020521_Quiz 9 Properties

1) Entanglements can be described using the “tube” model of Edwards.
   a) (20 pts.) **Explain** what a tube is by describing its diameter, length and mass-fractal dimension.

   b) (10 pts) **Is there** a connection between the tube model and blobs? **Explain**.

   c) (20 pts) **Is the** tensile modulus of an elastomer enhanced or diminished when calculated using the tube model? Explain.

2) Flory-Rehner theory involves a balance of free energy.
   a) (10 pts) **Describe** this balance with words.
   b) (10 pts) For a series of PDMS elastomers in benzene the swelling ratio, $Q = 1/\varphi$, was found to be 2, 5 and 10. If the first of these gels had a strand length of 1,000 g/mole and an interaction parameter of -0.05,
   What are the interaction parameter and strand length for the other two gels?
   c) (10 pts) **Would the swelling** ratio change with temperature? **Why**?

3) The limiting limiting coefficient for the first normal stress difference for a viscoelastic fluid, Ψ_1^0, can be written as a function of the recoverable shear compliance, J_e^0, and the plateau viscosity, η_0,

$$\Psi_1^0 = 2\, \eta_0^2 J_e^0$$

   which reflects the viscous and elastic nature of this feature of polymer flow.
   a) (10 pts) In words, **explain** why you might expect such a viscous and elastic contribution to Ψ_1^0 for simple shear flow. (You may want to draw a cartoon of simple shear flow and show a temporal network in the fluid to start.)
   b) (10 pts) **Why would** the time dependent shear modulus, G(t), be considered a "memory function"?

Answers: 020521_Quiz 9 Properties

1) a) The tube is formed by entanglements that define a confined path for the chain. This path, or tube has a diameter related to the entanglement molecular weight and the density of the polymer melt. The length of the tube along the tube path is $a\{(Nl^2)^{3/2}/a^3\}$. The tube forms a random walk in the melt, with a dimension of 2.

b) The tube is similar to the blob model in that the chain is decomposed into elements of size a^3 that form a random walk in the melt. The tube subunits are very similar to blobs.

c) It is enhanced in the tube model by a factor of a^2z^2/R_0^2. z is the number of tube subunits in the chain.

2) a) An elastomer swells since the solvent is compatible with the polymer similar to a chain dissolving in a solvent. Then the Flory Huggins equation can be used to calculate the free energy of mixing for the chains. This swelling is opposed by the elasticity of the network. A free energy based on Flory-Huggins and rubber elasticity can be minimized to find the degree of swelling at equilibrium,

$\varphi_c^{5/3} = V_c\rho/(M_c\ (1/2 - \chi))$

b) Q = 2, 5, 10
φ = 0.5, 0.2, 0.1

The interaction parameter is fixed for a given solvent and polymer combination at a fixed temperature, i.e. it is -0.05 for all three cases. Then,

$M_c \sim Q^{-5/3}$

so, $M_{c2} = M_{c1}\ (5/2)^{5/3}$ and
$M_{c3} = M_{c1}\ (5)^{5/3}$

c) Yes, the swelling ratio would increase with temperature since $\chi \sim 1/T$. Then,

$$Q \sim \left(\frac{M_c}{V_c\rho}\left\{\frac{1}{2}-\frac{B}{T}\right\}\right)^{3/5}$$

3) a) Viscous drag leads to a force that opposes the applied force in the z-direction for instance. This force is translated to the transverse direction by the elasticity of the temporal network created by entanglements and associated with the rubber elasticity term.

b) G(t) makes sense as a memory function since it accounts for the memory of stress with time for a fluid. It also works for the known limits, for a Newtonian fluid it is a delta function of time so there is no memory, and for a Hookean elastic it is a constant so it corresponds with infinite mechanical memory.