## 06/06/07 Final Polymer Propeties

1) In class we showed that the complex compliance, J*, is given by,

$$J^* = J_e^0 - i\frac{1}{\eta_0\omega}$$

    a) Define the terms $J_e^0$ and $\eta_0$.
    b) Calculate G* knowing that this is the inverse of the complex compliance.
    c) Give an expression for the storage modulus $G'(\omega)$.
    d) Sketch a plot of $\log(G'(\omega))$ versus $\log(\omega)$ for several molecular weight polymers in the flow regime.
    e) Show how your expression for $G'(\omega)$ can be used to predict these curves in the limits of very low frequency and moderate frequency.

2)     a) Show the behavior of viscosity with shear rate for a series of different molecular weight polymers of the same type.
    b) Show how $\eta_0$ is obtained from these plots.
    c) Show the dependence of $\eta_0$ on molecular weight.
    d) Explain the regimes observed in part "c".
    e) Show the dependence of $J_e^0$ on molecular weight.

3) Time and temperature are related for materials that follow Eyring rate theory by the Arrhenius equation (at high Temperature relative to $T_g$) or by the Vogel-Fulcher Equation (near $T_g$). Time-temperature superposition involves use of the Vogel-Fulcher equation in the Williams-Landel-Ferry formalism to correlate mechanical measurements made at one temperature and frequency or time-scale to another temperature by shifting the frequency or time-scale.
    a) Give the Arrhenius equation for relaxation time (or viscosity) as a function of temperature.
    b) If you measured the creep compliance from 0.01 s to $1 \times 10^8$ s at -80 C and wanted to plot the curve on a plot with a reference temperature of 25C how would you do this using the Arrhenius equation.
    c) If you measured the creep compliance from 0.01 s to $1 \times 10^8$ s at +80 C and wanted to plot the curve on a plot with a reference temperature of 25C how would you do this using the Arrhenius equation.
    d) If you were working with a tire compound that is 50% carbon black would this time temperature superposition work?
    e) For proteins biophysicists discuss a kind of glass transition where they propose that water in the protein hydration layer can display a glass transition restricting conformational changes in the protein. Do you expect this behavior to follow a simple time-temperature superposition? Explain your reasoning.

**Second Quiz from Quizes 3, 4 and 5**

Q3 2) The hydrodynamic radius is measured in a dynamic experiment such as observation of flow or diffusion.
a) Write an equation for the viscosity of a polymer solution that describes the increase in viscosity with concentration. (Give the units of all constants in this equation).
b) Write an expression for the intrinsic viscosity, $[\eta]$, based on the units of this constant using the hydrodynamic radius and the molecular weight.
c) Give a function of $[\eta]$ in terms of molecular weight for a Gaussian chain, a self-avoiding walk and for a rod.
d) How is the diffusion coefficient related to the hydrodynamic radius?
e) Explain qualitatively how the dynamic light scattering experiment (DLS) can measure the diffusion coefficient.

Q4 2) In class we considered 2 ways to obtain the RMS end-to-end distance, $\langle R^2 \rangle^{1/2}$ using the Gaussian distribution function.
a) Explain what these two approaches are.
b) Which approach gives a better value.
c) Sketch a plot of the Gaussian probability in 3D space versus end-to-end distance from $-Nl_k$ to $+Nl_k$, where N is the number of Kuhn units and $l_k$ is the Kuhn length. What happens beyond $Nl_k$?
d) Given the Boltzman probability function, $p_B(R) = \exp(-G(R)/k_BT)$, where G(R) is the free energy as a function of "R" and $k_B$ is Boltzmann's constant, write an expression for the free energy of a Gaussian chain by comparison with the Gaussian probability function.
e) What can you say about the enthalpic part of the free energy for an isolated Gaussian chain from this comparison (remembering that G = H - TS).

Q5 A polymer coil can accommodate to changing thermodynamic conditions because it is a molecule which spans several orders of size. Thermodynamic conditions on a small scale can differ from conditions at a large scale. This concept is the basis for the definition of a "blob".

Q5 1) a) Define a "blob".

b) Give the temperature dependence of the *thermal* blob for a polymer coil.

c) How can this temperature dependence describe structural changes that occur to a polymer in dilute solution? (Discuss these structural changes perhaps using scattering curves or using schematic magnification of the structure)

d) Sketch the dependence of $R_g$ and $R_H$ on temperature.

e) Is the concept of a thermal blob needed to explain this dependence?

