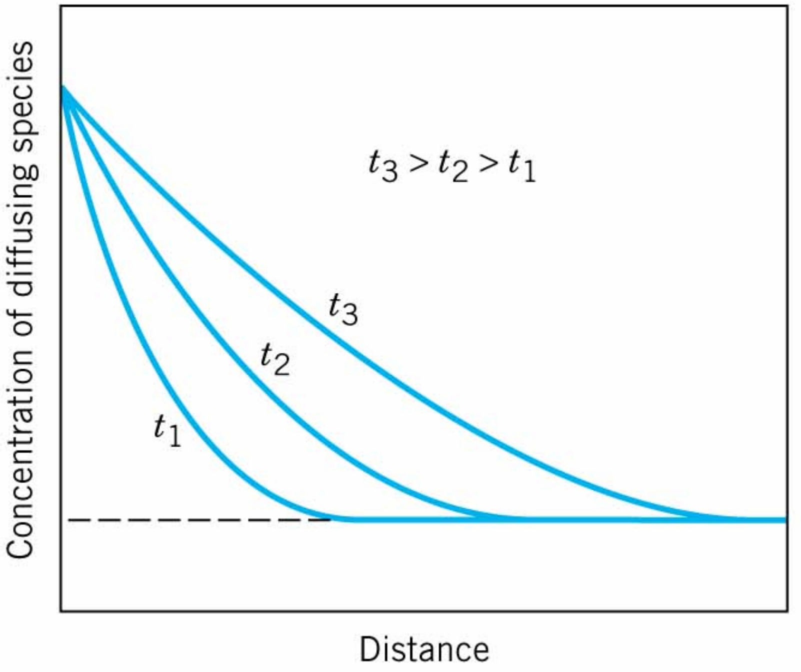
Fick’s Second Law of Diffusion

$$\boxed{\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}}$$

- Nonsteady-state
- Diffusion flux and concentration gradient vary with time
- Seen in practical situations
- Time (*t*)



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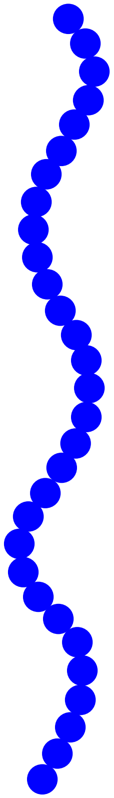
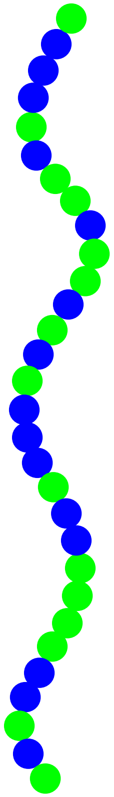
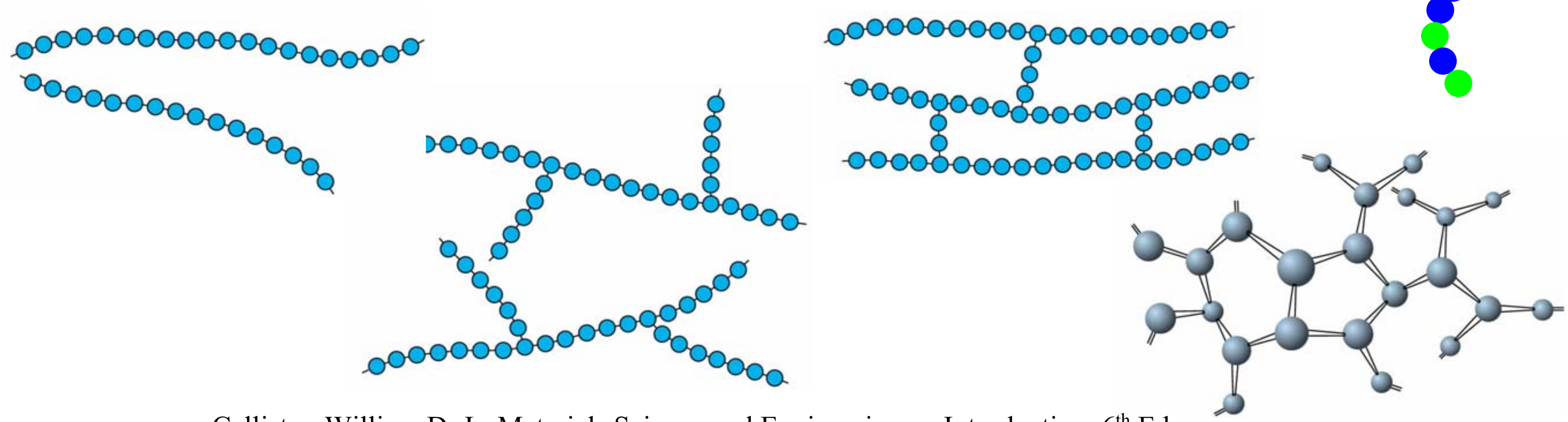
Introduction to Polymers



- Many monomers → polymer
  - Many possible functional groups: hydrocarbon, alcohol, ether, acid, aromatic, …
  - Monomers help determine properties and three-dimensional structure
- Linear, branched, crosslinked, network
- Homopolymer or copolymer
  - Examples: plastics, DNA, proteins





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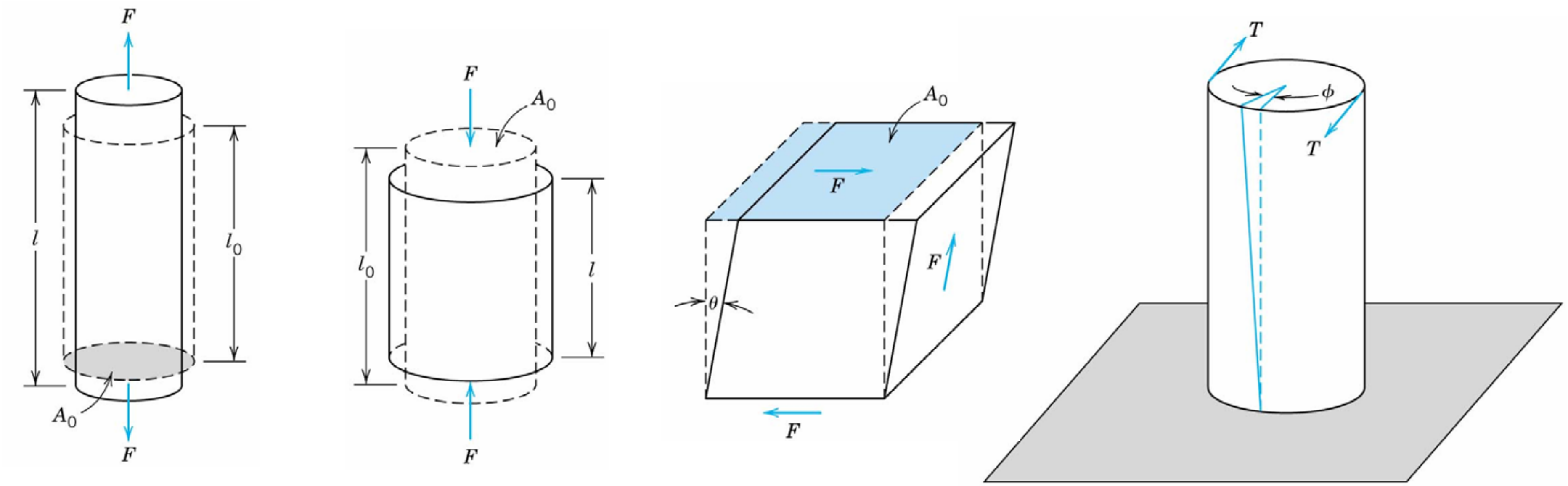
Mechanical Properties of Polymers

- Stress and strain tests
  - Tension
  - Compression
  - Shear and torsion
- Load is applied uniformly until material is deformed
- Adhesion



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Movement of a Polymer

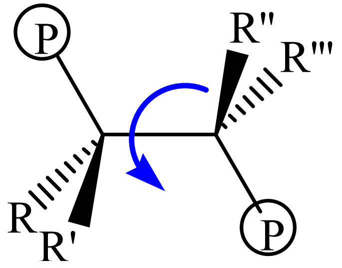
- Polymer movement in a solution is dominated by entropy

$$\boxed{\sigma = \log\left[\Re_N\left(\vec{r}\right)\right]}$$

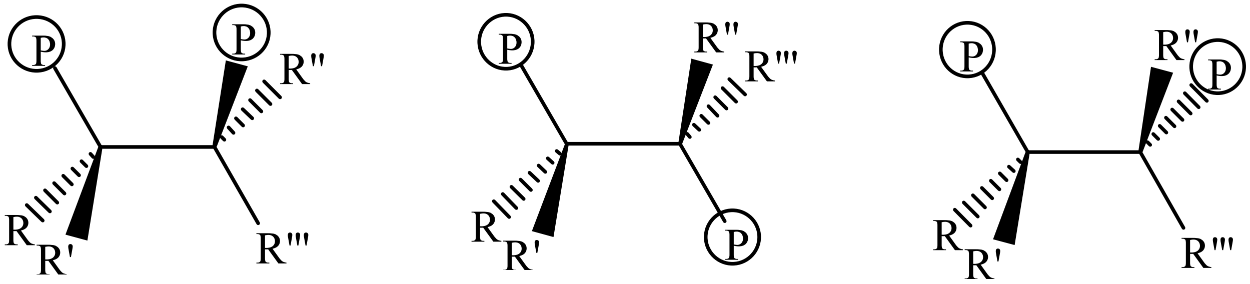
  - Number of conformations of the polymer ($\Re$)
- Without interactions movement is a random walk
- With interactions movement is a self-avoiding walk (saw)
- Interactions are either within a polymer chain or between two or more chains
- In different environments the conformation is affected
  - In different solutions, in blends, or if monomers are charged, etc.

Polymer Conformation

- Flexibility of polymers comes from rotation of single bonds in the backbone
  - Typically C-C bonds



- Steric repulsions cause the rotation to be hindered, with three staggered conformations energetically favored
  - Gauche (G), trans (T) and gauche' (G')

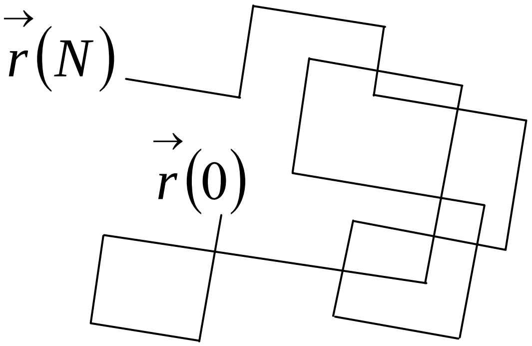


  - Calculation of the average shape of a flexible polymer chain, including all bonding details, is demanding
- The oversimplified model can be modified to describe the shape of real polymer molecules in statistical terms

Random Walk

- Freely jointed polymer moving by random walk in solution
  - Polymer solution concentration in a good solvent must be small enough so the polymer does not interact with itself or another polymer
- Multiple steps for polymer to get to one conformation
- Vector connecting one end of the polymer to the other

$$\boxed{\vec{r} = \vec{r}(N) - \vec{r}(0)}$$

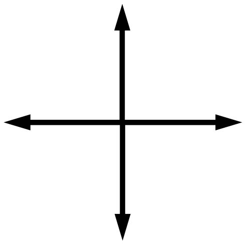


  - Vector ***r*** is also the sum of N jump vectors $\boldsymbol{l_i}$

$$\boxed{\vec{r} = \sum_{i=1}^{N} \vec{l}_i}$$

Random Walk

- For each jump, the polymer has an equal probability of moving in any direction
  - The vectors cancel when averaged



$$\boxed{< \vec{r} >= 0}$$

- The average square end-to-end distance is directly proportional to N

$$\boxed{< \vec{r} \cdot \vec{r} >=< \vec{r}^{\,2} >}$$

$$\boxed{< \vec{r}^{\,2} >= \left\langle \sum_{i=1}^{N} \vec{l}_i \cdot \sum_{k=1}^{N} \vec{l}_k \right\rangle = \sum_{1}^{N} \left\langle \vec{l}_i \cdot \vec{l}_k \right\rangle = \sum_{1}^{N} \left\langle \vec{l}_i^{\,2} \right\rangle}$$

  - All of the cross products cancel

$$\boxed{< \vec{r}^{\,2} >= l^2 N + 0 = l^2 N}$$

  - *l* is the persistence length, depends on rigidity of polymer

Random Walk

- Probability of the vector **r**
  - A gaussian shape is seen when N>>1

$$\boxed{P\left(\vec{r}\right) = \frac{\Re_N\left(\vec{r}\right)}{\sum_r \Re_N\left(\vec{r}\right)}}$$

- Probability of the vector **r** in three directions

$$\boxed{P\left(\vec{r}\right) = P(x, y, z)}$$

$$\boxed{P(x, y, z) \propto \exp\left(\frac{-x^2}{2<x^2>}\right) \cdot \exp\left(\frac{-y^2}{2<y^2>}\right) \cdot \exp\left(\frac{-z^2}{2<z^2>}\right)}$$

$$\boxed{P\left(\vec{r}\right) \propto \exp\left(\frac{-3r^2}{2l^2N}\right)}$$

- Relation of random walk to the Fick's second law of diffusion:

$$\boxed{\frac{\partial P}{\partial t} = D\nabla^2 P}$$

  - $t = N \; ; \; D = \frac{l^2}{6}$

Free Energy of Random Walk

- From statistical mechanics:

$$\boxed{F \equiv U - \tau\sigma}$$

- Therefore:

$$\boxed{\frac{F}{k_B T} = \frac{U}{k_B T} - \sigma}$$

- Negligible enthalpy: no interactions within or between polymer molecules
- Since:

$$\boxed{\sigma = \frac{3r^2}{2l^2 N}}$$

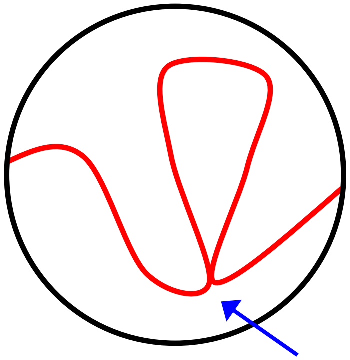
- Therefore:

$$\boxed{P\left(\vec{r}\right) \propto \exp\left(\frac{-F\left(\vec{r}\right)}{k_B T}\right)}$$

Self-avoiding Walks

- Concentration (c) of polymer solution is great enough there are interactions either within a polymer chain or between chains

$$\boxed{c = \frac{N}{\frac{4}{3}\pi \cdot r^3}}$$



  - Interaction causes a penalty in energy (υ)

- Have interactions: must consider enthalpy as well as entropy

$$\boxed{\frac{U}{k_B T} = \upsilon \int_0^r c^2(r) d^3 r = \upsilon \frac{N^2}{\frac{4}{3}\pi \cdot r^3}}$$

Free Energy of Self-avoiding Walk

- When υ > 0: good solvent or **SAW**
- The solvent wants to be homogeneously mixed causing swelling of the chains.
- Minimize F with respect to R to get the Flory exponent in good solvent, which is close to the numerical value
- F^{en}: from entropy

$$\boxed{F = F^{en} + F^{ex}}$$

- F^{ex}: from excluded volume
- From random walk:

$$\boxed{F^{en} = \frac{3r^2}{2l^2 N}}$$

- Using the Flory argument:

$$\boxed{F^{ex} \approx \upsilon \frac{\left(N/r^3\right)^2}{2} r^3 \approx \frac{\upsilon}{2} \frac{(N)^2}{r^3}}$$

Values of r

- When υ > 0 the chain is in a good solvent in SAW

$$\boxed{r \approx \upsilon^{1/5} N^{3/5}}$$

- When υ < 0 the chain is in a bad solvent: the structure collapses

$$\boxed{r \approx N^{1/3}}$$

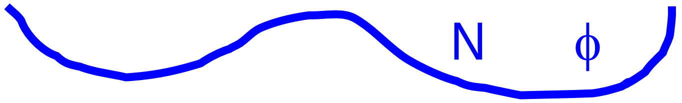
  - This situation has free energy with three terms

- When υ = 0 the chain is a random walk, because there are no interactions

$$\boxed{r \approx N^{1/2}}$$

Polymer Solution: what is v in solutions?

Flory-Huggins interaction parameter χ



$$\chi = \frac{z}{k_B T}\left(E_{AB} - \frac{E_{AA} + E_{BB}}{2}\right)$$

$\chi = 0$	Ideal No interaction
$\chi > 0$	Repulsive, immiscible Van der Waals

Free energy of mixing

$$\frac{F}{k_B T} = \frac{\phi}{N}\ln(\phi\ ) + (1-\phi)\ln(1-\phi) + \chi\phi\ (1-\phi)$$

Expand when solvent concentration is small

$$\frac{F}{k_B T} = \frac{\phi}{N}\ln(\phi\ ) + \frac{1}{2}(1-2\chi)\phi\ \phi$$

Degree of incompatibility: v=1- 2χ

χ → energetic

N → entropic

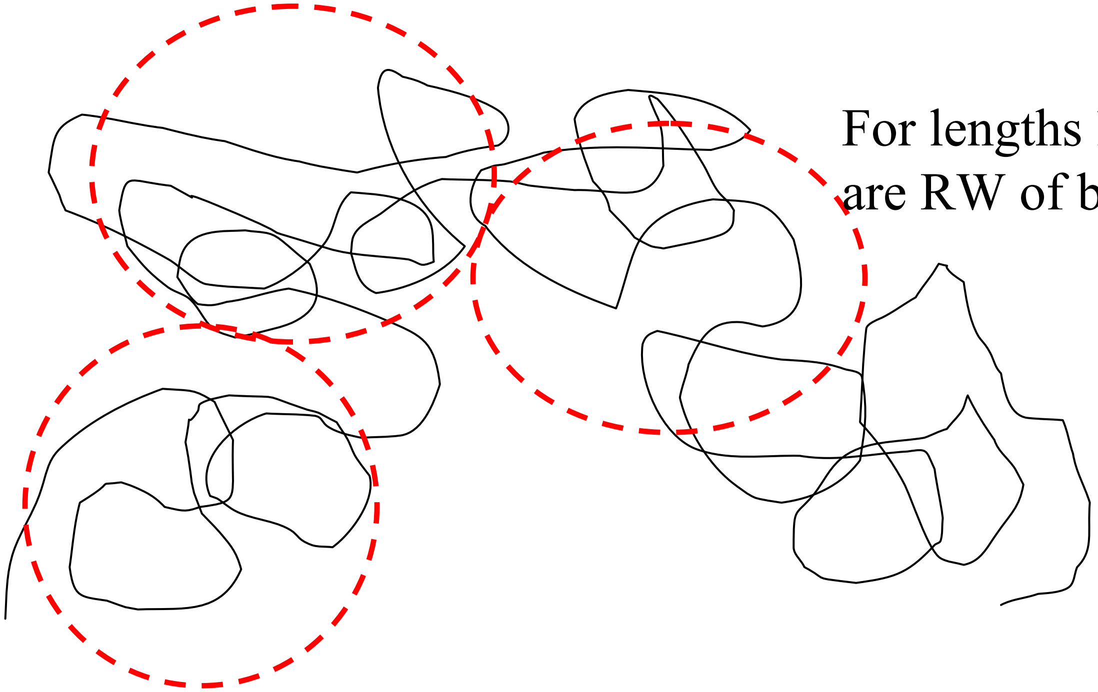
volume fraction ϕ

Semidilute Solutions

semi-dilute: overlapping of blobs:

