Macromolecular Engineering: Networks and Gels

Lecture 13: Swelling

Prof. Dr. Mark W. Tibbitt, 05. April 2022

Polymeric precursor

Complementary polymer

10 nm scale

Solution of polymeric species

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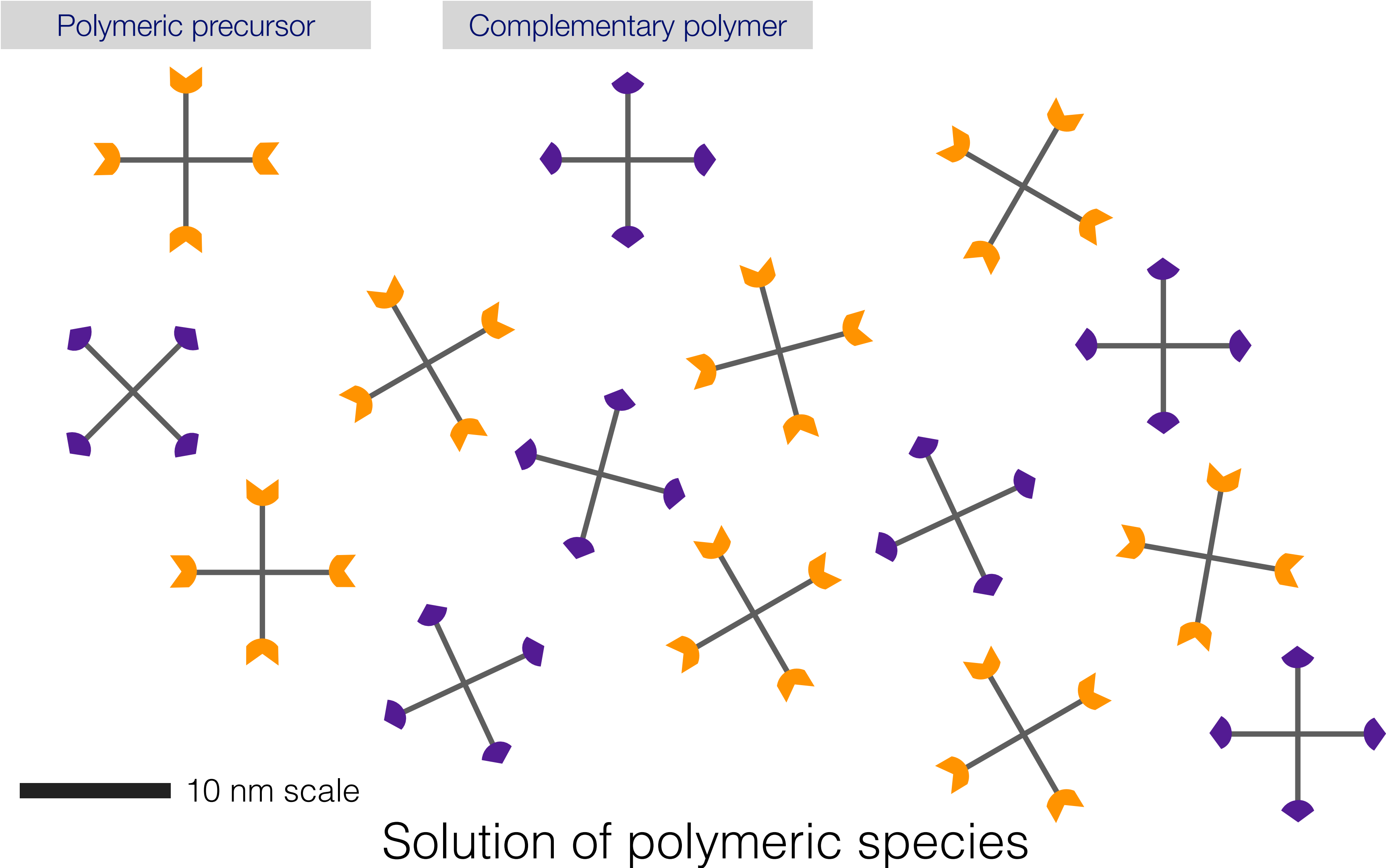
Polymer network or gel
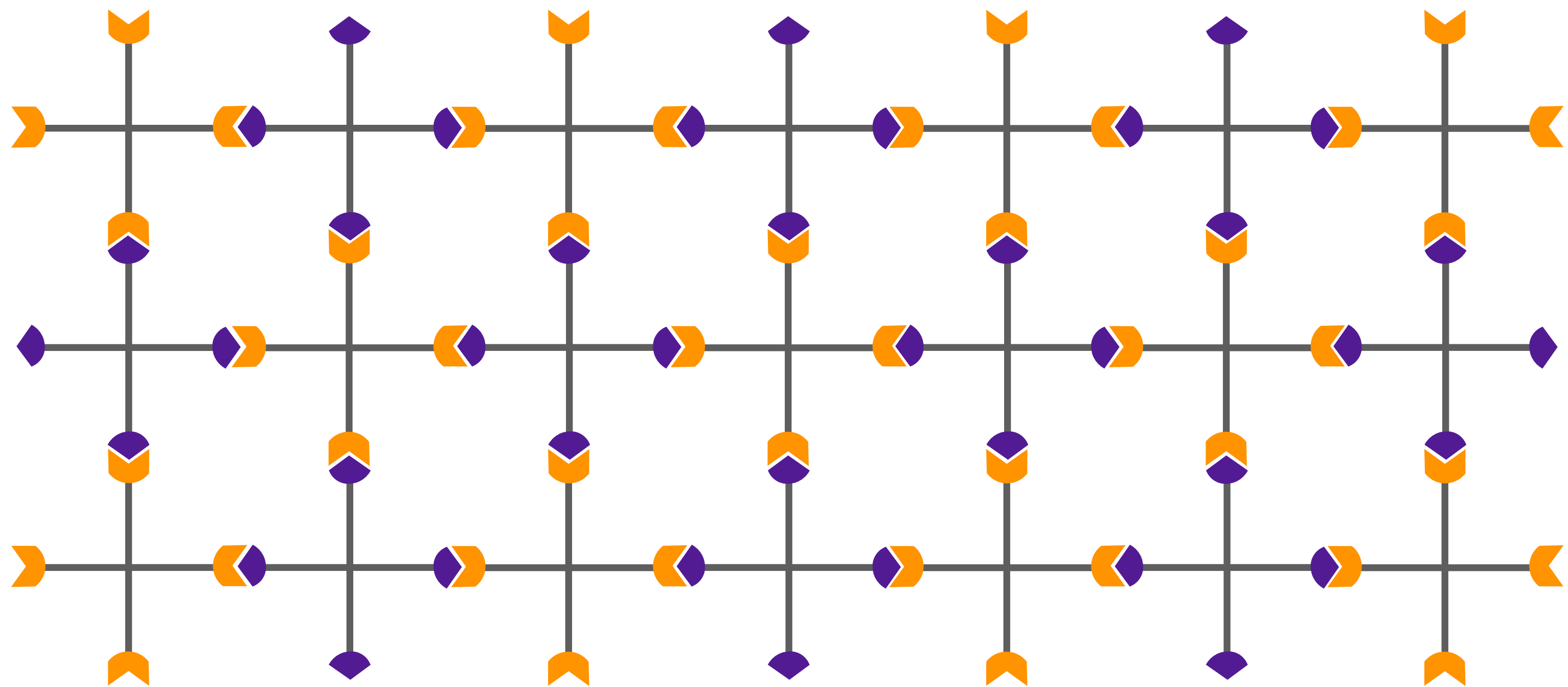
10 nm scale

