Gelation

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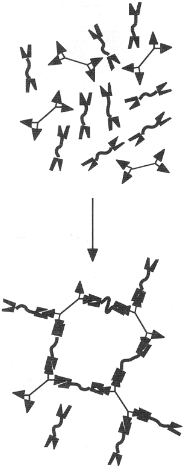
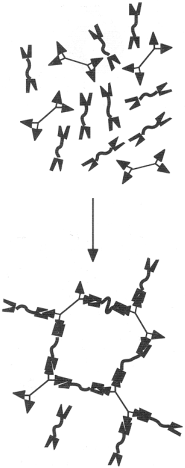
Gelation



Gelation chemical or physical process of linking subunits until a macroscopic network is formed.

Sol-Gel transition between liquid (sol) to a solid (gel) state, where the latter characterised by a non-zero shear modulus

Chemical gels



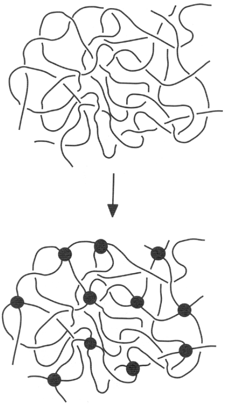
Crosslinking agent is strong chemical bonds

Thermosetting resins.

Short polymers + multi-functional linkers forms network.

The resulting material is glassy, hard, and stiff. e.g. Epoxy resins

Chemical gels

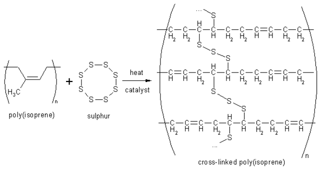


Crosslinking agent is strong chemical bonds

Irreversibly vulcanised rubber (Goodyear 1839).

The resulting material is a tough, rubbery solid.

Chemical gels



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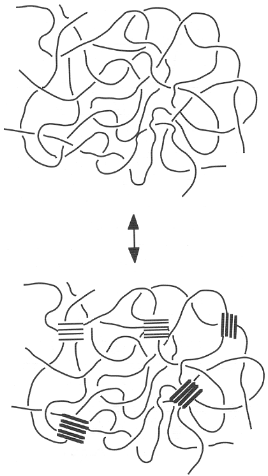
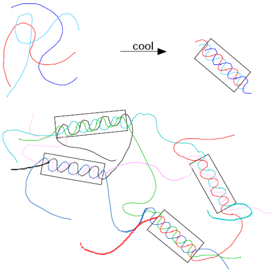
Physical gels



Crosslinking agent is weak physical interactions

Microcrystalline domains acts as crosslinkers.

Physical gels

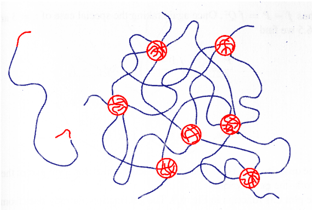


Crosslinking agent is weak physical interactions

Microcrystalline domains acts as crosslinkers.

For example jelly, where denatured collagen proteins forms triple helices upon cooling - junctions that joins chains.

Physical gels

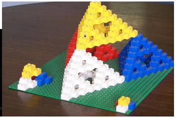


Crosslinking agent is weak physical interactions

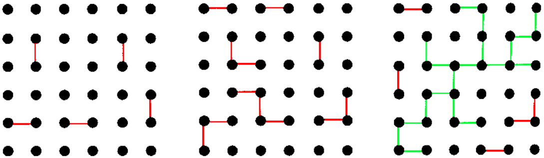
Microphase separation.

Block copolymers where one block forms glassy domains.

Styrene-butadiene-styrene (SBS) or acrylonitrile-butadiene-styrene (ABS)



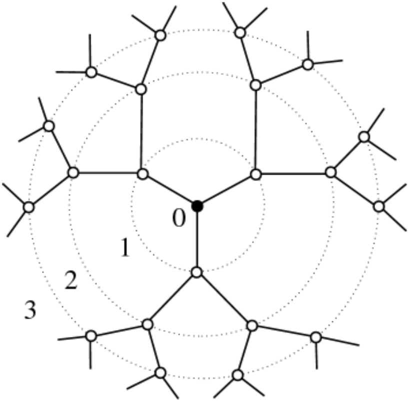
Percolation



Questions:

- fraction of bonds required to form infinite cluster?
- average cluster size vs. fraction of bonds?
- when infinite cluster is formed, how many bonds belong to it?

