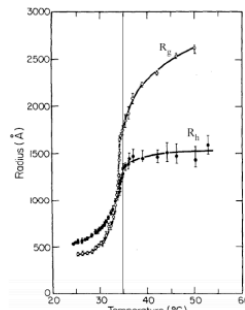


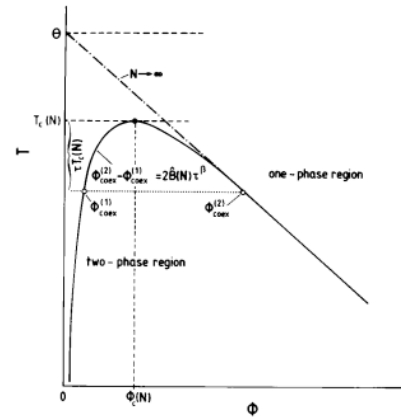
**121214 Final Polymer Properties**  
*6 questions 4 pages*

- 1) We often refer to a Gaussian chain when discussing a polymer in the theta-state.
  - a) What is the Gaussian function and how does it relate to a polymer in the theta-state?
  - b) Show how the Gaussian function can be used to determine the most probable chain end-to-end distance.
  - c) How can the Gaussian function be used to calculate  $\langle R^2 \rangle$ ? (Just outline the method to solve for  $\langle R^2 \rangle$  using the Gaussian probability.)
  - d) Show how the Gaussian probability can be used to quantify the energy associated with extension of a theta-chain.
  - e) Obtain an expression for the spring constant for a theta-chain.
  
- 2) In a computer simulation it was found that the Kuhn length is 1 for a random walk but is 1.2 for a chain that does not take a back step and is 1.4 for a chain with fixed bond angle.
  - a) Show that the absence of a back step leads to  $l_k = 1.22$ .
  - b) Show that a restricted bond angle of  $109^\circ$  leads to  $l_k = 1.4$ .
  - c) Experimental measurement for polyethylene finds  $C_\infty = 6.7$ . What is  $l_k$ ?
  - d) Why is this value for  $l_k$  larger than  $1.4 l_0$ ?
  - e) Do you expect  $C_n$  for polyethylene (finite molecular weight) to be larger or smaller than 6.7? Why?

- 3) The following plot (left) shows the behavior of  $R_g$  (and  $R_h$ ) as a function of temperature for polystyrene in cyclohexane. The plot to the right shows a schematic phase diagram of a polymer solution displaying UCST behavior near the overlap concentration,  $c^*$ .



**Figure 3.** Radius of gyration,  $R_g$ , and hydrodynamic radius  $R_h$  versus temperature for polystyrene in cyclohexane. Vertical line indicates the phase separation temperature. From Reference [21].



**FIG. 1.** Schematic phase diagram of a polymer solution in the space of the temperature  $T$  and the volume fraction  $\phi$ . The coexistence curve separates a dilute solution of collapsed chains [at  $\phi_{\text{cox}}^{(1)}$ ] from a semidilute solution of overlapping chains [at  $\phi_{\text{cox}}^{(2)}$ ]. These two branches of the coexistence curve merge at a critical point  $T_c(N)$ ,  $\phi_c(N)$ . For  $N \rightarrow \infty$  the critical point merges with the  $\Theta$  point of a dilute polymer solution [ $T_c(N \rightarrow \infty) \rightarrow \Theta$ ,  $\phi_c(N \rightarrow \infty) \rightarrow 0$ ] and the unmixing transition has a tricritical character. At  $T = \Theta$ , the chain configurations are ideal Gaussian coils, while their structure at  $T_c(N)$  is nontrivial.

Figure 1.

