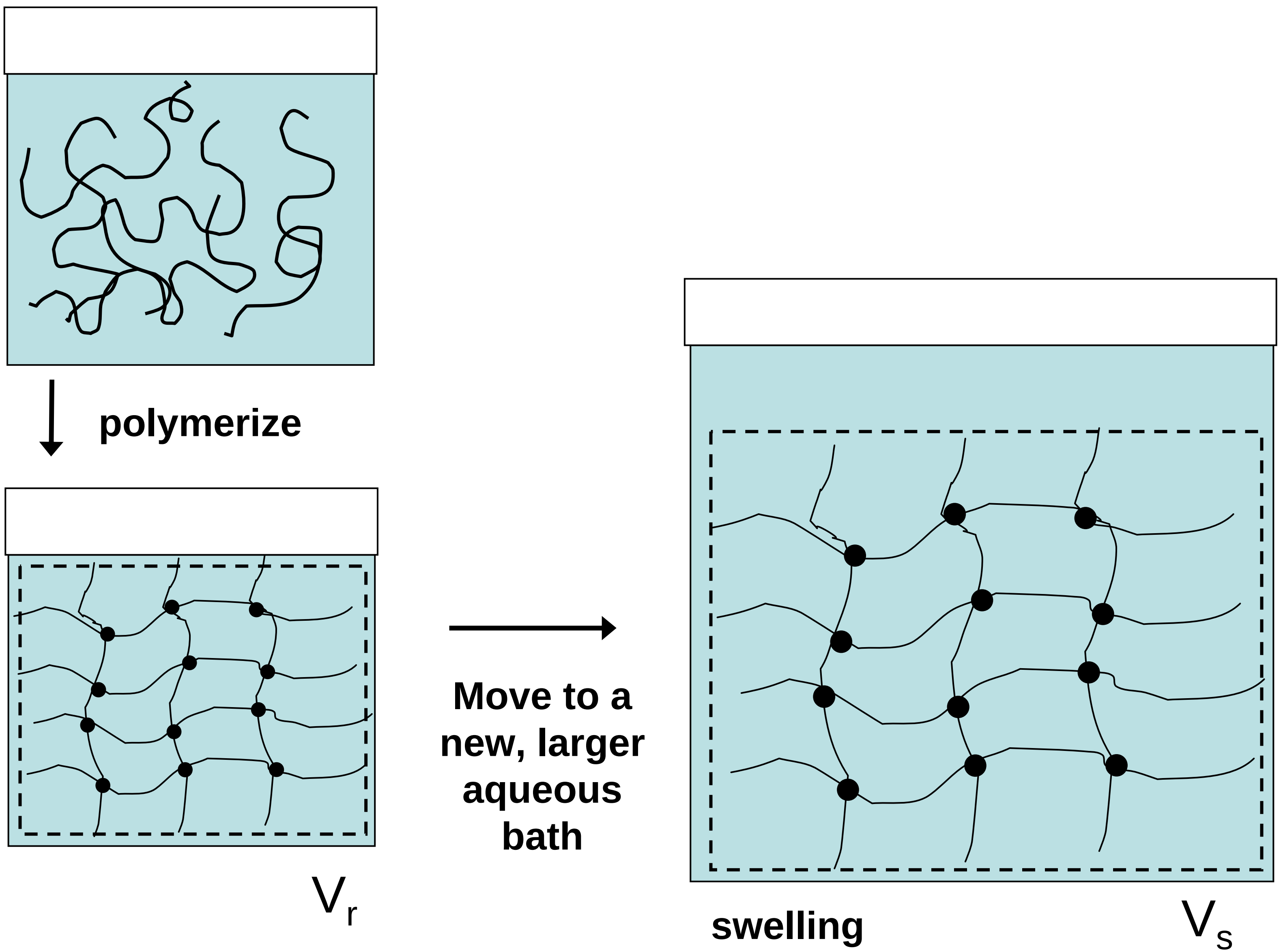
Thermodynamics of hydrogel swelling
Applications of hydrogels in bioengineering

