Example: Uniaxial Deformation

With Axi-symmetric sample cross-section

Deform along $\vec{x}$ $\quad l_0 \to l_x \;,\; \alpha_x = \frac{l_x}{l_0},\;\; d\alpha_x = \frac{dl_x}{l_0}$

$\alpha_x = \alpha_x, \quad \alpha_y = \alpha_z = \frac{1}{\sqrt{\alpha_x}}$ Poisson contraction in lateral directions

since $\alpha_x\alpha_y\alpha_z = 1$

Rewriting $\Delta S(\alpha_i)$ explicitly in terms of α_x

$$\Delta S(\alpha_i) = -\frac{k}{2}\left(\alpha_x^2 + \frac{1}{\alpha_x} + \frac{1}{\alpha_x} - 3\right)$$

$$F_x = -T\frac{\partial}{\partial l_x}\left(\Delta S(\alpha_x)\right)\Big|_{T,P} = \frac{kT}{2}\frac{\partial}{\partial l_x}\left(\alpha_x^{\,2} + \frac{2}{\alpha_x} - 3\right)$$

Uniaxial Deformation cont'd

$$F_x = \frac{kT}{2l_0}\left(2\alpha_x - \frac{2}{\alpha_x{}^2}\right) = \frac{kT}{l_0}\left(\alpha_x - \frac{1}{\alpha_x{}^2}\right)$$

At small extensions, the stress behavior is Hookean ($F_x \sim \text{const}\ \alpha_x$)

Stress-Extension Relationship

$$\sigma_{xx} = \text{total}\ \frac{F_x(\alpha_x)}{A_0} = \frac{zkT}{A_0 l_0}\left(\alpha_x - \frac{1}{\alpha_x{}^2}\right) \quad \text{for z subchains in volume V}$$

$$A_0 l_0 = V \qquad \frac{z}{V} = \#\ \text{of subchains per unit volume} = N_{xlinks}$$

Usually the entropic stress of an elastomeric network is written in terms of M_x where M_x = avg. molecular weight of subchain between x-links

$$\frac{mass/vol}{molesofcrosslinks/volume} = \quad M_x = \frac{\rho}{N_x / N_A}$$

$$\boxed{\sigma_{xx}(\alpha_x) = \frac{\rho N_A kT}{M_x}\left(\alpha_x - \frac{1}{\alpha_x{}^2}\right) \qquad \text{uniaxial}}$$

Young’s Modulus of a Rubber

$$E \equiv \lim_{\alpha_x \to 1} \frac{d\sigma_{xx}}{d\alpha_x} = \frac{\rho RT}{M_x}\left(1 + \frac{2}{\alpha_x^3}\right)$$

$$\boxed{E = 3\rho RT/M_x}$$

Notice that Young’s Modulus of a rubber is :

1. Directly *proportional* to temperature
2. Indirectly proportional to M_x

- Can measure modulus of crosslinked rubber to derive $\underline{\underline{M_x}}$

- In an analogous fashion, the entanglement network of a melt, gives rise to entropic restoring elastic force provided the time scale of the measurement is sufficiently short so the chains do not slip out of their entanglements. In this case, we can measure modulus of non-crosslinked rubber melt to derive M_e !

Stress-Uniaxial Extension Ratio Behavior of Elastomers

Uniaxial Stretching

tensile

$\sigma(\alpha)$

Image removed due to copyright restrictions.

Please see Fig. 5 in Treloar, L. R. G. “Stress-Strain Data for Vulcanised Rubber Under Various Types of Deformation.” *Transactions of the Faraday Society* 40 (1944): 59-70