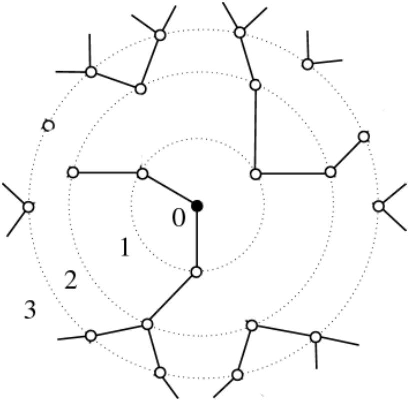
Cayley tree $z = 3$



Number of bonds:

$$
\begin{aligned}
N(g) &= \frac{z\left[(z-1)^g - 1\right]}{z-2} \\
&\sim (z-1)^g
\end{aligned}
$$

Cayley tree $z = 3$ f=1/3



Probability a bond is made/bond fraction f.

Number of bonds in cluster:

$$N(g) \sim [f(z-1)]^g$$

Percolation on a Cayley tree

Number of bonds in cluster:

$$N(g) \sim [f(z-1)]^g$$

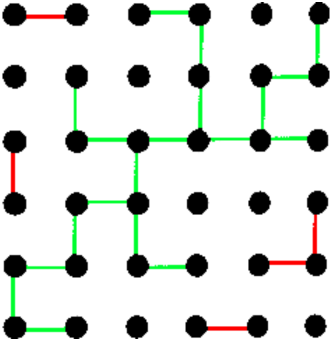
Two cases:

$$N(g) \to \begin{cases} 0 & \text{if } f < f_c \\ \infty & \text{if } f > f_c \end{cases} \quad \text{for} \quad g \to \infty$$

where the critical percolation threshold $f_c = (z-1)^{-1}$

Gel fraction

What is the fraction of bonds that belongs to the infinite cluster (red). The reacted fraction f (red+green).



Probabilities vs. language

For independent assertions A,B,C,D,..

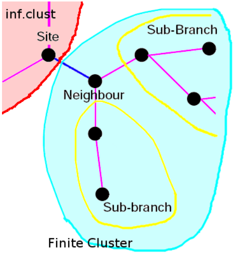
Probability of A AND B: $P(A \text{ and } B) = P(A)P(B)$.

Probability of A AND B AND C:
$P(A \text{ and } B \text{ and } C) = P(A)P(B)P(C)$.

Probability of A OR B: $P(A \text{ or } B) = P(A) + P(B)$.

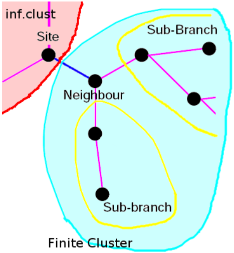
Probability of NOT A: $P(\text{not } A) = 1 - P(A)$.

Gel fraction



Prob(a certain bond belongs to an infinite cluster) $\equiv P$

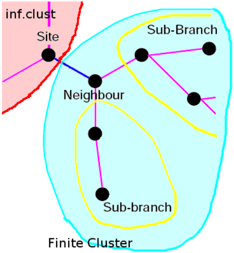
Gel fraction



Prob(a certain bond belongs to an infinite cluster) $\equiv P$

Prob(a certain site is connected to a finite cluster via one specified neighbour) $\equiv Q$

Gel fraction

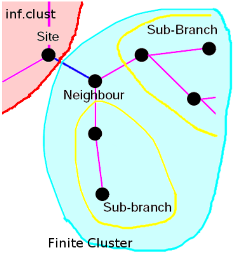


Prob(a certain bond belongs to an infinite cluster) $\equiv P$

Prob(a certain site is connected to a finite cluster via one specified neighbour) $\equiv Q$

a)Prob(that neighbours sub-branches $1, \cdots, z-1$ all belong to finite cluster) $= Q^{z-1}$

Gel fraction



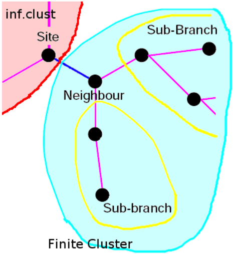
Prob(a certain bond belongs to an infinite cluster) $\equiv P$