**Third Quiz from Quizes 5, 6 and 7**

Q5 2) The Flory-Krigbaum model is based on the concept of excluded volume.
   a) For an ideal gas what is the excluded volume?

   b) A Gaussian chain is sometimes called an ideal chain or ideal coil. Explain why this term might be used.

   c) Why would you expect enthalpy to play a role in excluded volume? (Give an example of what enthalpy is in a model system and how it could effect excluded volume.)

   d) Give the Flory-Krigbaum expression for excluded volume. And sketch a plot of excluded volume versus temperature.

   e) Explain the logic of the equation in part "d" by considering the limits in temperature.

Q6 1) Polymer chains in a melt display ideal behavior. In dilute solution they display non-ideal behavior, for instance in terms of the second virial coefficient, $A_2$.

   a) Does this observation agree with the behavior of a gas? Explain.

   b) Give the virial expansion for pressure in a gas in terms of concentration (n/V) and explain how the deviation from ideality is effected by concentration.

   c) For a polymer in solution how would the first virial coefficient need to be modified compared with a gas?

   d) Explain (as best you can) what is the fundamental difference between a polymer and a gas that gives rise to different ideal limits in concentration.

   e) Give the Flory-Huggins expression for the second virial coefficient.

Q7 2) a) Plot the Flory-Huggins equation for the gas mixture,
   $(S/(NkT) = (\phi_A \ln\phi_A)/z + (1-\phi_A) \ln(1-\phi_A) + \phi_A(1-\phi_A)\chi)$,
   in a plot of free energy per kT per lattice site versus volume fraction of A for $\chi = 0$, $\chi = 0.5$, $\chi = 1$, $\chi = 2$, $\chi = 2.5$.

   b) Show graphically the location of the critical point, the binodal points and the spinodal points in part "a".

   c) The binodal regime is considered a meta-stable region of the phase diagram while the spinodal regime is considered unstable. Explain the difference between stable: meta-stable and unstable in the context of the free energy plot of part "a".

   d) Sketch a phase diagram for a gas mixture following the Flory-Huggins-like gas equation.

   e) Explain the connection between the plot in part "a" and the plot in part "d".

# Answers Final First 3 questions

1) a) $J_e^0$ is the recover shear compliance. It is the plateau value of compliance at moderate frequency. $\eta_0$ is the zero shear rate viscosity extrapolated from the viscosity versus rate of strain curve.

b)
$$G^* = 1/J^* = \dfrac{1}{\left/ J_e^0 - i\dfrac{1}{\eta_0\omega}\right.}$$

multiply numerator and denominator by the complex conjugate of the denominator times $\omega\eta_0$ yields,

$$G^* = 1/J^* = \dfrac{\left\{ J_e^0(\eta_0\omega)^2 + i\eta_0\omega \right\}}{\left\{ (\eta_0\omega J_e^0)^2 + 1 \right\}}$$

c)
$$G'(\omega) = \dfrac{J_e^0(\eta_0\omega)^2}{\left\{ (\eta_0\omega J_e^0)^2 + 1 \right\}}$$

d)


e) At low frequency the expression in "c" reaches the limit of $G'(\omega) = J_e^0\eta_0^2\omega^2$. At moderate frequency the limit of $G'(\omega) = \dfrac{J_e^0(\eta_0\omega)^2}{\left\{ (\eta_0\omega J_e^0)^2 \right\}} = \dfrac{1}{J_e^0}$ is reached so a constant plateau modulus is seen corresponding to the plateau in recoverable compliance.

**b)** The zero shear rate viscosity is found at the low shear rate intercept where the viscosity reaches the Newtonian plateau.



**d)** Below the entanglement molecular weight the viscosity follows Rouse behavior and is linear in molecular weight. Above the entanglement molecular weight we observe a 3.4 power-law dependence on molecular weight that remains unexplained by theory. The increase in molecular weight dependence is due to entanglements.