Last Day:	Structure of hydrogels
Today:	bioengineering applications of hydrogels Thermodynamics of hydrogel swelling
Reading:	
Supplementary Reading:	P.J. Flory, 'Principles of Polymer Chemistry,' Cornell University Press, Ithaca, pp. 464-469, pp. 576-581 (Statistical thermodynamics of networks and network swelling) P.J. Flory, 'Principles of Polymer Chemistry,' Cornell University Press, Ithaca, pp. 495-507 (Entropy of polymer-solvent mixing)

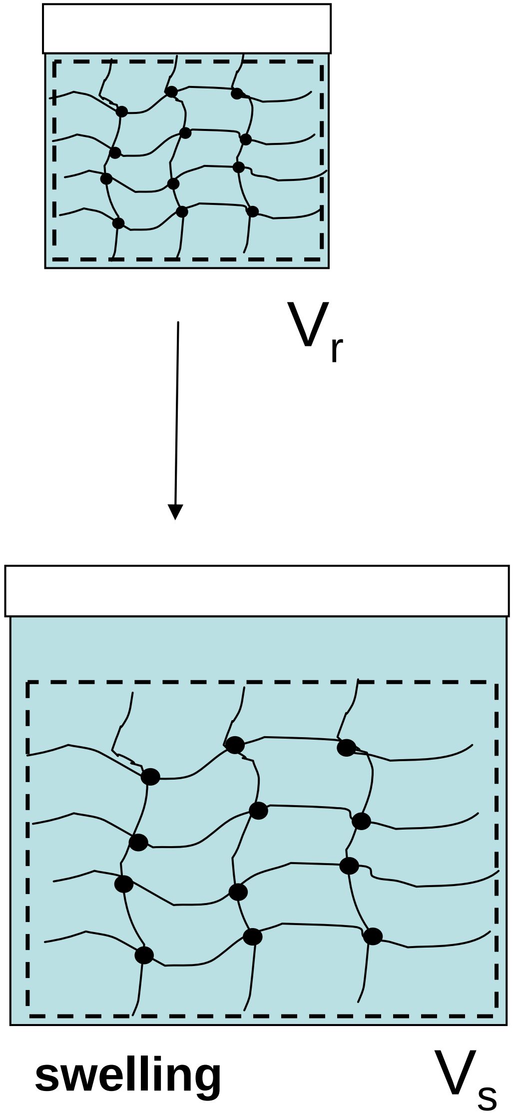
Announcements:

hydrogels

Thermodynamics of hydrogel swelling

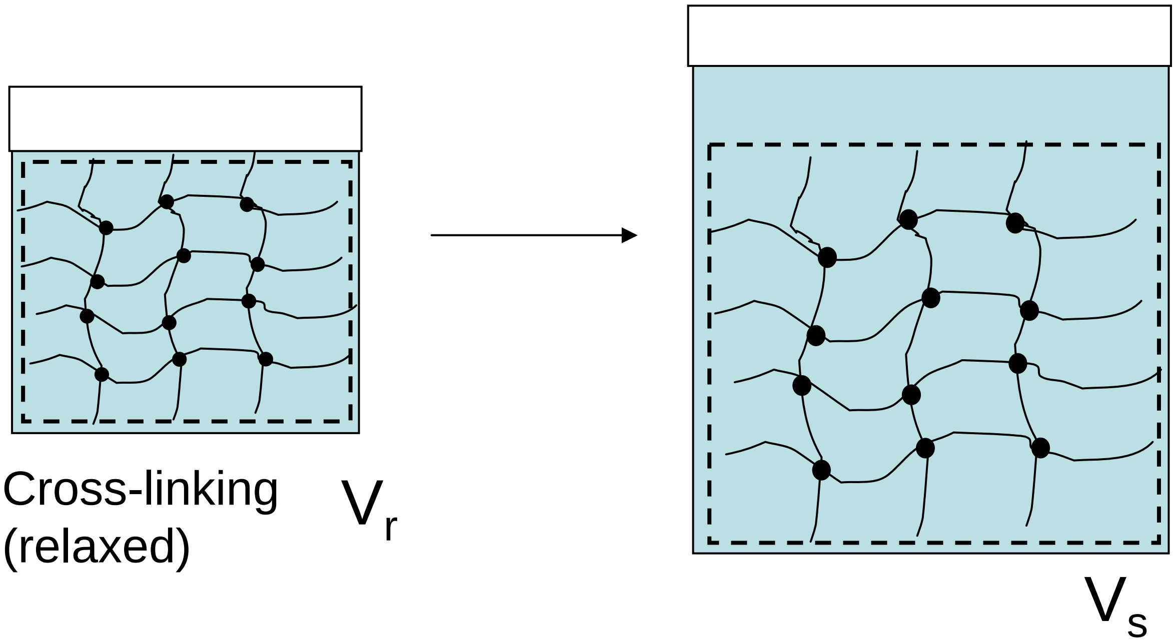


Thermodynamics of hydrogel swelling



Competing driving forces determine total swelling:

Description of cross-linked network



Expansion factor: α

$\alpha_x \alpha_y \alpha_z = \alpha^3 = V_s/Vr = (V_2 + n_1 v_{m,1})/V_r$ swelling

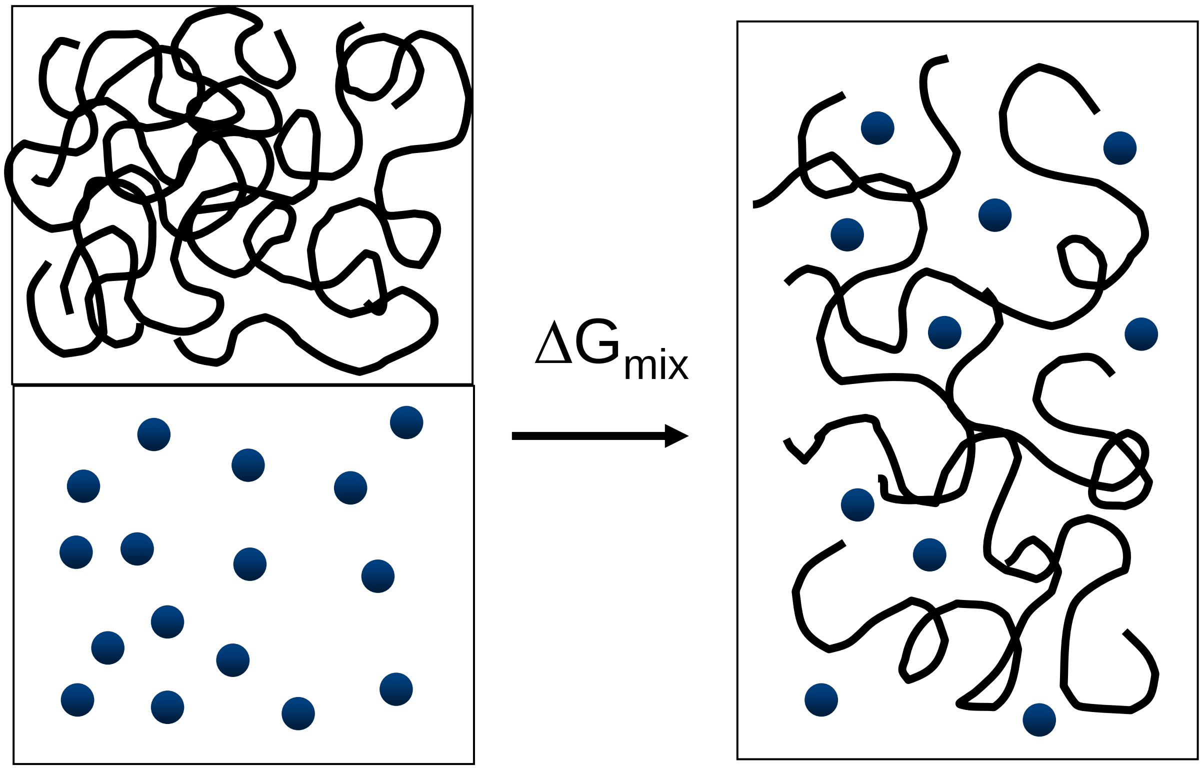
$\phi_{2,s} = V_2/(V_2 + n_1 v_{m,1})$ volume fraction of polymer in swollen gel