Prob(a certain site is connected to a finite cluster via one specified neighbour) $\equiv Q$

a)Prob(that neighbours sub-branches $1, \cdots, z-1$ all belong to finite cluster) $= Q^{z-1}$

b) Prob(site is connected to neighbour $[f]$ AND that neighbours $z-1$ sub-branches belong to finite cluster $[Q^{z-1}]$) $= fQ^{z-1}$

Gel fraction



Prob(a certain bond belongs to an infinite cluster) $\equiv P$

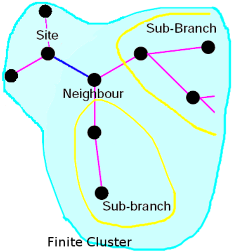
Prob(a certain site is connected to a finite cluster via one specified neighbour) $\equiv Q$

b) Prob(site is connected to neighbour $[f]$ AND that neighbours $z-1$ sub-branches belong to finite cluster $[Q^{z-1}]$) $= fQ^{z-1}$

c) Prob(site is connected to finite cluster via specified neighbour $[Q]$) $=$ Prob(site is NOT connected to neighbour $[1-f]$ OR that it is connected to neighbour AND neighbour belongs to finite cluster $[fQ^{z-1}]$)

Hence $Q = (1-f) + fQ^{z-1}$

Gel fraction

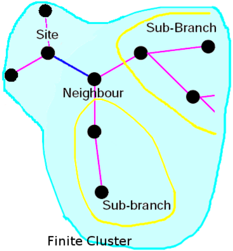


Prob(a certain bond belongs to an infinite cluster) $\equiv P$

Prob(a certain site is connected to a finite cluster via one specified neighbour) $\equiv Q$

e) Prob(site is connected to finite cluster via all neighbours) $= Q^z$

Gel fraction



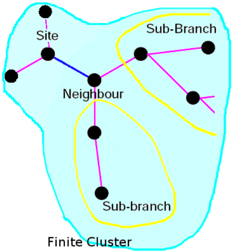
Prob(a certain bond belongs to an infinite cluster) $\equiv P$

Prob(a certain site is connected to a finite cluster via one specified neighbour) $\equiv Q$

e) Prob(site is connected to finite cluster via all neighbours) $= Q^z$

f) Prob(site is connected to finite cluster via all neighbours $[Q^z]$ AND is connected by a bond to a specified neighbour $[f]$) $= fQ^z$

Gel fraction



Prob(a certain bond belongs to an infinite cluster) $\equiv P$

Prob(a certain site is connected to a finite cluster via one specified neighbour) $\equiv Q$

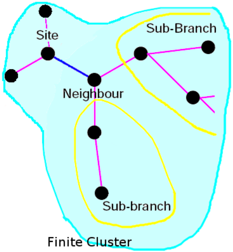
e) Prob(site is connected to finite cluster via all neighbours) $= Q^z$

f) Prob(site is connected to finite cluster via all neighbours $[Q^z]$ AND is connected by a bond to a specified neighbour $[f]$) $= fQ^z$

$=$ Prob(that the bond to the specified neighbour exists, but is not part of the infinite cluster)$=f - P$

Hence $f - P = fQ^z$

Gel fraction



Prob(a certain bond belongs to an infinite cluster) $\equiv P$

Prob(a certain site is connected to a finite cluster via one specified neighbour) $\equiv Q$

Solution:

$$fQ^{z-1} - Q + (1 - f) = 0$$

$$f - P = fQ^{z}$$

Special case $z = 3$

General Equations: $P/f = 1 - Q^z$ and $fQ^{z-1} - Q + (1-f) = 0$

Special case: $P/f = 1 - Q^3$ and $fQ^2 - Q + (1-f) = 0$

Solution:

$$Q = \begin{cases} 1 & \text{for } f < f_c \\ \frac{1-f}{f} & \text{for } f > f_c \end{cases} \tag{1}$$

Gel fraction:

$$P/f = \begin{cases} 0 & \text{for } f < f_c \\ 1 - \left(\frac{1-f}{f}\right)^3 & \text{for } f > f_c \end{cases} \tag{2}$$

$$\frac{P}{f} \approx 12(f - f_c) - 72(f - f_c)^2 + 304(f - f_c)^3 \ldots \tag{3}$$

Gel fraction