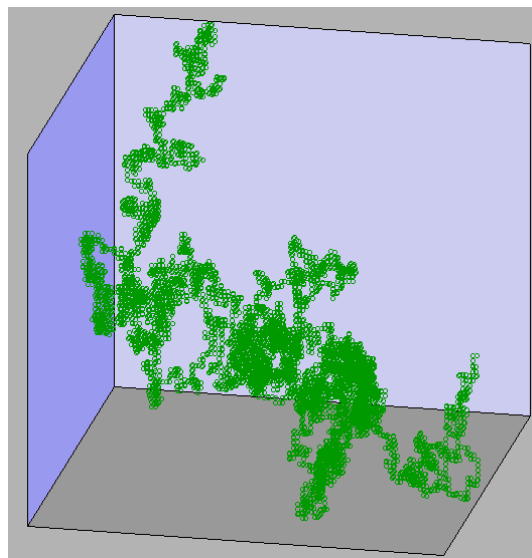
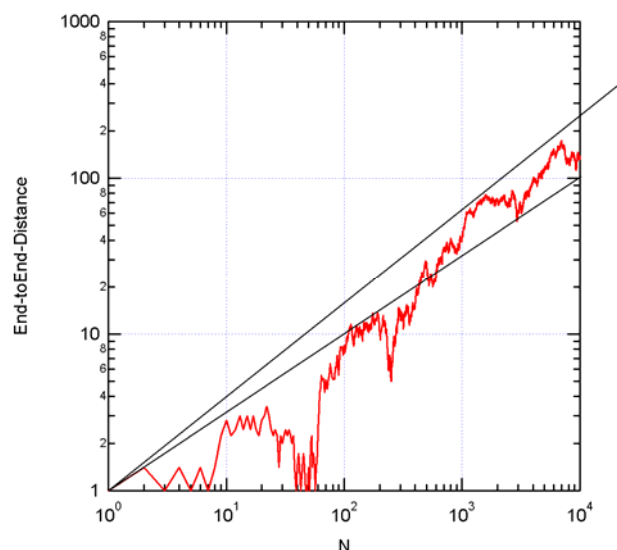


## 060331 Quiz 1 Polymer Properties

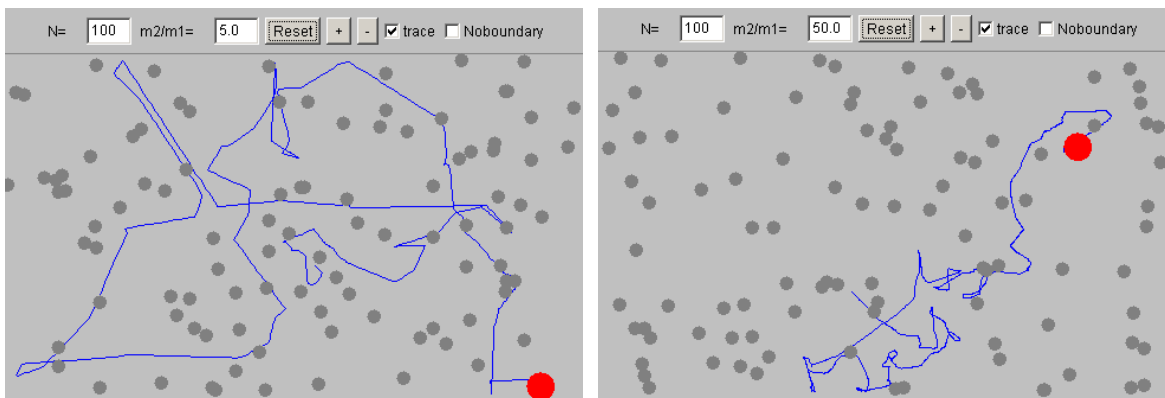
This week we discussed the difference between the view of a polymer chain by a chemist, physicist and engineer (rheologist). We also discussed differences between *models*, *simulations* and *experiments*. An example of the *assumptions* made in the development of a *simulation* for a simple polymer chain were given, which were framed on the concepts of *short* and *long range interactions*. The results for two *models* for long range interactions (Brownian and self-avoidance) were described. An outline for a simulation of a random walk including the assumptions involved was given.

