Gels

i) What is a gel?

ii) Types of gels
   - Chemical gels
   - Physical gels

iv) Relation to other liquid-solid transitions
A gel?

*A gel is a gel, as long as one cannot prove that it is not a gel*

K. te Nijenhuis
A gel?

A gel is a gel, as long as one cannot prove that it is not a gel

K. te Nijenhuis

Can we make any useful definition?

⇒ Solid-like properties - sustain shear stress
   network spanning the system

⇒ Undergoes liquid - solid transition - gelation

⇒ Heterogeneous - multi component systems
   dynamics on different time scales
   multiple length scales
Example - gelatine

**Gelatine:** Formed from *collagen*, a protein “found” in animals. When collagen is heated, it breaks down into the *protein gelatin*.

Gelatine swells in water $\Rightarrow$ *polymer solution (liquid)*

At low T gelatine+water forms a solid $\Rightarrow$ *a gel*

*water is trapped in a loose polymer network structure*

*Fig. 7. Phase Diagram for Gelatin Solution.*

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Applications

- Food
- Pharmaceuticals
- Batteries and fuel cells
- Epoxy resins
- Disposable napkins
A gel?

A gel is a gel, as long as one cannot prove that it is not a gel

K. te Nijenhuis

Can we make any useful definition?

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network spanning the system

⇒ Undergoes liquid - solid transition - gelation

⇒ Heterogeneous - multi component systems
  dynamics on different time scales
  multiple length scales
Gelation or sol-gel transition

At the gelation point an infinite cluster is created that spans the whole system.

Macroscopic properties changes abruptly ⇒ from liquid-like to solid-like.

Gelation can be described as a bond percolation transition
Gelation or sol-gel transition

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Macroscopic properties changes abruptly ⇒ from liquid-like to solid-like.

Gelation can be described as a bond percolation transition.

Fig. 6.10
Spreading of a disease in an orchard
Percolation theory

Gelation can be described as a connectivity transition - 
*bond percolation problem*

\[ p - \text{probability of bond to neighbour} \]

\[ p < p_c \quad \text{sol} \]

\[ p > p_c \quad \text{gel} \]

In general the problem has not an analytical solution

- *triangular lattice* \[ p_c \approx 0.347 \]
- *square lattice* \[ p_c \approx 0.5 \]
The gel-fraction

\( P_{\text{gel}} \) fraction of sites in the system spanning clusters

\( (gel \ fraction) \)

\( P_{\text{sol}} \) fraction of sites in finite clusters

\( (sol \ fraction) \)

\[ p \leq p_c \quad P_{\text{sol}} = 1 \quad \text{and} \quad P_{\text{gel}} = 0 \]

\[ p \geq p_c \quad P_{\text{sol}} < 1 \quad \text{and} \quad P_{\text{gel}} > 0 \]

Gelation is a continuous transition

**Fig. 6.15**
Mean-field prediction of sol and gel fractions for functionality \( f = 3 \).
Gel

Heterogeneous system: immobile network + mobile solvent
The family of gels

From Rubinstein & Colby: Polymer Physics
The family of gels

Reversible system

- Physical
  - Weak
  - Strong
    - Ex: gelatin

Irreversible system

- Chemical
  - Crosslinking polymers (vulcanization)
  - Addition (kinetic growth)
  - End-linking
    - Random crosslinking

- Reacting monomers

From Rubinstein & Colby: Polymer Physics
Chemical gels

Creating network by *chemical* cross links - covalent bonds

*Reacting monomers:*
Thermosetting resins with monomers and hardener (epoxy)
Chemical gels

Creating network by *chemical* cross links - covalent bonds

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*Reacting monomers:*
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*Cross-linking long polymer chains,*
e.g. vulcanised rubber
Chemical gels

Creating network by *chemical* cross links - covalent bonds

**Reacting monomers:**
Thermosetting resins with monomers and hardener (epoxy)

**Cross-linking long polymer chains,**
e.g. vulcanised rubber

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Short stiff segments/
High cross-link density

\[
G = \frac{\rho RT}{M_x}
\]

rigid gel/glassy
Example I: Fuel cell membranes

Polymer gel membrane
Combine mechanical stability of polymer with conductivity of a liquid phase

5-20 nm
Example I: Fuel cell membranes

Polymer gel membrane
Combine mechanical stability of polymer with conductivity of a liquid phase

Chemical gel:
Cross-linked polymer + acidic solution (H₂O+H₂SO₄)

PVA = poly(vinyl alcohol)

GLA (glutaraldehyde) = Pentane-1,5-dial
Example II: Superabsorbents

Superabsorbent - a gel that can swell >100 x weight

Volume change a balance between osmotic pressure and elasticity

Polyelectrolyte gels - control swelling by salt concentration

\[ q_W = \frac{W_s}{W_d} \]
Example II: Superabsorbents

Superabsorbent - a gel that can swell >100 x weight

Antigen responsive - control swelling by presence of a specific protein

Nature 399, 766 (1999)
Example II: Superabsorbents

Superabsorbent - a gel that can swell >100 x weight

Volume change a balance between osmotic pressure and elasticity

*Polyelectrolyte gels* - control swelling by salt concentration
*Antigen responsive* - control swelling by presence of protein
*Lipophilic absorbent* - swelling in non-polar solvent (oils)

…. 
Swelling an analogue to coil-globule transition

\[ F_{\text{rep}} + \Delta U_{\text{int}} = k_b T \nu (1 - 2\chi) \frac{N^2}{R^3} \]

\( \chi = 1/2 \) and the two energies cancel and we have a “theta solvent” with pure random walk conformation!