Viscoelastic insoluble network or gel

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Network architecture

Macroscale Properties

Viscoelasticity

Diffusivity

Surface chemistry

Swelling

Degradation
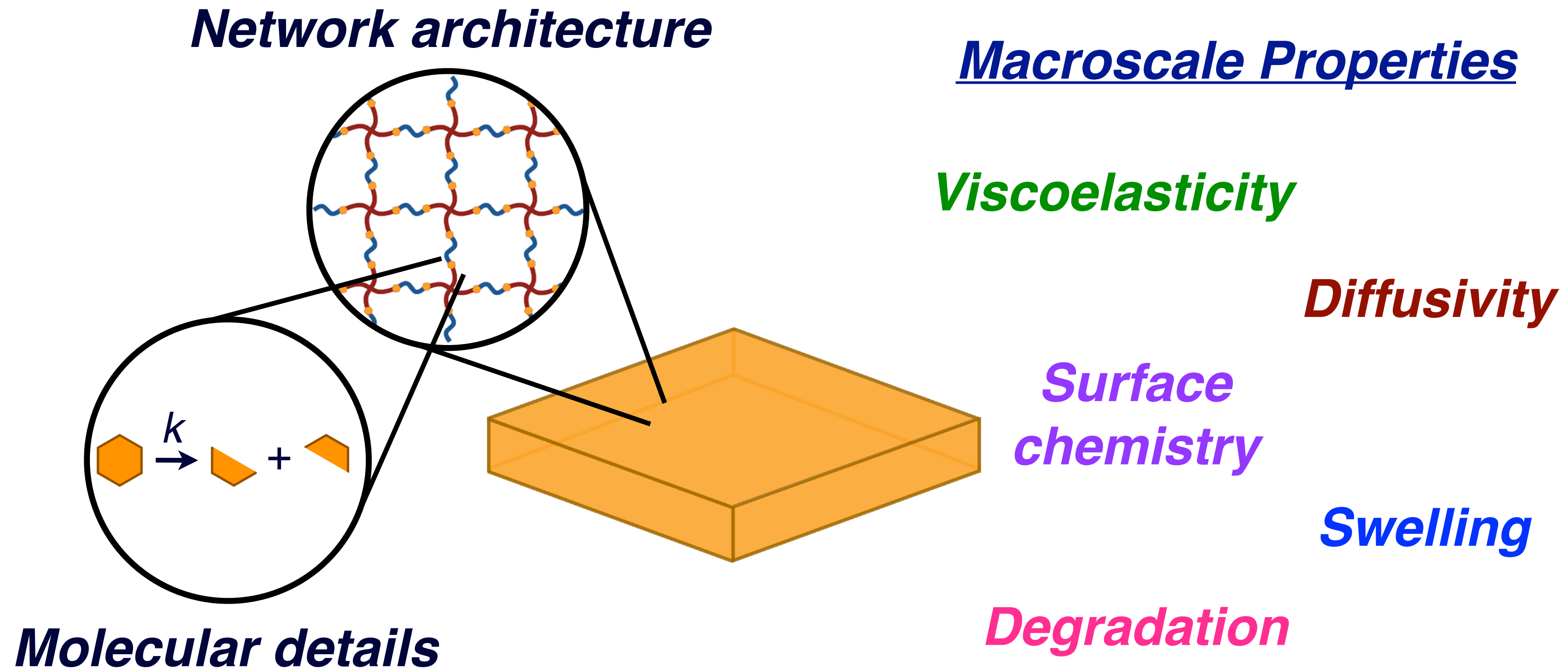
Molecular details

Macromolecular details inform material properties and provide a tunable handle in their design.

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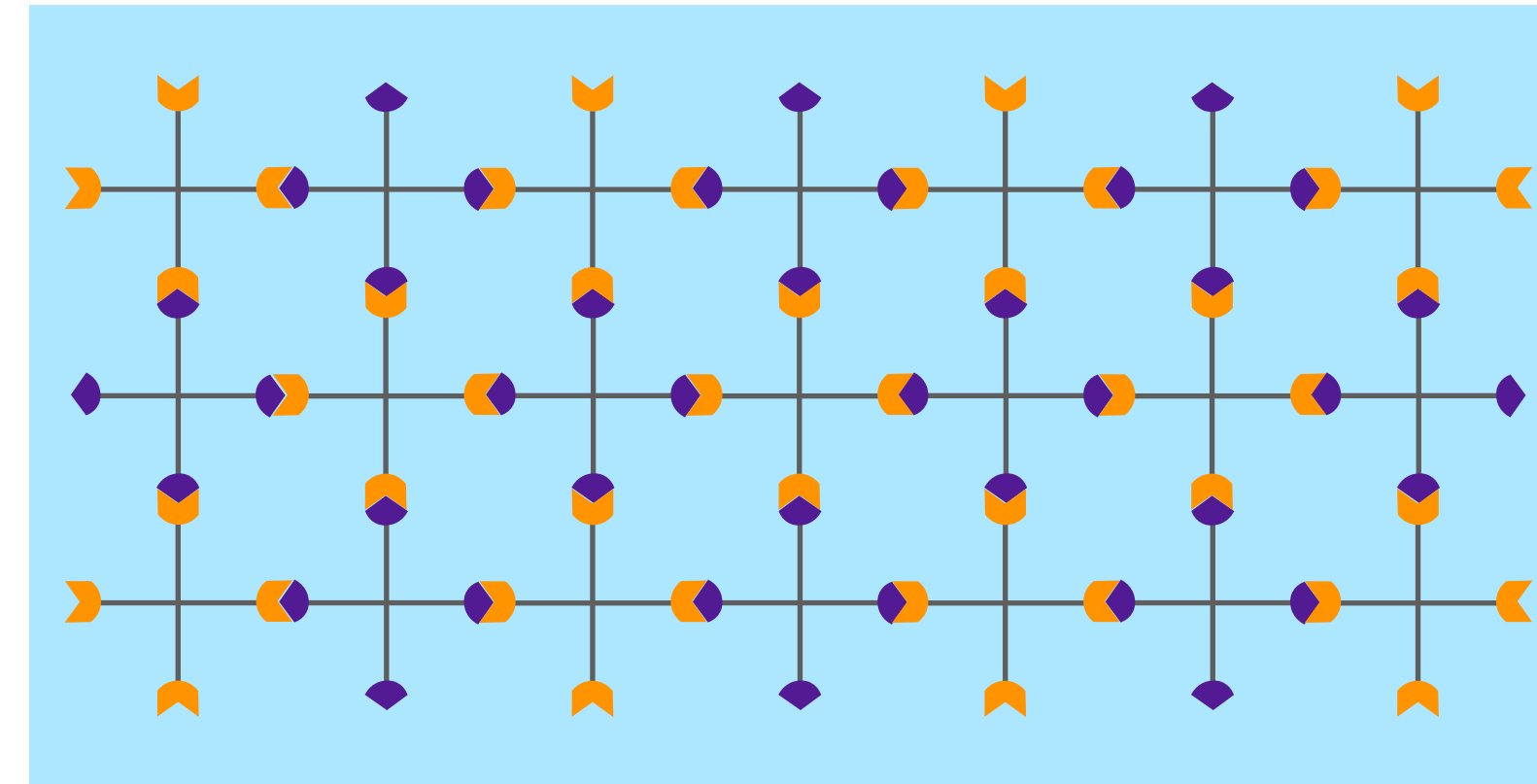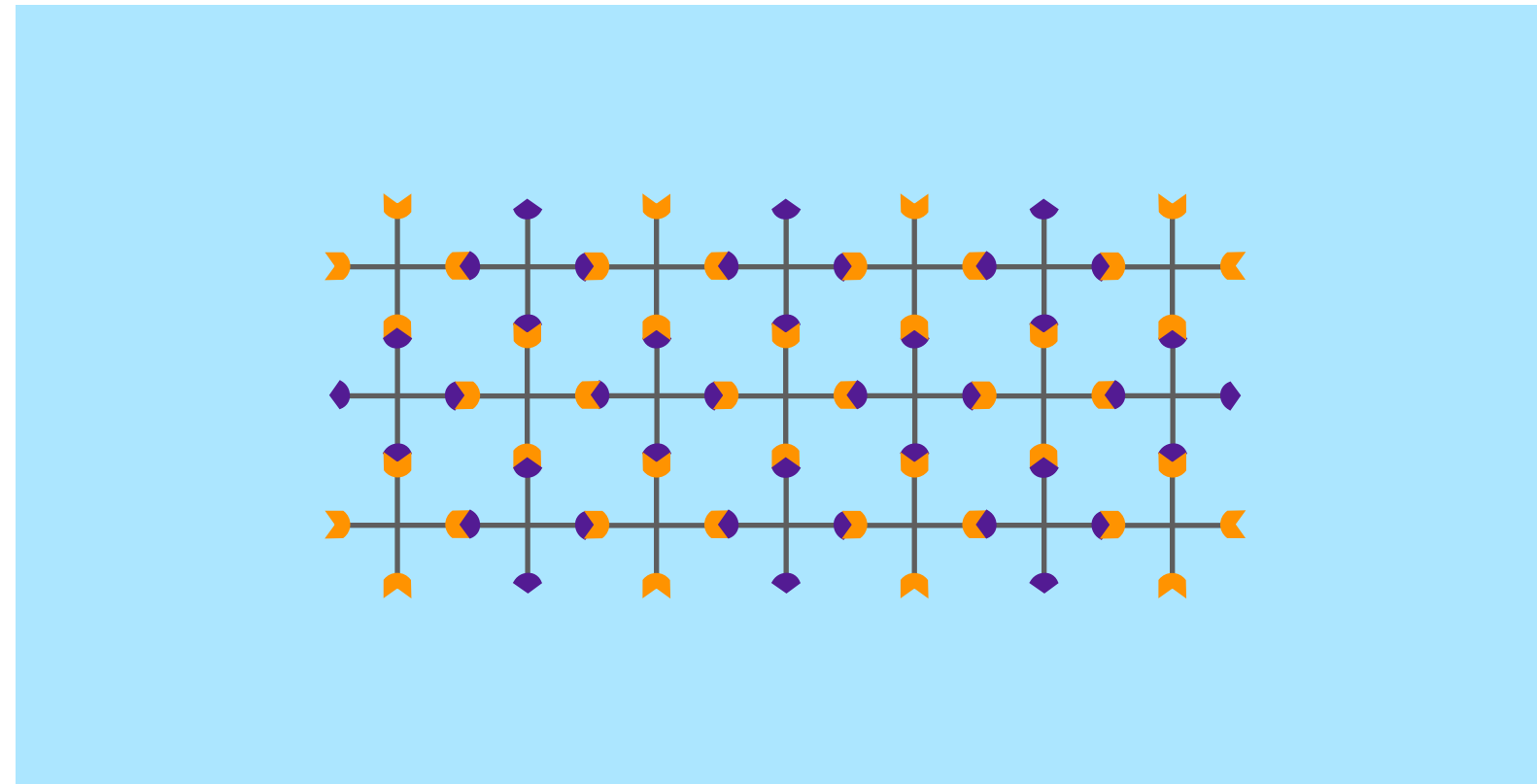
We are interested in the equilibrium swelling ratio once the network is placed in a solvent.