$\phi_{2,r} = V_2/V_r$ volume fraction of polymer in relaxed gel

Free energy of mixing in the network:

Starting point: thermodynamic description of simple polymer-solvent mixing:

Seek to derive an expression for the free energy of mixing:

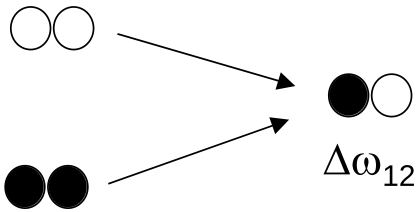


Free energy of mixing in the network:

Lattice model description of polymers: (Flory/Huggins)

ENTHALPY OF MIXING:

Energy of contacts:



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ENTROPY OF MIXING:

Image removed due to copyright reasons. Please see: Figure 110 in Flory, P. J. *Principles of Polymer Chemistry.* Ithaca, NY: Cornell University Press, 1953.

Free energy of mixing in the network:

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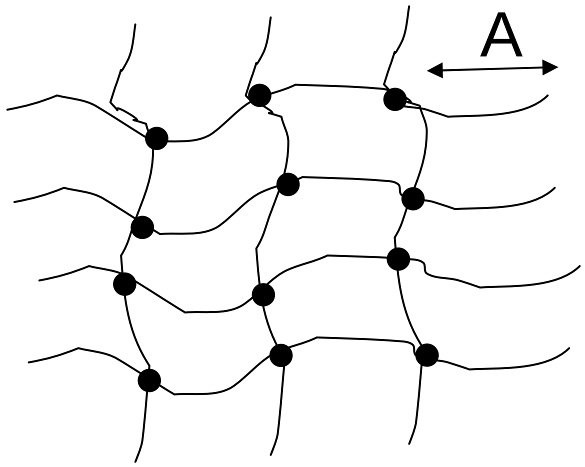
Description of cross-linked network



Assume cross-links are randomly placed; on average, all are equidistant:

ν = number of subchains in cross-linked network

ν_e = number of **'effective'** subchains: tethered at both ends

M = MW of original chains
M_c = MW of subchains = MW between cross-links

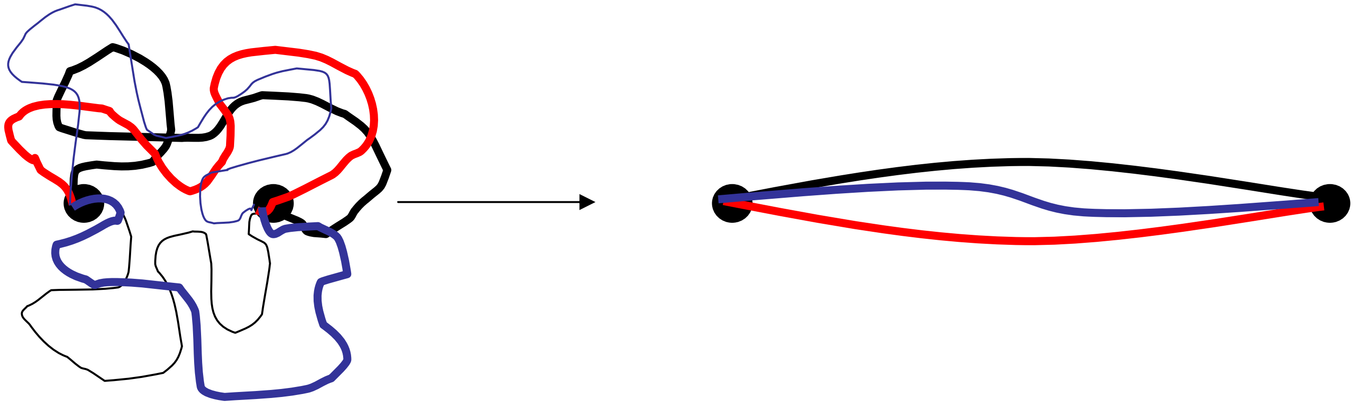
Example: assume polymer chains have a molecular weight M = 4A and each 'subchain' has molecular weight A:

Two useful relationships:

$\nu = V_2/v_{sp,2}M_c$
$\nu_e = \nu(1 - 2(M_c/M))$

Elastic contribution to hydrogel free energy: ΔG_{el}

•Account for entropic retraction force that restrains swelling:



$\Delta G_{el} > 0$

Elastic contribution to hydrogel free energy: ΔG_{el}

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Complete expression for the free energy of the gel:

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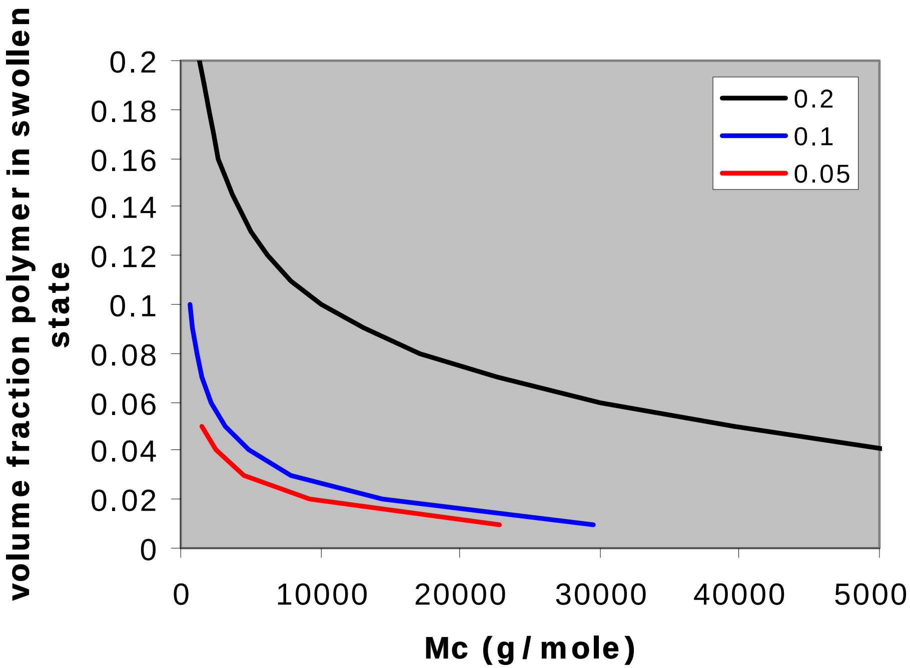
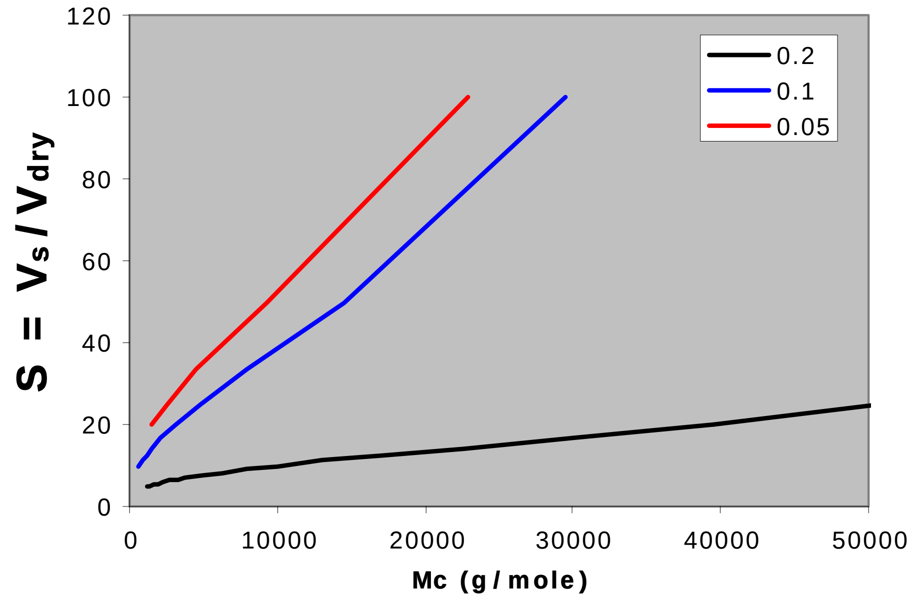
Predictions of Flory/Peppas theory