compressive

Small deformations

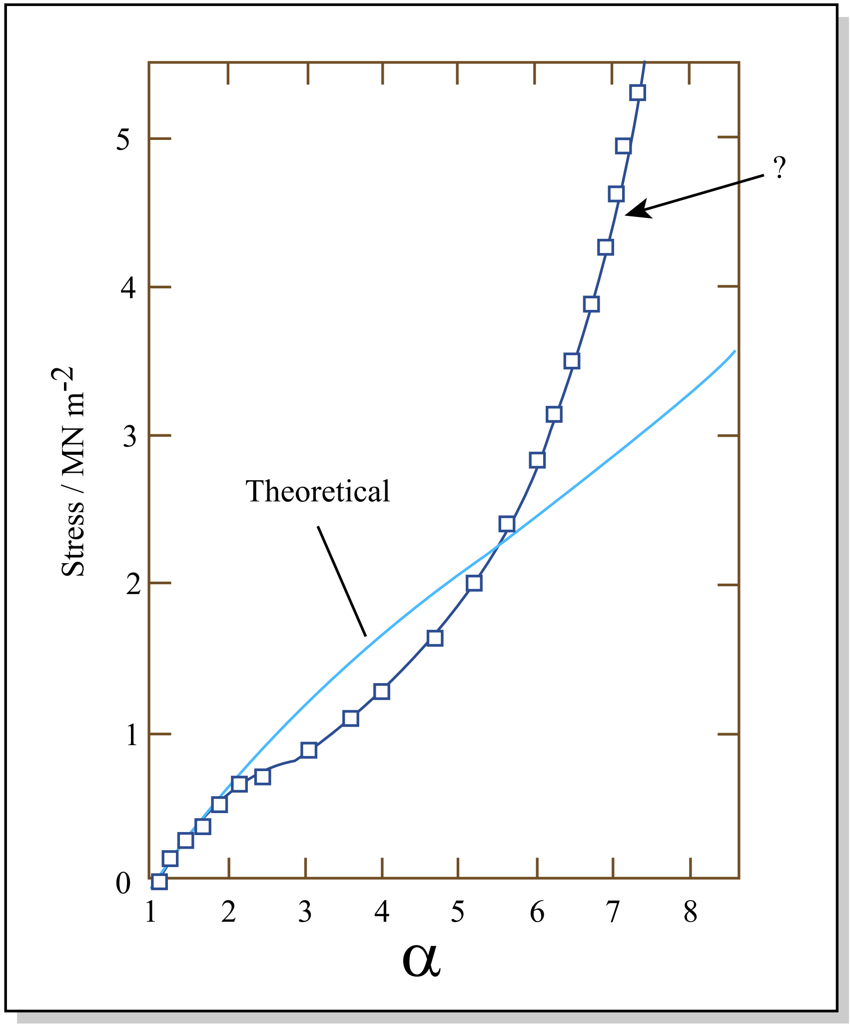


Figure by MIT OCW.

High tensile elongations

Rubber Demos

Tg for Happy Ball and Unhappy Ball

Deformation of Rubber to High Strains

Heating a Stretched Rubber Band

How stretchy is a gel?

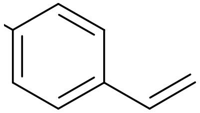
Gel – A Highly Swollen Network

Several ways to form a gel:

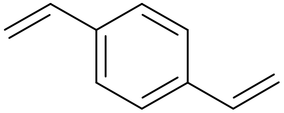
- Start with a polymer melt and produce a 3D network (via chemical or physical crosslinks) and then swell it with a solvent

Example:

styrene



divinyl benzene



- Start with a concentrated polymer solution and induce network formation, for example, crosslink the polymer by:
  - Radiation- (UV, electron beam) (covalent bonds)
  - Chemical- (e.g. divinyl benzene & PS) (covalent bonds)
  - Physical Associations - (noncovalent bonds induced by lowering the temperature or adding a nonsolvent)

Q: describe some types of physical (ie noncovalent) crosslinks

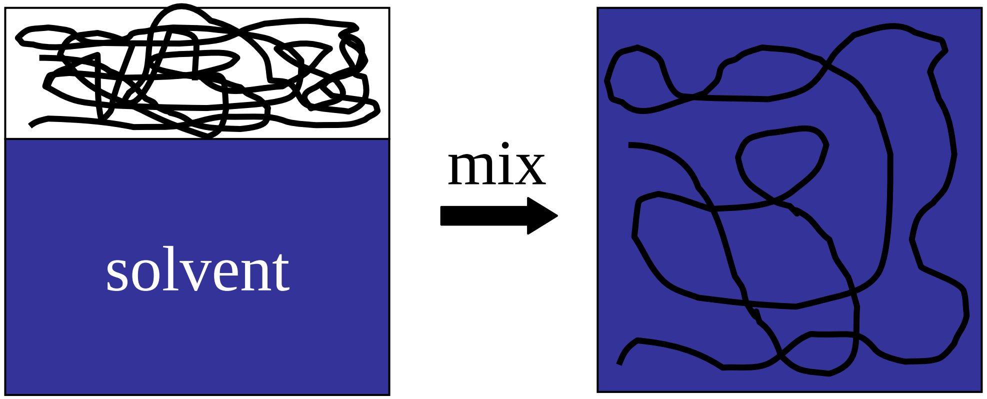
Flory-Rehner Treatment of Gels

- Assumes elastic effect and mixing effect are linearly *additive*

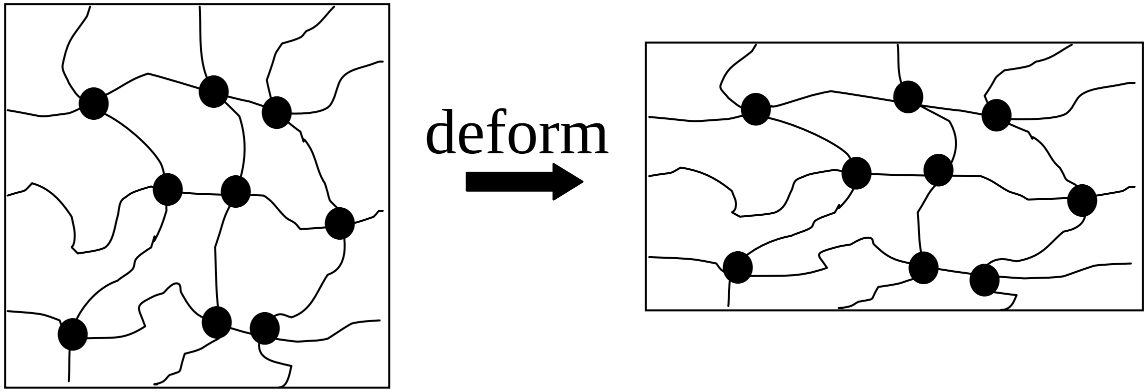
$$\Delta G = \Delta G_{mix} + \Delta G_{elastic}$$

Polymer-solvent Thermodynamics, ΔG_{mix}

Flory Huggins Theory (χ, x_1, x_2, ϕ_1, ϕ_2)



