PHYS 4xx Net 4 - Elasticity in three dimensions

Random chain networks

- model for vulcanized rubber (Flory, 1953; Treloar, 1975)
- scale factors Λ_x, Λ_y, Λ_z characterize the deformation:

- extension (compression) of the network corresponds to $\Lambda > 1$ ($\Lambda < 1$)
- after a lot of algebra (given in *Mech of Cell* or the extra material on networks):

$$S = -(k_B n/2)[\Lambda_x^2 + \Lambda_y^2 + \Lambda_z^2 - 3 - \ln(\Lambda_x\Lambda_y\Lambda_z) - \ln\,(n/2)! - (n/2)\ln(2\delta V\,/\,V_o)] \qquad (1)$$

n is the total number of chains, V_o is the undeformed volume and δV specifies the volume of the weld between chains; note that the last two terms are independent of the deformation

- ΔS with respect to the reference state $\Lambda_x = \Lambda_y = \Lambda_z = 1$ is

$$\Delta S = -(k_B n/2)[\Lambda_x^2 + \Lambda_y^2 + \Lambda_z^2 - 3 - \ln(\Lambda_x\Lambda_y\Lambda_z)]. \qquad (2)$$

- the chains have no internal energy scale, so $\Delta F = -T\Delta S$, and

$$\Delta F = (k_B Tn/2)[\Lambda_x^2 + \Lambda_y^2 + \Lambda_z^2 - 3 - \ln(\Lambda_x\Lambda_y\Lambda_z)]. \qquad (3)$$

- under a uniform change of scale $\Lambda_x = \Lambda_y = \Lambda_z = \Lambda$, (3) becomes

$$\Delta F = (3k_B Tn/2)\bullet(\Lambda^2 - 1 - \ln\Lambda) \qquad \text{(uniform scaling)} \qquad (4)$$

- note: $\Delta F = 0$ at $\Lambda_x = \Lambda_y = \Lambda_z = 1$, but the minimum of ΔF is at $\Lambda = 1/\sqrt{2}$.

- extract the shear modulus from ΔF by performing a pure shear on (3), with $\Lambda_x = \Lambda = 1/\Lambda_y$ and $\Lambda_z = 1$, yielding

$$\Delta F = (k_B Tn/2)\bullet(\Lambda^2 + 1/\Lambda^2 - 2) \qquad \text{(pure shear).} \qquad (5)$$

- but $(\Lambda^2 + 1/\Lambda^2 - 2) = (\Lambda - 1/\Lambda)^2 = 4\delta^2$ when $\Lambda = 1+\delta$ and δ is small

- divide (5) by the volume V_o (unchanged by shear)

$$\Delta \mathcal{F} = 2\delta^2 \rho k_B T, \qquad (\rho = \text{density of chains} = n\,/\,V) \qquad (6)$$

- evaluate $\Delta\mathcal{F}$ in terms of strain tensor under pure shear conditions of $\Lambda = 1+\delta$,

  ---->$u_{xx} = \delta$, $u_{yy} = -\delta$, $u_{zz} = 0$

  then

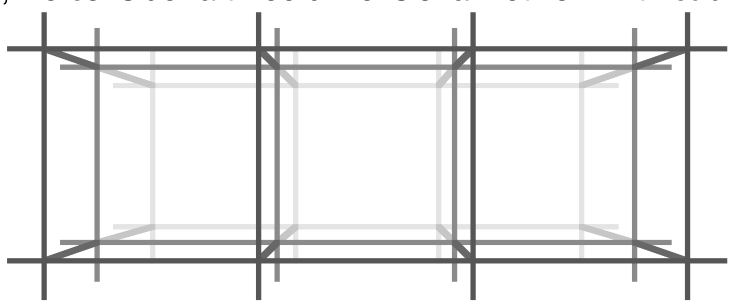
  $$\Delta\mathcal{F} = 2\delta^2\mu \qquad (7)$$

- comparing (6) and (7)

  $$\mu = \rho k_B T. \qquad (8)$$

Spring networks

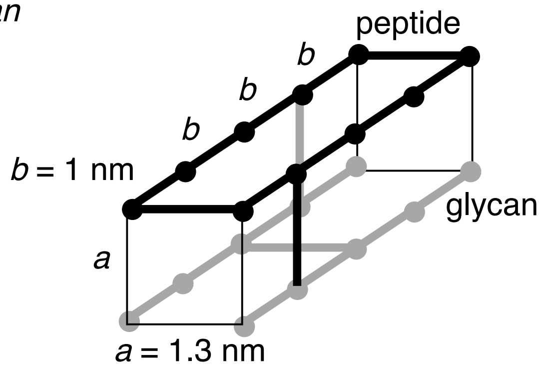
- as an example, we consider a three dimensional network with cubic symmetry



- go through the usual reduction of elastic constants and deformation modes to find the volume compression modulus:

  $$K_V = k_{sp} / 3s_o \qquad \text{(rigid cubic symmetry)}, \qquad (9)$$

Example: peptidoglycan



network "bonds" are drawn as heavy lines and their junctions are shown as disks

The rectangular box:

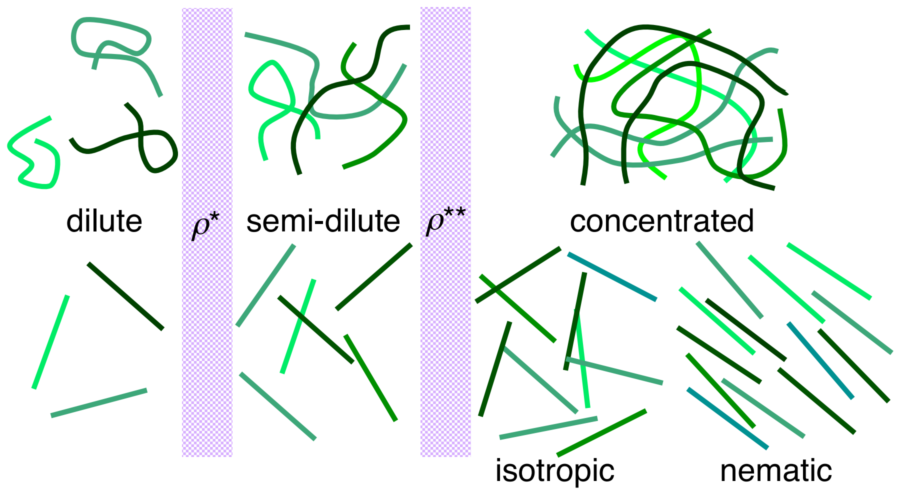
- has a volume of a x a x $4b = 4a^2b$
- contains four vertices; the eight vertices at the corners are each shared with eight adjoining boxes, while the twelve vertices along the edges are shared with four adjoining boxes, giving a net total of 8/8 + 12/4 = 4 vertices
- ---> the density of vertices = $1 / a^2b$.

- a vertex joins two glycans and one peptide – each of which is shared by another vertex - so there are 3/2 bonds per vertex; ---> bond density $\rho = 3 / 2a^2b$

- if a = 1.3 nm and b = 1 nm, we expect $\mu = \rho k_B T$ = 3.6 x 10^6 J/m^3.
- for many materials, $Y = (8/3)\mu$ --> Y = 1 x 10^7 J/m^3 in this representation
- Y = 2-3 x 10^7 J/m^3 is observed experimentally

Polymer solutions

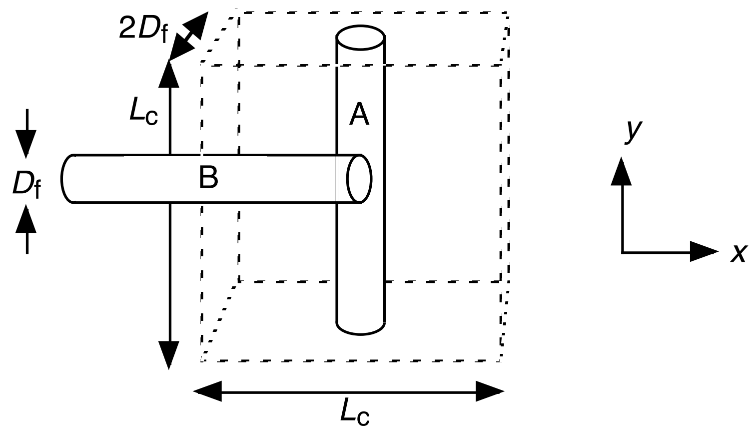
What happens if there are no permanent cross-links between filaments? Then the network can relax when subjected to a shear, although the relaxation time may be long. There are several concentration regimes, each with different properties:



- dilute regime ($\rho < \rho^*$): filaments do not touch, on average
  - rods: density < $1 / L_c^3$
  - chains: density < $3 / 4\pi R_g^3$

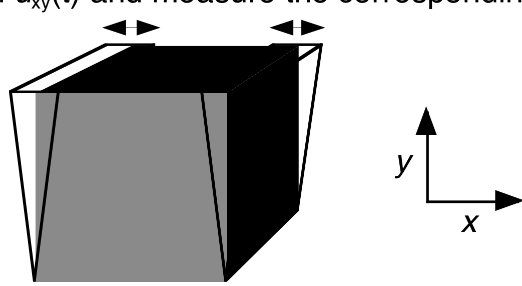
- concentrated regime ($\rho > \rho^{**}$): filaments in frequent contact
  - rods: density > $1 / D_f L_c^2$ (D_f = filament diameter, as below)
  - chains: density > $v_{ex} b^6$ (v_{ex}, b are the excluded volume and chain segment length; proof not trivial; see Doi and Edwards)

- semidilute regime lies between ρ^* and ρ^{**}



Viscoelasticity

- time evolution of polymer solution characterized by frequency-dependent elastic moduli
- apply a periodic strain $u_{xy}(t)$ and measure the corresponding stress $\sigma_{xy}(t)$



- system driven at an angular frequency ω
- introduce two new moduli
  - $G'(\omega)$ = shear storage modulus: $G' \rightarrow \mu$ as $\omega \rightarrow 0$
  - $G''(\omega)$ = shear loss modulus: $G'' \rightarrow \eta / \omega$ as $\omega \rightarrow 0$
- response of system is
  - $\sigma_{xy} = G'(\omega) u_{xy}(t) + G''(\omega) \cdot (\mathrm{d}u_{xy}/\mathrm{d}t)/\omega$

for 1 mg/ml actin:
$G' \sim 10^0$ to 10^2 J/m^3 at
$10^{-2} < \; < 10^{+2}$ rad/sec

rises to 10^9 J/m^3 like plastics
at high frequencies