$$Q \equiv \frac{V_p + V_s}{V_p} \quad \text{swelling ratio}$$
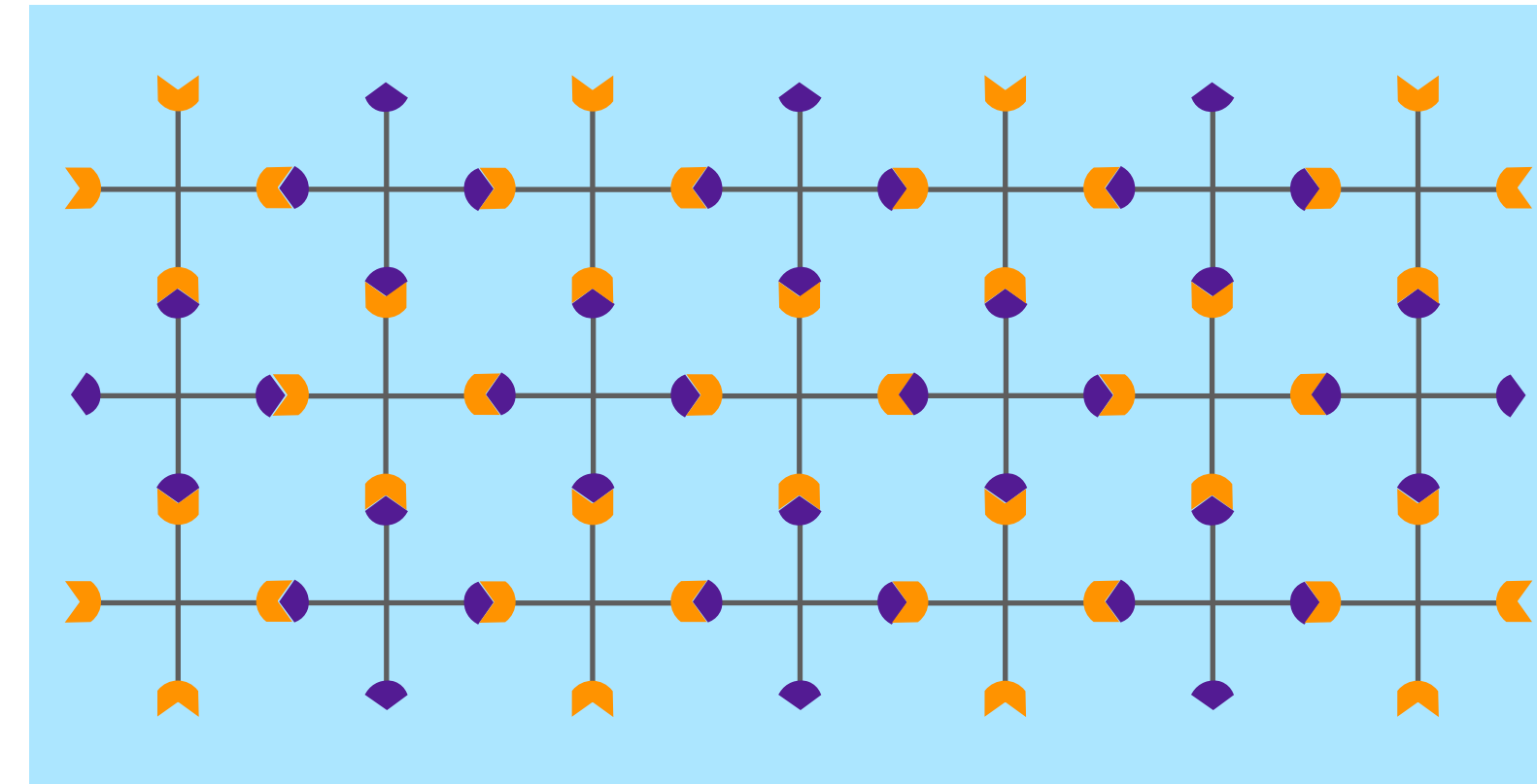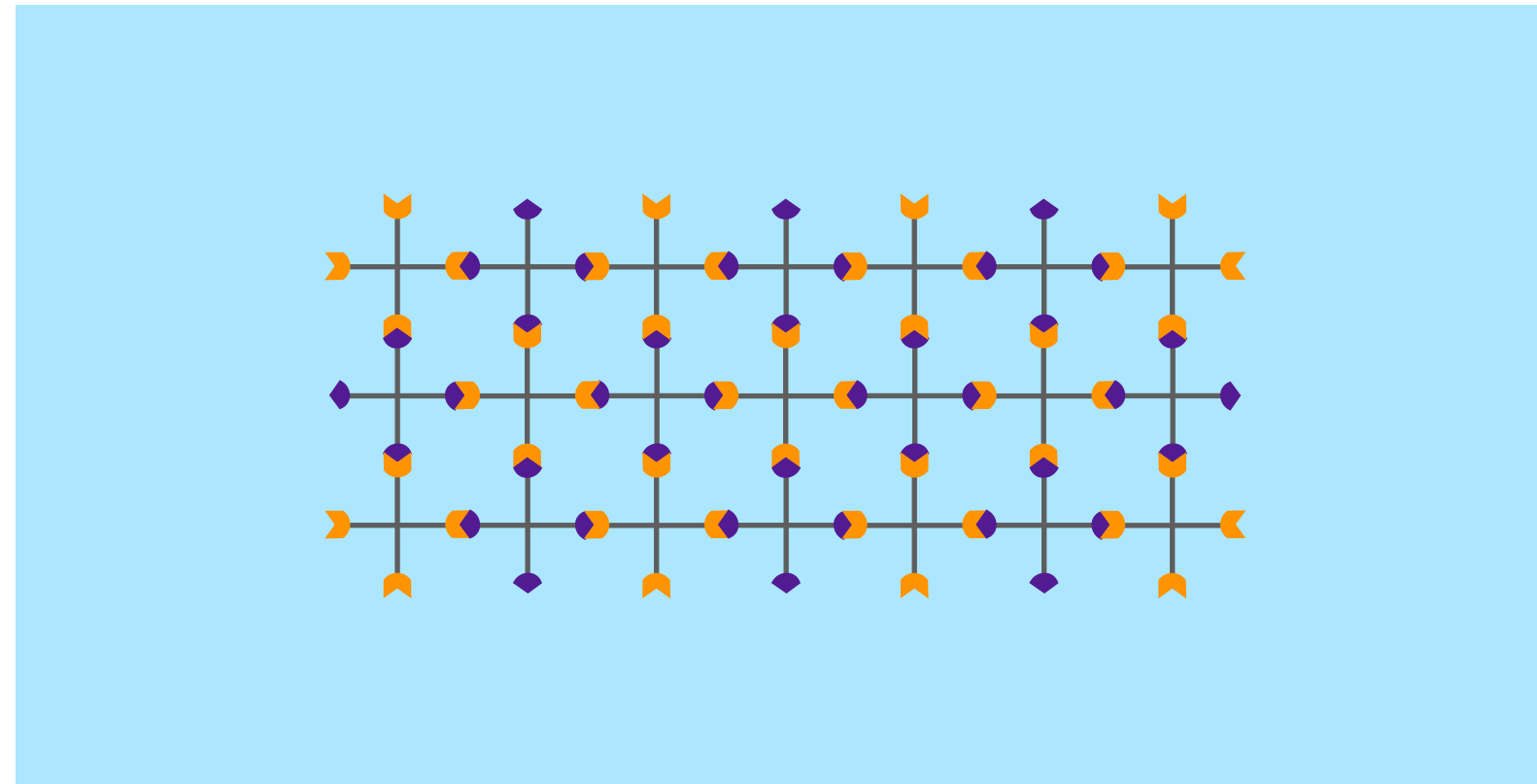
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$$\Delta G = \Delta G_{mix} + \Delta G_{elastic}$$