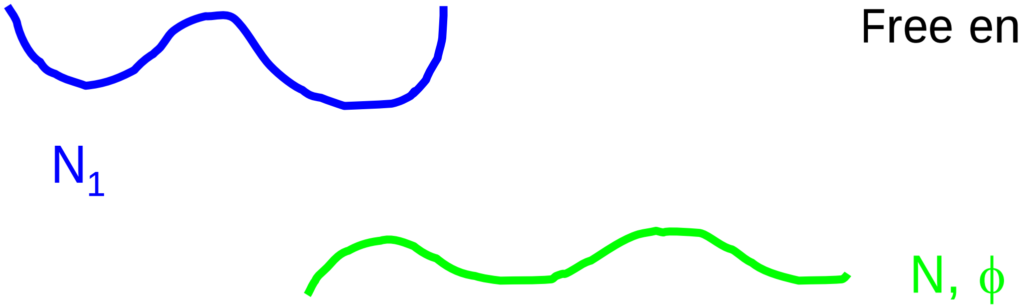
Inside the blobs chains are SAW
or swollen

For lengths larger than blobs chains
are RW of blobs



Polymer melt state: Mean Field

Free energy of mixing



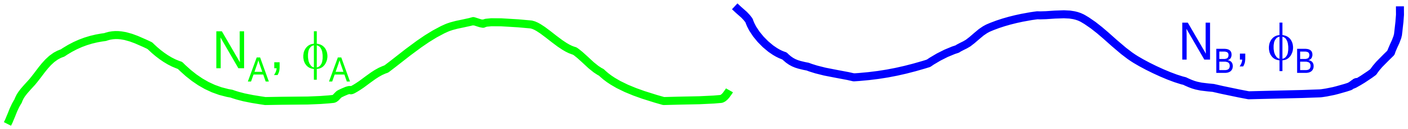
$$\frac{F}{k_B T} = \frac{\phi}{N}\ln(\phi\ ) + \frac{1-\phi}{N_1}\ln(1-\phi\ )$$

Expand when solvent concentration is small (virial expansion)

$$\frac{F}{k_B T} = \frac{\phi}{N}\ln(\phi\ ) + \frac{1}{N_1}\phi\ \phi$$

Degree of incompatibility: v is reduced by N then ideal chains if $N_1=N$
Expansion of F(R) for $R \sim R_o\ (1 + 4z/3 + \ldots)$ $z \sim v\ N^{1/2}/b^3$
(from Flory at $R=R_o$) then if $v \sim 1/N_1$ then $z \sim N^{1/2}/N_1$

Polymer blend phase diagram



Flory-Huggins interaction parameter χ

$$\chi = \frac{z}{k_B T}\left(E_{AB} - \frac{E_{AA} + E_{BB}}{2}\right)$$

$\chi = 0$	Ideal mixing No interaction
$\chi < 0$	Attractive, miscible Hydrogen bonding
$\chi > 0$	Repulsive, immiscible Van der Waals

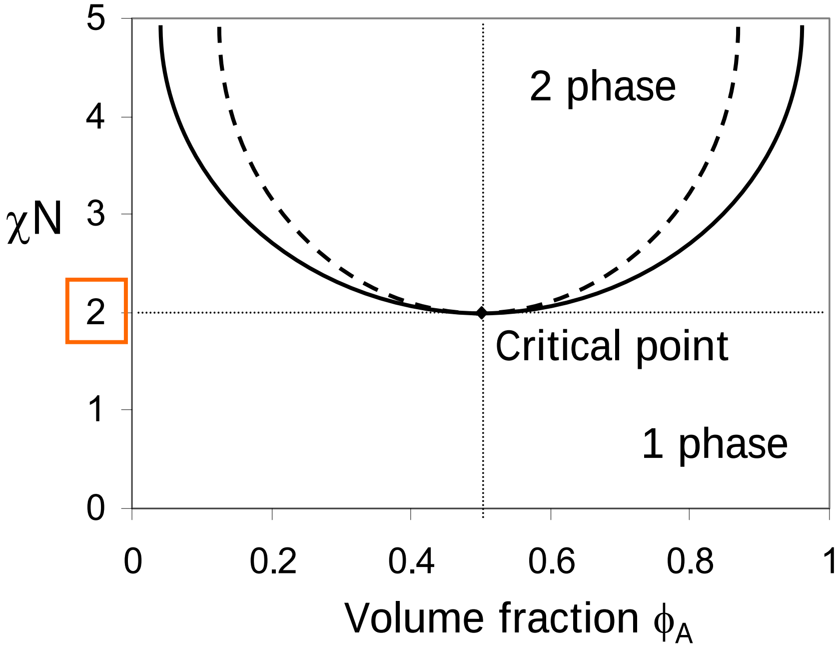
Degree of incompatibility: χN

χ → energetic

N → entropic

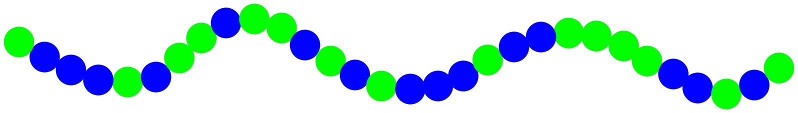
Free energy of mixing

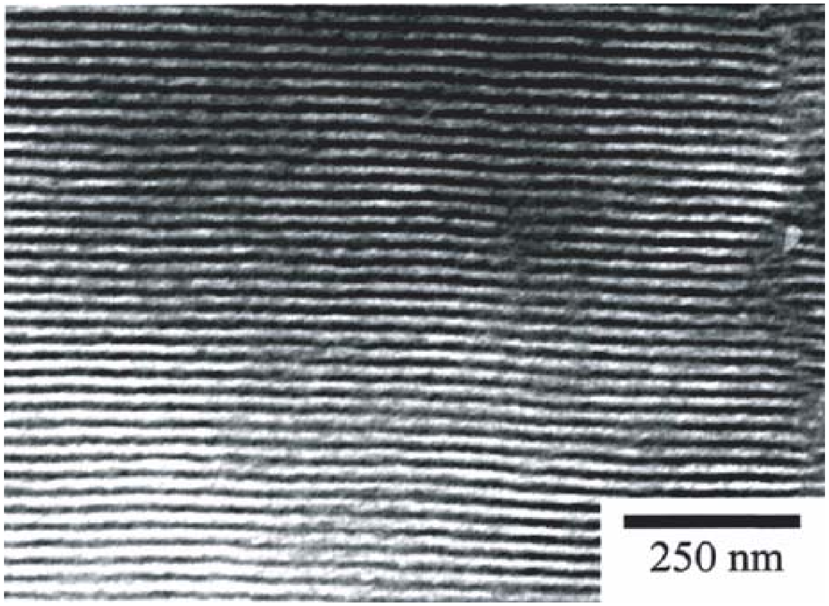
$$\frac{F}{k_B T} = \frac{\phi_A}{N_A}\ln(\phi_A) + \frac{\phi_B}{N_B}\ln(\phi_B) + \chi\phi_A\phi_B$$



Copolymers

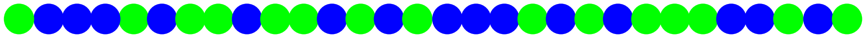
- Covalently linked repeat units with different chemistries into the same polymer chain
- Combining existing monomers is more financially feasible than inventing new monomers
- The copolymer retains properties of both constituent repeat groups





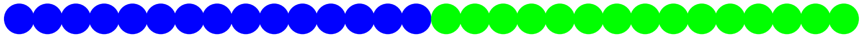
Copolymer Sequence Distributions

Random copolymer



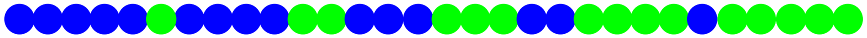
- ABS: acrylonitrile, butadiene, styrene

Block copolymer



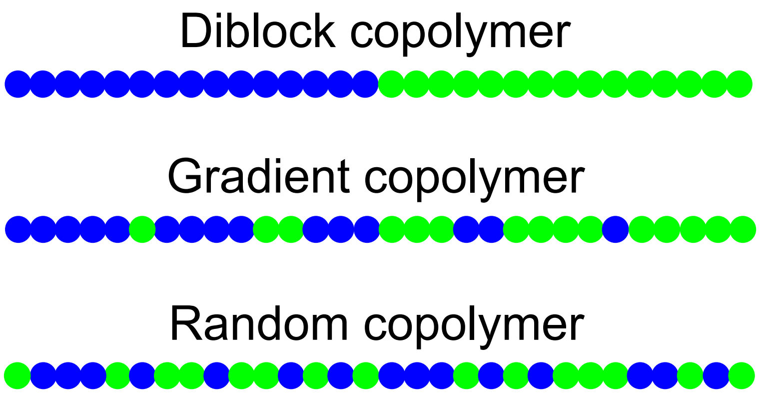
- SBS: styrene-butadiene-styrene

Gradient copolymer



- Controlled polymerization varies composition along the chain

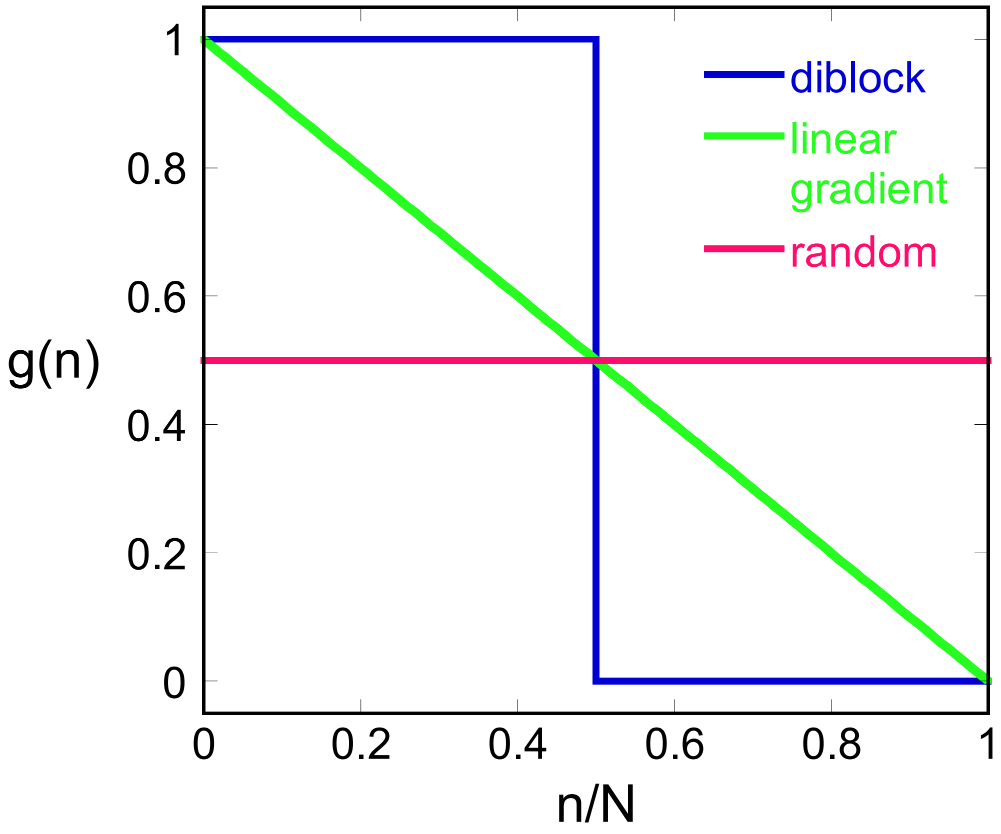
Copolymer sequence distributions



Diblock copolymer

Gradient copolymer

Random copolymer



g(n) = the average composition of repeat unit A
along the backbone of the chain

Theory

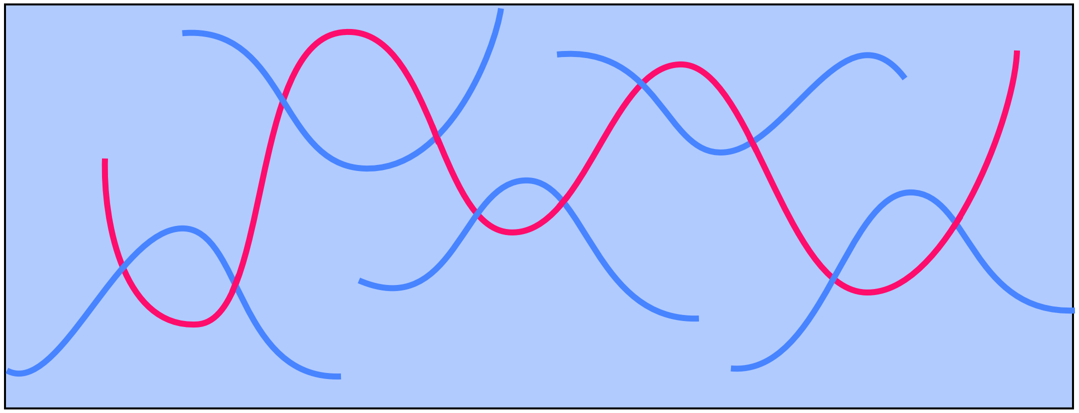
There are many possible sequence distributions and monomers to choose from when designing new polymeric materials

↓

Theory can be used to explore the parameter space and guide the design process

Polymers have a high coordination number

Mean field theory is accurate when fluctuations are not important



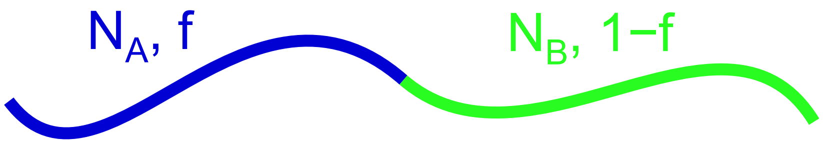
<u>Use theory to explore different copolymer sequence distributions</u>

Ordering in the melt

Interfacial behavior

Ordering in blends

Microphase separation: block copolymers



Two incompatible segments are covalently linked

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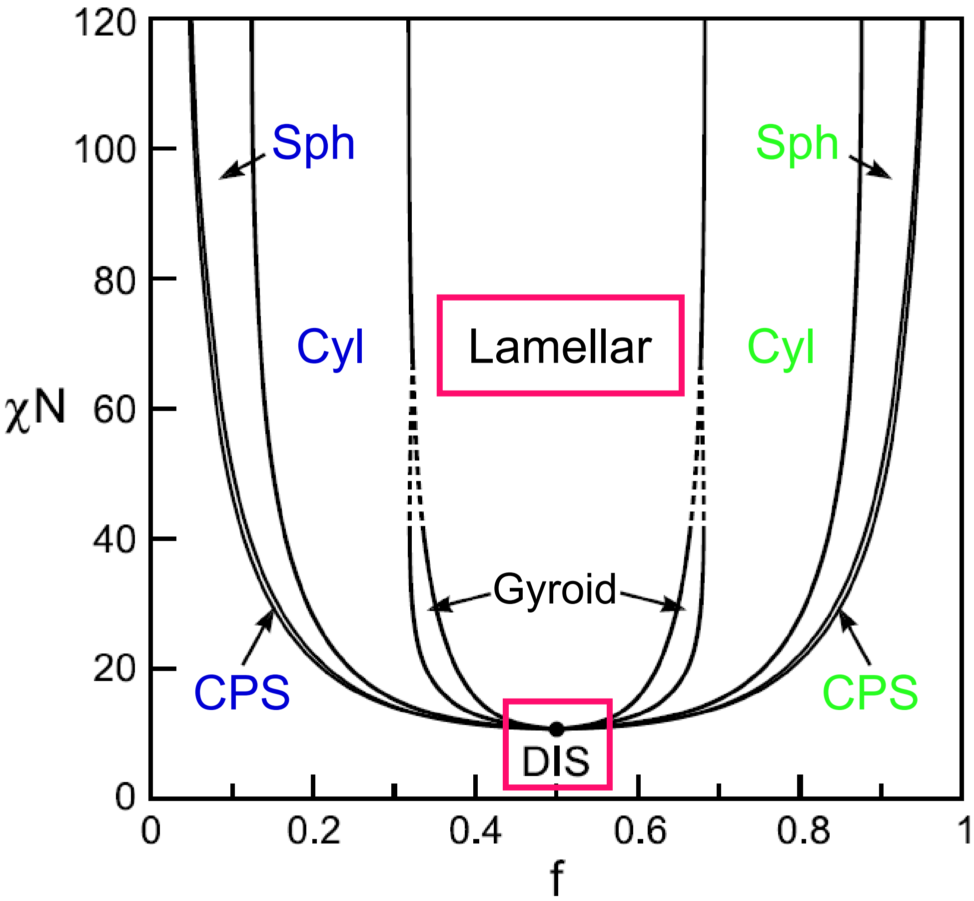
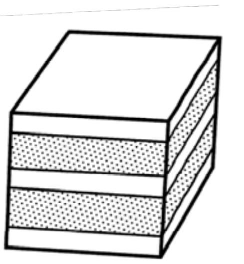
Phase separation occurs microscopically above $(\chi N)_c$

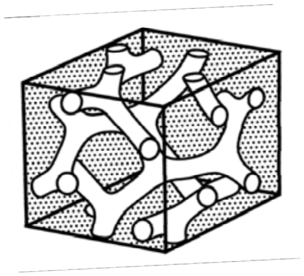
Geometry determined by f

Size determined by balance between repulsion and stretching

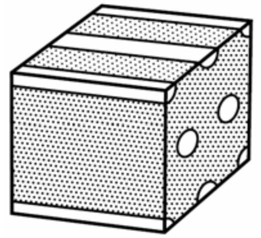




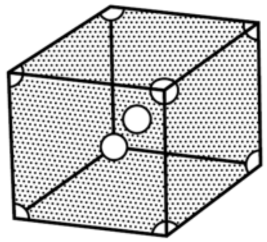
Lamellar



Gyroid



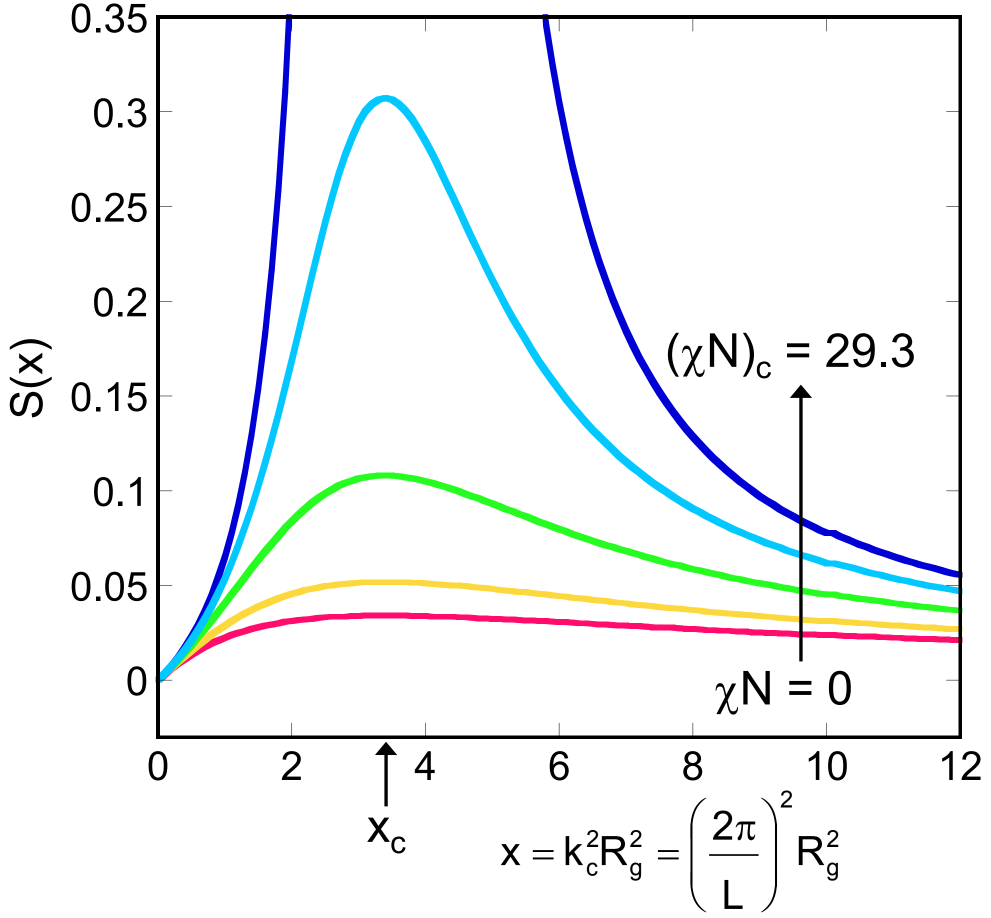
Hexagonal cylinders



BCC spheres

Scattering function

The scattering function measures composition
fluctuations in the disordered phase



