3. Polymer Gels

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M. Rubinstein, R.H. Colby,
Polymer Physics,
Oxford University Press 2003
3.1 Applications: cosmetics, medicine, food

www.aloe-vera-gel-flp.de

gel from aloe vera plant:
96 % water
4 % polysaccharides,
e.g. cellulose, Xylose
vitamins, enzymes, minerals etc.
Application: gel-electrophoresis
Superabsorbers

storage of humidity, e.g. in wound draps, gardening, fire fighting, concrete

deep sea cable
Superabsorbers

\[
\text{CH}_2\text{CH}_2\text{COOH} \quad \text{CH}_2\text{CH}_2\text{COO}^-\text{Na}^+ \\
\text{acrylic acid} \quad \text{sodium acrylate}
\]

polyacrylic acid
- main component of network
- does not dissociate
- low cross-linking density

few sodium acrylate groups in polymer network:
\[\rightarrow \text{Na}^+ \text{ ion can dissociate in water}\]

strong swelling in water
Superabsorbers

dry polyelectrolyte network

polyelectrolyte network swollen in water

addition of water

→

→

→

→
Supertough polymer gels

conventional gels:

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→

slide-ring gel (rings may be cyclodextrines):
uniform distribution of cross-links → very hard to break

NC gel: high deformability of more than 10 times

tetra-PEG gels: extraordinarily high compression modulus higher than the one of articular cartilage

3.2 The sol-gel transition

4 cross-links 8 cross-links 10 cross-links

bold line: largest branched polymer
10 or more cross-links: gel
cross-linking of a solution of polymer chains (‘sol’) → one molecule spans the entire system (‘gel’)

‘infinitely’ large, branched polymer: ‘gel’ or ‘network’ (sample contains also finite branched polymers)

sol-gel transition (gelation, gel formation): solution of finite branched polymers → system with infinite, branched polymer

gel point: critical point where gel appears for the first time

growth models (mean-field theories):
• critical percolation theory
• diffusion-limited aggregation
• cluster-cluster aggregation
• kinetic gel formation
3.3 Chemical and physical gels

chemical cross-links:

• condensation of di- and trifunctional groups $A_2$ and $B_3$

cluster-cluster aggregation
Chemical gels

Vulcanization
- cross-linking of overlapping linear chains
- mean-field percolation model
- end-cross-linkable chains or random cross-linking
- the latter e.g. by sulfur in cis-polyisoprene (Goodyear 1839)

end cross-linking vulcanization

random cross-linking
Physical gels

strong physical gels:

- lamellar microcrystals
- glassy cross-links
- double helices
Physical gels

weak physical gels

- H-bonds
- block copolymer micelles
- ionic association
3.4 Models: percolation transition

gel formation = percolation transition

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- 
- 
- 
-
Fractions of gel and sol

fraction of the sol:

fraction of the gel:

fraction of the sol decreases as the fraction of the gel increases

continuous phase transition
Experimental determination of the sol and the gel fraction

Soxhlet extraction

- solvent boils in the bottom and condenses in the top, drips into the thimble, in which the gel is located on a fine glass filter
- solvent dissolves sol fraction and flows into solvent flask
- after a few days: sol fraction in the solvent flask, gel fraction in the thimble
- determination of the masses of the swollen and the dried gel by weighing → degree of swelling
- characterization of the molar mass distribution in the sol by gel permeation chromatography
Mean-field model for gelation

Model for gelation: place monomers onto an infinite Bethe lattice

functionality of the lattice $f$

$= \text{functionality of the monomers}$

assumptions of the bond percolation model on the Bethe lattice:

- 
- 

random bond percolation model:

limitation of the model:
choice of a certain site and cross-linking outwards

starting site (parents) has already bond with neighbor (grand parents) average number of additional bonds of the starting site with the $f$-1 remaining neighbors (possible children): $p(f-1)$

if $p(f-1) < 1$:
if $p(f-1) > 1$:

