

PHYS 4xx Net 4 - Elasticity in three dimensions

Random chain networks



- model for vulcanized rubber (Flory, 1953; Treloar, 1975)
- scale factors $\Lambda_x, \Lambda_y, \Lambda_z$ 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):

$$S = -(k_B n/2)[\Lambda_x^2 + \Lambda_y^2 + \Lambda_z^2 - 3 - \ln(\Lambda_x \Lambda_y \Lambda_z) - \ln(n/2)! - (n/2)\ln(2\delta V / V_0)] \quad (1)$$

n is the total number of chains, V_0 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

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

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

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

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

$$\Delta F = (3k_B T n/2) \cdot (\Lambda^2 - 1 - \ln \Lambda) \quad (\text{uniform scaling}) \quad (4)$$

- 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

$$\Delta F = (k_B T n/2) \cdot (\Lambda^2 + 1/\Lambda^2 - 2) \quad (\text{pure shear}). \quad (5)$$

- 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_0 (unchanged by shear)

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

- evaluate ΔF in terms of strain tensor under pure shear conditions of $\Lambda = 1 + \delta$,
 $\text{---} \rightarrow u_{xx} = \delta, u_{yy} = -\delta, u_{zz} = 0$

then

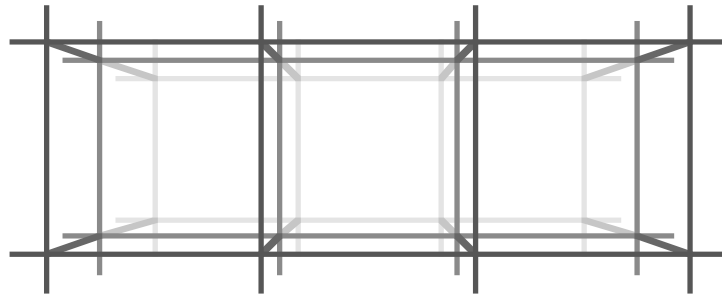
$$\Delta F = 2\delta^2 \mu \tag{7}$$

- comparing (6) and (7)

$$\mu = \rho k_B T. \tag{8}$$

Spring networks

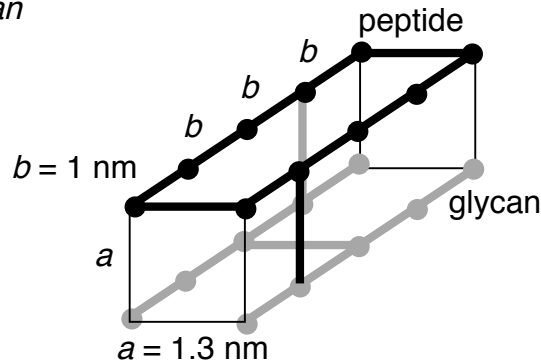
- as an example, we consider a three dimensional network with cubic symmetry



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

$$K_V = k_{sp} / 3s_0 \quad (\text{rigid cubic symmetry}), \tag{9}$$

Example: peptidoglycan



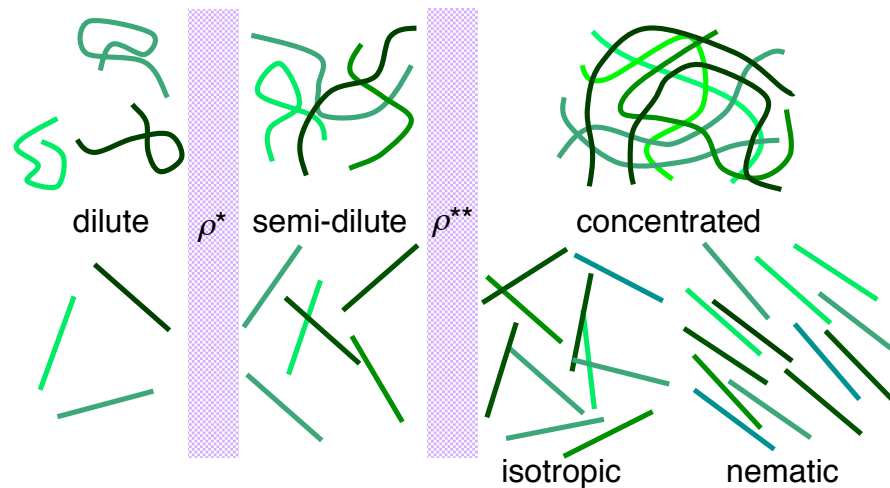
network "bonds" are drawn as heavy lines and their junctions are shown as disks
 The rectangular box:

- has a volume of $a \times a \times 4b = 4a^2b$
- 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 = $1 / a^2b$.

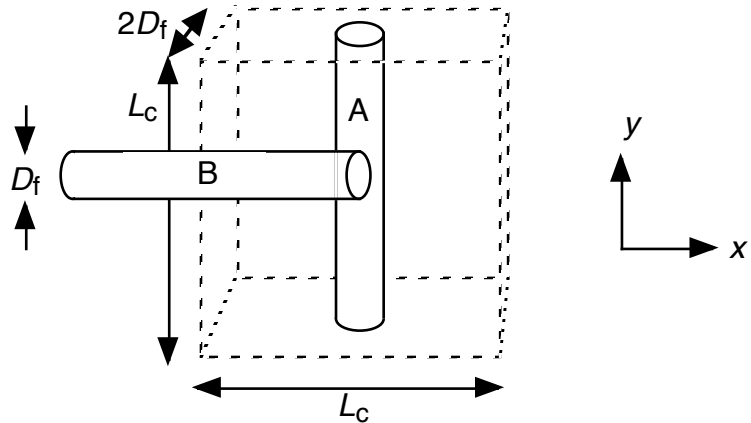
- a vertex joins two glycans and one peptide – each of which is shared by another vertex - so there are 3/2 bonds per vertex; ---> bond density $\rho = 3 / 2a^2b$
- if $a = 1.3 \text{ nm}$ and $b = 1 \text{ nm}$, we expect $\mu = \rho k_B T = 3.6 \times 10^6 \text{ J/m}^3$.
- for many materials, $Y = (8/3)\mu$ --> $Y = 1 \times 10^7 \text{ J/m}^3$ in this representation
- $Y = 2\text{-}3 \times 10^7 \text{ J/m}^3$ 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:

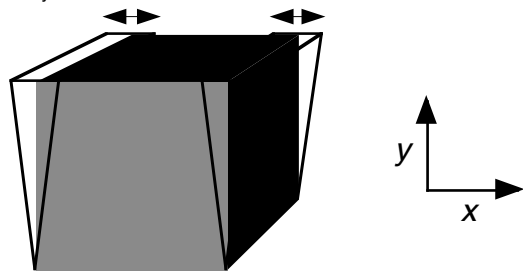


- dilute regime ($\rho < \rho^*$): filaments do not touch, on average
 rods: density $< 1 / L_c^3$
 chains: density $< 3 / 4\pi R_g^3$
- concentrated regime ($\rho > \rho^{**}$): filaments in frequent contact
 rods: density $> 1 / D_f L_c^2$ (D_f = filament diameter, as below)
 chains: density $> v_{ex} b^6$ (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

$$\sigma_{xy} = G'(\omega)u_{xy}(t) + G''(\omega) \cdot (du_{xy}/dt) / \omega$$

for 1 mg/ml actin:

$$G' \sim 10^0 \text{ to } 10^2 \text{ J/m}^3 \text{ at } 10^{-2} < \omega < 10^2 \text{ rad/sec}$$

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

