Rheology Gels and Networks

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March 31, 2011

Outline

Crosslinks

Terms

Gel Solid formed by linking molecular strands into network

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  - **Strong** effectively permanent
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    - Hydrogen bonds
    - Hydrophobic association
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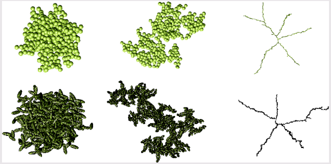
- Chemical linking
  - **Covalent** bonds.

Chemical Gelation

Chemical Gelation Mechanisms

Condensation of monomers in a melt or solution



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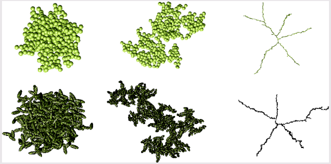
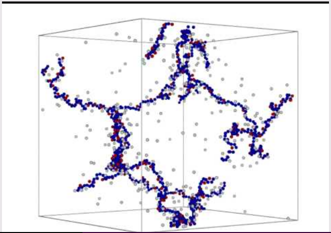


Vulcanization cross-linking of long chains



Formation

Linking

Sol polydisperse mixture of branched polymers in a **sol**vent

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Gel "*Infinite Polymer*"

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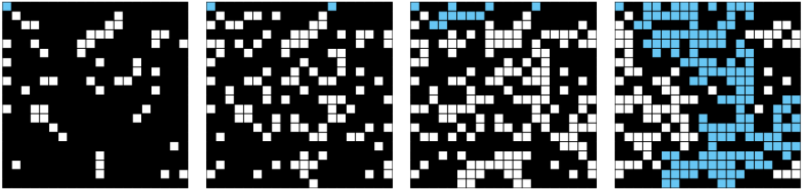
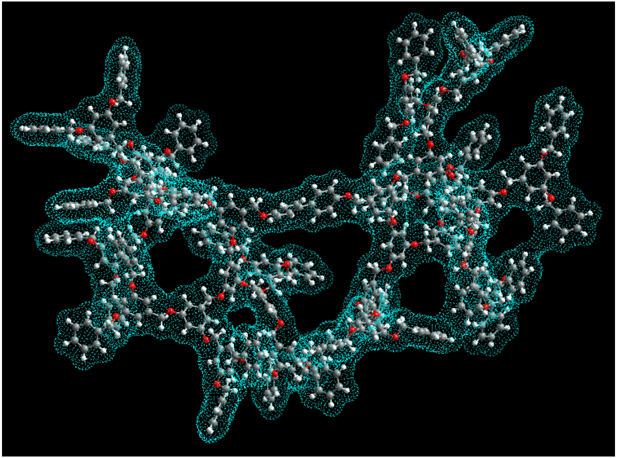
Incipient Gel One structure perculates the entire system

Sol-gel Transition The moment the incipient gel forms



Gel Point



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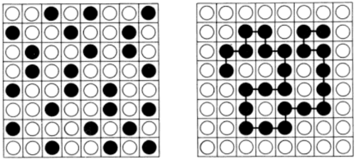

(a) (b)

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Mean-Field Theory

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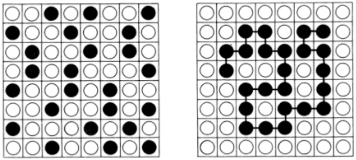
- Coordination number?



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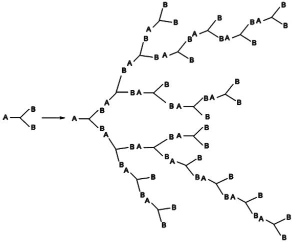

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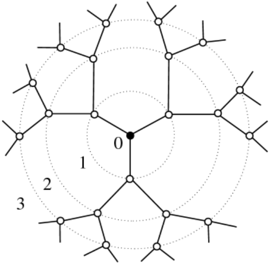

Bethe Lattice

- Monomers have some **functionality** f

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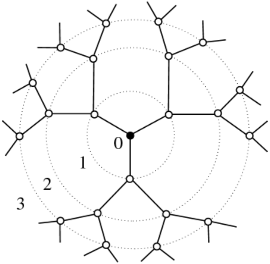

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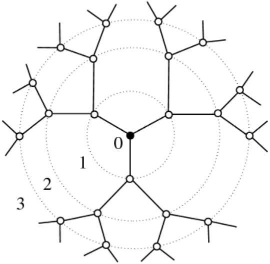

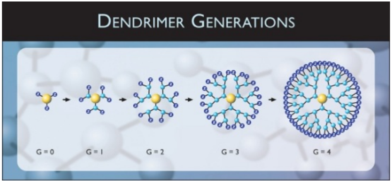

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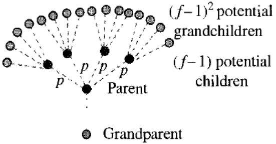

Bond Percolation Model (Mean-Field Model of Gelation)

- Consider some parent site (who has a definite grandparent)

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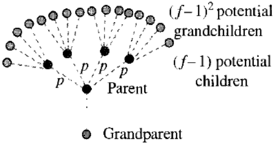

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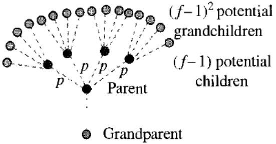

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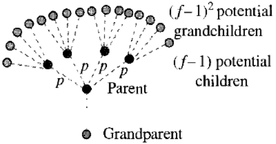

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- **If** $p\,(f-1) < 1$ then the next generation has a smaller population than the last and the sol must be finite
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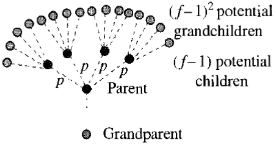

Conclusion

The transition occurs when

$$p_c = \frac{1}{f-1}$$

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Assessment

Comments

- The probablity p is often called the **extent of reaction** and can be used to specify the sol fraction and the gel fraction, the moments of the size distribution.
- Mean-field percolation only holds on a Bethe Lattice and so in 2 and 3D the number of functional groups and the degree of polymerization are not easily related (researchers resort to numerical studies).
- **But** Mean-field percolation works exceptionally well for vulcanization (where f is now the the number of crosslinkable monomers).