ΔG_{mix}

Promotes swelling
  - Entropy gain by mixing solvent and polymer
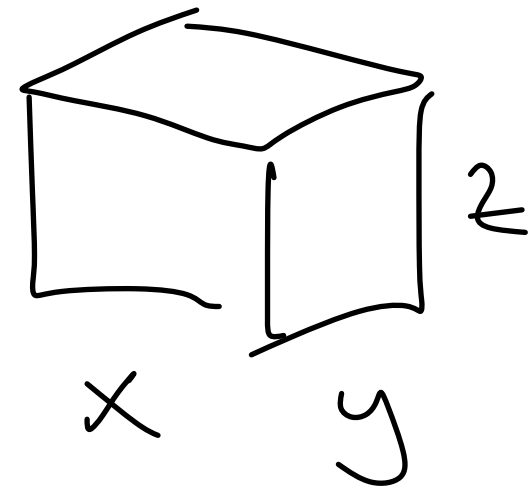 - Potential enthalpic gain from polymer-solvent contacts

$\Delta G_{elastic}$

Resists swelling
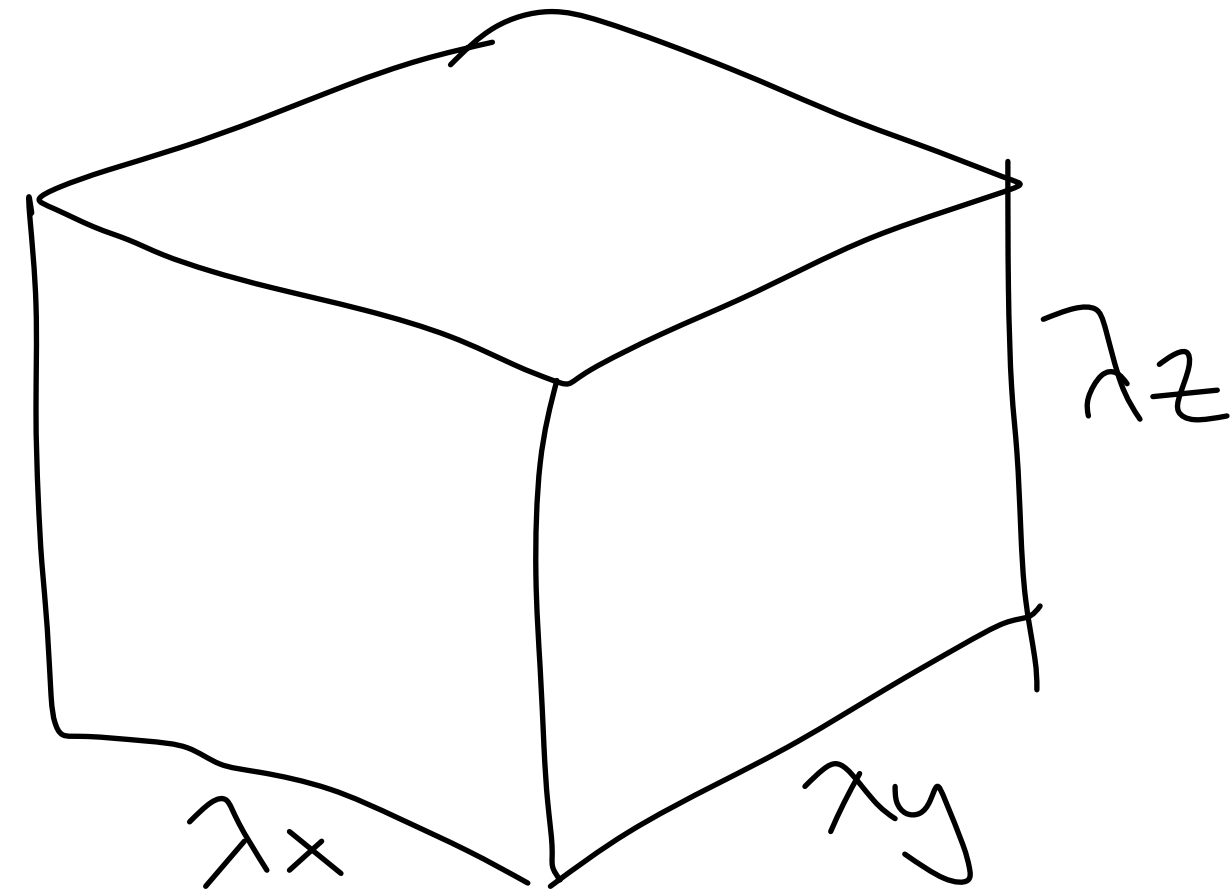 - Loss in entropy as the network chains are stretched

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V_r relaxed state

V_s swollen state

Swell

x y z

λx λy λz

Linear expansion factor λ

$$\lambda_x \lambda_y \lambda_z = \lambda^3 = \frac{V_s}{V_r} = \frac{V_2 + V_{m,1} n_1}{V_r}$$
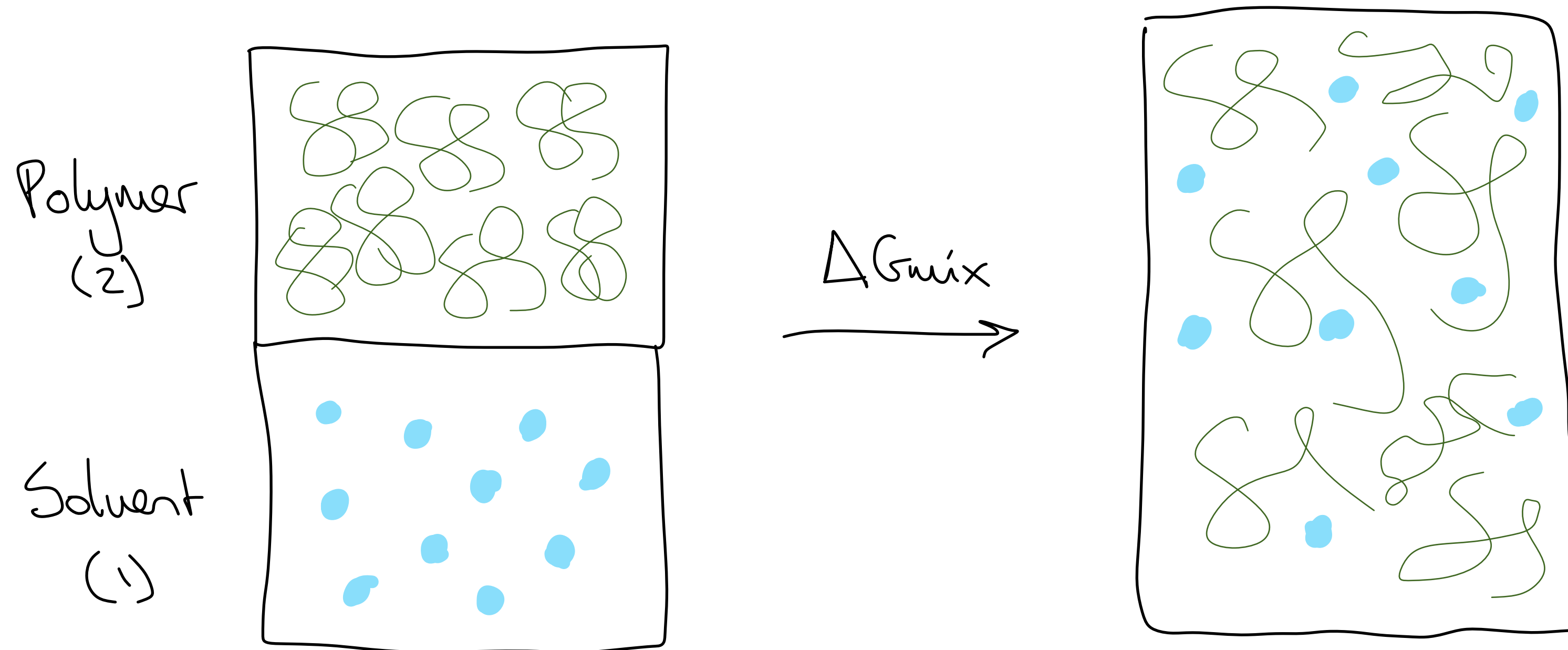
$$\phi_{2,r} = \frac{V_2}{V_r}$$

$$\phi_{2,s} = \frac{V_2}{V_2 + V_{m,1} n_1}$$

$$Q = \frac{1}{\phi_{2,s}}$$

V_2 = polymer volume

n_1 = # of solvent molecules

$V_{m,1}$ = volume of a solvent molecule

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Thermodynamic calculation of polymer-solvent mixing

$$\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix}$$

Polymer
(2)