Scattering increases with χN

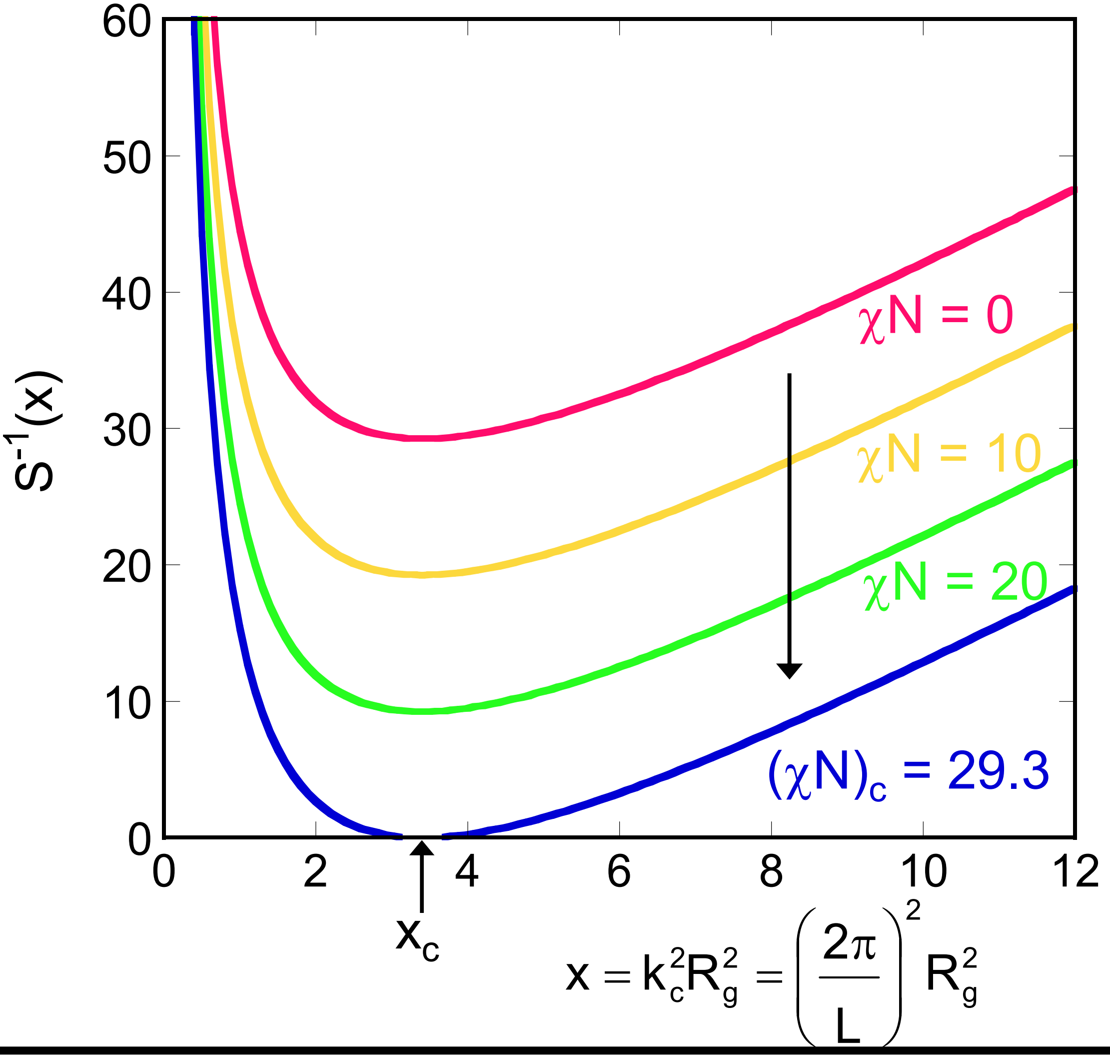
At $(\chi N)_c$: transition to ordered phase
$S(x) \rightarrow \infty$

S(x) derived analytically
using the random phase
approximation (RPA)

Scattering peak forms at L_c from
disordered periodic fluctuations

Inverse scattering function

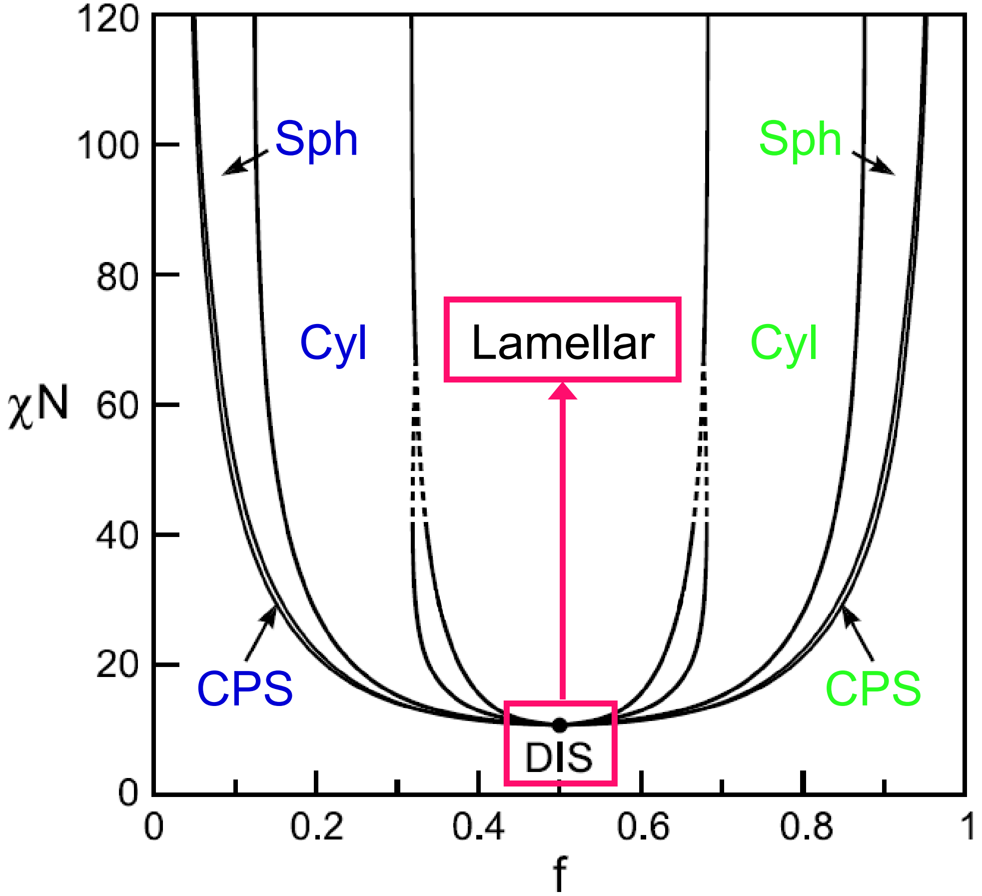
$S^{-1}(x) = 0$ at $(\chi N)_c$, L_c



Copolymer	$(\chi N)_c$
λ=0 linear	10.5
λ=0.5 linear	13.9
λ=0.5 tanh	17.9
λ=1 linear	29.3

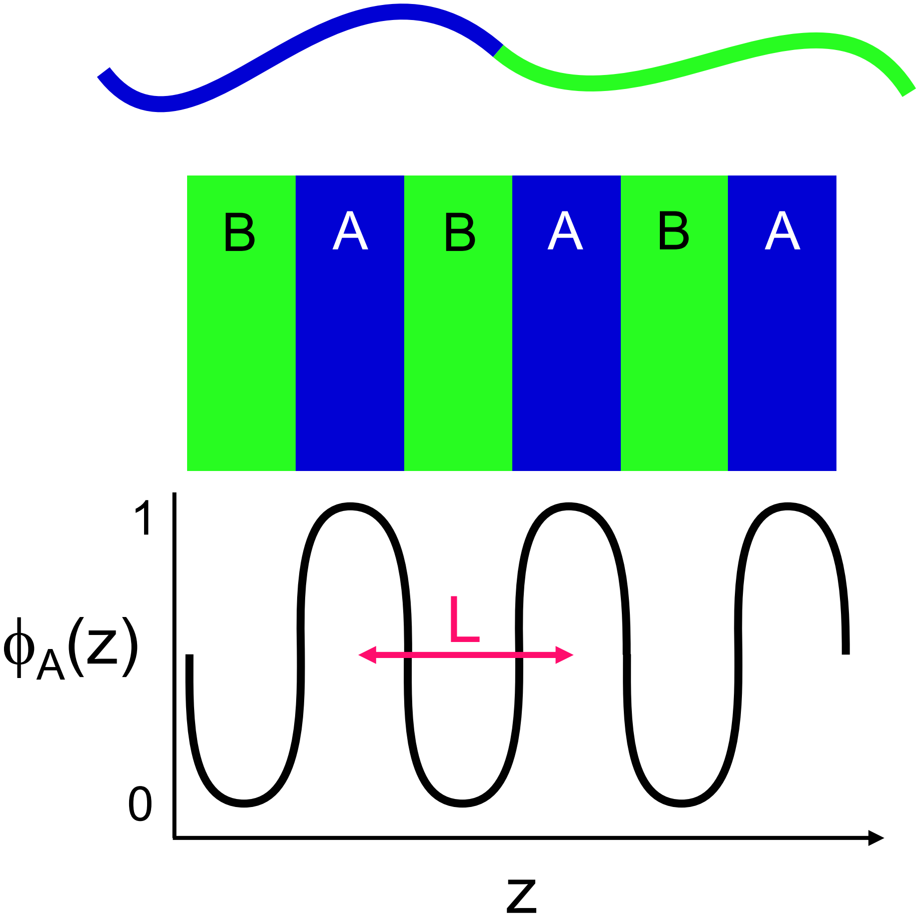
Higher order-disorder transition may be useful in applications where phase separation needs to be suppressed

Lamellar phase separated region

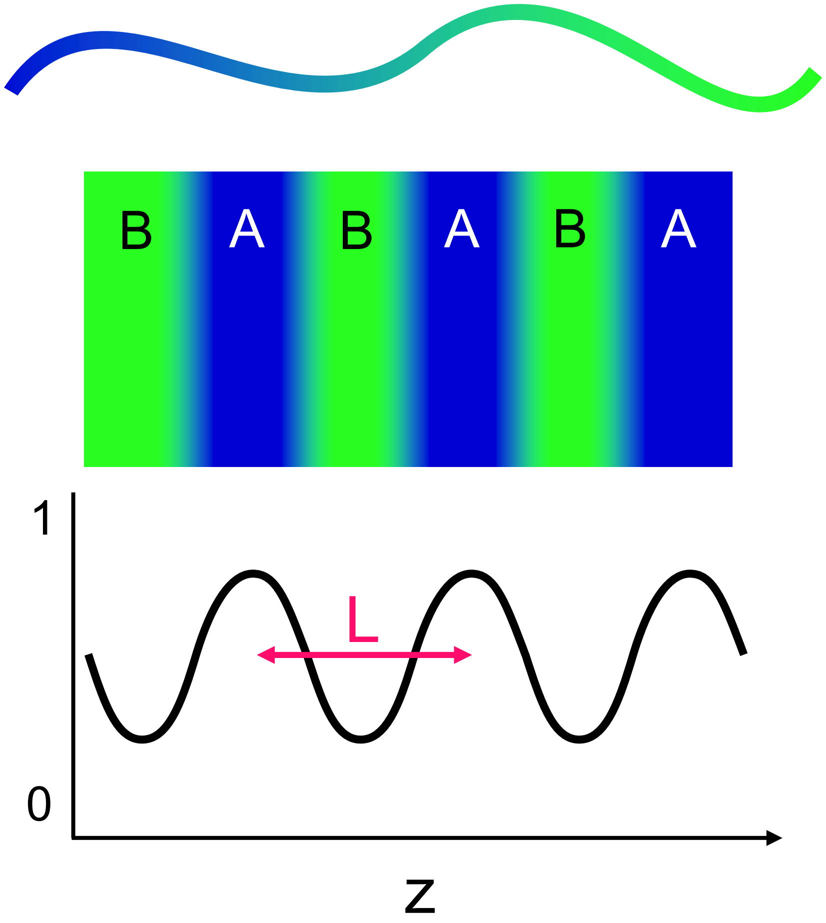


Lamellar microphases

Block copolymer



Gradient copolymer

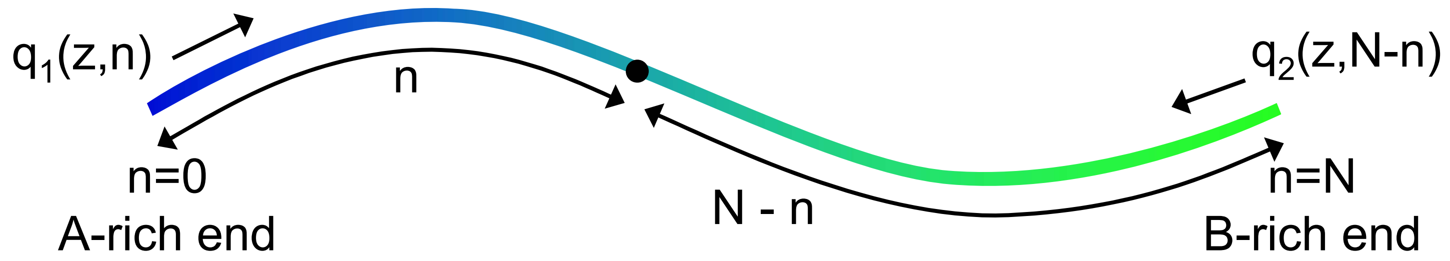


L = wavelength of the composition fluctuation
= repeat distance of the lamellar layers

Self-consistent mean field theory

Polymers in the melt obey a modified diffusion equation

$$\frac{dq(z,n)}{dn} = \frac{a^2}{6}\frac{d^2q(z,n)}{dz^2} - w(z,n)q(z,n)$$



$q_1(z,n)$

n

n=0

A-rich end

$q_2(z,N\text{-}n)$

N - n

n=N

B-rich end

Probability distribution functions

$$\boxed{\phi_A(z)} = \frac{1}{N}\int_1^N g(n)\,q_1(z,n)\,q_2(z,N-n)\,dn$$

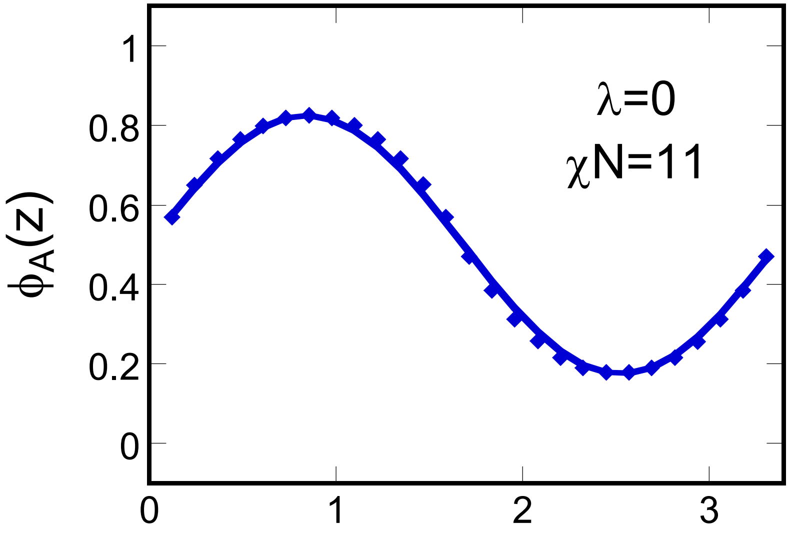
Solve equations self-consistently
for volume fraction profiles

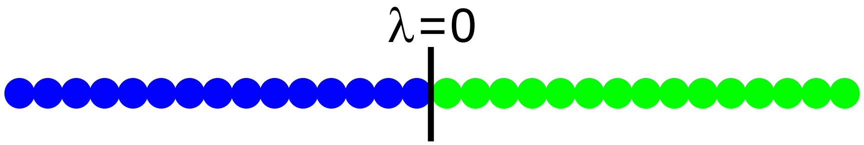
Mean composition field

$$w(z,n) = \chi\left(g(n) - \phi_a(z)\right)^2 - \Delta w(z)$$

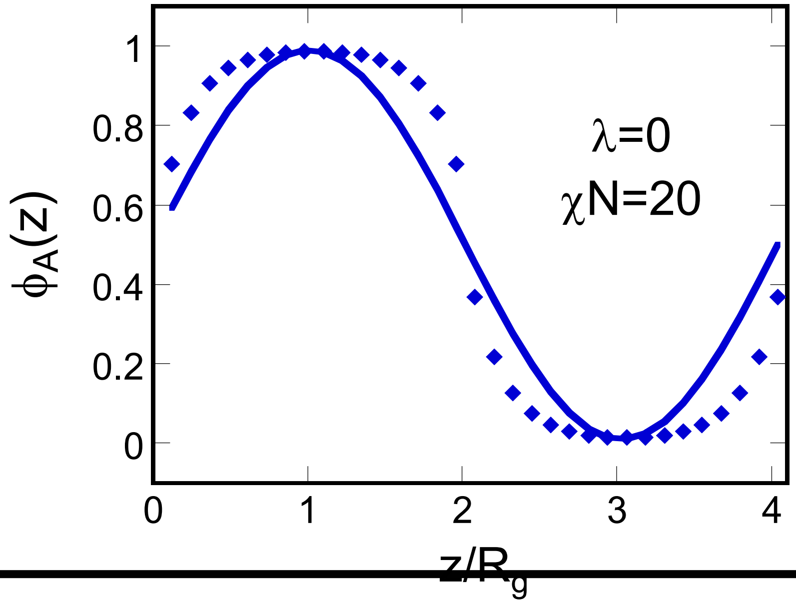
$$\Delta w(z) = \zeta\left(1 - \phi_A - \phi_B\right)$$