Rubber Elasticity Theory $\Delta G_{elastic}$

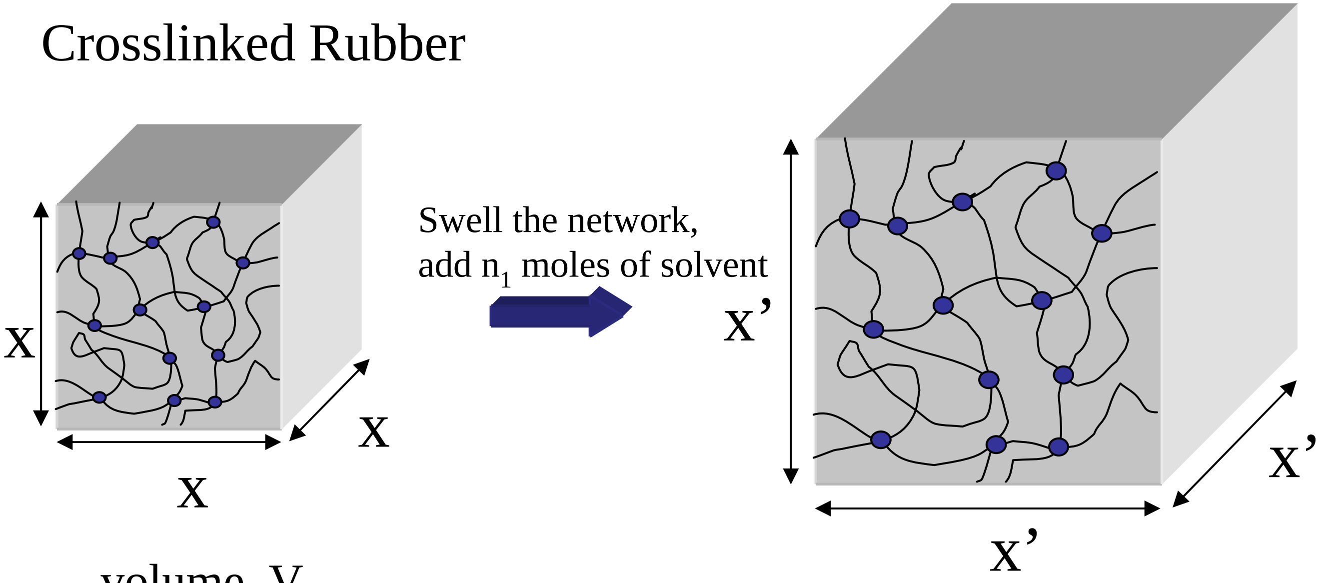


Flory-Rehner Theory

$$\Delta G = \Delta G_{mix} + \Delta G_{elastic}$$

At equilibrium, $\Delta G_{mix} = -\Delta G_{elastic}$

1. Thermodynamically good solvent swells rubber
    - favorable χ interaction
    - favorable ΔS_{mix}
2. BUT Entropy elasticity of network ($\Delta S_{elastic}$) exerts retractive force to to oppose swelling



Crosslinked Rubber

Swell the network, add n_1 moles of solvent

Swollen Rubber

volume, V_o
subchain, $\langle r_0^2 \rangle^{1/2}_{subchain}$

volume, V
subchain, $\langle r^2 \rangle^{1/2}_{subchain}$

Thermo of Swollen Network cont'd

α_x = linear swelling ratio $= \frac{x'}{x}$

ϕ_2 = volume fraction polymer = $\frac{V_0}{V}$

N = # of subchains in the network = $\frac{\rho V_0 N_A}{M_x}$

Isotropic swelling $\alpha_x = \alpha_y = \alpha_z = \alpha_s$

$$V_0 \alpha_s^3 = V \qquad \phi_2 = \frac{V_0}{V} \qquad \text{so} \quad \alpha_s^3 = \frac{1}{\phi_2}$$

chemical potential, $\mu_i = \left(\frac{\partial \Delta G_{tot}}{\partial n_i} \right)_{T,P,n_j}$

$\mu_1 - \mu_1^0 =$ chemical potential difference for solvent in gel vs pure solvent

$$\Rightarrow \quad \mu_1 - \mu_1^0 = \left(\frac{\partial \Delta G_{mix}}{\partial n_1} \right)_{T,P,n_2} + \left(\frac{\partial \Delta G_{elastic}}{\partial \alpha_s} \right) \left(\frac{\partial \alpha_s}{\partial n_1} \right)_{T,P,n_2}$$

ΔG_{mix} and Flory Huggins

- n_1 moles of solvent
- n_2 moles of polymer

$$[n_1 + n_2 x_2] N_A = N_0$$

recall

$$\boxed{\frac{\Delta G_m}{N_0} = kT\left[\chi\phi_1\phi_2 + \frac{\phi_1}{x_1}\ln\phi_1 + \frac{\phi_2}{x_2}\ln\phi_2\right]}$$

equivalently

$$\Delta \mathrm{G}_{\mathrm{mix}} = RT[n_1\ln\phi_1 + n_2\ln\phi_2 + n_1\chi_{12}\phi_2]$$

some math

$$\left(\frac{\partial \Delta \mathrm{G}_{\mathrm{mix}}}{\partial \mathrm{n}_1}\right) = RT[\ln\phi_1 + \phi_2(1 - \frac{1}{x_2}) + \chi_{12}\phi_2^2]$$

Since $x_2 \to \infty$ for a network (one megamolecule)

$$\left(\frac{\partial \Delta \mathrm{G}_{\mathrm{mix}}}{\partial \mathrm{n}_1}\right) = RT[\ln\phi_1 + \phi_2 + \chi_{12}\phi_2^2]$$