(a)

(b)

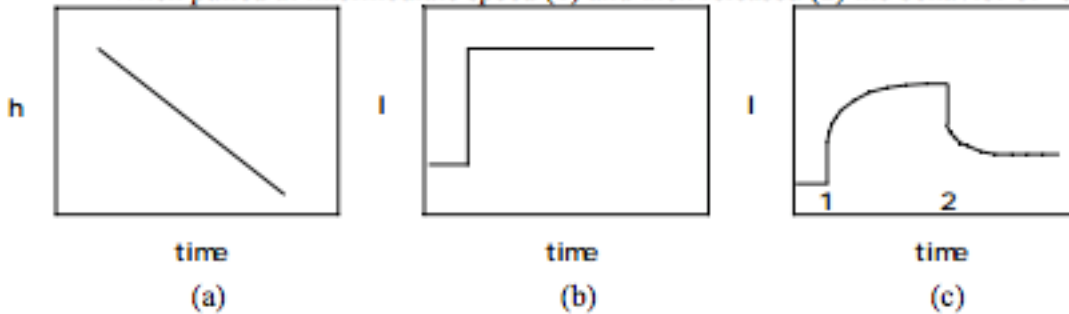
- At what composition on the right plot would the behavior seen in the left plot be observed? Why.
  - How would the left plot differ if a concentration to the right side of the right plot were used?
  - Define  $c^*$ .
  - At the lowest concentrations on the right plot the phase boundary is physically not achievable. Explain what happens to the right plot at very low concentrations if  $c^*$  is accounted for.
  - Explain why the theta temperature is the critical point (critical temperature) for an infinite molecular weight polymer. At what composition does the critical point for an infinite molecular weight polymer occur? In the context of  $c^*$  is it possible to achieve this critical point?
- 4) a) Write the Flory-Huggins expression and explain what it describes, i.e. “the ... free energy of mixing for ... per ... and per ...”.
- Explain how the chemical potential for the solvent in a polymer solvent mixture can be obtained from this expression.
  - For a mixture of two polymers of the same molecular weight,  $N$ , what is the value of the critical interaction parameter? Why does this differ from the critical interaction parameter for a high molecular weight polymer in a solvent (1/2)?
  - Sketch a plot of the Flory Huggins equation as a function of concentration for  $\chi$  below the critical  $\chi$ ,  $\chi$  at the critical  $\chi$  and  $\chi$  above the critical  $\chi$ .
  - For the plot with  $\chi$  above the critical  $\chi$  show where the meta-stable region is and explain why it is meta-stable.

5)

Silly Putty® is a typical viscoelastic material made from polydimethylsiloxane, silica and oils.

a) **Propose 3 functions** for the following behavior of Silly Putty.

- When left on the table for a long period of time the height,  $h$ , decays in the manner of figure "a".
- When rapidly pulled and observed over only short times the length,  $l$ , follows "b".
- When pulled at intermediate speed (1) and then released (2) the behavior of "c" results.



b) -For question "a" which terms are related to permanent set in the silly putty?

-What relaxation times are involved in your answer to question "a"?

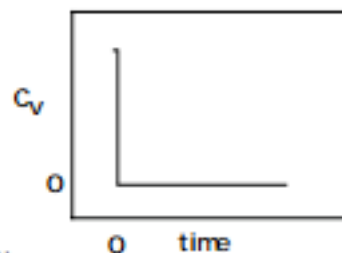
c) If the Silly Putty were subjected to an oscillatory stress following a cosine function,

-which of terms in your equations would be related to the in-phase and out-of-phase parts of the dynamic strain?

-On a plot of real and imaginary modulus versus frequency,  $\omega$ , at room temperature, where would you expect to see the behavior of figures "a" and "b"?

-What do you expect to be the behavior of creep compliance,  $J(t) = \epsilon(t)/\sigma_0$ , at long times for Silly Putty?

d) In addition to the two relaxation times related to Silly Putty, briefly **describe two other** characteristic times discussed in class related to a bell and a grain of pollen subjected to thermal motion. (In your description of the bell mention the basic features of the delta function.)



e) If the velocity correlation function,  $C_v$ , had the form:

What could you say about  $\tau_v$ ?

What type of particles display such behavior? Why (give relationship)?

6)

The Rouse model represents a polymer coil as a series of beads and springs.

- a) The Rouse spring has a spring constant based on rubber elasticity theory. This is sometimes called the ideal rubber law in analogy to an ideal gas.

-What is the association between an ideal rubber and an ideal gas?

- b) The Maxwell model for visco-elasticity is based on a dash pot (viscous element) and a spring (Hookean elastic). This is similar to the Rouse model.