Solvent
(1)

ΔG_{mix}

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Lattice model with mean-field approximation (Flory-Huggins)

$z = $ # nearest neighbors

$\Delta \omega$

$$\Delta \omega = \omega_{SP} - \frac{\omega_{SS} + \omega_{PP}}{2}$$
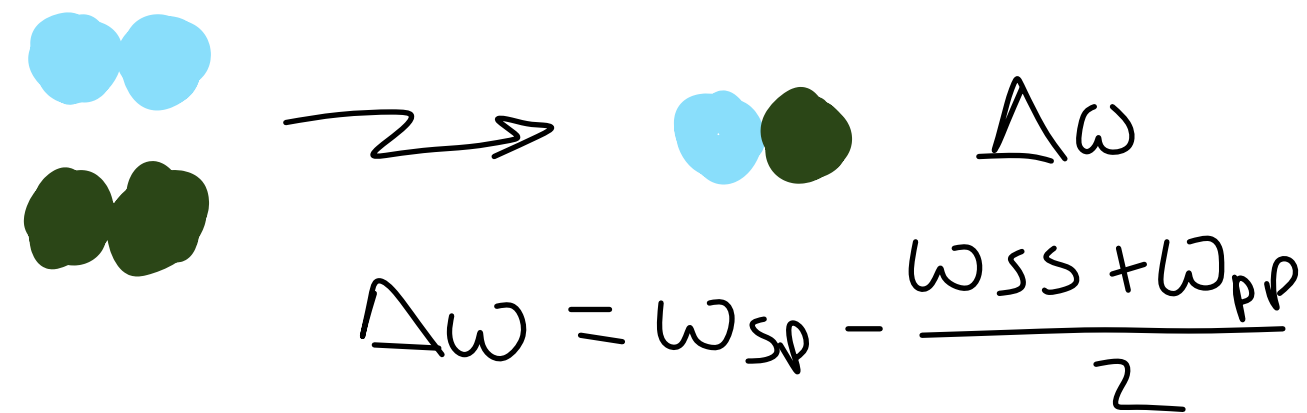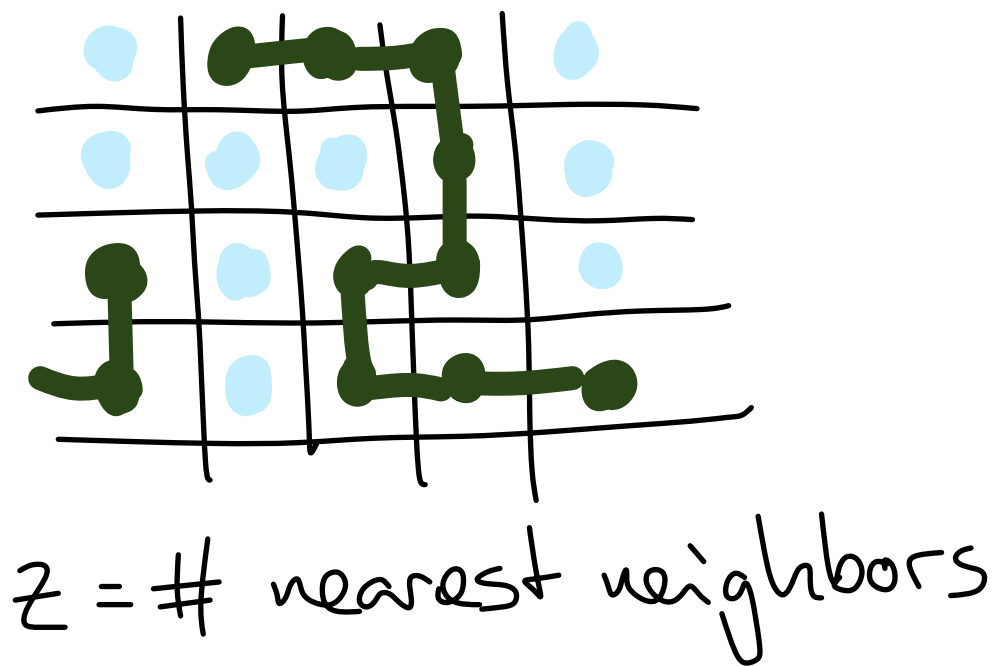
solvent -polymer contacts (δ):

$\delta = ($ # of polymer segments $) \cdot ($ # of contacts w/ solvent molecules per segment $)$

$= n_2 \cdot N_K \cdot z \, \underline{\phi_1}$ Mean-field approach

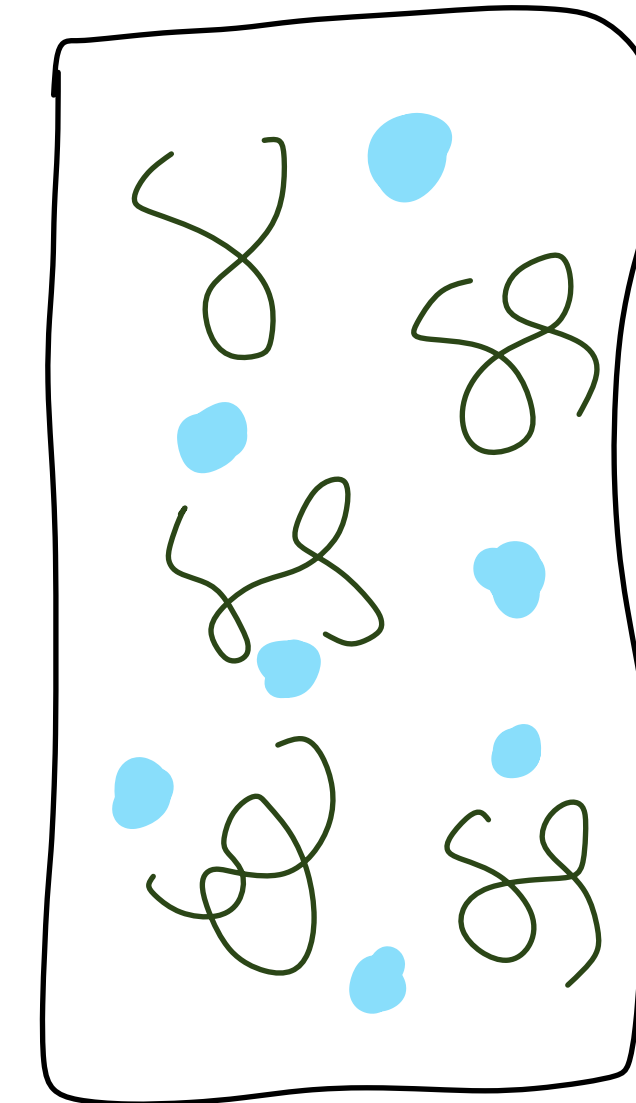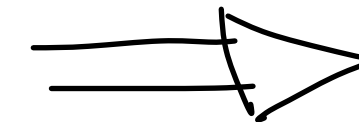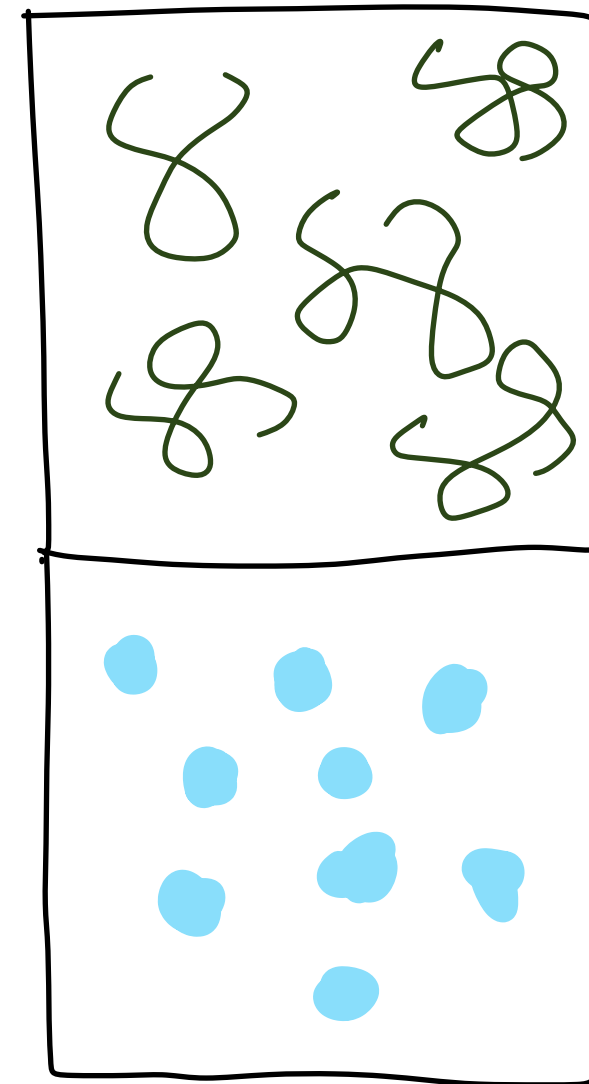Macromolecular Engineering: Networks and Gels
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Lattice model with mean-field approximation (Flory-Huggins)