$\Delta G_{\text{elastic}}$ and Rubber Elasticity

new term

$$\Delta G_{\text{elastic}} = -T\Delta S_{elastic}$$

$$\Delta S_{elastic} = -\frac{k}{2}\left(\left[\ (\alpha_x^2+\alpha_y^2+\alpha_z^2)-3\ \right]-\ln\frac{V}{V_0}\right)$$

- new term is an additional entropy increase per subchain, due to increased volume available on swelling, of

$$\frac{k}{2}\ln\left(\frac{V}{V_0}\right)$$

- for N subchains

$$\Delta S_{elastic} = -\frac{k}{2}N\left(3\alpha_s^2-3-\ln\frac{V}{V_0}\right)$$

$\Delta G_{\text{elastic}}$ cont'd

$$\left(\frac{\partial \Delta G_{\text{elastic}}}{\partial n_1}\right) = \underline{\left(\frac{\partial \Delta G_{\text{elastic}}}{\partial \alpha_s}\right)}\underline{\left(\frac{\partial \alpha_s}{\partial n_1}\right)}$$

$$\underline{\left(\frac{\partial \Delta G_{\text{elastic}}}{\partial \alpha_s}\right)} = \frac{NkT}{2}\frac{\partial}{\partial \alpha_s}\left(3\alpha_s^2 - 3 - \ln\frac{\alpha_s^3 V_0}{V_0}\right)$$

$$= \frac{NkT}{2}\left(6\alpha_s - \frac{1}{\alpha_s^3}(3\alpha_s^2)\right) = \frac{NkT}{2}\left(6\alpha_s - \frac{3}{\alpha_s}\right)$$

To calculate $\underline{\dfrac{\partial \alpha_s}{\partial n_1}}$

$$\alpha_s^3 = \frac{V}{V_0} = \frac{V_0 + n_1 v_1}{V_0} \quad \text{or} \quad \alpha_s = \left(1 + \frac{n_1 v_1}{V_0}\right)^{1/3}$$

where v_1 is the molar volume of the solvent

$$\frac{\partial \alpha_s}{\partial n_1} = \frac{1}{3}\left(1 + \frac{n_1 v_1}{V_0}\right)^{-2/3}\frac{v_1}{V_0} = \frac{1}{3\alpha_s{}^2}\frac{v_1}{V_o}$$

$\Delta G_{\text{elastic}}$ cont’d

collecting terms

$$\left(\frac{\partial \Delta G_{\text{elastic}}}{\partial n_1}\right) = \left(\frac{\partial \Delta G_{\text{elastic}}}{\partial \alpha_s}\right)\left(\frac{\partial \alpha_s}{\partial n_1}\right) = \frac{NkT}{2}\left(6\alpha_s - \frac{3}{\alpha_s}\right)\frac{1}{3\alpha_s^2}\frac{v_1}{V_0}$$

Now express
in terms of $\phi_2 \quad and \quad M_x$

$$\left(\frac{\partial \Delta G_{\text{elastic}}}{\partial n_1}\right) = NkT\frac{v_1}{V_0}\left(\phi_2^{1/3} - \frac{\phi_2}{2}\right) = \frac{RT\rho v_1}{M_x}\left(\phi_2^{1/3} - \frac{\phi_2}{2}\right)$$

Collecting the terms we’ve worked out,

$$\mu_1 - \mu_1^0 = RT[\ln \phi_1 + \phi_2 + \chi_{12}\phi_2^2] + \frac{RT\,\rho v_1}{M_x}\left(\phi_2^{1/3} - \frac{\phi_2}{2}\right)$$

At equilibrium, $\mu_1 = \mu_1^0$

$$\ln(1-\phi_2) + \phi_2 + \chi_{12}\phi_2^2 = -\frac{\rho v_1}{M_x}\left(\phi_2^{1/3} - \frac{\phi_2}{2}\right)$$

Determination of χ_{12}, M_x from Swelling Experiments

I. Generally ρ, v_1 are known

ϕ_2 measured from equilibrium swelling ratio $\frac{V}{V_0}$

If M_x is known from elastic modulus of dry rubber then, χ_{12} available from single swelling experiment

---

II. ρ, v_1, ϕ_1, ϕ_2 known as above

Assume, χ_{12} known from $\frac{\pi}{c_z}$ measurements for polymer-solvent solution. Then, M_x available from single swelling experiment

---

The Most Relaxed Gel: Swell polymer in a θ solvent so that the chains overlap and then crosslink. In this case, swollen chains have their unperturbed dimensions. M_x will be large since there are fewer subchains per unit volume in the dilute and swollen state ($c_2 \sim c_2^*$ in order to form network). The maximum extension of this type of gel can be HUGE!!

Practice Problems to Try

(1) Calculate M_x from known swelling ratio and χ

$$\frac{V}{V_0} = 4 \qquad \rho = 1.0 \text{g/cm}^3 \qquad \overline{v}_1 = 40 \ \text{cm}^3\text{/mole}$$