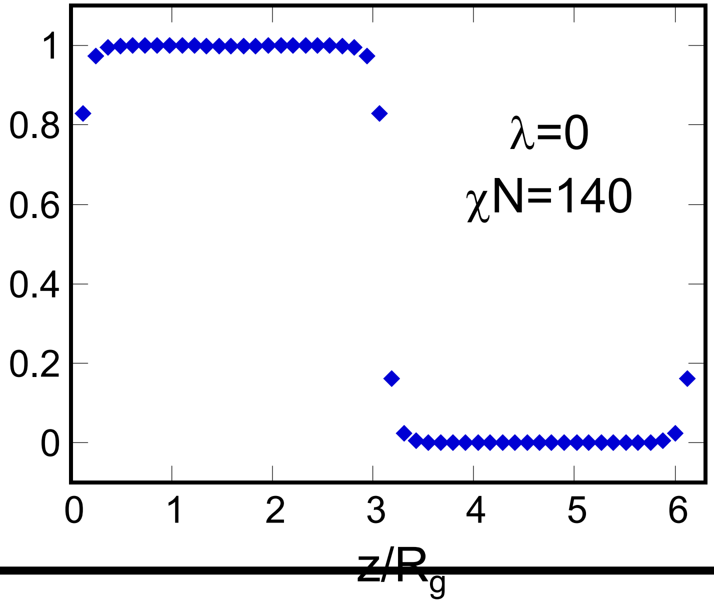
Volume fraction profiles





- Weakly segregated layers just above $(\chi N)_c = 10.5$
- Layers quickly become strongly segregated

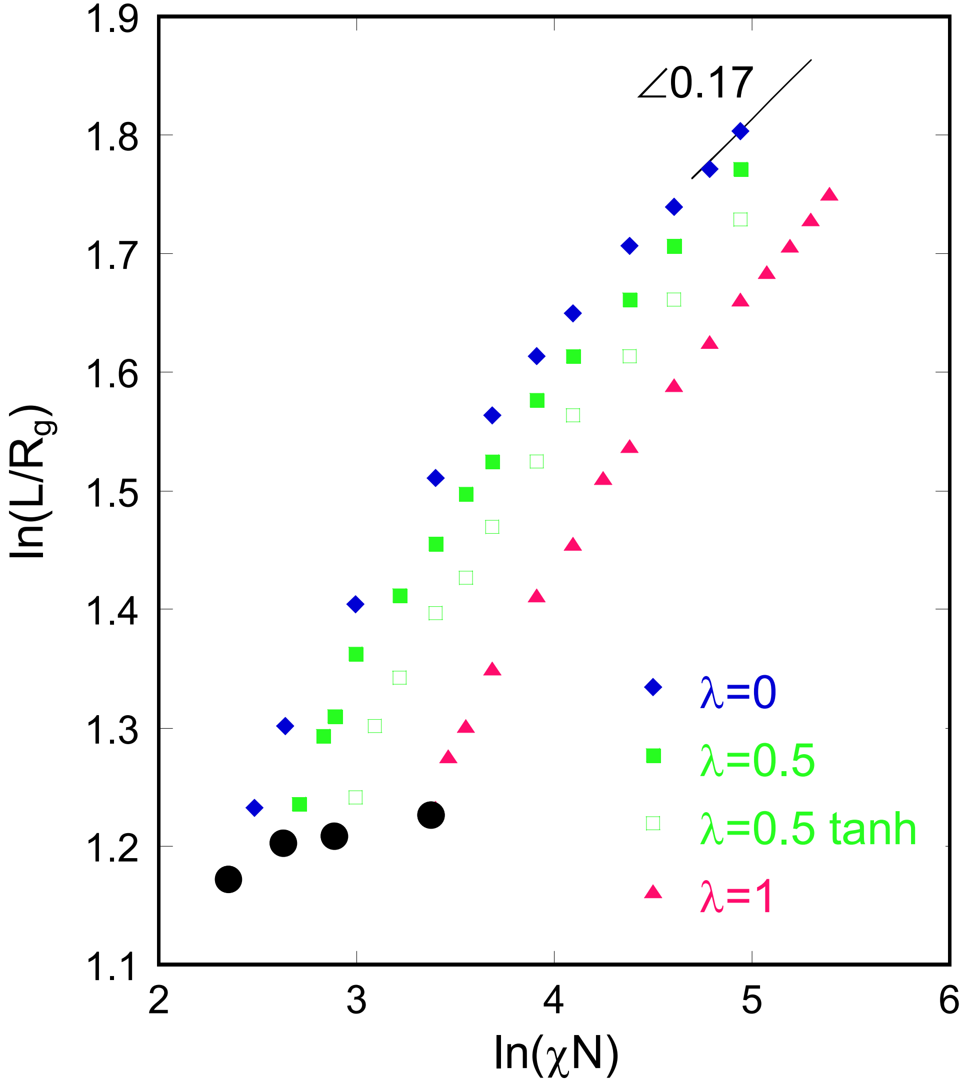




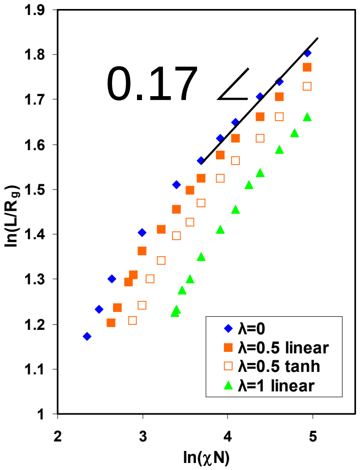
Equilibrium repeat length

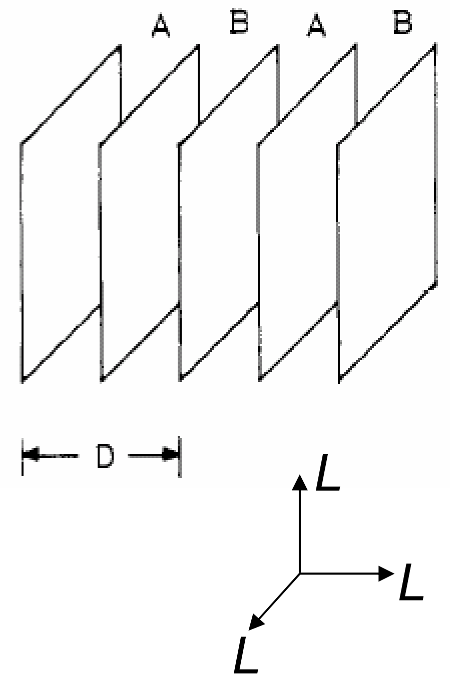
- L/R_g found for each χN from minimum in free energy
- For a given χN, L/R_g decreases with increasing gradient
- For block copolymers, the repeat length scales as:

$$\frac{L}{R_g} \propto (\chi N)^{1/6}$$



Strong Segregation Power Law





$$F = F_{\text{entropy}} + F_{\text{interface}}$$

$$F = n_p \frac{D^2}{R_0^2} + n_{\text{int}} A\gamma$$

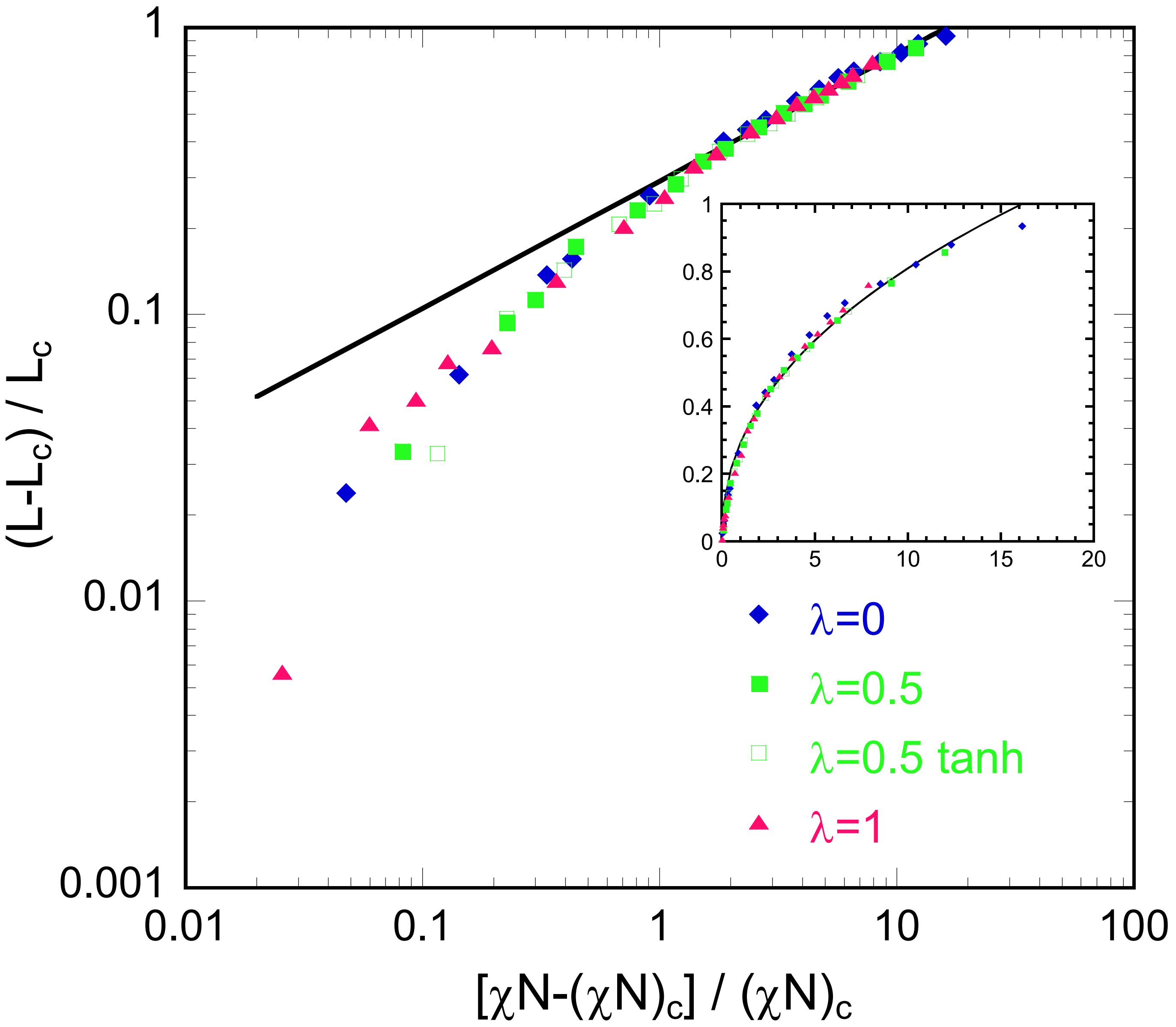
$$R_0^2 \sim N \qquad n_{\text{int}} = \frac{L}{D} \qquad A = L^2 \qquad \rho_0 = \frac{n_p N}{V} = \frac{n_p N}{L^3}$$

$$\frac{F}{n_p} = \frac{D^2}{N} + \frac{L}{D}\frac{N}{\rho_0 L^3} L^2 \gamma = \frac{D^2}{N} + \frac{N\gamma}{D\rho_0}$$

Minimize $\longrightarrow D \sim \gamma^{1/3} N^{2/3} \longrightarrow \gamma \sim \sqrt{\chi - \chi_c} \sim \sqrt{\chi} \longrightarrow D \sim \chi^{1/6} N^{2/3}$

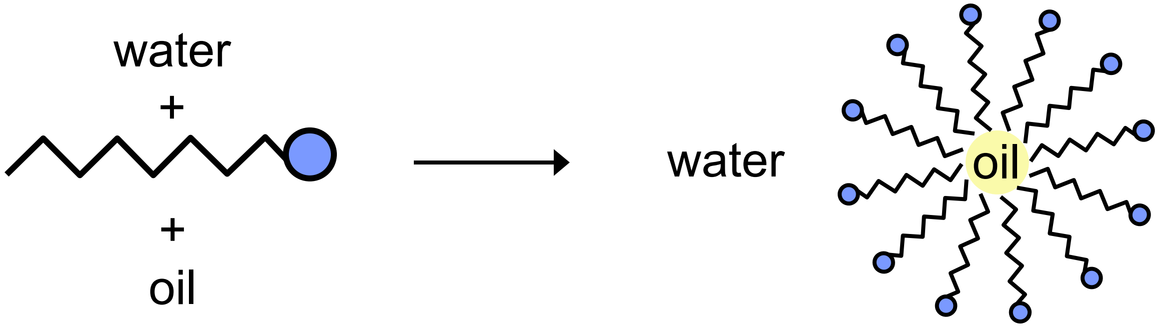
$$R_g \sim N^{1/2} \longrightarrow \frac{D}{R_g} \sim \chi^{1/6} \frac{N^{2/3}}{N^{1/2}} \longrightarrow \boxed{\frac{D}{R_g} \sim (\chi N)^{1/6}}$$