-What is the difference between the Maxwell model and the Rouse model consider:

-The assumptions involved in defining a Rouse unit,

-The molecular and theoretical basis of a Rouse spring,

-The molecular and theoretical basis for a Rouse bead,

-The ability of the 2 models to predict behavior in terms of molecular features.

- c) The relaxation time for a Maxwell element is the viscosity of the dash pot divided by the spring constant for the spring,  $\tau = \eta/k_{sp}$ . The following expression,

$\tau = \zeta_R / \{4b_R \sin^2(\delta/2)\}$ , was obtained for a Rouse chain of infinite molecular weight.

-What are the similarities between the two relaxation times?

-What are the differences?

-Describe the terms in the Rouse relaxation time with respect to the Rouse Model.

-What is  $\delta$  and what values can it take for an infinite chain?

- d) The term "Free-Draining" is often associated with the Rouse model. Free draining means that solvent or other polymer chains have no effect on the dynamic response of a chain, i.e. the solvent can freely move in and out of the Rouse chain.

-Explain why free-draining might be associated with the Rouse model.

-Why would the ratio of the Rouse friction factor, to the mean square Rouse size,  $\zeta_R/a_R^2$ , be constant in the number of mer units for a Rouse unit under a free-draining model?

- e) The Rouse model is in some ways identical in dynamic behavior to the dumb bell model. This similarity relies on the dominance of the lowest order modes on the dynamic response as will be discussed in class.

-Give expressions for the relaxation time for the dumb-bell and Rouse models.

-How does the dumb-bell model compare with a Maxwell element in terms of the relaxation time?

## ANSWERS: 121214 Final Polymer Properties

1) a) The Gaussian function is  $P(R) = K \exp(-3R^2/(2n_k l_k^2))$ . In the theta-state the chain adopts a Gaussian conformation displaying a mass fractal dimension of 2.

b) The most probable end-to-end distance,  $R^*$ , can be obtained by taking the derivative of  $d(R^2 P(R))/dR$  which yields  $(R^*)^2 = 2/3 n l^2$  for the Gaussian distribution function. The most probable end-to-end distance also scales with  $n^{1/2}$  so it reflects a 2-dimensional chain.

$$c) \langle R^2 \rangle = \frac{\int_{-\infty}^{\infty} R^2 P(R) dR}{\int_{-\infty}^{\infty} P(R) dR}.$$

d) The entropy can be obtained from  $S = \ln(P(R)) \sim -3R^2/(2n_k l_k^2)$  and the chain energy can be obtained from  $E = -k_B T S = 3 k_B T R^2/(2n_k l_k^2)$  for chains with no enthalpic interactions (athermal chains).

e) For extension the change in energy,  $dE$ , with extension is equal to the applied force,  $F$ , times the change in end-to-end distance,  $dR$ ,  $dE/dR = F = (3 k_B T/(n_k l_k^2)) R = k_{spr} R$ .

2)

$$\langle r_{i+1} \rangle = \sum_{k=1}^{k=z} b_k = 0$$

a)

For exclusion of the previous step this sum does not equal 0

$$\langle r_{i+1} \rangle_{Random} = \sum_{k=1}^{k=z} b_k = 0 = (z-1) \langle r_{i+1} \rangle_{ShortRangeInteraction} - r_i$$

so

$$\langle r_{i+1} \rangle_{ShortRangeInteraction} = \frac{r_i}{(z-1)}$$

$$\langle r_i \cdot r_j \rangle = \frac{b^2}{(z-1)^{|i-j|}} \quad \text{and} \quad \langle R^2 \rangle = \sum_{i=1}^n \sum_{j=1}^n \langle r_i \cdot r_j \rangle \equiv \sum_{i=1}^n \sum_{k=-\infty}^{\infty} \frac{b^2}{(z-1)^{|k|}} = n b^2 \frac{z}{z-2} = n b_{effective}^2$$

The second to the last equality is the result of the Sum of Geometric Progression Rule,  $\lim_{n \rightarrow \infty} \text{of } a + ar + ar^2 + \dots = a/(1-r)$  substituting  $x=1/(z-1)$  results in  $2/(1-x) - 1 = 2(z-1)/(z-2) - 1 = z/(z-2)$

For Cartesian simulation  $z = 6$  and  $b_{eff}$  is 1.22 b so about a 25% increase for one step self-avoidance.