$z = \#$ nearest neighbors

$$\phi_2 = \frac{n_2 N k}{V} \qquad \phi_1 = \frac{n_1}{V}$$

$$\frac{1}{V} = \frac{\phi_2}{n_2 N k} = \frac{\phi_1}{n_1}$$

$$\therefore \; n_2 N k \phi_1 = n_1 \phi_2$$

$$\Rightarrow \quad \delta = z n_1 \phi_2$$

$$\Delta H_{mix} = z n_1 \phi_2 \Delta \omega$$

$$\chi = \frac{z}{k_B T} \Delta \omega$$

$$\Rightarrow \quad \boxed{\Delta H_{mix} = k_B T \, n_1 \phi_2 \chi}$$

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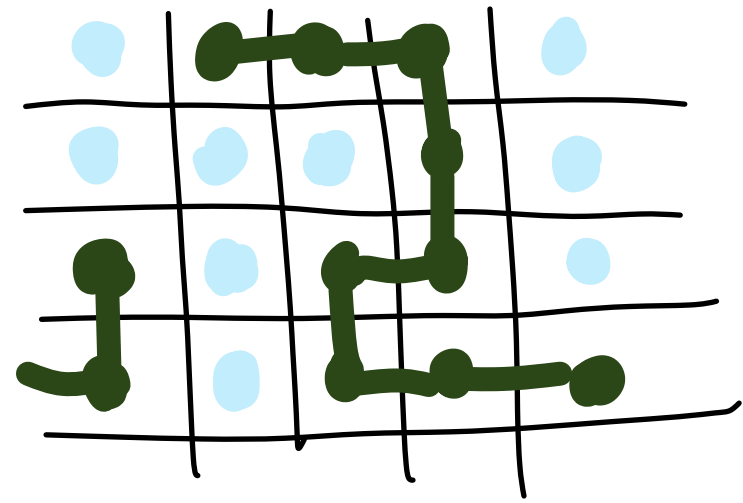
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Lattice model with mean-field approximation (Flory-Huggins)
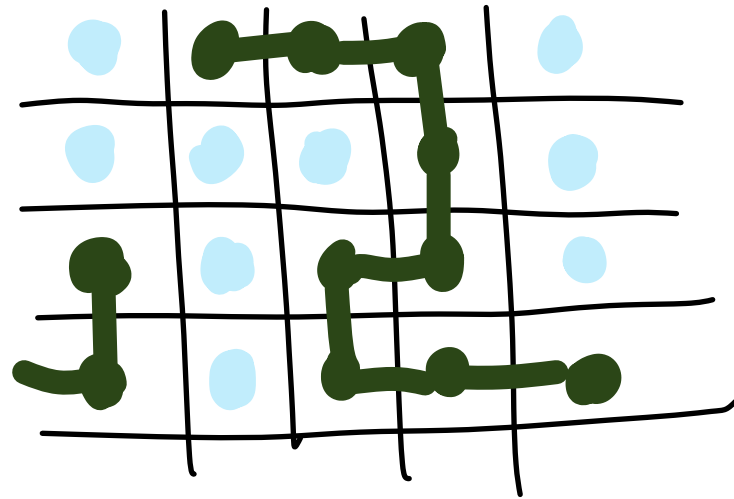
$$S = k_B \ln \omega$$

$$\omega = \frac{N!}{n_1! \, n_2!} \qquad \therefore S = -k_B \left[n_1 \ln x_1 + n_2 \ln x_2 \right]$$

For the polymer-solvent system:

$$\Delta S_{mix} = -k_B \left[n_1 \ln \phi_1 + \frac{n_2}{N_2} \ln \phi_2 \right]$$

In the case of a network/gel, $n_2 = 0$ b/c there are no free chains

$$\boxed{\Delta S_{mix} = -k_B \, n_1 \ln \phi_1}$$

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Lattice model with mean-field approximation (Flory-Huggins)

Total Free Energy of Mixing:

$$\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix}$$

$$= k_B T n_1 \phi_2 \chi - T \left(-k_B n_1 \ln \phi_1 \right)$$

$$\boxed{\Delta G_{mix} = k_B T \left[n_1 \phi_2 \chi + n_1 \ln \phi_1 \right]}$$

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Affine deformations [can substitute w/ other models]:

Individual chain

Also stretched by λ
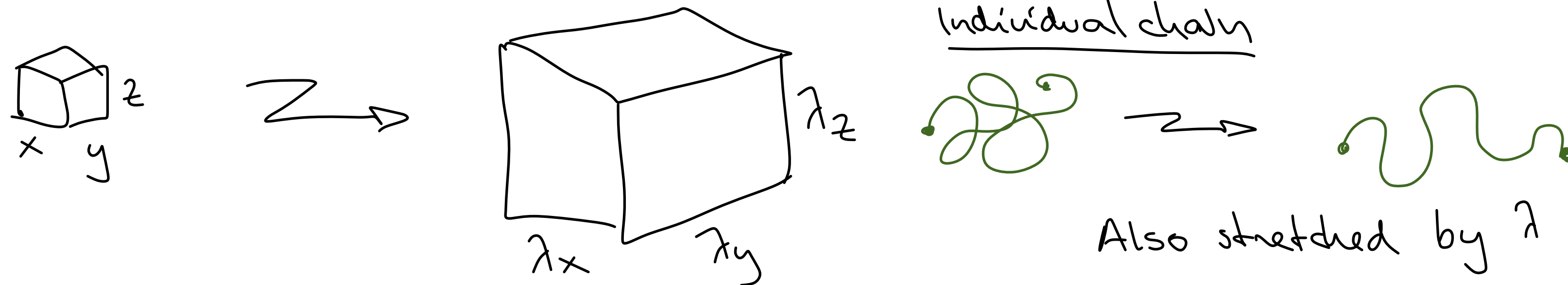
Follow same derivation as in Lectures 11 & 12:

Terms:

$$\nu = \frac{V_2}{V_{sp,2} M_c}$$

$V_2 \equiv$ volume of polymer

$V_{sp,2} \equiv$ specific volume of polymer

$$\nu_e = \nu \left(1 - 2 \frac{M_c}{M_n} \right)$$

number of
elastically active network strands

$M_c \equiv$ molecular weight between cross-links

$M_n \equiv$ chain molecular weight before cross-linking

$$\Delta G_{el} = -T \Delta S_{el}$$

[RUBBER ELASTICITY THEORY]