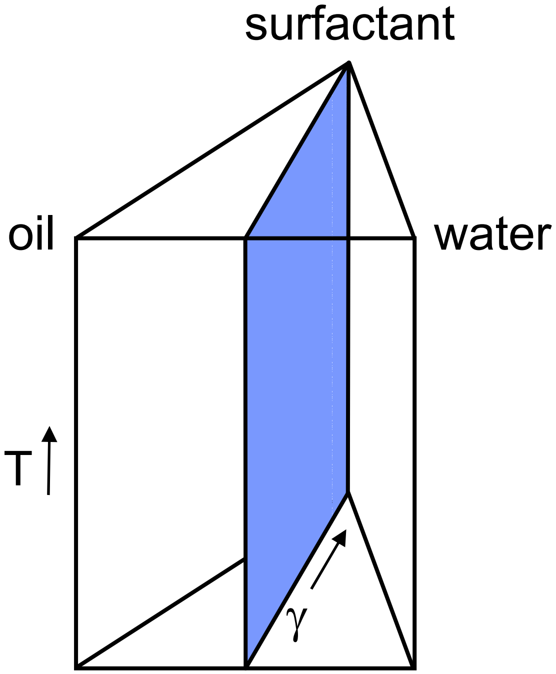
Universal curve

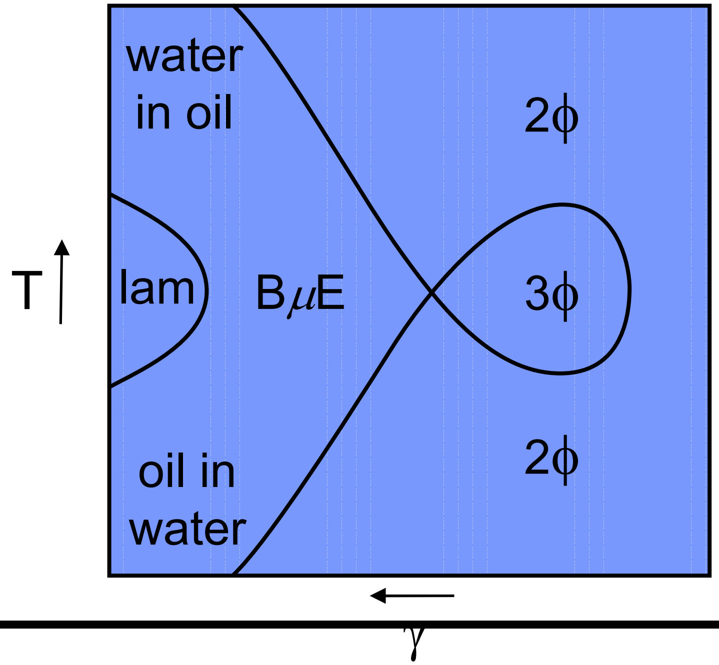


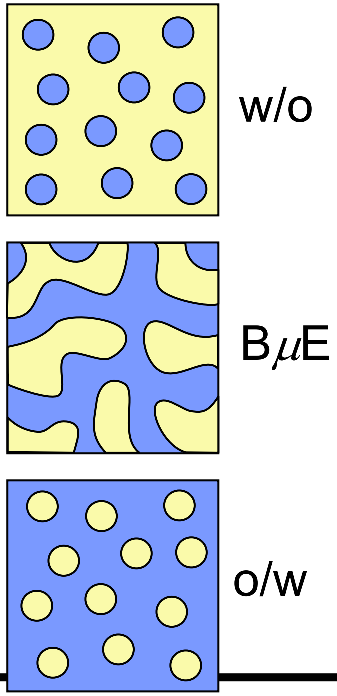
Microemulsions

Oil and water can be made miscible by adding a surfactant

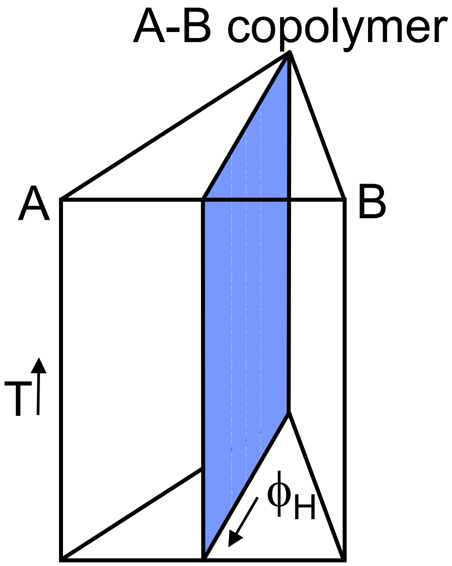


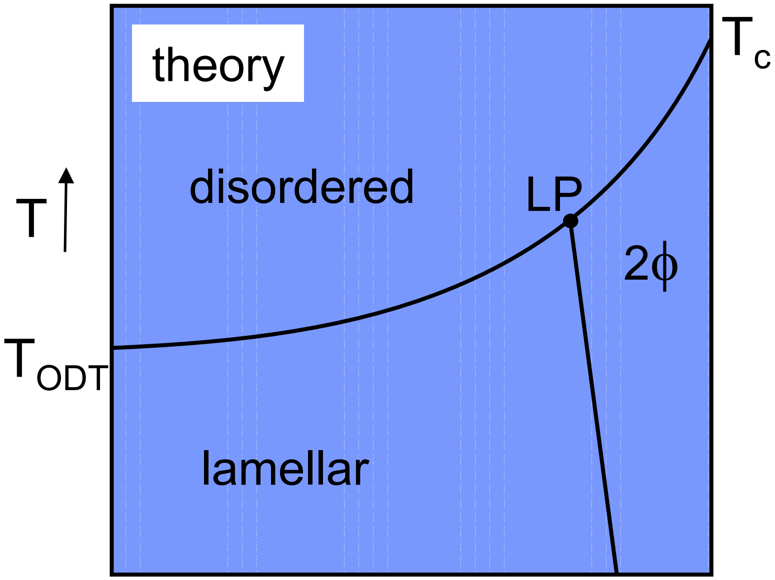


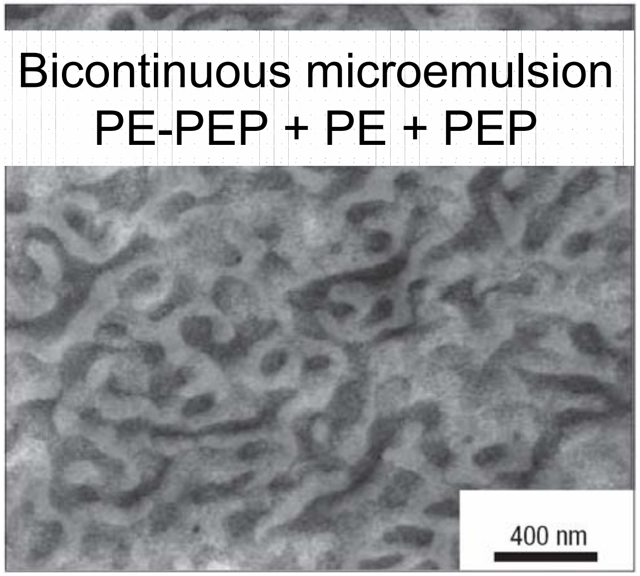


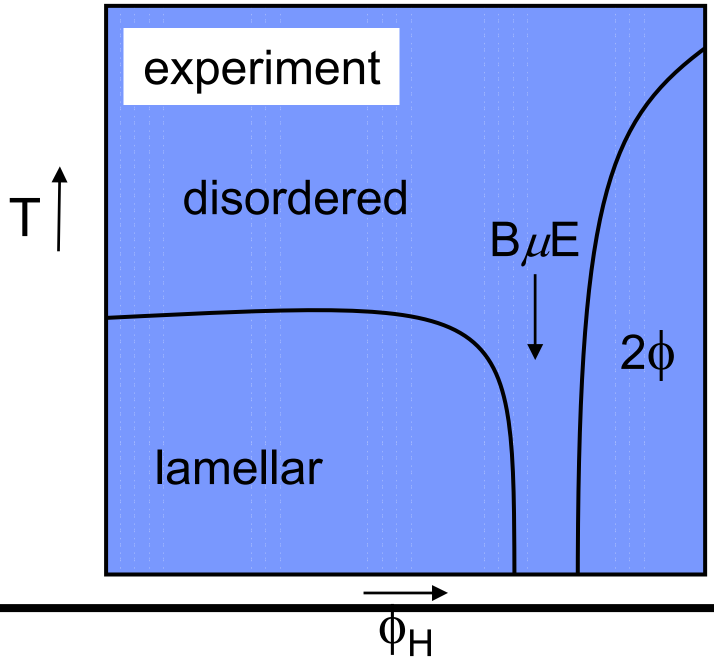


Polymeric microemulsions





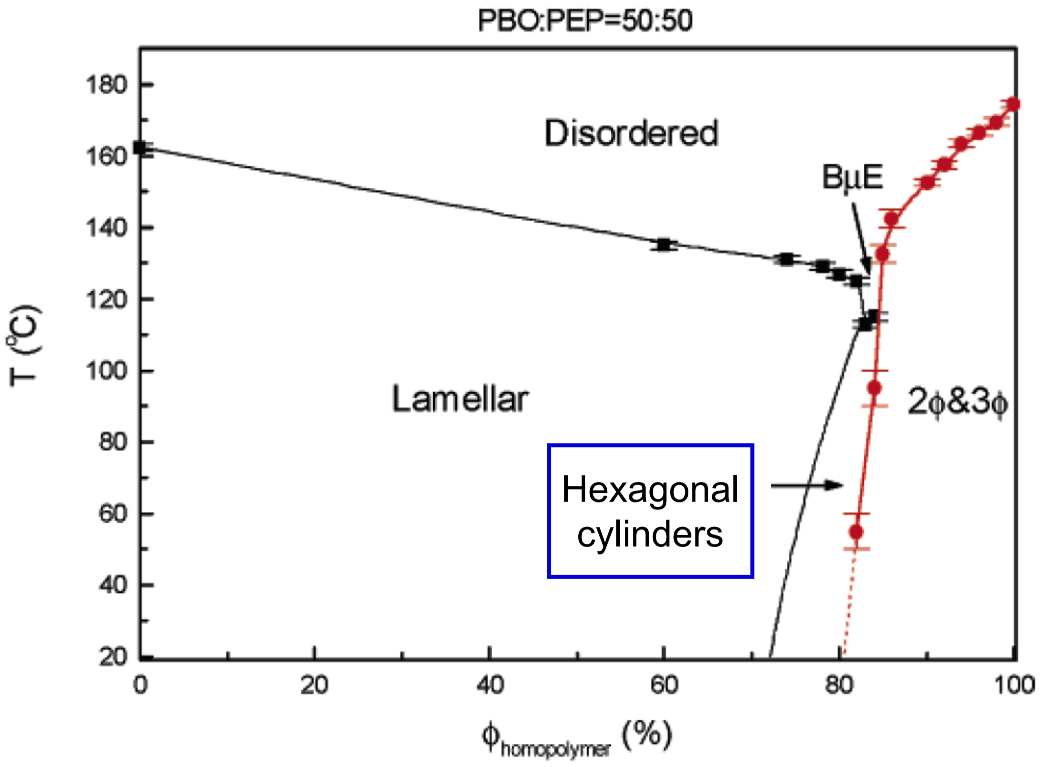

Bicontinuous microemulsion
PE-PEP + PE + PEP



Bates et al. *Phys. Rev Lett.* 79 849 (1997)

Asymmetric microemulsions

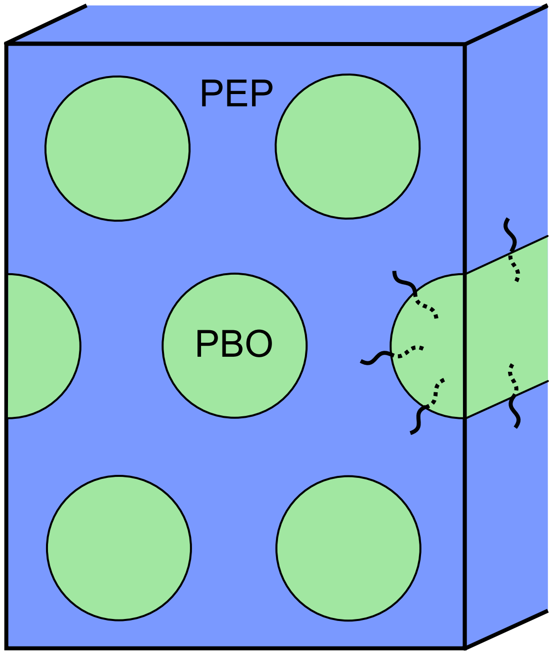
Poly(ethylene-propylene) and Poly(butylene oxide)
PEP-PBO + PEP + PBO



Hexagonal cylinders

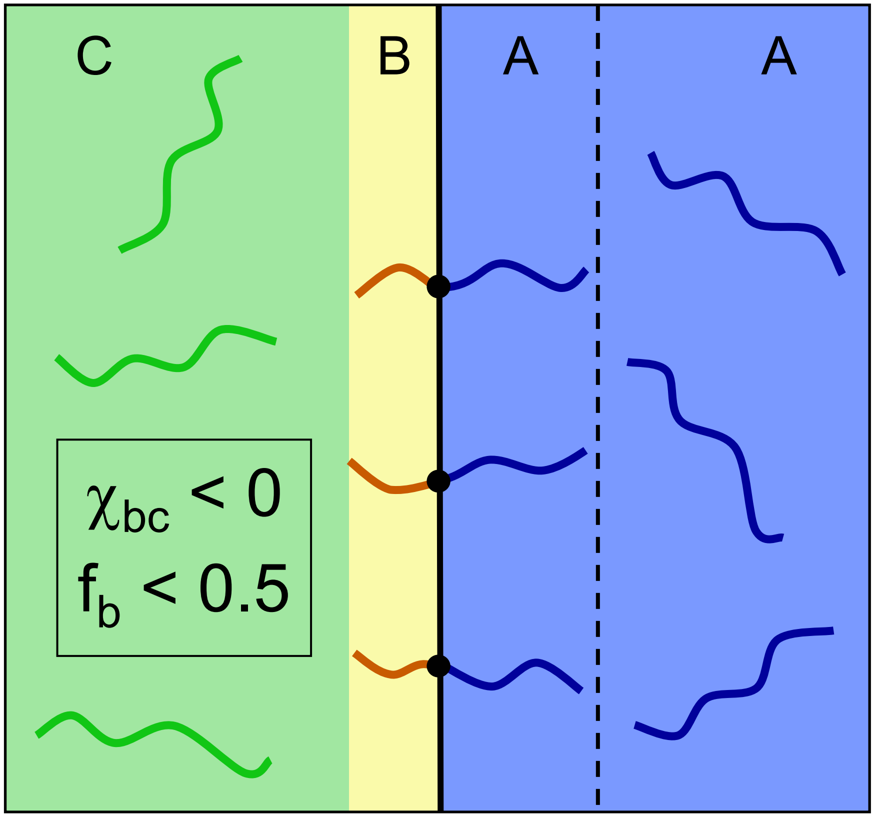
Zhou, Lodge, Bates, *J. Phys. Chem. B.* 110 3979 (2006)

The more flexible PBO component induces a spontaneous curvature toward the PBO domains



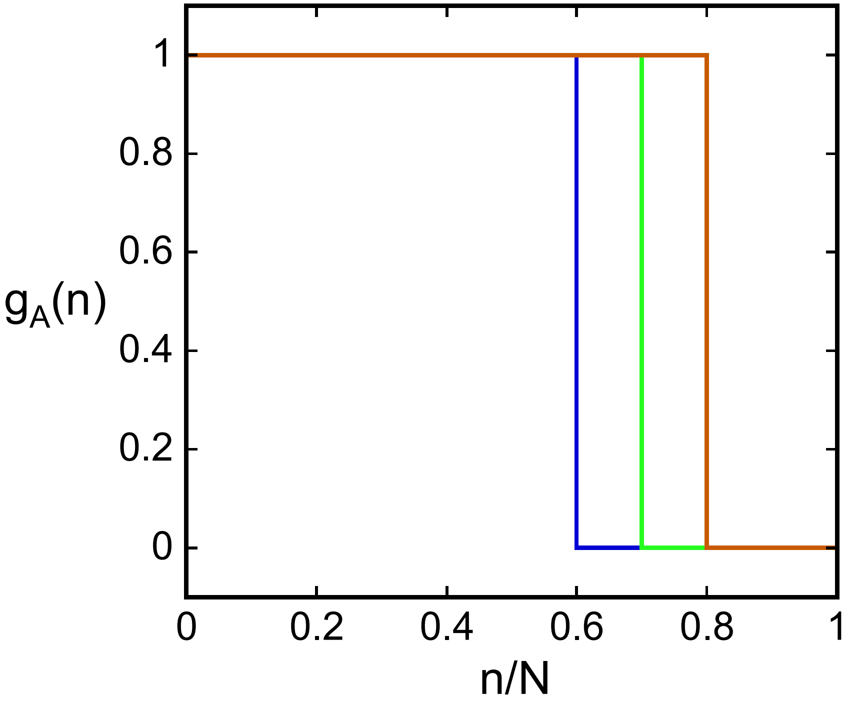
Can a spherical micellar microemulsion form?

Three component system



$\chi_{bc} < 0$
$f_b < 0.5$

Copolymer sequence distributions



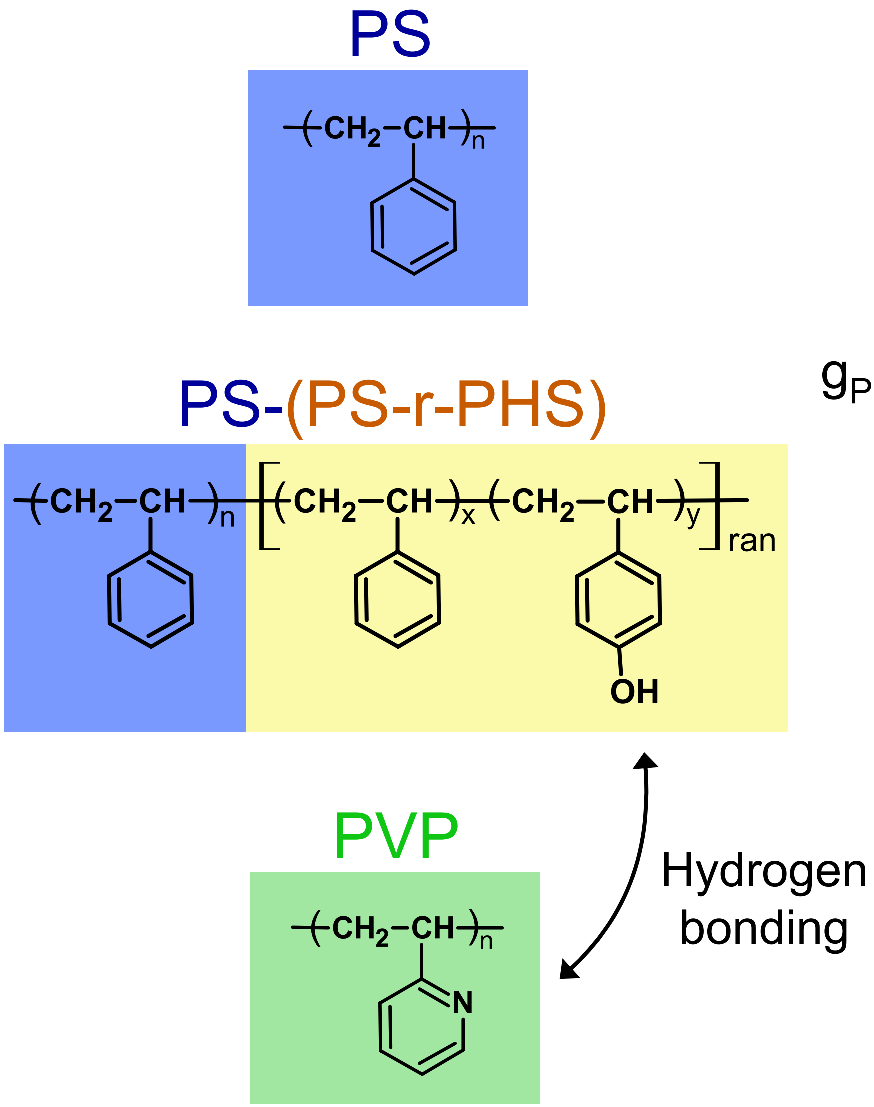
Copolymer segregates to the interface

Preferred interfacial curvature changes as copolymer accumulates

f_b = 0.2 to 0.4

$\chi_{bc}N_{cb}$ = 0 to −6

Experimental system

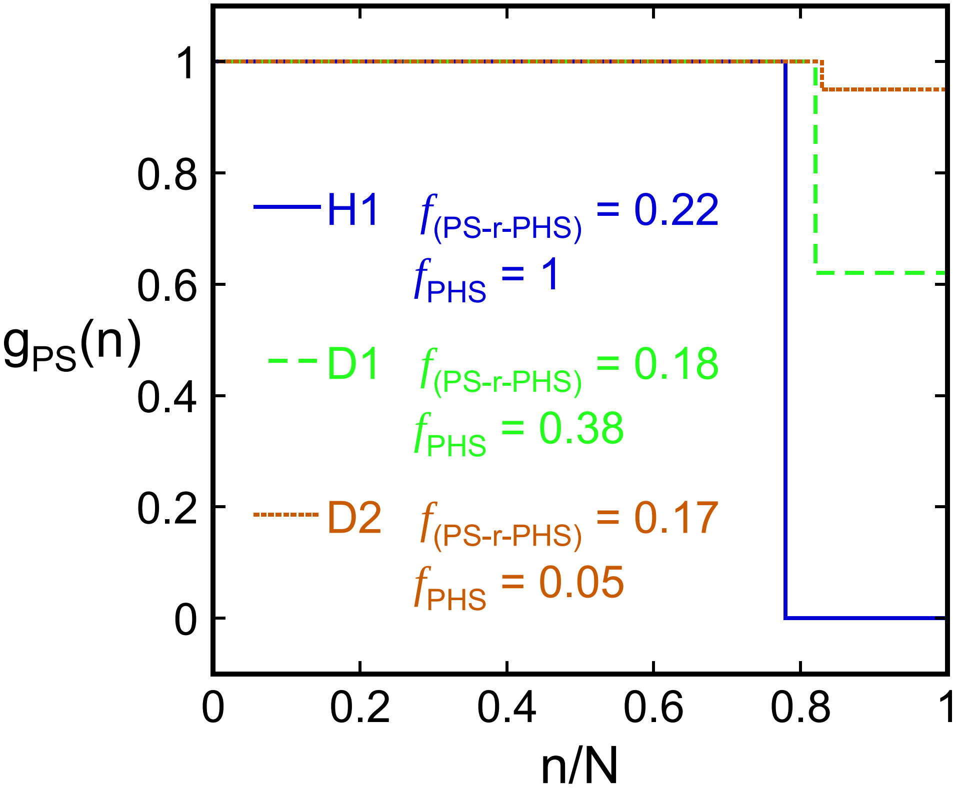

PS

PS-(PS-r-PHS)

PVP

Hydrogen bonding

Copolymer sequence distributions

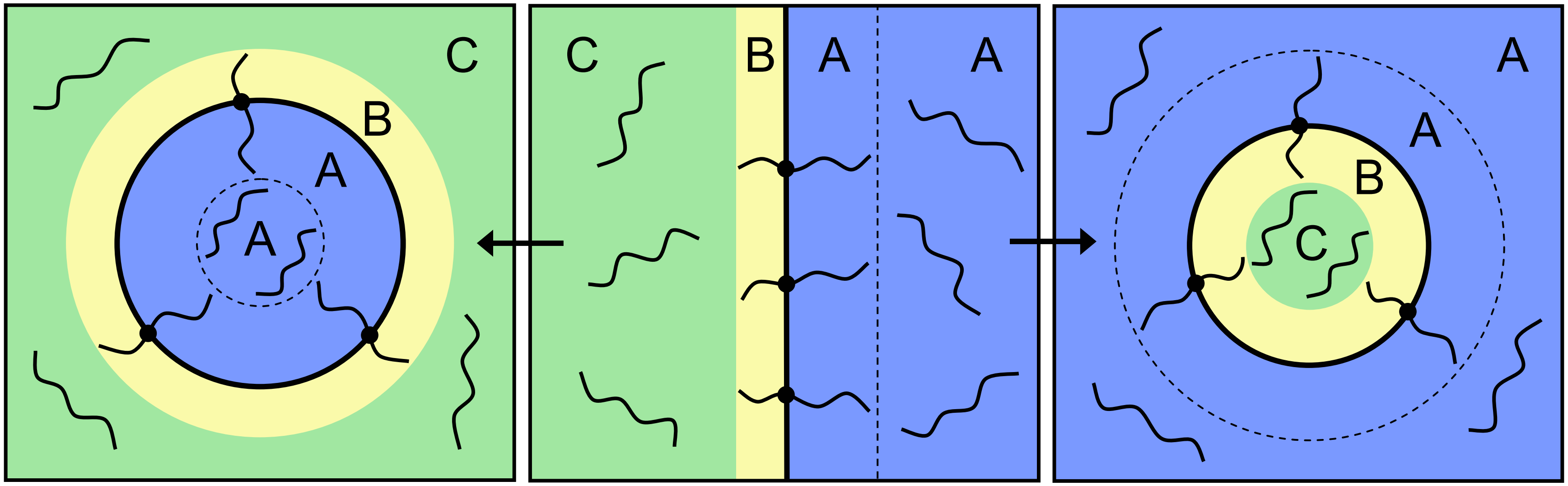


Copolymer synthesis

- Anionic polymerization of PS
- NM-CRP of PS-r-PAS
- Hydrolysis to PS-b-(PS-r-PHS)

Curved interfaces

When the curvature changes, swollen micelles can “pinch off” from the interface to accommodate the preferred curvature and maximize B-C contacts