$\chi =$ Š 0.2

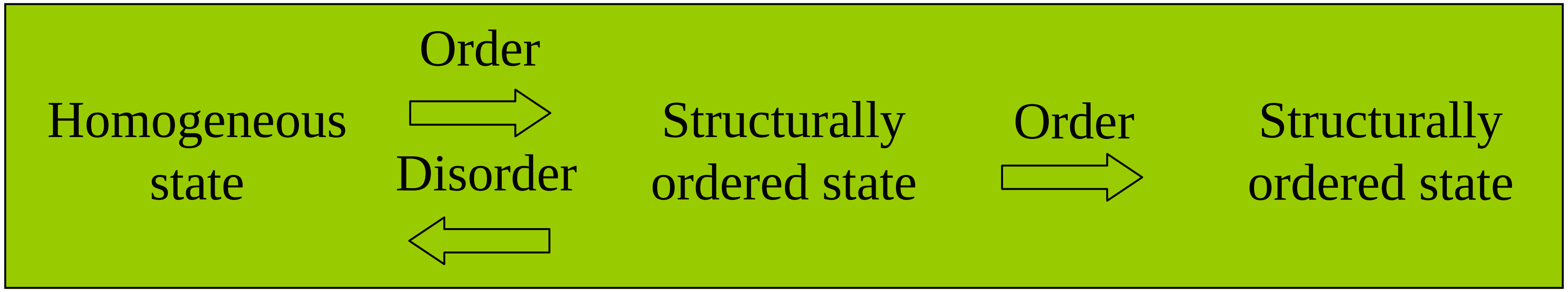
ANS:400 g/mole

(2) Suppose M_x=5,000 g/mole and $\chi = 0.5$,
ρ=1.0g/cm^{3,} $\overline{v}_1 = 40 \ cm^3 / mole$

What is the % solvent in the network for equilibrium swelling?

End of material that will be covered by the 1st exam.

Self Organization



Homogeneous state

Order

Disorder

Structurally ordered state

Order

Structurally ordered state

- Competing interactions: Enthalpy (H) vs. Entropy (S)
- Free energy landscape: entropic frustration, multiple pathways
- Order forming processes
  - (Macro)Phase separation
  - Microphase separation
  - Mesophase formation
  - Adsorption/complexation
  - Crystallization
- Selection of symmetries and characteristic lengths
  - Chemical affinities (long range correlations)
  - Interfacial tension

Muthukumar, M., Ober, C.K. and Thomas, E.L., "Competing Interactions and Levels of Ordering in Self-Organizing Materials," *Science*, 277, 1225-1237 (1997).

Competing Interactions and Levels of Ordering in Self-Organizing (Soft) Materials

Materials

- liquid crystals
- block copolymers
- hydrogen bonded complexes
- nanocrystals

Structural order over many length scales

- atomic
- molecular
- mesogens
- domains
- grains

increasing size scale

Outcome:

Precise shapes, structures and functions

Strategic Design for Materials with Multiple Length Scales

- **Synthetic design strategy**
  - Intramolecular shapes and interaction sites (molecular docking, etc)
  - Control multistep processing to achieve long range order
- **Interactions**
  - sequential
  - simultaneous
  - synergistic
  - antagonistic

Reduction of disorder (S ↓)

Strengthening of intra- and inter-molecular interactions (H ↑)

- **Structural design strategy**
  - organize starting from initially homogeneous state
  - organize from largest to smallest length scale

(induce a global pattern, followed by sequential development of finer details)

- **Selection of growth directions**
  - applied bias field(s)
  - substrate patterning
- **Prior-formed structures impose boundary conditions**
  - commensuration of emergent and prior length scales
  - compatibility of structures across interfaces

Principles of Self Organization:
Microphase Separation Block Copolymers

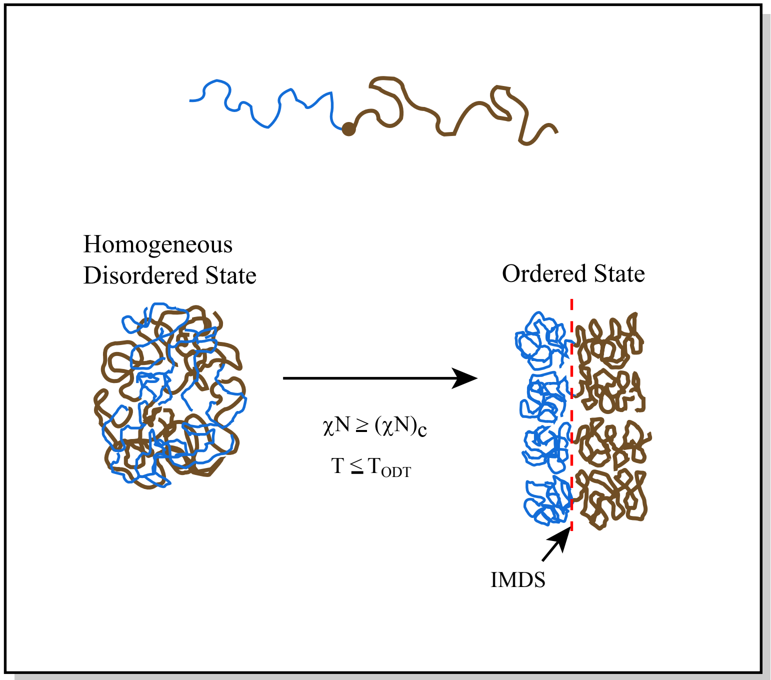
The min - max principle:

- *Minimize* interfacial area
- *Maximize* chain conformational entropy

Result:

- Morphology highly coupled to molecular characteristics
- Morphology serves as a sort of molecular probe

Gas of junctions



Junctions on Surfaces

Figure by MIT OCW.

