Example: Uniaxial Deformation

With Axi-symmetric sample cross-section

Deform along $l_0 \rightarrow l_x$, $\alpha_x = \frac{l_x}{l_0}$, $d\alpha_x = \frac{dl_x}{l_0}$

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

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

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

$$F_x = -T \frac{\partial}{\partial l_x} \left( \Delta S(\alpha_x) \right) \bigg|_{T,P} = \frac{kT}{2} \frac{\partial}{\partial l_x} \left( \alpha_x^2 + \frac{2}{\alpha_x} - 3 \right)$$
Uniaxial Deformation cont’d

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

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

Stress-Extension Relationship

\[ \sigma_{xx} = \frac{F_x(\alpha_x)}{A_0} = \frac{zkT}{A_0l_0} \left(\alpha_x - \frac{1}{\alpha_x} \right) \text{ for } z \text{ subchains in volume } V \]

\[ A_0l_0 = V \quad \frac{z}{V} = \# \text{ of subchains per unit volume} = N_{\text{xlinks}} \]

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

\[ \text{mass/vol moles of crosslinks/volume} = M_x = \frac{\rho}{N_x/N_A} \]

\[ \sigma_{xx}(\alpha_x) = \frac{\rho N_A kT}{M_x} \left(\alpha_x - \frac{1}{\alpha_x^2} \right) \text{ uniaxial} \]
Young’s Modulus of a Rubber

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

\[ E = 3\rho RT/M_x \]

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 \( M_x \)
- 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

$\sigma(\alpha)$

Small deformations

High tensile elongations

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

Figure by MIT OCW.
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?
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](attachment:styrene.png) ![divinyl benzene](attachment:divinyl_benzene.png)

- 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, \( \Delta G_{mix} \)

**Flory Huggins Theory** \((\chi, x_1, x_2, \phi_1, \phi_2)\)

**Rubber Elasticity Theory** \(\Delta G_{elastic}\)
At equilibrium, $\Delta G_{\text{mix}} = -\Delta G_{\text{elastic}}$

1. Thermodynamically good solvent swells rubber
   - favorable $\chi$ interaction
   - favorable $\Delta S_{\text{mix}}$

2. BUT Entropy elasticity of network ($\Delta S_{\text{elastic}}$) exerts retractive force to oppose swelling

Crosslinked Rubber

Swollen Rubber

volume, $V$

subchain, $\left\langle r_0^2 \right\rangle^{1/2}_{\text{subchain}}$
Thermo of Swollen Network cont’d

\[ \alpha_x = \text{linear swelling ratio} = \frac{x'}{x} \]

\[ \phi_2 = \text{volume fraction polymer} = \frac{V_0}{V} \]

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

Isotropic swelling \( \alpha_x = \alpha_y = \alpha_z = \alpha_s \)

\[ V_0 \alpha_s^3 = V \quad \phi_2 = \frac{V_0}{V} \quad \text{so} \quad \alpha_s^3 = \frac{1}{\phi_2} \]

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

\( \mu_1 - \mu_1^0 = \text{chemical potential difference for solvent in gel vs pure solvent} \)

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

- $n_1$ moles of solvent \[ [n_1 + n_2x_2]N_A = N_0 \]
- $n_2$ moles of polymer

recall \[
\frac{\Delta G_m}{N_0} = kT \left[ \chi \phi_1 \phi_2 + \frac{\phi_1}{x_1} \ln \phi_1 + \frac{\phi_2}{x_2} \ln \phi_2 \right]
\]
equivalently \[\Delta G_{\text{mix}} = RT[n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \chi_{12} \phi_2] \]
some math \[
\left( \frac{\partial \Delta G_{\text{mix}}}{\partial n_1} \right) = RT[\ln \phi_1 + \phi_2(1 - \frac{1}{x_2}) + \chi_{12} \phi_2^2]
\]
Since $x_2 \rightarrow \infty$ for a network (one megamolecule)

\[
\left( \frac{\partial \Delta G_{\text{mix}}}{\partial n_1} \right) = RT[\ln \phi_1 + \phi_2 + \chi_{12} \phi_2^2]
\]
$\Delta G_{\text{elastic}}$ and Rubber Elasticity

\[ \Delta G_{\text{elastic}} = -T \Delta S_{\text{elastic}} \]

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

• 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

\[ \Delta S_{\text{elastic}} = -\frac{k}{2} N \left( 3\alpha_s^2 - 3 - \ln \frac{V}{V_0} \right) \]
\[ \Delta G_{\text{elastic}} \text{ cont'd} \]

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

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

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

To calculate \( \frac{\partial \alpha_s}{\partial n_1} \)