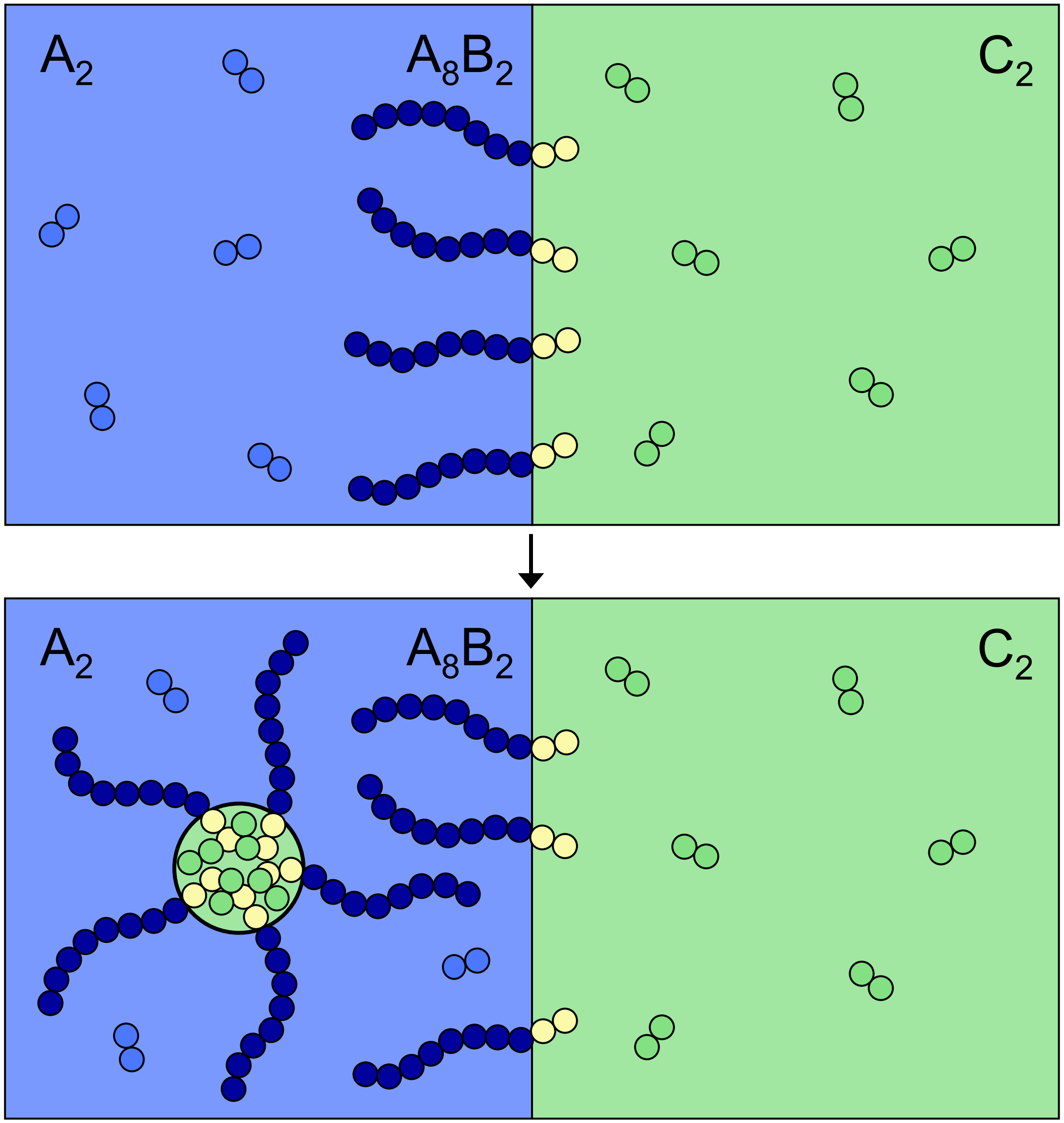


Inverse swollen micelles   Flat interface   Swollen micelles

Spherical microemulsions

- Short amphiphiles: Molecular dynamics
- Polymers: Self-consistent mean field theory

Short amphiphiles



Short amphiphilic chain of 10 units with $f_b = 0.2$:

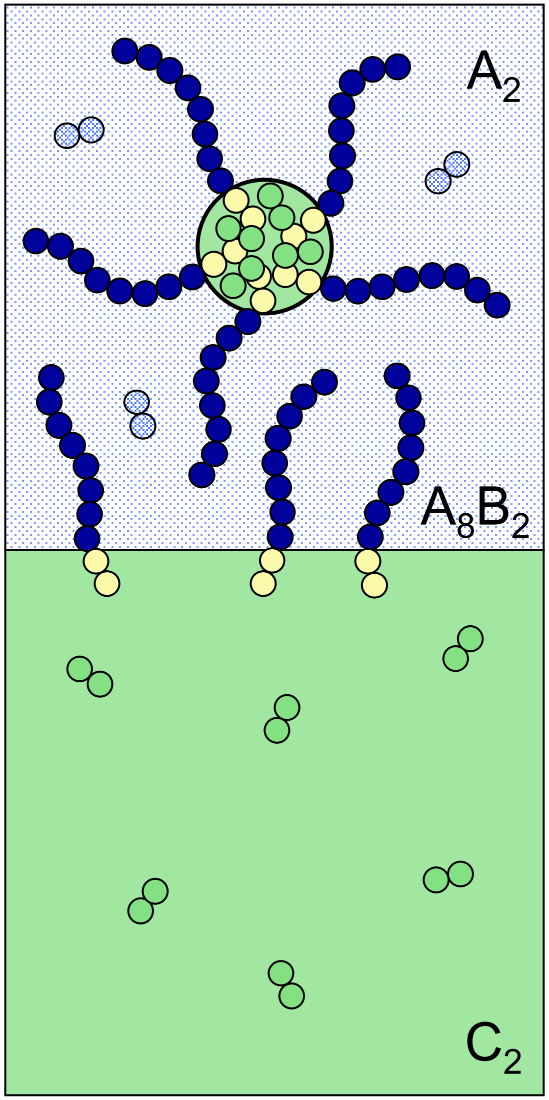
A_8B_2

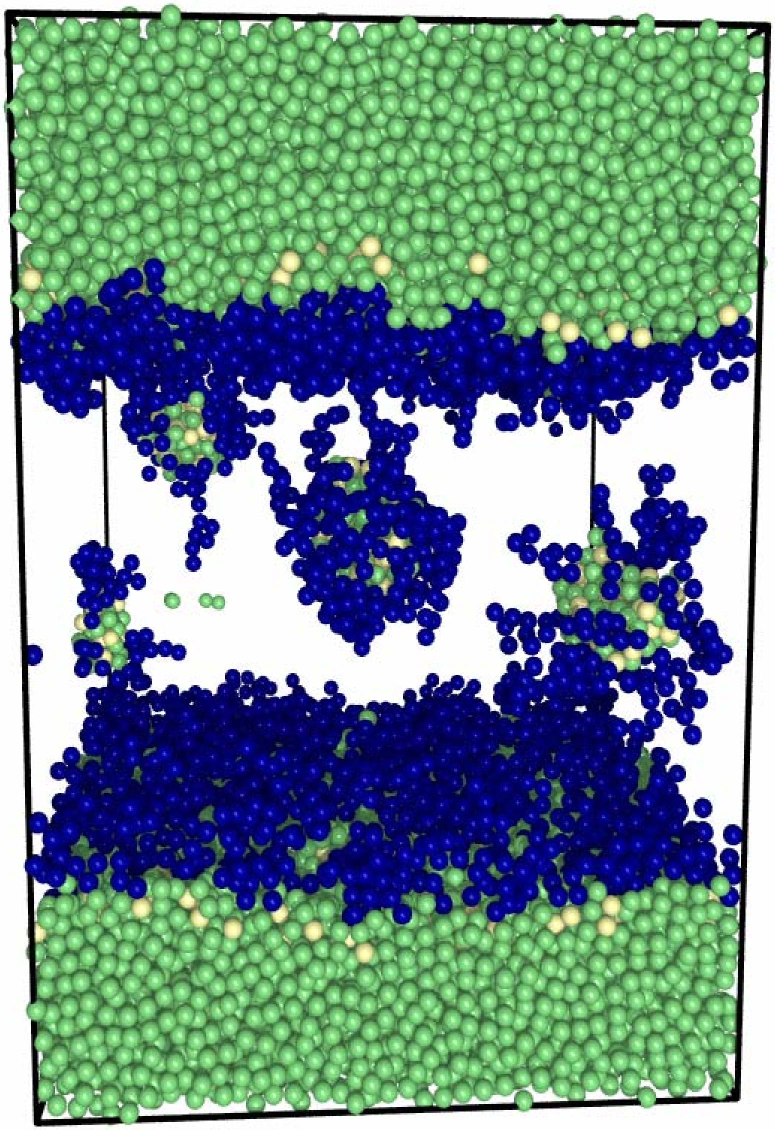
Short 2-unit solvents:

A_2 and C_2

Swollen micelles form in the A_2 matrix

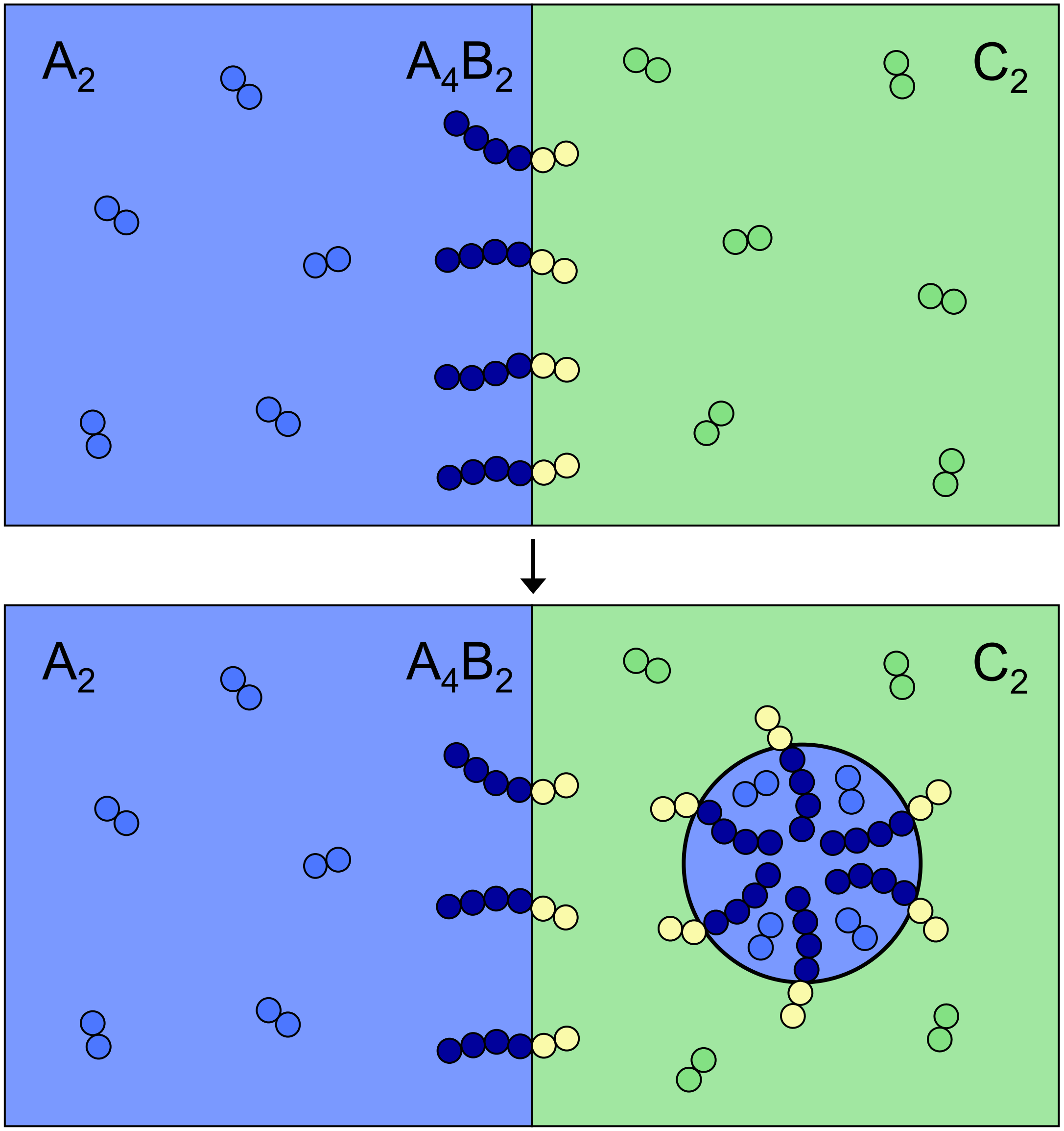
MD – Swollen micelles





$\phi_{cop} = 9.3\%$ $\chi_{ab}N_{cop} \approx 30$

Inverse swollen micelles

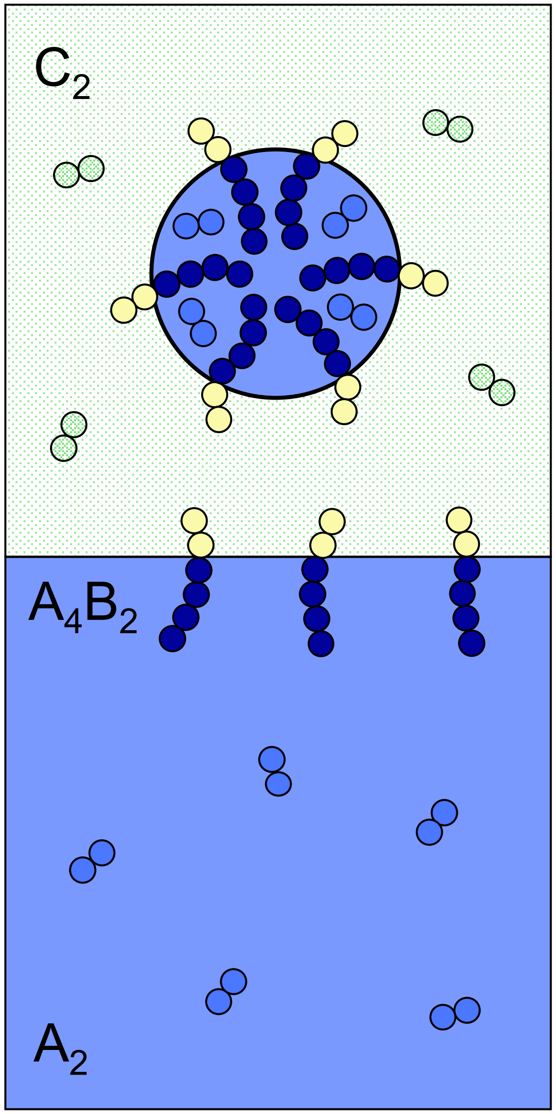


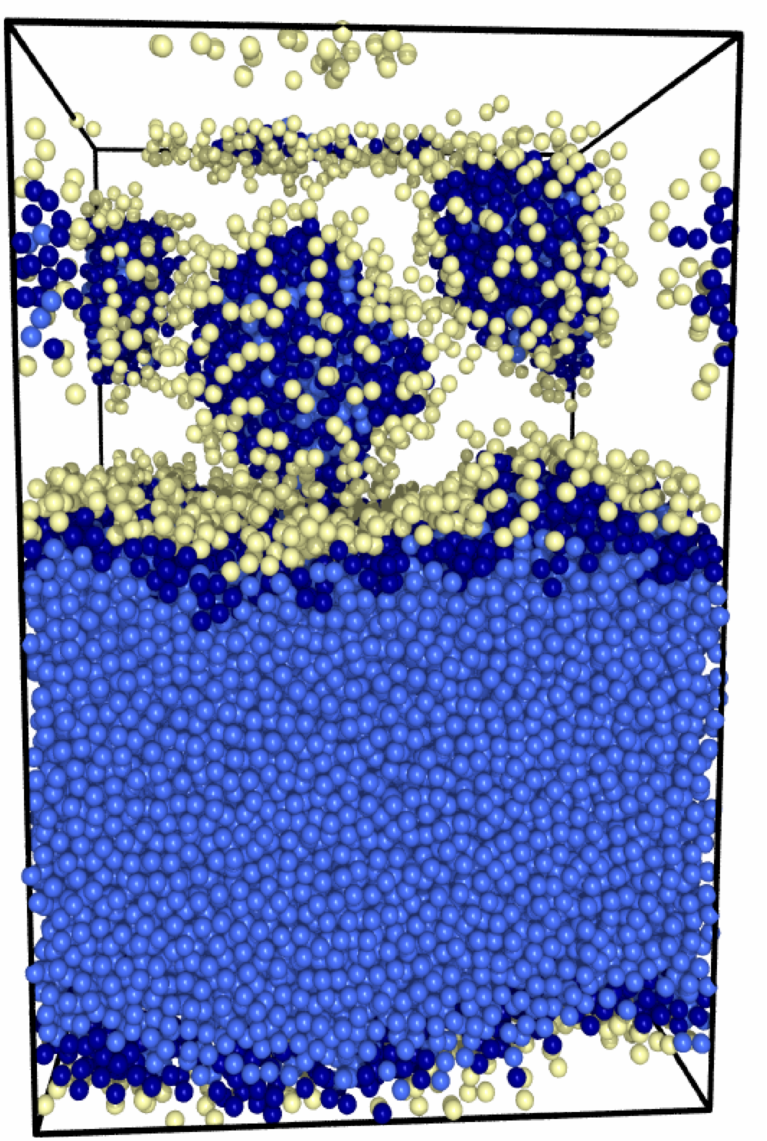
Shorter amphiphilic chain of 6 units with $f_b = 0.33$:
A_4B_2

Short 2-unit solvents:
A_2 and C_2

Inverse swollen micelles form in the C_2 matrix

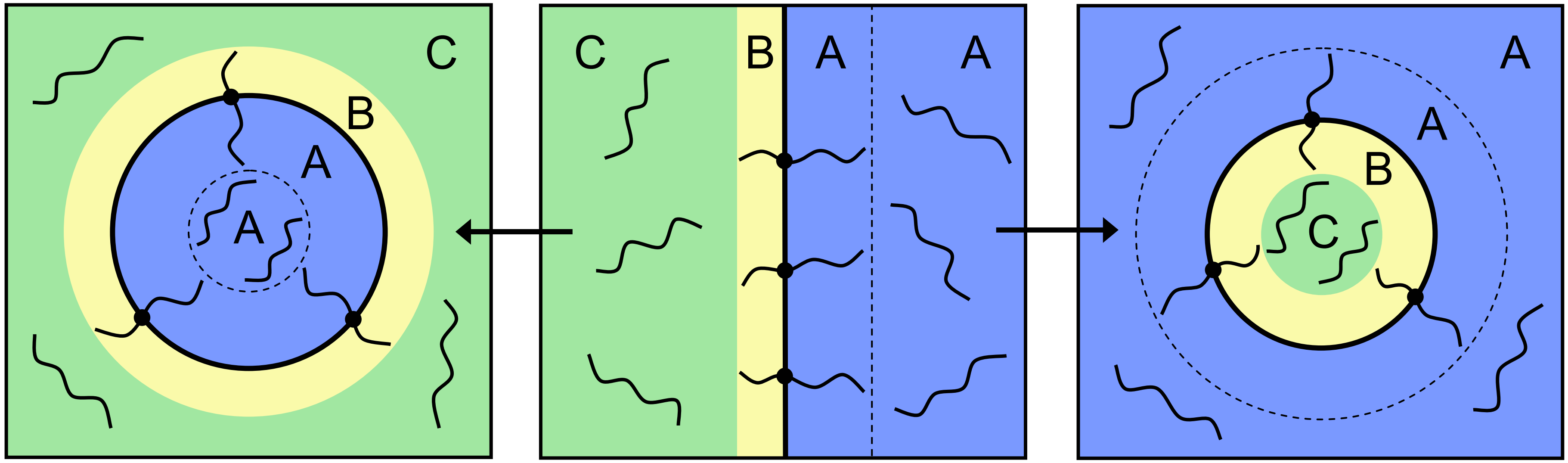
MD – Inverse swollen micelles





$\phi_{cop} = 7.5\%$ $\chi_{ab}N_{cop} \approx 20$

Polymers



$C < 0$
Inverse swollen micelles
A-centered

$C = 0$
Flat interface

$C > 0$
Swollen micelles
C-centered

Find the equilibrium curvature as f_b and χ_{bc} are varied

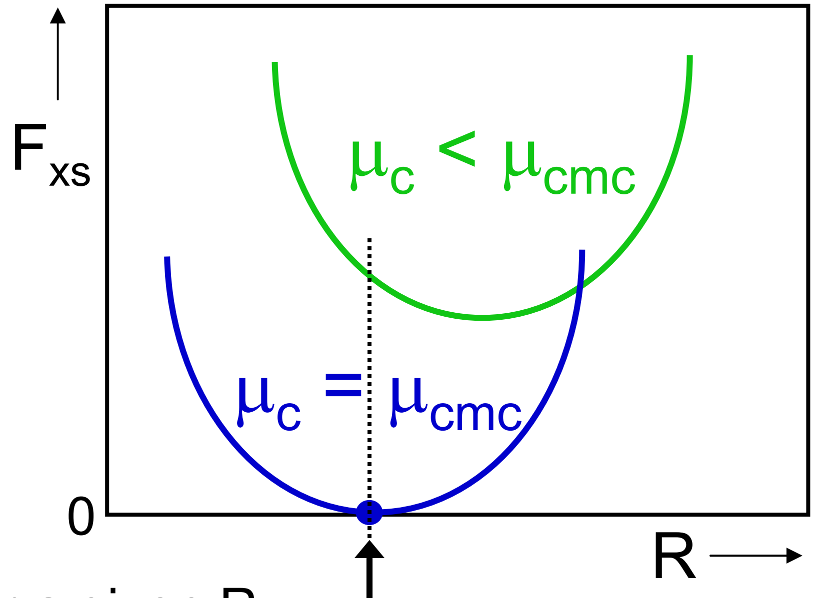
Self-consistent mean field theory

Matsen, M.W. *J. Chem. Phys.* 110 4658 (1999)