Microdomain Morphologies and Symmetries - Diblock Copolymers

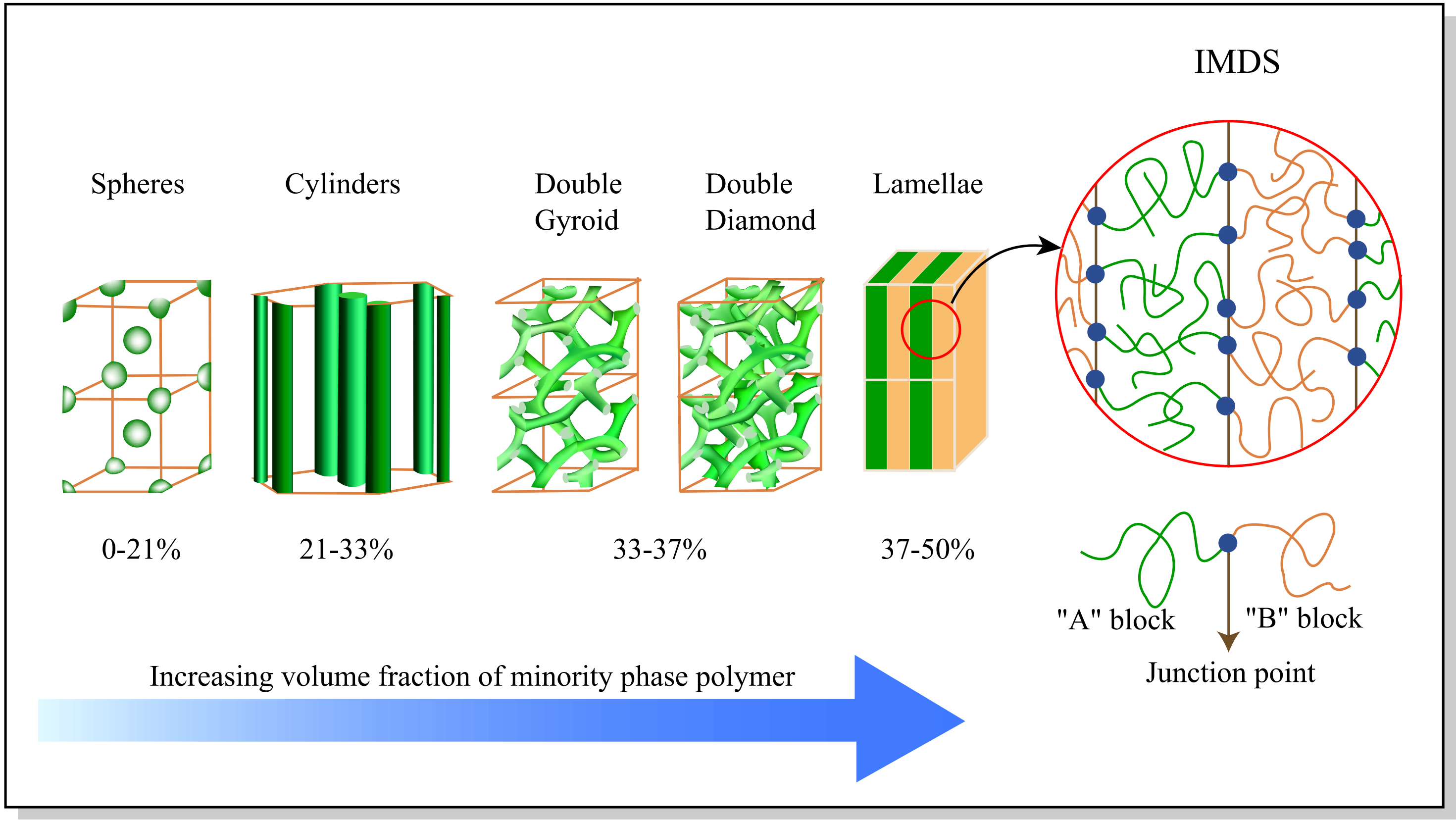


Figure by MIT OCW.