\( \chi < 1/2 \) the coil is swollen (A good solvent)

\( \chi > 1/2 \) the coil forms a globule (A bad or poor solvent)
The family of gels

Reversible system

Physical
- Weak
- Strong
  - Ex: gelatin

Irreversible system

Chemical
- Crosslinking polymers (vulcanization)
- Addition (kinetic growth)
- End-linking
- Random crosslinking

Gelation
- Reacting monomers
- Condensation (critical percolation)

Ex: epoxy

From Rubinstein & Colby: Polymer Physics
Physical gels

Creating network by *physical* cross links

**Reversible cross-links**

⇒ micellar crystallites  
⇒ helix formation  
⇒ glassy entanglements  
⇒ micro-phase separation  
⇒ hydrogen or ionic bonds

**Gelation induced by:**

⇒ temperature  
⇒ pH  
⇒ salt concentration  
⇒ …

*Fig. 3A–F. Schematic view of various kinds of Flory’s type 3 gels: A PVC/plasticizer; B aqueous gelatin; C atactic PS in CS₂; D triblock copolymer SBS in tetradecane; E PO-EO-PO triblock copolymer in water; F 5-PMMA and 3-PMMA in toluene; G dissolved SCLCP*

*Te Nijenhuis, Thermoreversible Networks*
Thermoreversible gelation

**Reversible transition from liquid-like to solid-like behavior**

Found for a large range of macromolecular systems, biological as well as synthetic polymers (polymer solutions)

**Gelation mechanism?**
- crystalline cross links
- entanglement
- phase separation
- aggregation/jamming
- …
Measuring the gel-point

Rheology experiment
Transition from liquid-like to solid-like behavior
⇒ development of a shear modulus ($\omega=0$)

Easy in the lab method
⇒ Falling ball
⇒ TTT (tilt-test-tube)
Measuring the gel-point

Rheology experiment
Transition from liquid-like to solid-like behavior
⇒ development of a shear modulus (\(\omega=0\))

\[ G(t) = St^{-n} \]

Winter-Chambon method
At the gel-point

\[ G(t) = St^{-n} \]

Te Nijenhuis, Thermoreversible Networks
Example - gelatine

Gelatine: Formed from collagen, a protein “found” in animals. When collagen is heated, it breaks down into the protein gelatin.

A thermoreversible system - gelatine+water
Example - gelatine

Gelatine: Formed from collagen, a protein “found” in animals. When collagen is heated, it breaks down into the protein gelatin.

A thermoreversible system - gelatine+water
Crosslinks from helix formation

Fig. 6.4 Collagen molecules in their native conformation. Each chain is a left-handed helix; the three chains assemble to form a right-handed superhelix.

Fig. 7. Phase Diagram for Gelatin Solution.

Te Nijenhuis, Thermoreversible Networks
**Example - gelatine**

**Gelatine:** Formed from *collagen*, a protein “found” in animals. When collagen is heated, it breaks down into the *protein gelatin*.

*A thermoreversible system - gelatine+water*

*Crosslinks from helix formation*

**Time dependence of gleetion**

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*Te Nijenhuis, Thermoreversible Networks*
Gelation and phase separation

Phase diagram for aPS/toluene
Gelation by phase separation

For polymer solutions we can form

- homogeneous gels
- heterogeneous gels (phase separated)

Fig. 84. Phase diagram, shown schematically, of solutions of monodisperse polymer for which the glass transition curve (---) crosses the bimodal boundary curve. 

Te Nijenhuis, Thermoreversible Networks
Gelation by phase separation

For polymer solutions we can form
- homogeneous gels
- heterogeneous gels (phase separated)

Te Nijenhuis, Thermoreversible Networks
Gelation by phase separation

For polymer solutions we can form
- homogeneous gels
- heterogeneous gels (phase separated)

Creating different textures in the material
⇒ important for e.g. taste

Fig. 86. Schematic illustration of the three classes of gels: i molecularly connected; ii phase connected (continuous); iii phase connected (adhesive). Reproduced from Makromol Chem [Ref. 276] by the courtesy of the authors and of Hüthig & Wepf Verlag Publishers, Zug, Switzerland

Fig. 86. Detail of Upper Critical Temperature phase diagram of sPS (M_n = 2730 kg/mol) in cyclohexanol, including expected variation in gel morphology with concentration. Reproduced from Makromol Chem [Ref. 276] by the courtesy of the authors and of Hüthig & Wepf Verlag Publishers, Zug, Switzerland
Solid - liquid transitions

gelation

Hydrogel's viscosity changes dramatically with temperature

Glass transition

colloidal aggregation
Solid - liquid transitions

gelation

Arrest of molecular/structural motion

Dramatic change in viscosity

Non-equilibrium transitions

Similar relaxation patterns

Colloidal aggregation

glass transition
Jamming?

A unifying picture of glass formation, gelation and colloidal aggregation?
Next lecture

Thursday 4/10 8.00

⇒ Experimental techniques for soft matter