b) Use same approach as in (a) replacing  $1/(z-1)$  with  $\cos(71^\circ)$ . The final equation is  $n b^2 (1 + \cos(71^\circ)/(1 - \cos(71^\circ))) = 2 n b^2$ . So  $b_{eff} = 1.4 b$ .

$$c) l_k = 1.54 \text{ \AA} \cdot 6.7 = 10.3 \text{ \AA}.$$

d) It is larger due to bond rotation restrictions and higher order restrictions to chain flexibility.

e)  $C_n$  should be smaller due to end group effects that serve to reduce persistence due to a higher degree of flexibility for chain ends. In class we suggested an end-group functionality,

$$\frac{1}{C_n} = \frac{1}{C_\infty} - \frac{2K}{M_n}.$$

3) a) The left plot is for a single coil going through the collapse transition. This occurs at concentrations below the overlap concentration and presumably below the critical composition (peak value on the miscibility limit curve in figure 1) b. So the behavior would be seen to the far left of the right plot.

b) In more concentrated conditions the coils would overlap (above  $c^*$ ) so that interactions would be screened at large scales. This means that a different mechanism for coil collapse would be observed. At large scales the coils would be in the theta state at all temperatures, at small scales we would observe coil collapse. The situation would be complex. On reaching the miscibility limit the system would separate into two distinct phases with the less dense phase on the top, like oil and water.

c)  $c^*$  is the concentration where polymer coils (or other structures) just begin to overlap. It is the mass of the molecule divided by the volume of the molecule  $z/R^3$ . For a mass fractal object  $z \sim R^{df}$  so  $c^* = z/R^3 \sim z^{1-3/df}$ .

d) Below  $c^*$  the coil can not be diluted further since it maintains a concentration of  $c^*$  within the coil. Under these conditions the miscibility limit is frozen at the  $c^*$  value and the phase diagram would have a horizontal line to lower concentrations. That is, coil collapse would happen at the same temperature for all compositions more dilute than  $c^*$ .

e) The critical point on the phase diagram follows .

$$T_c(N) = \Theta / (1 + 1/\sqrt{N})^2 \approx \Theta - 2\Theta/\sqrt{N}, \quad N \rightarrow \infty, \quad (1)$$

$$\phi_c(N) = 1 / (1 + \sqrt{N}) \approx 1/\sqrt{N}, \quad N \rightarrow \infty. \quad (2)$$

so as  $N \Rightarrow \infty$   $T_c \Rightarrow \Theta$  and  $\Phi_c \Rightarrow 0$ . It is not possible to reach this critical concentration since we are limited to concentrations above  $c^*$ . However, as we approach  $N \Rightarrow \infty$ ,  $c^* \Rightarrow 0$  so in the limit of an infinite chain we can reach this critical composition.



4) a) The Flory Huggins equation

describes the Helmholtz mixing free energy per lattice site,  $kTf_m(\phi)$  for a Polymer/Solvent system in terms of the volume fraction polymer,  $\phi$ , the degree of polymerization,  $N$ , and the Flory-

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Huggins interaction parameter,  $\chi = (z/2kT) [\epsilon_{pp} + \epsilon_{ss} - 2\epsilon_{ps}]$ , where  $z$  is the coordination number for the lattice,

$$f_m(\phi) = \phi \ln \phi / N + (1-\phi) \ln(1-\phi) + \chi \phi (1-\phi)$$

The features of this equation should be familiar to you. The Helmholtz (Volumetric) free energy change on mixing for a given system is given by the above expression times the number of lattice sites in the system,  $\Omega$ ,  $F_m(\Omega, \phi) = \Omega kT f_m(\phi)$ .

b)

The chemical potential, here  $\mu_p$  or  $\mu_s$ , for one component of a mixture is the derivative of the Gibbs free energy for the system with respect to the number of moles of that component. The Gibbs free energy is related to the Helmholtz free energy by,  $G = F + PV$ . For the Flory lattice system the volume equals the number of lattice sites time the volume of one site,  $V = \Omega V_c$ , where  $\Omega = n_s + n_p N$  and  $N$  is the degree of polymerization. Changing the number of moles of one component in the Flory lattice model, while retaining the number of moles of the other component will result in a change in the lattice size,  $\Omega$  and the volume fraction  $\phi$ , and system volume,  $V$ . This means,

$$\mu_{s: np, T, P \text{ constant}}(\phi, P, T) - \mu_s^0(T) = (\delta F / \delta \Omega)_{\phi, T} (\delta \Omega / \delta n_s)_{np} + (\delta F / \delta \phi)_{\Omega, T} (\delta \phi / \delta n_s)_{np} + PV_c$$

Where  $\mu_s^0(T)$  is the chemical potential of the pure solvent.