Hierarchical Structure & Length Scales

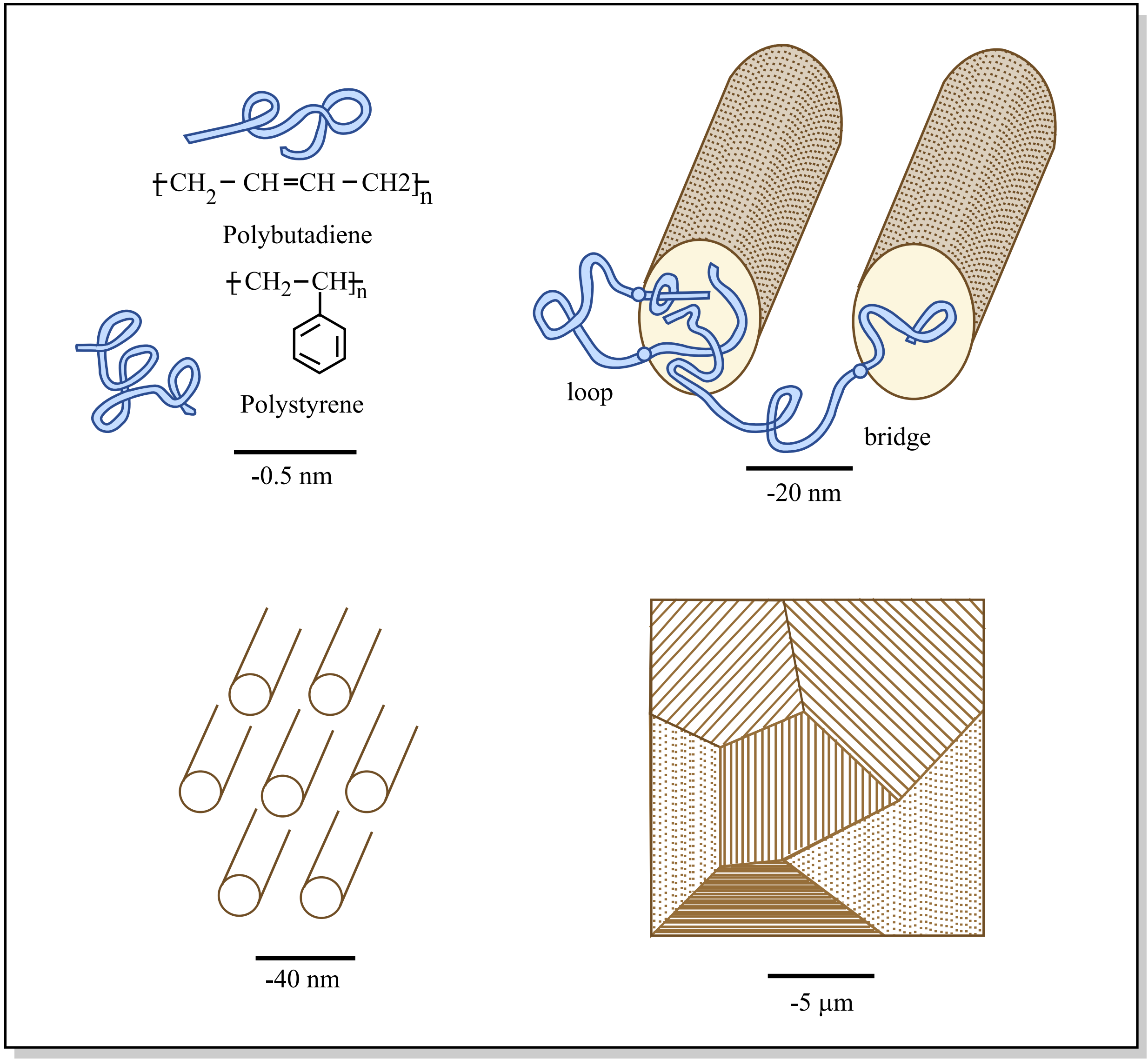
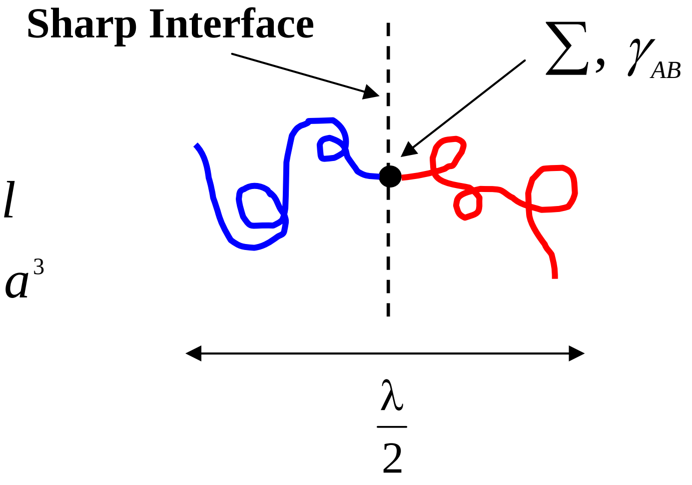


Figure by MIT OCW.

Computing the characteristic length scale:
Equilibrium Domain Spacing

Min-Max Principle



G = Free Energy per Chain
N = # of segments = $N_A + N_B$
a = Step Size $a_A \sim a_B$
λ = Domain Periodicity
Σ = Interfacial Area/Chain
γ_{AB} = Interfacial Energy = $\frac{kT}{a^2}\sqrt{\frac{\chi_{AB}}{6}}$

segmental volume $\sim a^3$

$$\chi_{AB} = \text{Segment - Segment Interaction Parameter} = \frac{z}{kT}\left[\varepsilon_{AB} - \frac{1}{2}\left[\varepsilon_{AA} + \varepsilon_{BB}\right]\right]$$

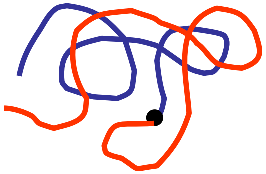
Strong Segregation Limit → **$N\chi$ very large (high MW and positive χ),**

=> **pure A domains & pure B microdomains**

Characteristic Period (Lamellae)

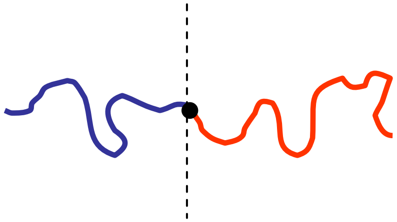
State 1

Melt



State 2

Microdomains



$$\Delta G = \Delta H - T\Delta S$$

$$= \underbrace{\gamma_{AB}\sum - N\chi_{AB}\phi_A\phi_B kT}_{\textbf{Enthalpic}\text{ Term}} + \underbrace{\frac{3}{2}kT\left[\frac{(\lambda/2)^2}{Na^2}-1\right]}_{\textbf{Entropic}\text{ Spring Term}}$$