**3) a)** $\eta = \eta_0 \exp\left(\dfrac{A}{kT}\right)$ where A is the barrier energy for molecular flow and $\eta_0$ is the viscosity at infinite temperature. An identical equation applies to relaxation time, $\tau = \tau_0 \exp\left(\dfrac{A}{kT}\right)$.

b)

$$\tau_{-80°C} = \tau_0 \, exp\left(\frac{A}{K \, 193k}\right)$$

$$\tau_{25°C} = \tau_0 \, exp\left(\frac{A}{K \, 298k}\right)$$

$$\frac{\tau_{25}}{\tau_{-80}} = exp\left(\frac{A}{K}\left\{\frac{1}{298} - \frac{1}{193}\right\}\right)$$

The -80°C time scale is multiplied by

$$t_{25} = t_{-80} \cdot exp\left(\frac{A}{K}\left\{-0.00183\right\}\right)$$

c) $t_{25C} = t_{T_1} \exp\left(\frac{A}{k}\left\{\frac{1}{298} - \frac{1}{T_1}\right\}\right) = t_{80C} \exp\left(\frac{A}{k}\left\{\frac{1}{298} - \frac{1}{353}\right\}\right) = t_{80C} \exp\left(\frac{0.00052A}{k}\right)$

d)  No this will not work since filled elastomers first contain at least two phases one of which can display time temperature superposition while the other, carbon black, can not.  Also, some elastomer is trapped in the filler particles and might not display the expected behavior due to confinement.  A real tire has a large fraction of oil which makes the material essentially a reinforced gel.  Simple time temperature superposition will not generally apply to gels since the solvent component does not display time temperature superposition with the same reference energy, A, as the elastomer.

e)  No this is an extremely complex system.  Water can only display this behavior, apparently, while it is enthalpically associated with the polymer.  This could introduce an enthalpic property to the proposed "glass transition" making it possibly indistinguishable from a first order transition.  Two component systems do not display simple time-temperature superposition.  See review on protein glass transition linked at
http://www.eng.uc.edu/~gbeaucag/Classes/Properties/Protein%20Glass%20Transition%20Review.pdf.

**Second Quiz Answers**

Q3 2) a) $\eta = \eta_s(1 + \phi[\eta])$ where $[\eta]$ is the intrinsic viscosity with units of volume per mass.

b) $[\eta] = R_H^3/N$, where N is the molar mass.

c) For a Gaussian Chain we have $R \sim N^{1/2} l_p$

For a SAW $R \sim N^{3/5} l_p$

For a Rod $R \sim N l_p$, so,

$[\eta] \sim N^{1/2}$

$[\eta] \sim N^{0.8}$

$[\eta] \sim N^2$

d) $D = 3kT/(6\pi\eta_0 R_H)$

e) In DLS we observe the intensity at a fixed scattering angle. The intensity is recorded as a function of time and the flickering that results from motion of particles in and out of the beam leads to a randomly oscillating pattern in time. The time correlation function decays in time difference between measurements and this is fit with $I(q,t) = \exp(-tq^2 D)$ to yield D.

Q4 2) a) The first approach is to integrate the probability function times $R^2$ and normalize by the integral of the probability function. The second approach is to set the first derivative of the probability function to 0 and solve for R* at the peak, the most probable value.

b) The integral gives the true value for the second moment.