From the definition of  $\Omega$ ,  $(\delta \Omega / \delta n_s)_{np} = 1$ ; and given that  $\phi = n_p N / (n_p N + n_s) = n_p N / \Omega$ , so  $(\delta \phi / \delta \Omega)_{np} = -n_p N / \Omega^2$ .  $(\delta \phi / \delta n_s)_{np} = (\delta \phi / \delta \Omega)_{np} (\delta \Omega / \delta n_s)_{np} = -n_p N / \Omega^2 = -\phi / \Omega$ .  $(\delta F / \delta \Omega)_{\phi, T} = kT f_m(\phi)$ , and  $(\delta F / \delta \phi)_{\Omega, T} = \Omega kT (\delta f_m / \delta \phi)_{\Omega, T}$ , so,

$$\mu_{s: np, T, P \text{ constant}}(\phi, P, T) = \mu_s^0(T) + kT (f_m(\phi) - \phi (\delta f_m / \delta \phi)_{\Omega, T}) + PV_c$$

c) In general, the critical interaction parameter is given by,

$$\chi_{Critical} = \frac{\left(N_A^{1/2} + N_B^{1/2}\right)^2}{2N_A N_B}$$

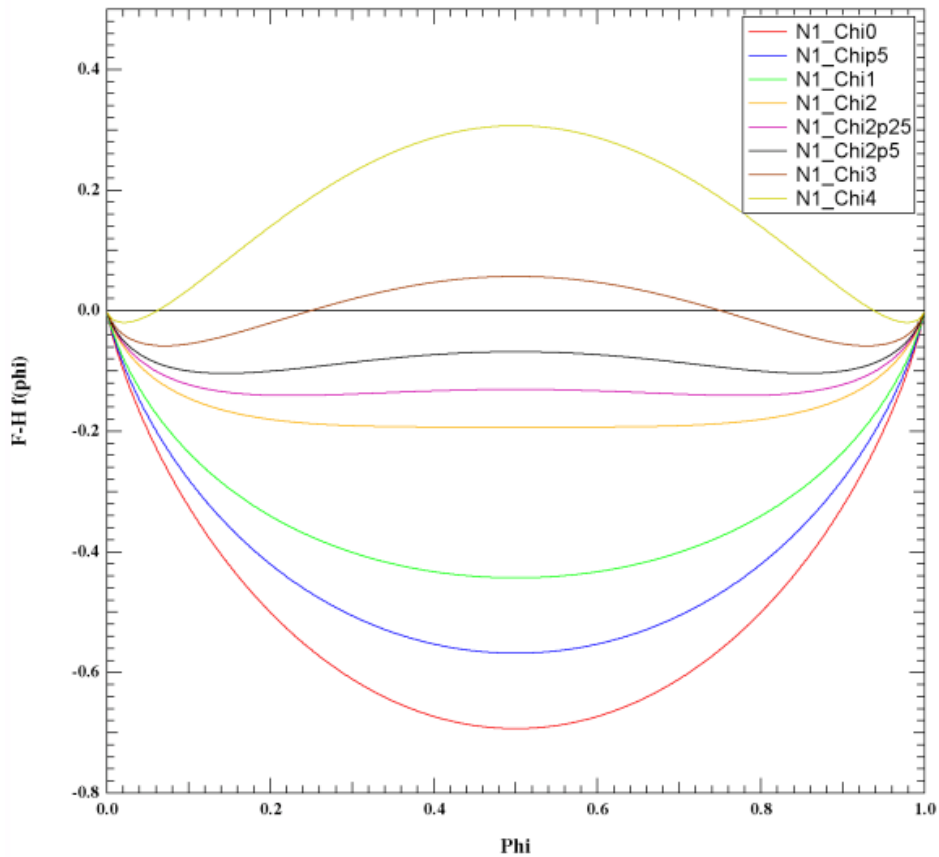
If  $N_A = N_B = N$ , for a symmetric blend,