λ_z

λ_x λ_y
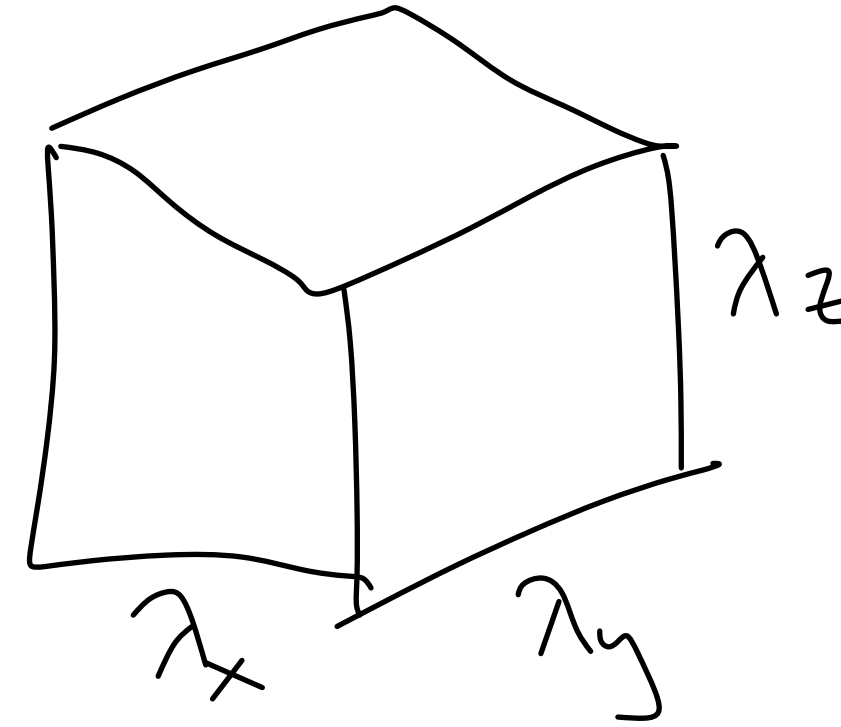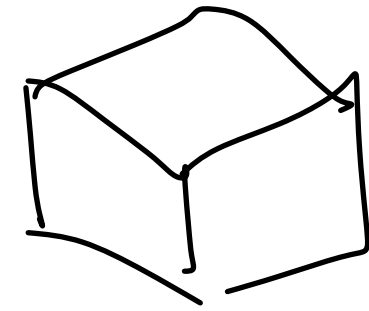
Isotropic
swelling:

$\lambda_x = \lambda_y = \lambda_z = \lambda$

$$\Delta G_{el} = \frac{3}{2} k_B T \, \nu_e \left(\lambda^2 - 1 - \ln\lambda \right)$$

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$$\Delta G = \Delta G_{mx} + \Delta G_{el}$$

$$= k_B T \left[n_1 \ln \phi_1 + n_1 \phi_2 \chi + \frac{3}{2} \nu_e \left(\lambda^2 - 1 - \ln \lambda \right) \right]$$

Equilibrium constraint:

$$\mu_1^{\circ} = \mu_1 \qquad \Longrightarrow \qquad \Delta \mu_1 = 0 = \Delta \mu_1^{mx} + \Delta \mu_1^{el}$$

$$\Delta \mu_1^{mix} = \left(\frac{\partial \Delta G_{mix}}{\partial n_1} \right)_{T, P, n_2}$$

$$\Delta \mu_1^{el} = \left(\frac{\partial \Delta G_{el}}{\partial n_1} \right)_{T, P, n_2}$$

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$$\Delta \mu_1^{wx} = \left(\frac{\partial \Delta G_{mix}}{\partial n_1} \right)_{T,P,n_2} = \frac{\partial}{\partial n_1} \left[k_B T \left[n_1 \ln \phi_1 + n_1 \phi_2 \chi \right] \right]$$

$$= \frac{\partial}{\partial n_1} \left[k_B T \left[n_1 \ln \phi_1 + \chi \frac{n_1 n_2 N_k}{n_1 + n_2 N_k} \right] \right]$$

$$= \boxed{k_B T \left[\ln (1-\phi_2) + \phi_2 + \chi \phi_2^2 \right]}$$

$$\Delta \mu_1^{el} = \left(\frac{\partial \Delta G_{el}}{\partial n_1} \right)_{T,P,n_2} = \left(\frac{\partial \Delta G_{el}}{\partial \lambda} \right)_{T,P,n_2} \left(\frac{\partial \lambda}{\partial n_1} \right)_{T,P,n_2}$$

$$\left(\frac{\partial \Delta G_{el}}{\partial \lambda} \right) = \frac{3}{2} k_B T \, \nu_e \left[2\lambda - \frac{1}{\lambda} \right]$$

$$\frac{\partial \lambda}{\partial n_1} = \frac{V_{m,1}}{3\lambda^2 V_r} \qquad \therefore \Delta \mu_1^{el} = \boxed{k_B T \nu_e \frac{V_{m,1}}{V_r} \left(\frac{1}{\lambda} - \frac{1}{2\lambda^3} \right)}$$

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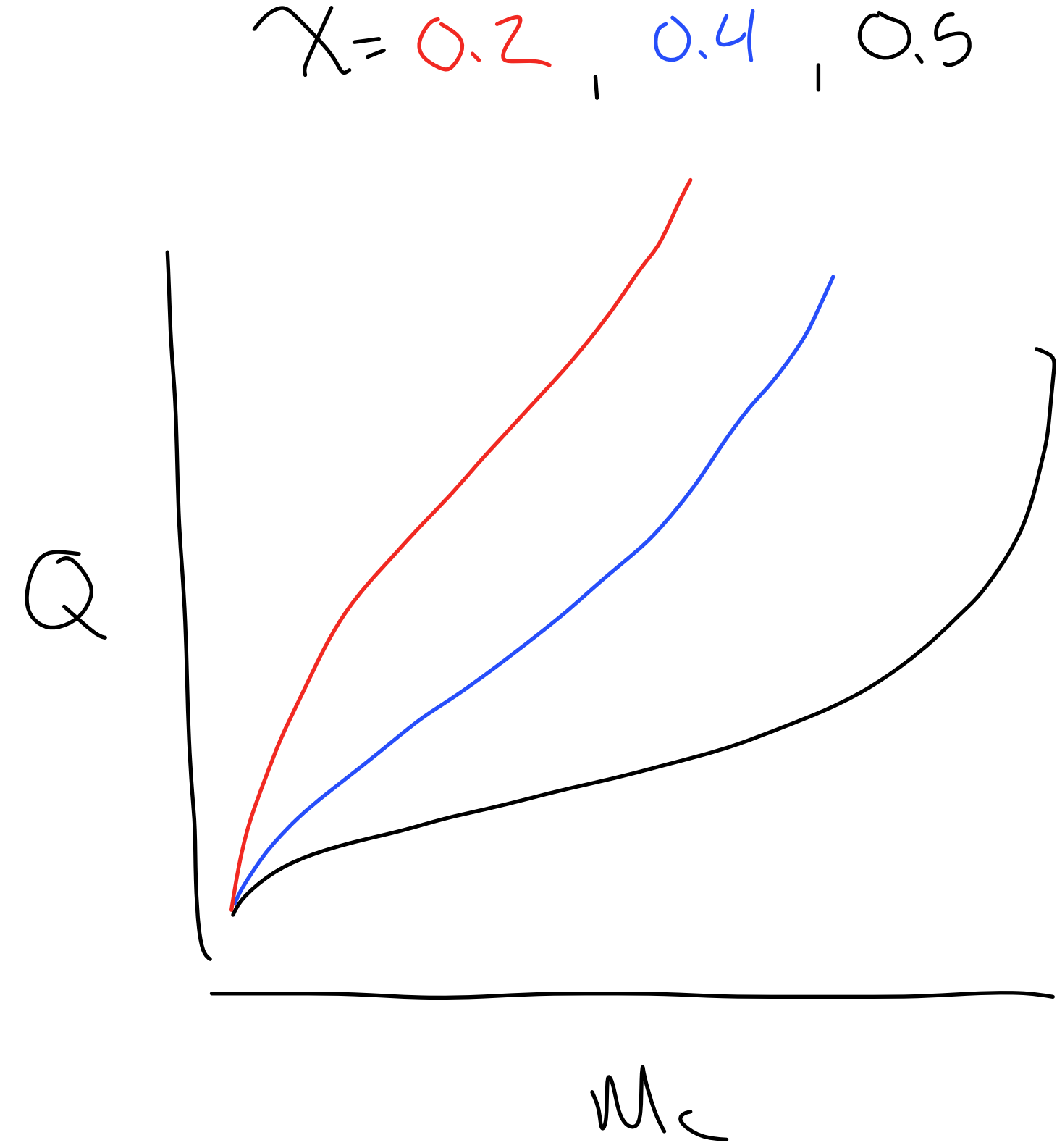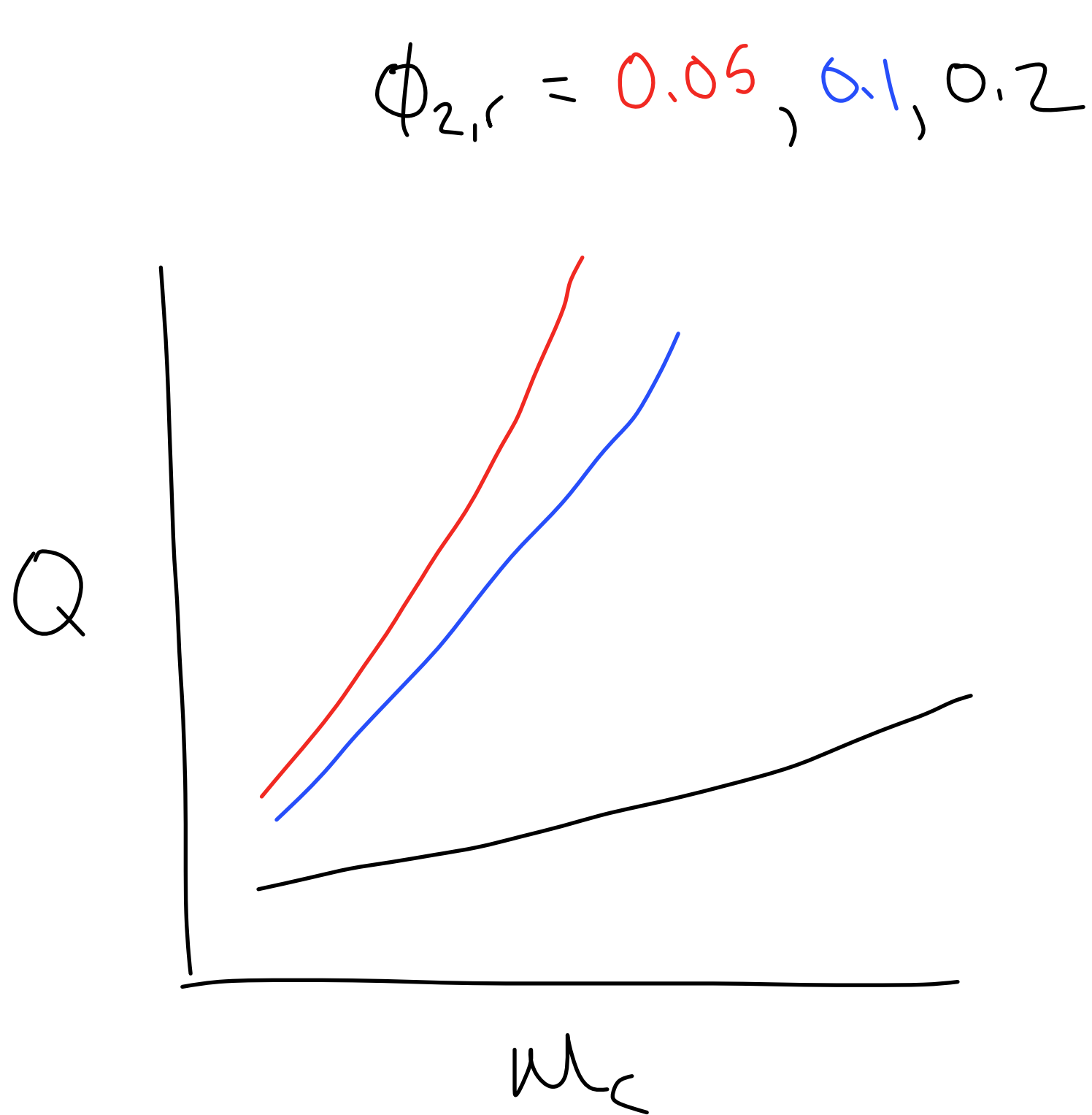Instructor: Prof. Tibbitt