$\rightarrow$ gel point:

for $p < p_c$:
for $p > p_c$:
Fraction of the sol

two possibilities:
1. no bond between A and B: 1-\( p \)
2. bond between A and B: \( p \)

in this case, there are \( f-1 \) paths from B which can react with the gel
probability that none of these bonds is formed: \( Q^{f-1} \)
probability that there is a bond between A and B and that B is not connected with the gel: \( pQ^{f-1} \)
recursion:

\[ P_{\text{sol}}: \text{fraction of monomers in the sol} = \text{probability that an arbitrary monomer is not connected with the gel, i.e. with none of its } f \text{ bonds} \]

for \( f = 3 \) and \( p > p_c \):

curve s. slide 13
3.5 Swelling behavior of polymer gels

Polymeric networks can take up a solvent mass which is many times their own mass

Here: swelling of non-entangled networks

Volume fraction of polymer in the swollen state:

during cross-linking: $\phi = \phi_0, \ V = V_0$

Mass conservation of the polymer:

Uptake of solvent

→ network is stretched equally in all spatial dimensions

→ linear deformation in each spatial direction:

M. Rubinstein, R.H. Colby, Polymer Physics, Oxford 2003, p. 274
Free energy of swelling

free energy of stretching
of a single, ideal chain:

quadratic average end-to-end distance
between two cross-links: $R_0^2$

for affine deformation:
elastic energy of a swollen piece of
chain between two cross-links:

$R_{\text{ref}}$: fluctuation of the end-to-end distance
of the piece of chain between two
cross-links
$= \text{end-to-end distance of a free chain}
\text{with the same number of monomers}$
Elasticity

upon swelling of the network, the elasticity of the chain pieces changes, because $R_{\text{ref}}^2$ changes

modulus $G(\phi)$ is proportional to the product of the number density of chains $\nu$ and the elastic free energy per chain
Equilibrium

at equilibrium swelling:
elasticity is balanced by osmotic pressure $\Pi$ of semidilute solution of uncrosslinked polymer chains at the same concentration

modulus proportional to elastic free energy

→ gel swells until modulus and osmotic pressure are balanced

→ degree of swelling in equilibrium, $Q$:

$$ Q \equiv \frac{V_{eq}}{V_{dry}} \quad \text{when} \quad G \approx \Pi $$

$V_{eq}$: volume in fully swollen state
Swelling in $\theta$ solvent

average end-to-end distance of a free chain in $\theta$ solvent is independent of concentration:

$$R_0^2 \approx b^2 N$$

fluctuations of the chain between the cross-links are also independent of concentration:

$$R_{ref}^2 \approx R_0^2 \approx b^2 N$$
Number of monomers between cross-links

osmotic pressure of a semidilute solution in $\theta$ solvent:

$\rightarrow$ equilibrium degree of swelling

if the network was cross-linked in the dry state: $\phi_0 = 1$
Gelatine – a physical gel


• binder in jogurts, aspic,…
• capsules for medical drugs
• silver halogenide photography

preparation from fibrous collagen
(from skin and bones)
From collagen to gelatine

- linearly linked amino acids
- carboxy group and $\alpha$-amino group make intermolecular peptide bond

tripel helical structure:
3 protein chains wind around each other

from collagen to gelatine by thermal partial hydrolysis: cleavage within single collagen chains
Properties of gelatine

thermoreversible sol-gel transition

cooling of an aqueous solution of gelatine (0.5%) to 35-40°C
→ increase of viscosity
→ at even lower temperatures gel formation

three steps:
1. aggregation of individually dissolved chains
   via hydrophobic structure elements
   → helical structures
2. crystallite formation by association of
   two or three ordered segments
3. stabilization of the structure by
   local formation of H-bonds
   within single helices and between the helices
Use of gelatine

granulate or leaves from highly concentrated solution solidified and dried

addition of cold water → swelling up to 10 times the own volume

heating to ~75°C → particles dissolve

cooling: gel forms again
3.6 Self-healing polymer gels

http://www.youtube.com/watch?v=qzl5Vfpe9lA&feature=relmfu

rubber-like material
- soft
- high extensibility
- relaxes back completely

when sample is cut into pieces and pieces are brought into contact for some time → self-heal without need to heat → or press strongly

- mended samples sustain large deformations
- the longer the healing time the better the healing
- healing also possible after some time after cutting

Supramolecular rubber

not made from long, cross-linked polymers but from small molecules which can form 2 (blue) or 3 (red) hydrogen bonds → a kind of polymer network

H-bonds: weak but long-lived high number density of H-bonding groups