$$\chi_{Critical} = \frac{4N}{2N^2} = \frac{2}{N}$$

If  $N_A = 1$  for a solvent and  $N_B$  is large then,

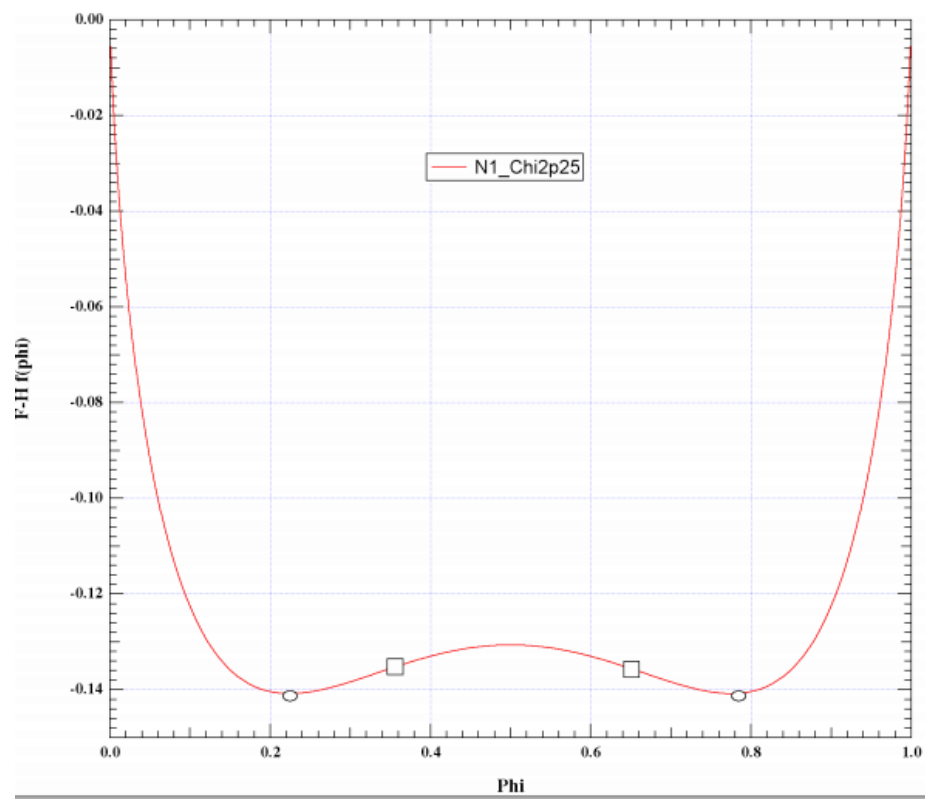
$$\chi_{Critical} = \frac{N_B}{2N_B} = \frac{1}{2}$$

d) Critical chi is 2 in plot below.



e) In the plot below, the meta-stable region is between the circle and square. In this region for small fluctuations in composition the system is stable since the curve is a smile (positive curvature) and the upward fluctuation always contributes more positive free energy than the downward fluctuation. For large fluctuations that overcome the central peak all fluctuations decompose. So if a large enough nucleation site is present the system will phase separate but for small fluctuations the system is stable.





5)