Note: $Na^3 = \frac{\lambda}{2}\Sigma$

$$\Delta G(\lambda) = \frac{kT}{a^2}\sqrt{\frac{\chi_{AB}}{6}}\,\frac{Na^3}{(\lambda/2)} - N\chi_{AB}\phi_A\phi_B kT + \frac{3}{2}kT\left[\frac{(\lambda/2)^2}{Na^2}-1\right]$$

$$\Delta G(\lambda) = \frac{\alpha}{\lambda} - const1 + \beta\lambda^2 - const2$$

$$\frac{\partial \Delta G}{\partial \lambda} = 0 \longrightarrow 0 = \frac{-\alpha}{\lambda^2} + 2\beta\lambda$$

Free Energy of Lamellae con't

Thus, the optimum period of the lamellae repeat unit is :

$$\boxed{\lambda_{opt} = \sqrt[3]{\frac{\alpha}{2\beta}} \cong aN^{2/3}\chi^{1/6}}$$

Important Result: Domain dimensions scale as $\lambda \sim N^{2/3}$
Chains in microdomains are therefore stretched
compared to the homogeneous melt state

$$\Delta G(\lambda_{opt}) = 1.2kTN^{1/3}\chi_{AB}{}^{1/3} - \frac{3}{2}kT$$

Order-Disorder Transition (ODT)

Estimating the Order-Disorder Transition:

$$G_{LAM} \cong G_{Disordered}$$

$$1.2kTN^{1/3}\chi^{1/3} \approx N\chi_{AB}\phi_A\phi_B kT$$ since both terms $>> \frac{3}{2}kT$

For a 50/50 volume fraction, $\phi_A\phi_B = 1/4$ so

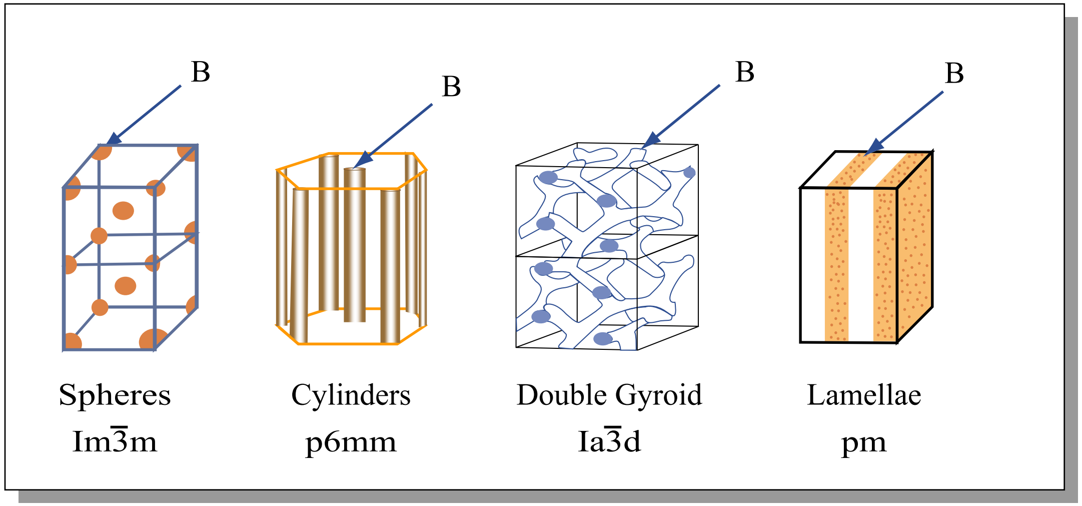
$$1.2N^{1/3}\chi^{1/3} = N\chi/4$$

The critical Nχ is just $(N\chi)_c = (4.8)^{3/2} \sim 10.5$

$N\chi < 10.5$	**Homogeneous, Mixed Melt**
$N\chi > 10.5$	**Lamellar Microdomains**

Original Order-Disorder Diblock Phase Diagram computed by L. Leibler , *Macromolecules*, 1980

Diblock Copolymer Morphology Diagram



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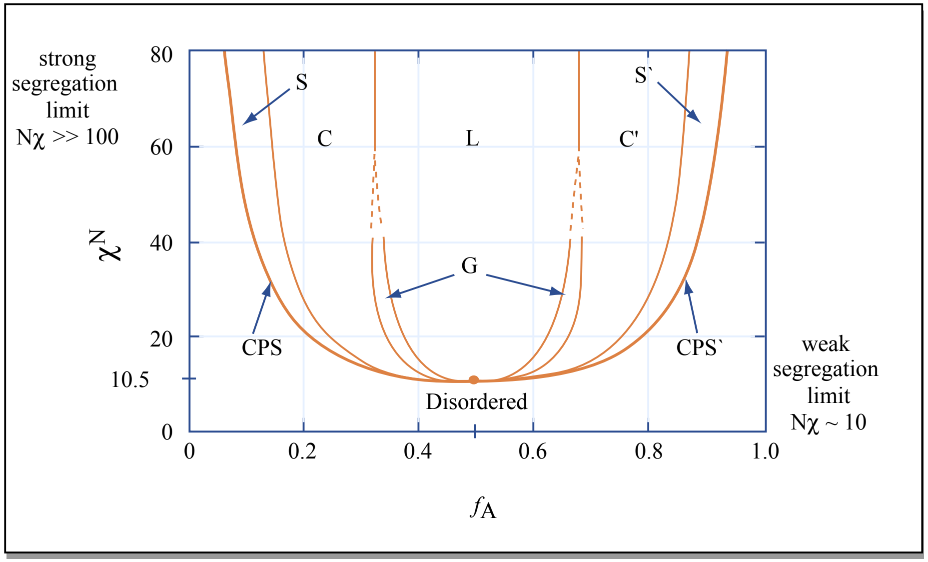

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