Entropy

Helmholtz Free Energy

The fascinating elastic properties arise from the entropy as follows:

$$
\begin{aligned}
F &= U - TS \\
dF &= -SdT - pdV + fdL \\
&= \left.\frac{\partial F}{\partial T}\right|_{V,L} dT + \left.\frac{\partial F}{\partial V}\right|_{T,L} dV + \left.\frac{\partial F}{\partial L}\right|_{T,V} dL
\end{aligned}
$$

Therefore,

$$
\begin{aligned}
f &= \left.\frac{\partial F}{\partial L}\right|_{T,V} \\
S &= -\left.\frac{\partial F}{\partial T}\right|_{V,L}
\end{aligned}
$$

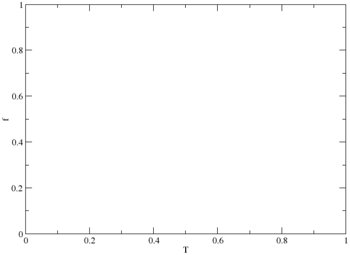
Maxwell Relation

$$
-\left.\frac{\partial S}{\partial L}\right|_{T,V} = \left.\frac{\partial f}{\partial T}\right|_{V,L}
$$

Entropy

Force to Deform Network

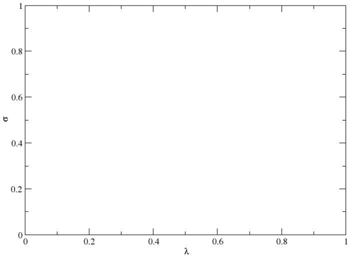
$$f = \frac{\partial F}{\partial L}\Big|_{T,V} = \frac{\partial U}{\partial L}\Big|_{T,V} + \frac{\partial f}{\partial T}\Big|_{V,L}$$



Stress-Elongation

Shear Modulus

$$\sigma = G\lambda$$



Free Energy of Deformation

$$L_i = \lambda_i L_{0,i}$$

$$S\left(N, \vec{R}\right) = -\frac{3}{2} k_{\mathrm{B}} \frac{\vec{R}^2}{Nb^2} + S_0$$

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Shear Modulus

$$G = \frac{\rho R T}{M_s}$$

Phantom Network

Fluctuating Crosslinks

This does not take into account fluctuations which should lower free nergy by reducing cummulative stretch.

Effective Free Chains

The fluctuations of some monomer in an ideal chain with ficed ends is identical to the fluctuations of the end monomer with an effective length

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Shear Modulus

$$G = \frac{\rho RT}{M_s}\left(\frac{f-2}{f}\right)$$

Entanglement

Can entanglement give us the softening?

Entanglement

The tube diameter is

$$a \approx bN_e^2$$

So a can be interpreted as the end-to-end distance between entanglement points. If an entanglement is equivalent to a crosslink and the shear modulus is $k_B T$ per crosslinked strand then

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where $M_e = N_e m$. **Which** is independent of N **but** has not changed the deformation dependence.

Subtle Tube

Tube

However, the tube also limits fluctuations.

- When the network is deformed by some λ_i, we expect the tube diameter to change. Instead of

$$a \approx bN_e^{1/2}$$

we expect $N_e' \cong N_e N_e \lambda$ (since $L \propto N$ between entanglements). The effective tube diameter is only

$$\begin{aligned} a' &\approx bN_e'^{1/2} \\ &= bN_e^{1/2}\lambda^{1/2} \\ &= a\lambda^{1/2} \end{aligned}$$

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Shear Modulus

The effective entanglement molar mass goes like the effective entanglement number so the shear modulus becomes:

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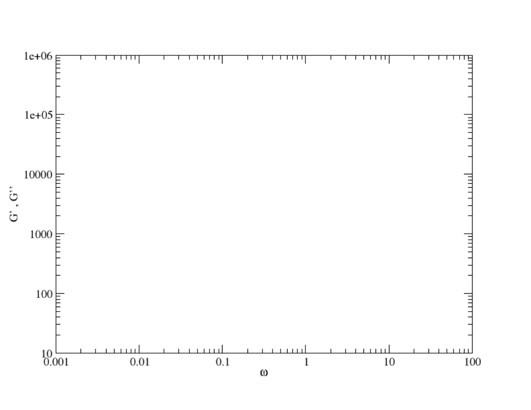
- Mooney-Rivlin Equation:

$$G = C_1 + \frac{C_2}{\lambda}$$

- Non-affin Tube Model:

$$G = G_x + \frac{G_e}{\lambda - \lambda^{1/2} + 1}$$

Maxwell Fluid



Network