- a) "a" is typical of Newtonian flow,  $\sigma = \eta (d\epsilon/dt)$  so  $\epsilon = \sigma_0 t/\eta$ .  
 "b" is typical of a Hookean Elastic,  $\sigma = E \epsilon$  or  $\epsilon = J \sigma$ .  
 "c" is typical of a complex viscoelastic response composed of flow, elasticity and an anelastic response,  $\epsilon = K_1 t + K_2 + K_3 (1 - e^{-t/\tau})$ .
- b) The flow term (term linear in time) is related to the set of the silly putty seen in figure "c".  
 The viscosity is proportional to a characteristic relaxation time for flow in the material.  
 The anelastic relaxation is also governed by a characteristic time given by tau in the equation.
- c) -Flow is related to the imaginary modulus,  $\eta/\omega = E''$ , the real modulus is related to the Hookean response,  $E = E'$ .  
 -The long time, flow behavior would be seen at low frequencies, the short time Hookean behavior would be seen at high frequencies. The loss modulus is related to flow and the real modulus is related to Hookean behavior.  
 - $J(t) = t/\eta$  at long times where Newtonian behavior dominates.
- d) Two other characteristic times.  
 -Translational velocity relaxation time for center of mass thermal motion of a pollen grain subjected to Brownian motion,  $\tau_v = m/\xi$ , where  $\xi$  is the friction factor given by Stokes law for a sphere, and m is the mass of the pollen grain.  $V = V_0 \exp(-t/\tau_v)$ , describes random thermal motion dampened by a Stokes friction factor.  
 -A bell resonates at a frequency  $\omega_0$  that is inversely related to a characteristic time,  $\tau = 1/\omega_0$ . The bell responds to a delta function stress,  $\sigma(t) = \sigma_0 \delta(t - t_1)$ , where  $\delta(t_1)$  has a value of 0 at all times except  $t_1$ , and has a value of  $\infty$  at  $t_1$ . The integral of  $\delta(t_1)$  over all time is equal to 1.
- e) The translational velocity correlation function shown is similar to that of a polymer coil in that the relaxation time can be assumed to be 0 for all times accessible to experiment. Under the assumption of simple spherical particles in a dilute solution subjected to thermal motion,  $\tau_v = m/(6\pi\eta a)$ , where m is the mass of the particle,  $\eta$  is the solvent viscosity and a is the radius of the spherical particle. m is typically very small for polymer coils compared to colloidal particles such as pollen grains.

6)

a) Both the ideal rubber and the ideal gas assume no change in enthalpy with deformation. That is, both are based on a purely entropic response for the systems. Because of this, both cases result in a responding force that is proportional to temperature.

b) The difference between the Maxwell model and the Rouse model involves the molecular basis for the springs and viscous elements in the Rouse model. The Rouse units are physically linked to the real structure of the chain while the Maxwell units are empirical constructions. The Rouse unit must be large enough so that rubber elasticity and Stokes law can be applied but small enough so that a preferred direction of dynamic response can be observed, i.e. the definition of a Rouse unit is identical to the definition of a sub-volume element, "v" in our discussion of the fluctuation dissipation theorem. The Rouse spring will follow,  $b_R = 3kT/a_R^2$ . The Rouse bead will follow  $F_R = \zeta_R dz_i/dt$ . Where  $\zeta_R$  is the friction factor for a Rouse bead that follows the ideal rubber law,  $\zeta_R = 3kT/\langle a_R^2 \rangle$ .

c) The similarity is that the viscosity,  $\eta$  and the friction factor  $\zeta_R$  describe viscous features for the system and the spring constant,  $k$ , and rubber elasticity term,  $b_R$ , describe Hookean behavior. The phase factor,  $\delta$ , gives a description of the temporal relationship in response between Rouse units. For an infinite chain  $\delta$  is a continuous function between  $-\pi$  and  $\pi$ . The Rouse equation is based on molecular structure while the Maxwell equation is empirical, i.e. the viscosity and spring constant do not have a connection with the structure of the material in any real way.

d) The "free-draining limit" pertains to polymers in dilute solution. Under a non-draining assumption the coil is assumed to trap all solvent molecules within the coil leading to the expected behavior or the intrinsic viscosity for theta and good solvents (Mark-Houwink parameter of 0.5 and 0.8 respectively). For a "free draining coil", i.e. a Rouse coil, no solvent is trapped and only the effect of the added Rouse segments or chain units with molecular weight is observed. The Mark-Houwink parameter is 1.0 under these conditions. The assumption that  $(\zeta_R/a_R^2)$  is constant means that each chain unit or Rouse segment adds linearly to the dynamic response. For a free draining chain the size of the Rouse unit is of no consequence.

e) The Rouse expression is given in question "a". The dumb-bell model yields  $\tau = \zeta_R/k_{spr}$ . The dumb-bell model is basically the same as a Maxwell model.