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

where \( v_1 \) is the molar volume of the solvent

\[
\frac{\partial \alpha_s}{\partial n_1} = \frac{1}{3} \left( 1 + \frac{n_1 v_1}{V_0} \right)^{-2/3} \frac{v_1}{V_0} = \frac{1}{3} \frac{v_1}{\alpha_s^2 V_0}
\]
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 $\chi_{12}$, $M_x$ from Swelling Experiments

I. Generally $\rho$, $v_1$ are known

$\phi_2$ measured from equilibrium swelling ratio $\frac{V}{V_0}$

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

II. $\rho$, $v_1$, $\phi_1$, $\phi_2$ known as above

Assume, $\chi_{12}$ known from $\frac{\pi}{c_z^2}$ measurements for polymer-solvent solution. Then, $M_x$ available from single swelling experiment

The Most Relaxed Gel: Swell polymer in a $\theta$ 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 $\chi$

\[
\frac{V}{V_0} = 4, \quad \rho = 1.0 \text{g/cm}^3, \quad \bar{v}_1 = 40 \text{ cm}^3/\text{mole}
\]

\[
\chi = 0.2
\]

ANS: 400 g/mole

(2) Suppose $M_x = 5,000$ g/mole and $\chi = 0.5$

\[
\rho = 1.0 \text{g/cm}^3, \quad \bar{v}_1 = 40 \text{ cm}^3/\text{mole}
\]

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

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

- 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

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 Reduction of disorder (S ↓)
  - simultaneous
  - synergistic Strengthening of intra- and inter-molecular interactions (H ↑)
  - antagonistic

- **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

0-21% 21-33% 33-37% 37-50%

Increasing volume fraction of minority phase polymer

Figure by MIT OCW.
Hierarchical Structure & Length Scales

\[ \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 \]_n
Polybutadiene

\[ \text{CH}_2 - \text{CH}_n \]
Polystyrene

-0.5 nm

-20 nm

Loop

Bridge

-40 nm

-5 \mu m

Figure by MIT OCW.
Computing the characteristic length scale:
Equilibrium Domain Spacing

**Min-Max Principle**

\[ G = \text{Free Energy per Chain} \]
\[ N = \# \text{ of segments} = N_A + N_B \]
\[ a = \text{Step Size} \quad a_A \sim a_B \]
\[ \lambda = \text{Domain Periodicity} \]
\[ \Sigma = \text{Interfacial Area/Chain} \]
\[ \gamma_{AB} = \text{Interfacial Energy} = \frac{kT}{a^2} \sqrt{\frac{\chi_{AB}}{6}} \]

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

**Strong Segregation Limit**  \[ \rightarrow \quad N\chi \text{ very large (high MW and positive } \chi), \]
\[ \rightarrow \quad \text{pure A domains & pure B microdomains} \]
Characteristic Period (Lamellae)

\[ \Delta G = \Delta H - T\Delta S \]

\[ = \gamma_{AB} \sum - N \chi_{AB} \phi_A \phi_B kT + \frac{3}{2} kT \left[ \frac{\left( \lambda/2 \right)^2}{Na^2} \right] - 1 \]

- **Enthalpic Term**
- **Entropic Spring Term**

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

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

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

\[ \frac{\partial \Delta G}{\partial \lambda} = 0 \quad \Rightarrow \quad 0 = -\frac{\alpha}{\lambda^2} + 2\beta \lambda \]
Thus, the optimum period of the lamellae repeat unit is:

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

**Important Result:** Domain dimensions scale as $\lambda \sim N^{2/3}$

Chains in microdomains are therefore stretched compared to the homogeneous melt state

$$\Delta G(\lambda_{opt}) = 1.2kTN^{1/3} \chi_{AB}^{1/3} - \frac{3}{2}kT$$
Estimating the Order-Disorder Transition:

\[ G_{LAM} \approx G_{\text{Disordered}} \]

\[ 1.2kTN^{1/3}\chi^{1/3} \approx N\chi_{AB}\phi_A\phi_BkT \]

since both terms \( \gg \frac{3}{2}kT \)

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 \( N\chi \) is just \( (N\chi)_c = (4.8)^{3/2} \approx 10.5 \)

\( N\chi < 10.5 \) Homogeneous, Mixed Melt

\( N\chi > 10.5 \) Lamellar Microdomains

Diblock Copolymer Morphology Diagram

Spheres
Im\textsuperscript{3}m

Cylinders
p6mm

Double Gyroid
Ia\textsuperscript{3}d

Lamellae
pm

Figure by MIT OCW.

![Diagram of Diblock Copolymer Morphology](image)

Figure by MIT OCW.