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After applying the equilibrium condition $\Delta \mu = 0$ & a lot of algebra we arrive at the <u>Flory-Rehner Eq.</u>:

$$\frac{1}{M_c} = \frac{2}{M_n} - \frac{V_{sp,2}}{V_1} \frac{\left[\ln\left(1-\phi_{2,s}\right) + \phi_{2,s} + \chi \phi_{2,s}^2\right]}{\left[\phi_{2,s}^{1/3} - \frac{1}{2}\phi_{2,s}\right]}$$

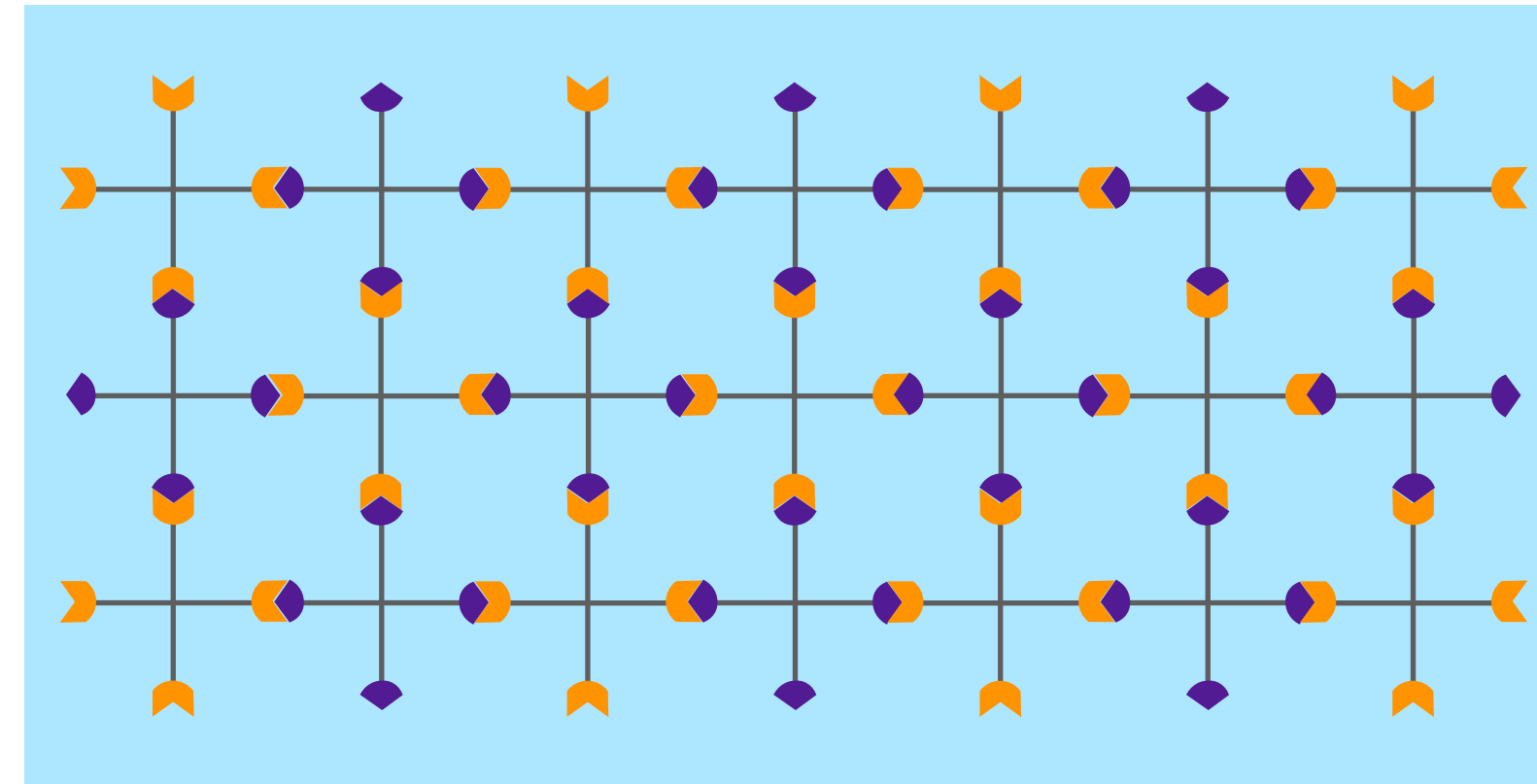If formed in the non-dry state we have the Peppas-Merrill Eq.:

$$\frac{1}{M_c} = \frac{2}{M_n} - \frac{V_{sp,2}}{V_1} \frac{\left[\ln\left(1-\phi_{2,s}\right) + \phi_{2,s} + \chi \phi_{2,s}^2\right]}{\phi_{2,r}\left[\left(\frac{\phi_{2,s}}{\phi_{2,r}}\right)^{1/3} - \frac{1}{2}\left(\frac{\phi_{2,s}}{\phi_{2,r}}\right)\right]}$$

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$\phi_{2,r} = 0.05, 0.1, 0.2$

$\chi = 0.2, 0.4, 0.5$

Q

M_c

$\hat{Q}$

M_c

Swelling increases with increasing Mc, decreasing polymer volume fraction, and decreasing χ.

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

ΔG_{mix}

Promotes swelling
  - Entropy gain by mixing solvent and polymer
  - Potential enthalpic gain from polymer-solvent contacts

$\Delta G_{elastic}$

Resists swelling
  - Loss in entropy as the network chains are stretched

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