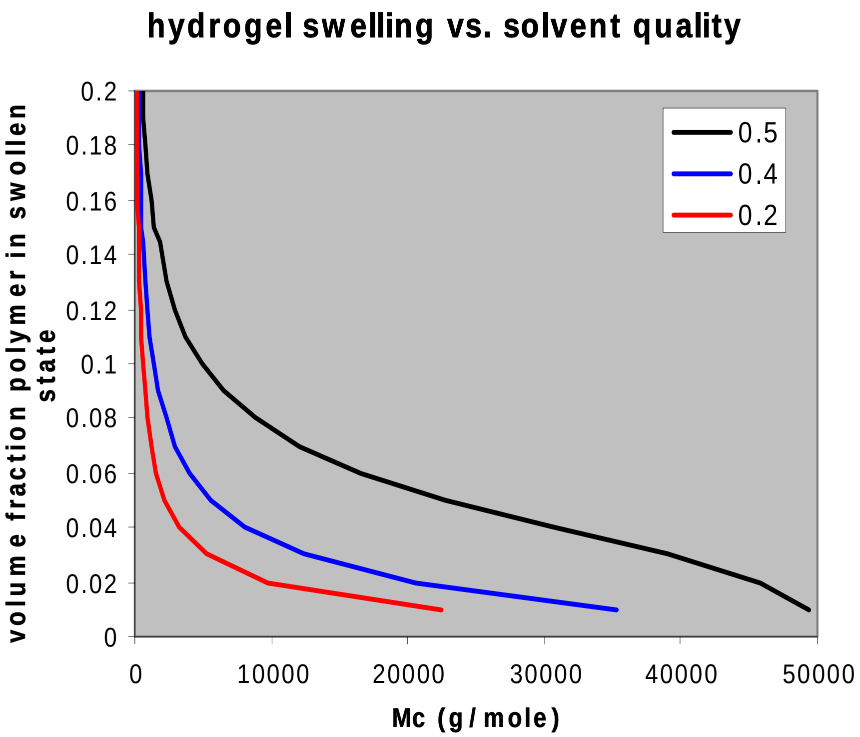
Varying $\phi_{2,r}$:

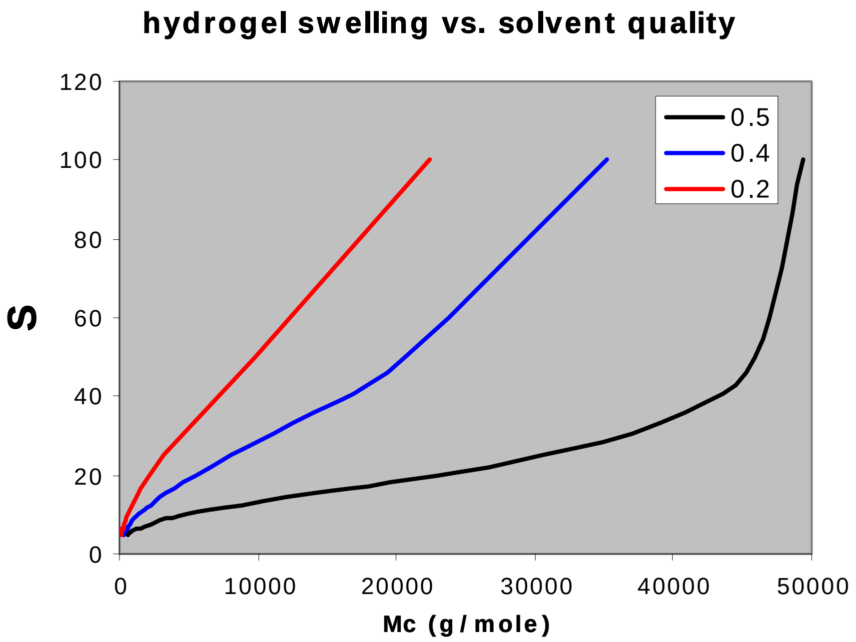




Predictions of Flory/Peppas theory

Varying χ:





Model parameters

μ_1^{bath}	chemical potential of water in external bath (= μ_1^0)
μ_1	chemical potential of water in the hydrogel
μ_1^0	chemical potential of pure water in standard state
Δw_{12}	pair contact interaction energy for polymer with water
z	model lattice coordination number
x	number of segments per polymer molecule
M	Molecular weight of polymer chains before cross-linking
M_c	Molecular weight of cross-linked subchains
n_1	number of water molecules in swollen gel
χ	polymer-solvent interaction parameter
k_B	Boltzman constant
T	absolute temperature (Kelvin)
$v_{m,1}$	molar volume of solvent (water)
$v_{m,2}$	molar volume of polymer
$v_{sp,1}$	specific volume of solvent (water)
$v_{sp,2}$	specific volume of polymer
V_2	total volume of polymer
V_s	total volume of swollen hydrogel
V_r	total volume of relaxed hydrogel
ν	number of subchains in network
ν_e	number of ‘effective’ subchains in network
ϕ_1	volume fraction of water in swollen gel
$\phi_{2,s}$	volume fraction of polymer in swollen gel
$\phi_{2,r}$	volume fraction of polymer in relaxed gel

Key properties of hydrogels for bioengineering applications:

Further Reading

1. Flory, P. J. & Rehner Jr., J. Statistical mechanics of cross-linked polymer networks. II. Swelling. *J. Chem. Phys.* **11**, 521-526 (1943).
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3. Peppas, N. A. & Merrill, E. W. Polyvinyl-Alcohol) Hydrogels - Reinforcement of Radiation-Crosslinked Networks by Crystallization. *Journal of Polymer Science Part a-Polymer Chemistry* **14**, 441-457 (1976).
4. Flory, P. J. *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, 1953).
5. An, Y. & Hubbell, J. A. Intraarterial protein delivery via intimally-adherent bilayer hydrogels. *J Control Release* **64**, 205-15 (2000).
6. Brannonpeppas, L. & Peppas, N. A. Equilibrium Swelling Behavior of Ph-Sensitive Hydrogels. *Chemical Engineering Science* **46**, 715-722 (1991).
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11. Peppas, N. A., Huang, Y., Torres-Lugo, M., Ward, J. H. & Zhang, J. Physicochemical foundations and structural design of hydrogels in medicine and biology. *Annu Rev Biomed Eng* **2**, 9-29 (2000).