c)
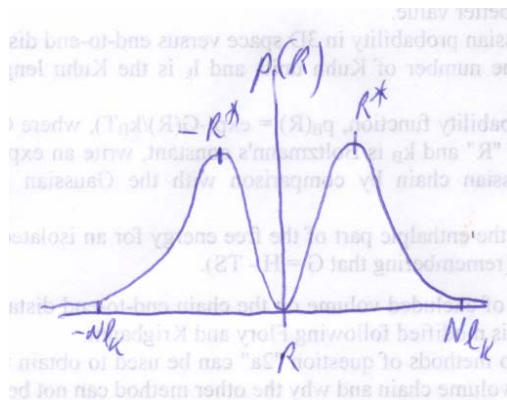


Beyond $Nl_k$ the function should go to 0 since it is impossible to extend the chain beyond this point but the Gaussian continues with a finite probability.
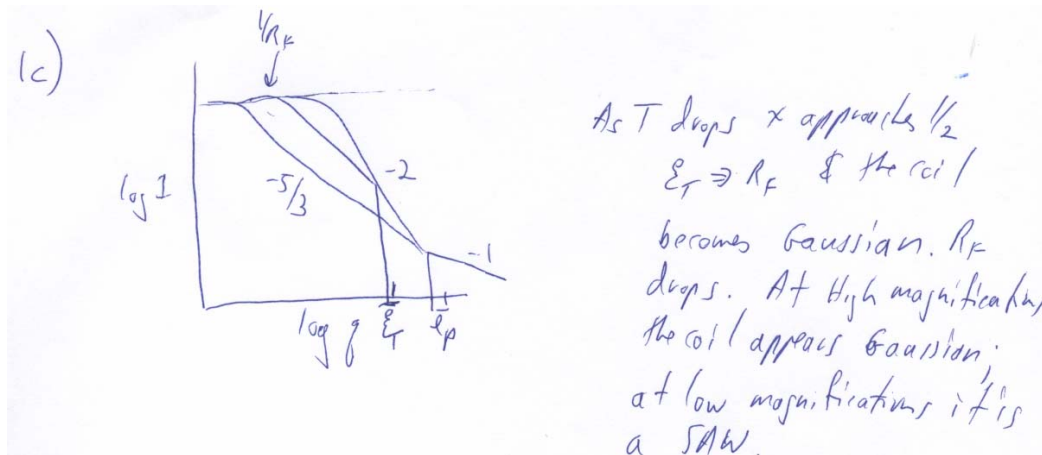
d) $3R^2/(2Nl_k^2) = 3R^2/(2R_0^2) = G(R)/k_BT$ so $G(R) = 3k_BT \, R^2/(2R_0^2)$

e) The free energy from part "d" has only an entropic part TS and no enthalpic part so this is the free energy for a chain with no enthalpic interactions or excluded volume.
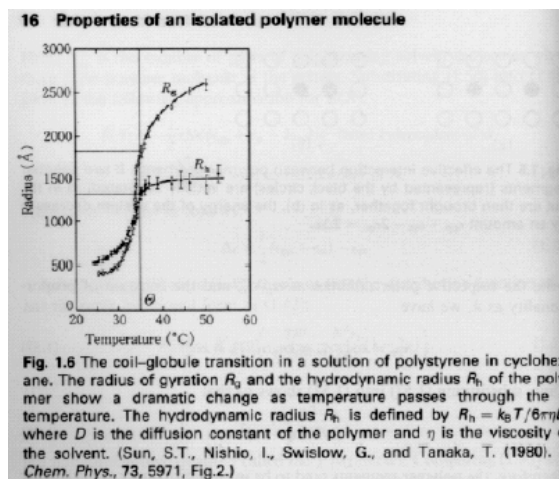
Q5 1) a) A blob is a size scale associated with a change in structural scaling. It is used to renormalize a chain structure.

b) $\xi_T = l_p/(1-2\chi) = l_p/(1-2z\Delta\varepsilon/kT)$

c)

(c)



As T drops χ approaches ½
$\xi_T \Rightarrow R_F$ & the coil
becomes Gaussian. $R_F$
drops. At high magnifications
the coil appears Gaussian;
at low magnifications it is
a SAW.

d)



**16  Properties of an isolated polymer molecule**

**Fig. 1.6** The coil–globule transition in a solution of polystyrene in cyclohexane. The radius of gyration $R_g$ and the hydrodynamic radius $R_h$ of the polymer show a dramatic change as temperature passes through the θ temperature. The hydrodynamic radius $R_h$ is defined by $R_h = k_B T / 6\pi\eta D$, where $D$ is the diffusion constant of the polymer and $\eta$ is the viscosity of the solvent. (Sun, S.T., Nishio, I., Swislow, G., and Tanaka, T. (1980). *J. Chem. Phys.*, 73, 5971, Fig.2.)

e)  No, the dependence can be shown just using the Flory-Krigbaum function.  The thermal blob model is needed to explain the structural meaning of the Flory-Krigbaum function.

**Quiz 3**

Q5  2)  a)  An ideal gas is composed of molecules of no volume so there is no excluded volume.

b)  A Gaussian chain is called an ideal chain in analogy to an ideal gas since a Gaussian chain displays no excluded volume.

c)  Enthalpy involves binary interactions between molecules in a system.  The simplest binary interaction involves the volume that is excluded from one molecule by the presence of another.  More complicated interactions might involve bonding, electrostatic charge forces, and van der Waals and London forces.  There is little or no distinction between the kind of ineraction involved in excluded volume and the kind of interaction involved in enthalpy.