- Numerical solution to the modified diffusion equation
- Use spherical or planar geometry
- Find volume fraction profiles of each polymer
- Equilibrium when the chemical potential of each component is uniform
- Find copolymer chemical potential where $F_{xs} = 0$

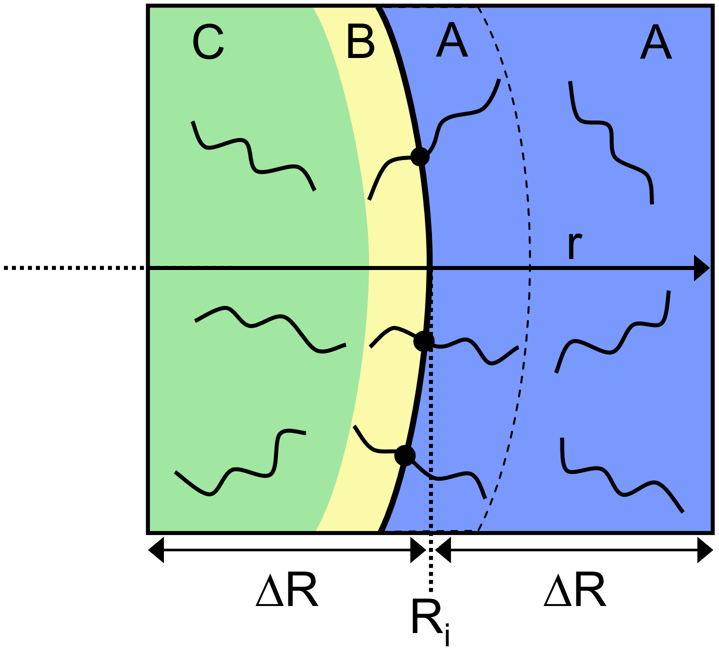
$$\text{Free energy} = \sum_i n_i \mu_i + F_{xs}$$

Excess free energy = 0 at
chemical potential of
micelle formation



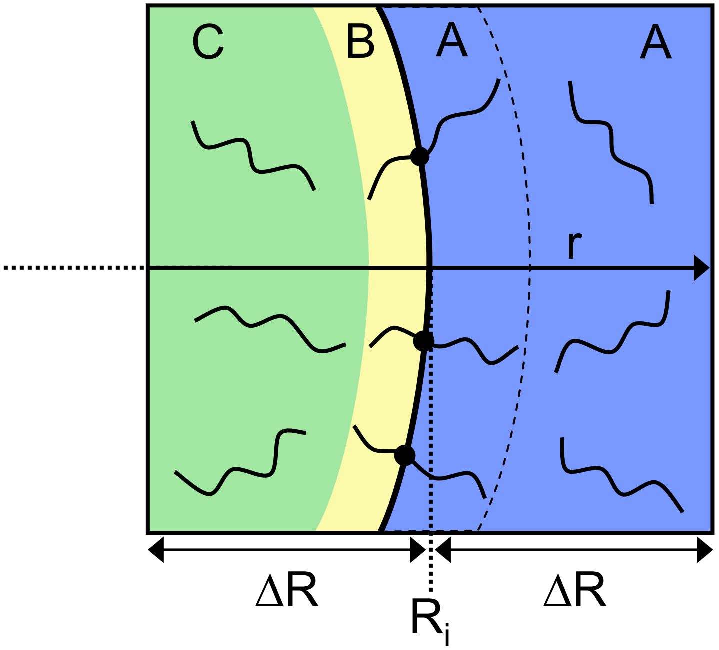
Find μ_{cmc} where F_{xs} = 0 for a given R

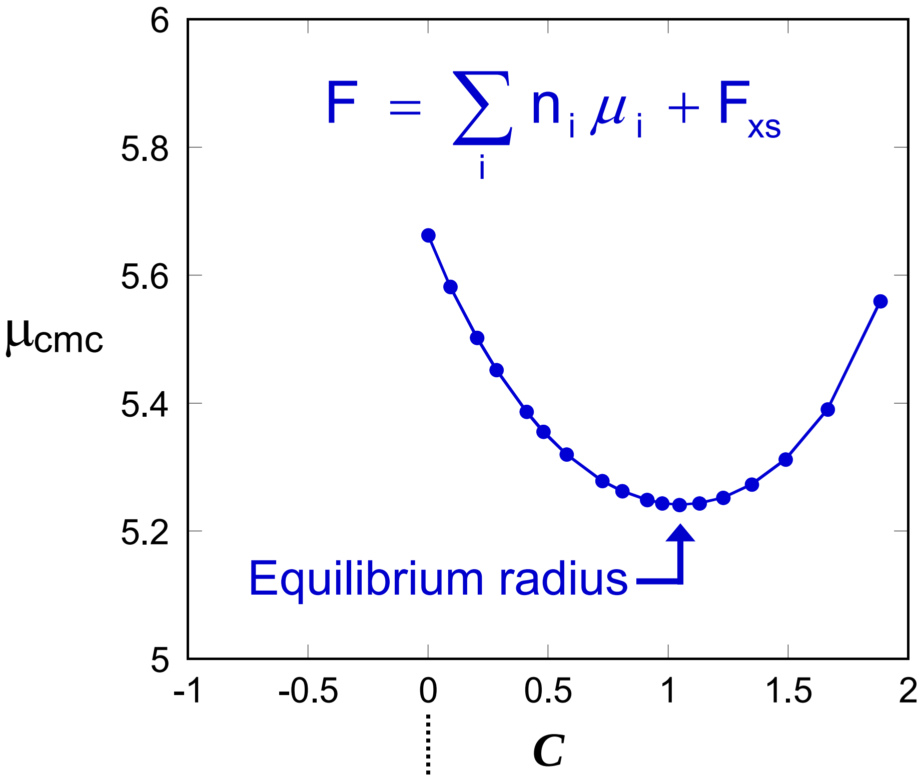
Equilibrium radius



- Fix the radius of the interface
- Solve the equations between R_i-ΔR and R_i+ΔR
- Use spherical or planar geometry
- At each radius find μ_{cmc}

Equilibrium radius





$$F = \sum_i n_i \mu_i + F_{xs}$$

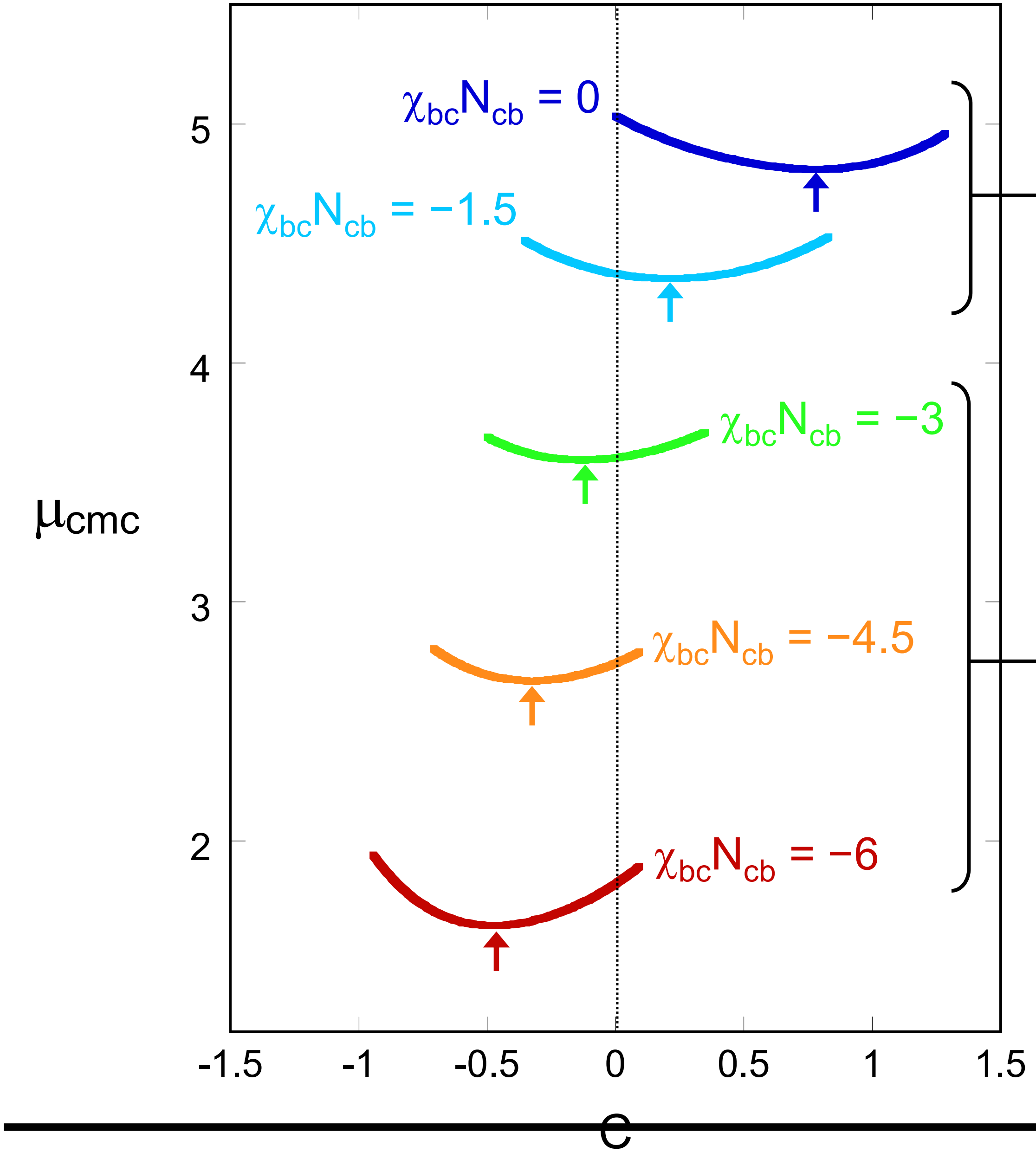
$C < 0$ ←
A-centered

→ $C > 0$
C-centered

- Fix the radius of the interface
- Solve the equations between R_i-ΔR and R_i+ΔR
- Use spherical or planar geometry
- At each radius find μ_{cmc}

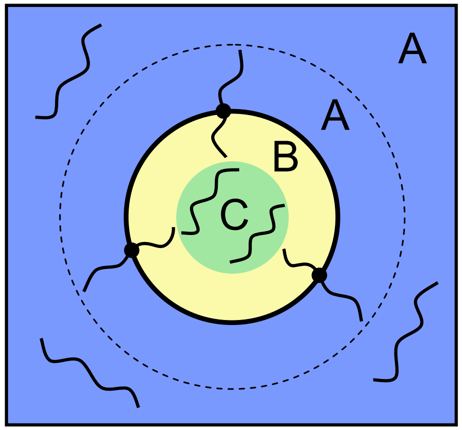
$$C = \frac{R_0}{R_i} = \frac{aN^{1/2}}{R_i}$$