d)  $V = V_0(1-2\chi)$
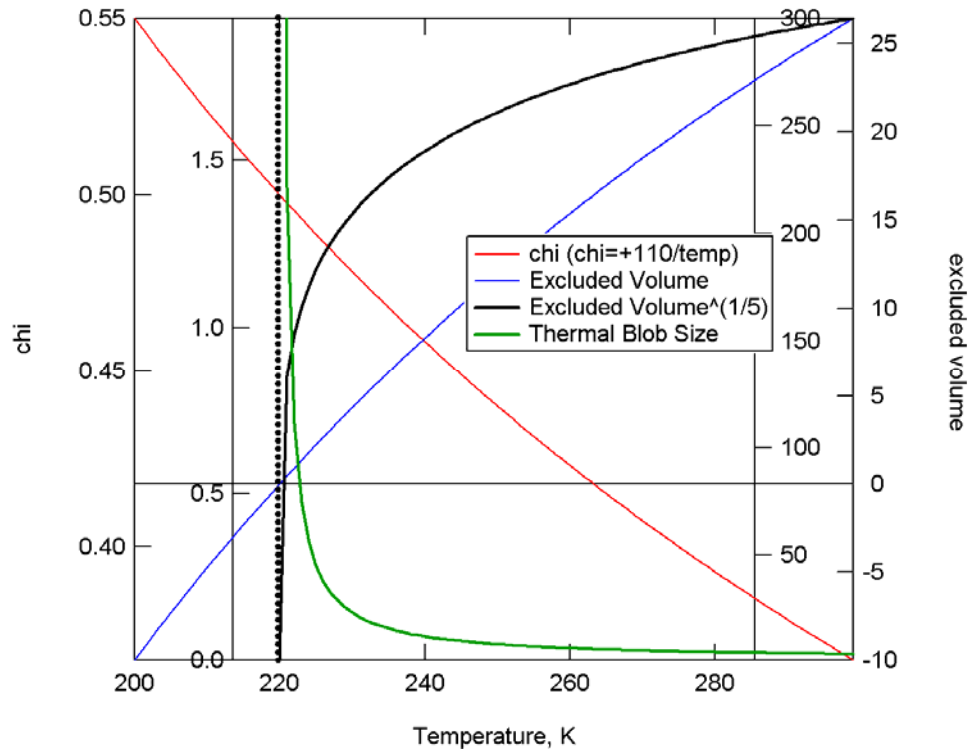
e)  As temperature drops the excluded volume decreases until it is 0 at the theta temperature (about 220 K above).  At high temperature the excluded volume gradually approaches $V_0$.

Q6  1)  a)  For a gas ideal behavior is seen in dilute conditions.  Higher concentrations lead to non-ideal behavior so this is in direct contrast to the behavior of a polymer.
b)  $P = (n/V) kT + A_2 (n/V)^2 + A_3 (n/V)^3 + \dots$
At higher concentration, $(n/V)$, the non-ideal behavior, $A_2$ and $A_3$ terms, are enhanced.
c)  For a polymer each chain is composed of N units so the first term becomes $(n/V) * (1/N)$.
d)  The polymer chain has essentially a fixed internal concentration because it is connected together.  For this reason, the dilute condition is already quite high in local concentration compared to a gas and we observed non-ideal behavior with an expanded coil structure.  At high concentration these effects are screened due to interpenetration of the coils above $(n/V)*$.
e)  $A_2 = (1/2 - \chi)$

Q7  2)
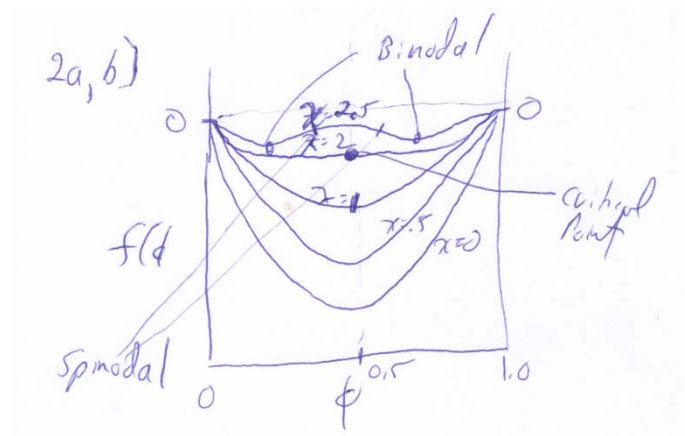


c)  Stable indicates the one phase region where any fluctuation in composition leads to a net increase in the free energy.  Unstable indicates the spinodal region where any fluctuation in composition lowers the free energy so phase separation is spontaneous.  Meta-Stable indicates the binodal region where small fluctations dissipate due to a weak increase in free energy but large fluctuations decay into phase separation with a net lowering of the free energy.