Equilibrium curvature



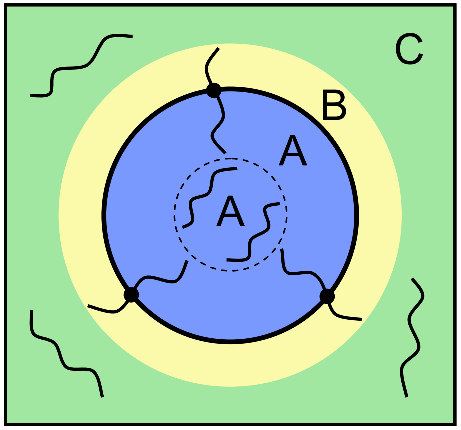
Swollen micelles

C > 0



Inverse swollen micelles

C < 0

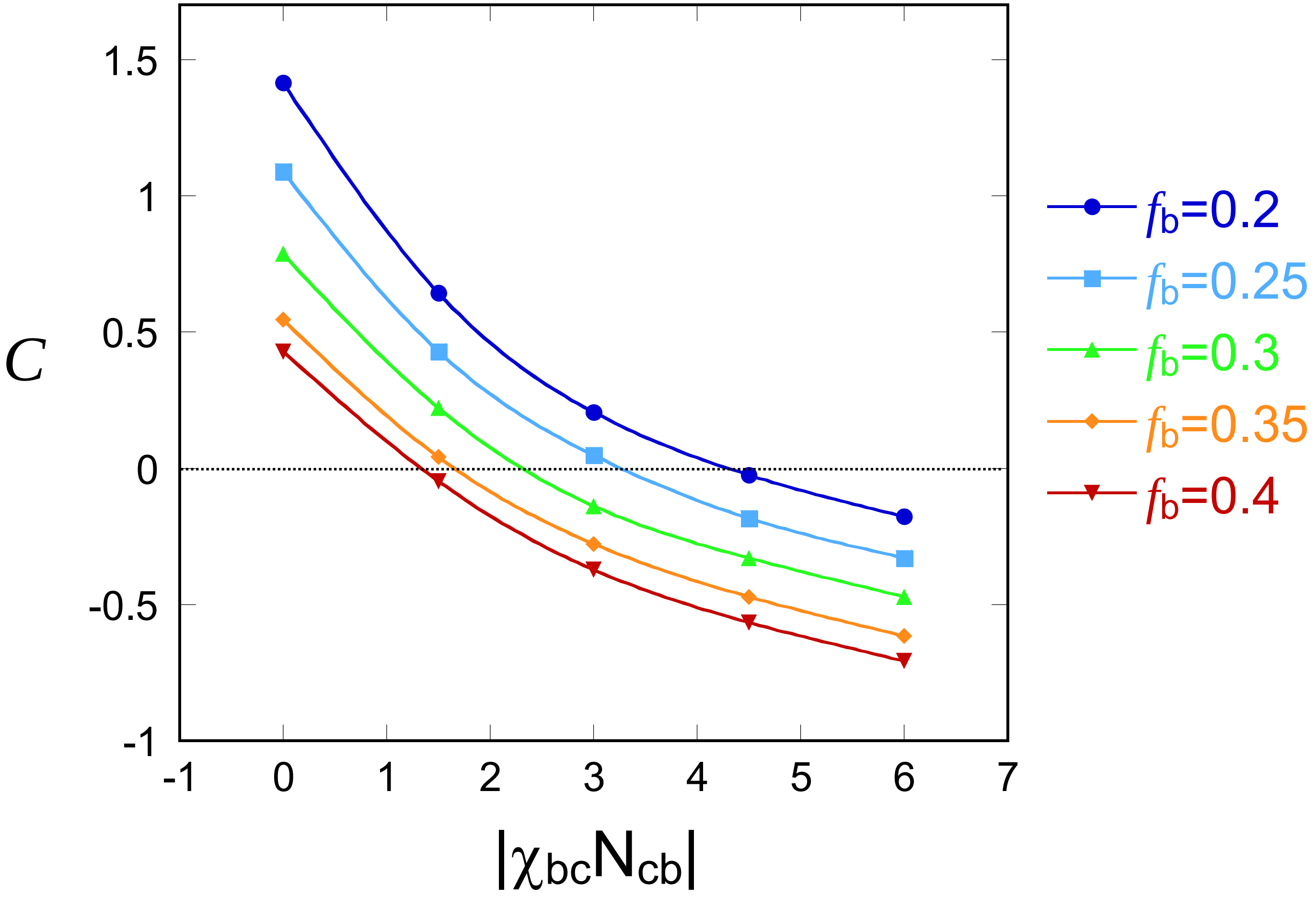


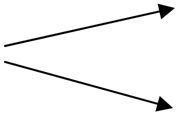
$N_{cop} = N_{ha} = N_{hc}$

$f_b = N_{cb}/N_{cop} = 0.3$

$\chi_{ab}N_{cop} = \chi_{ac}N_{cop} = 40$

Equilibrium curvature



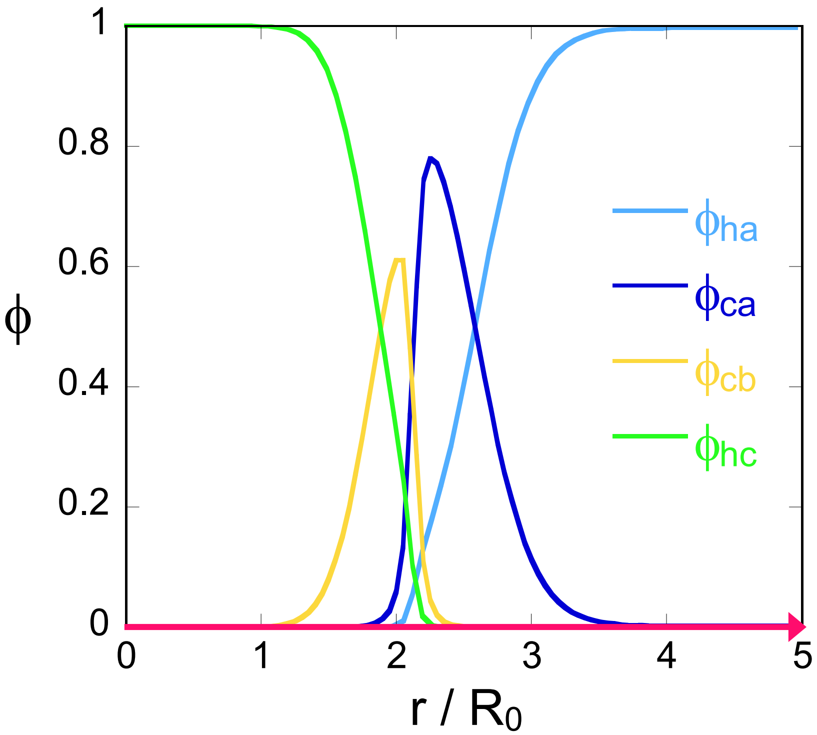


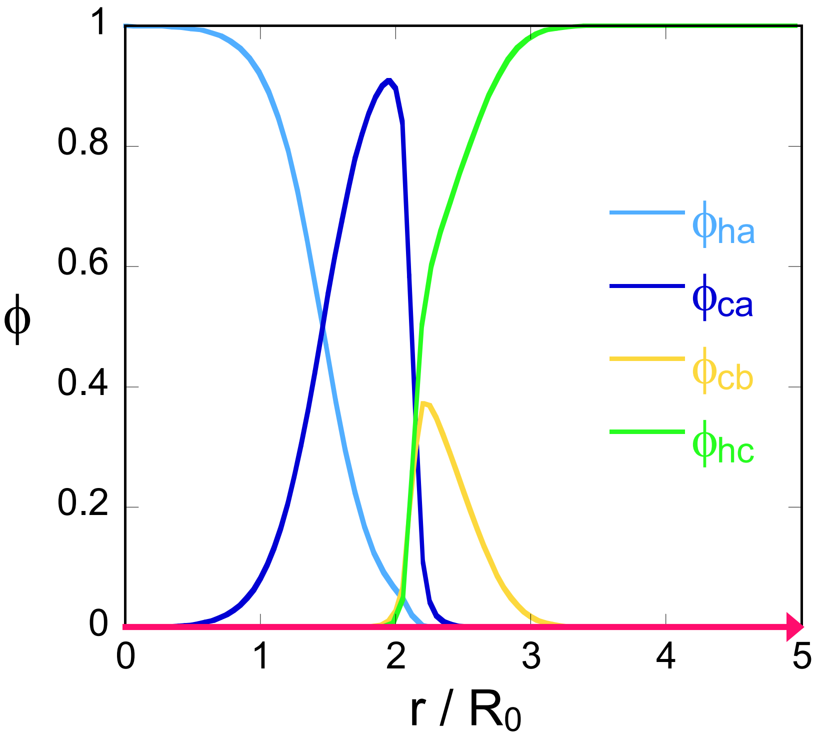
Curvature inverts by

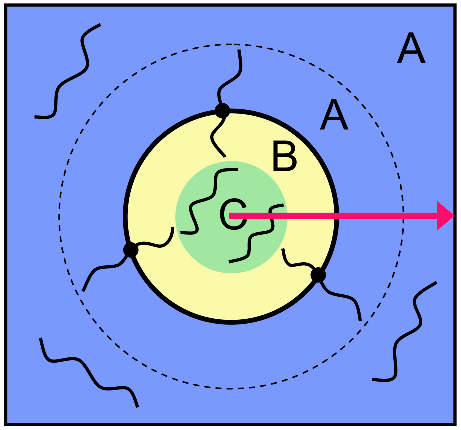
Holding f_b constant and increasing $|\chi_{bc}|$

Holding $|\chi_{bc}|$ constant and increasing f_b

Volume fraction profiles

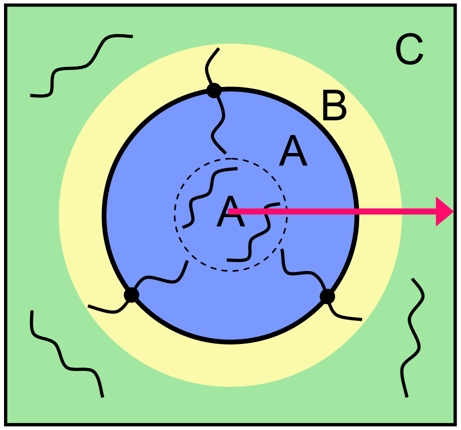






$f_b = 0.25$

$\chi_{bc} N_{cb} = -1.5$

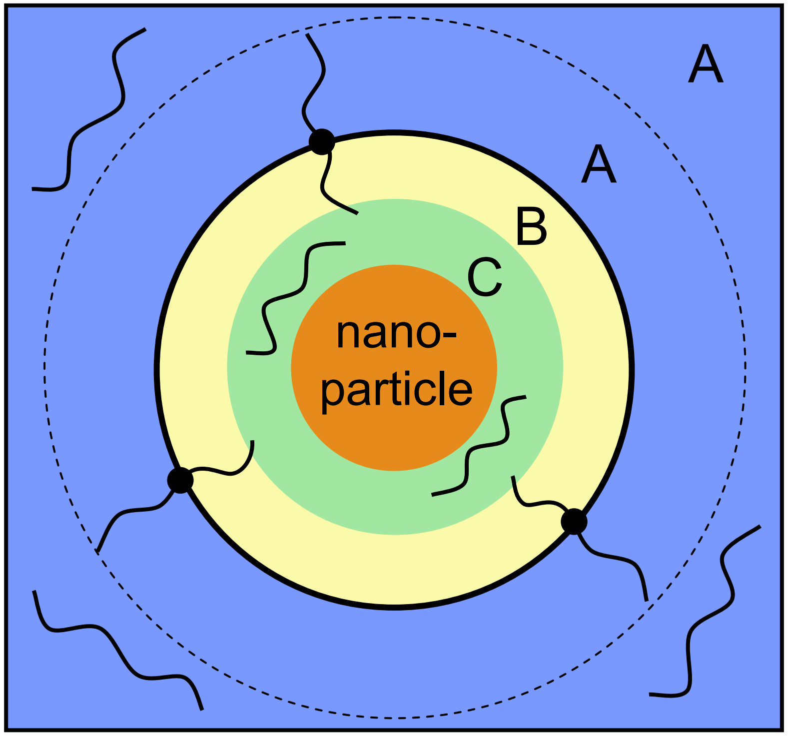


$f_b = 0.35$

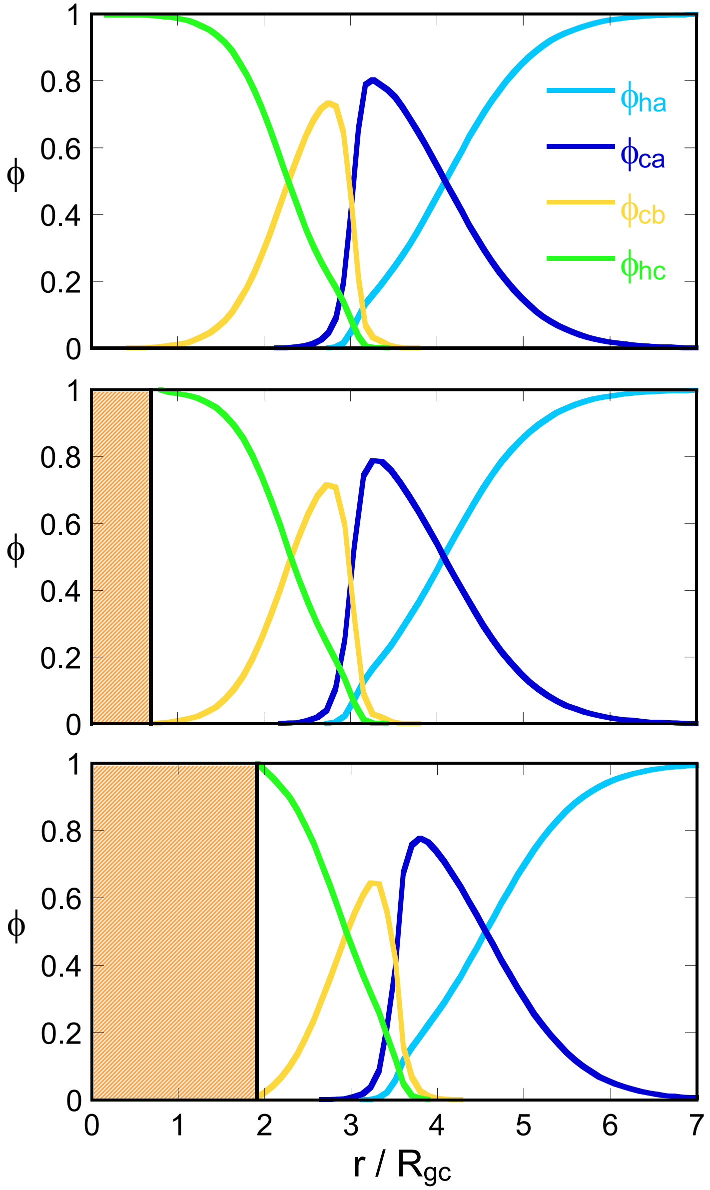
$\chi_{bc} N_{cb} = -4.5$

Polymer-metal nanocomposites

A nanoparticle can be encapsulated in the center of a swollen micelle

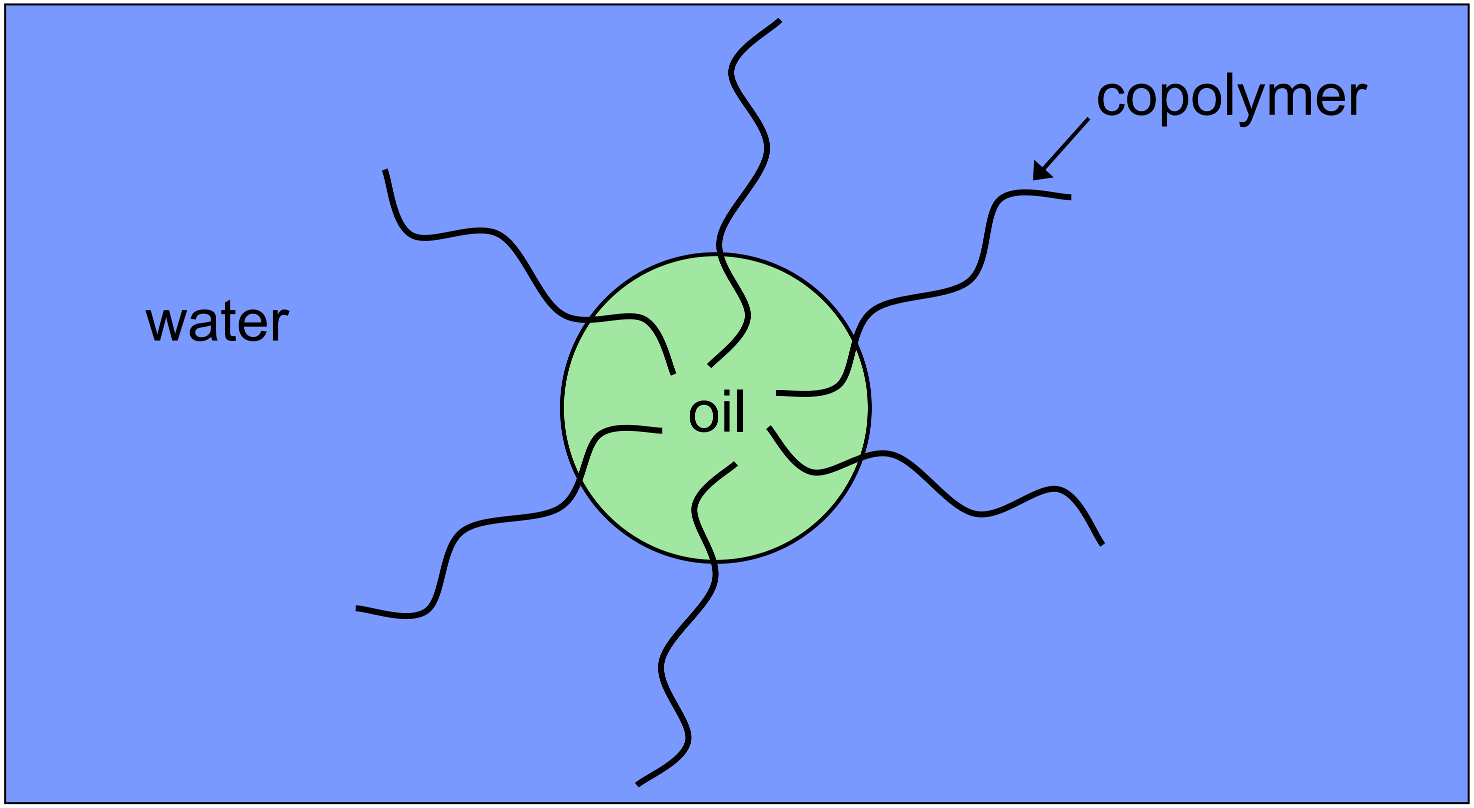


Choose a particle that has attractive interactions with the C homopolymer



Future directions: Copolymers in liquids

SCFT works well for concentrated polymer solutions



Important to use aqueous systems for drug delivery

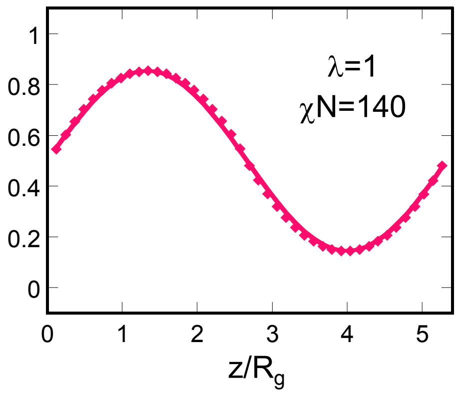
Can use polymers in many applications where surfactants are used

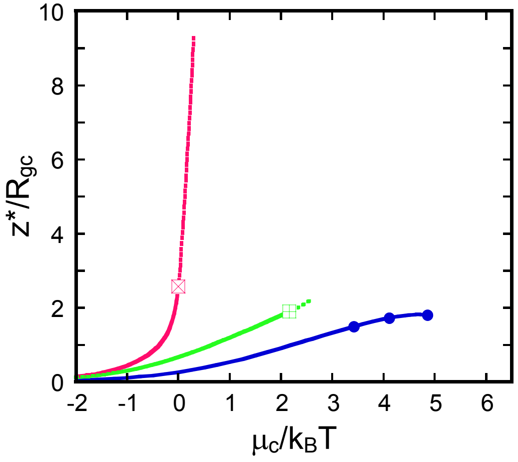
Summary

I. Phase segregation in gradient copolymer melts

RPA – gradient copolymers have higher order-disorder transitions than block copolymers

SCFT – gradient copolymers have weakly segregated lamellar layers even at high χN





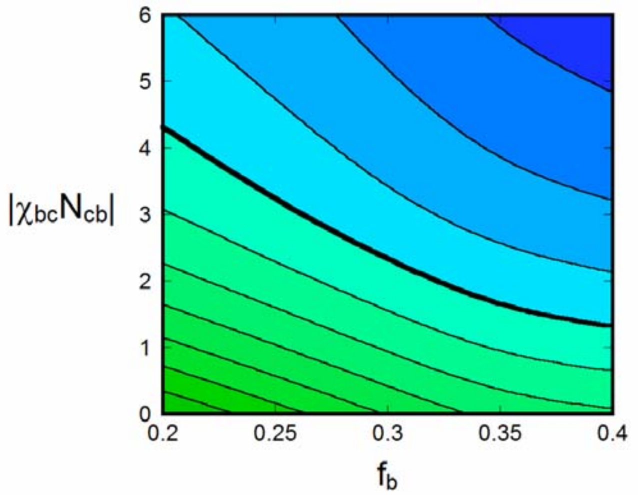
II. Interfacial behavior of block, random, and gradient copolymers

SCFT and interfacial experiments show that gradient copolymers exhibit intermediate interfacial behavior

III. Interfacial curvature of diblock copolymer monolayers

SCFT – predicts the formation of spherical micellar microemulsions

Can use results as a guide when designing future interfacial segregation experiments



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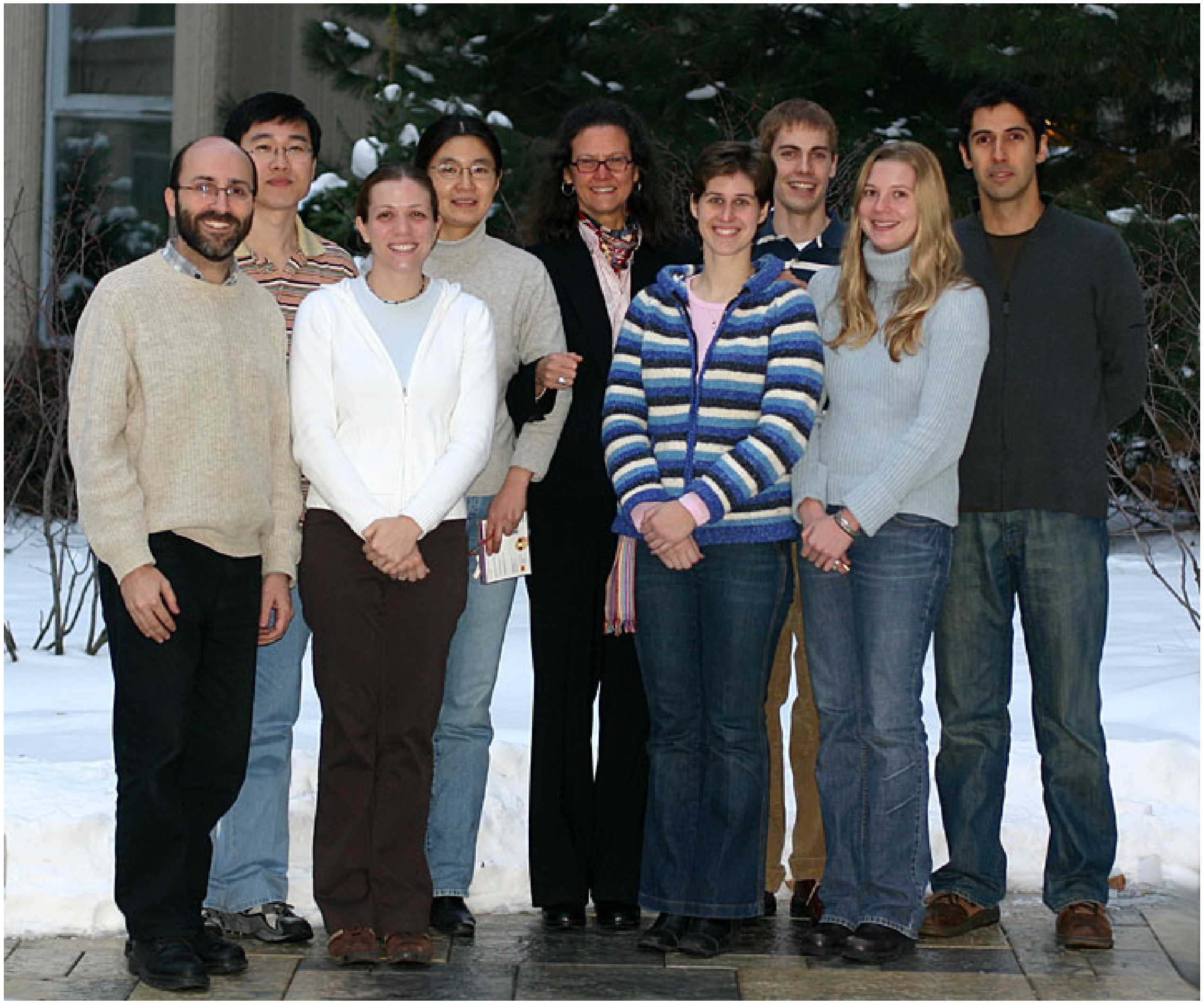

Sharon Loverde
Hao Cheng
Yuri Velichko
Graziano Vernizzi
Megan Greenfield
Kevin Kohlstedt
Hongxia Guo