- 1) A chemist views the polymer chain as composed of chemical units called mers. Flory followed this approach when he developed the *rotational isomeric state model (RISM)* which is based on calculations of chain energy for various bond rotations. Consider the difference between Flory's *model* to calculate chain energy based on bond rotations and a *simulation* of a polymer chain conformation.
  - a) Make a Neumann projection of 4 carbons showing how the bond rotation angle  $\psi$  might affect the chain segment energy. (Plot energy versus  $\psi$  and show the projection to explain the plot).
  - b) List the assumptions given in class for a simulation of a *random walk*.
  - c) Discuss the application of a model (*RISM*) and the use of a simulation to determine the melting point of a polymer (as best you can, i.e. guess if you need to).
  - d) Discuss the application of a model (*Random Walk*) or the use of a simulation to determine the total size of a polymer chain (you shouldn't have to guess much here).
  - e) Explain why a *simulation* that included *long-range interactions* would take longer to run than a *simulation* that ignored *long-range interactions*.



**Left:** End to end distance versus chain index for Gaussian Chain shown to the right. **Right:** Position for spherical units on a Cartesian coordinate system following Brownian chain scaling. (Simulation by Beaucage using Igor by Wavemetrics.)

- 2) We discussed two *models* for long range interactions (Gaussian and Excluded Volume) that yield two functions for mean chain size,  $R$ , in terms of the number of persistence steps,  $N$ , and the persistence length,  $l_p$ .
- What are the assumptions for these two models?
  - Give these two functions.
  - For a chain of 10,000 persistence units what difference in chain size is expected between the two models?
  - For a single *simulation* of a polymer chain following a Gaussian assumption (figure above) the chain size (end to end distance) fell between the expected result from the two models (Left above). Explain this result. Which line is predicted to be correct?
  - A 3d plot for this *simulation* (Right above) seems to show non-random behavior with clustering of the chain path into nodules. Explain this observation. Is this truly a random path?
- 3) In class you saw a simulation of a Brownian walk (below) where a large bead was driven in 2d space by collisions from a large number of smaller beads (this should mimic pollen grains and gas atoms).
- Describe in words the persistence length for this simulation.
  - What is the effect of changing the mass ratio ( $m_2/m_1$ ) between the two types of beads on persistence length? Explain.
  - In a polymer chain simulation what assumptions (initial values) play the role of the mass ratio in this simulation? Explain.
  - How would long-range exclusion (if the path of the large particle avoided itself on long distances) affect persistence?
  - If the left image below were scaled smaller (shrunk) it might look identical to a small part of the right image. Guess at why this might be important.

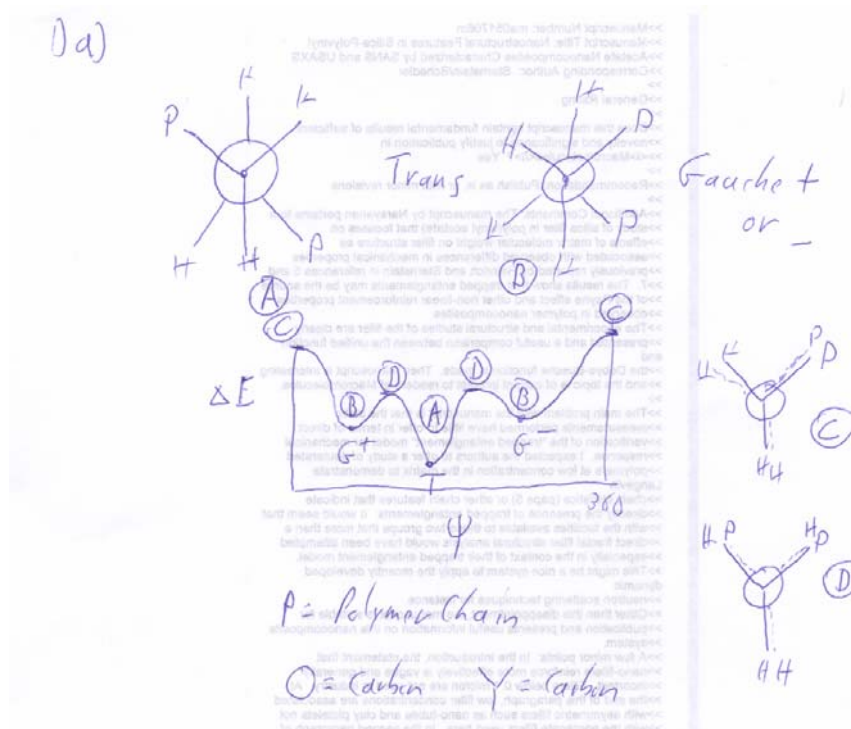


<http://www.phy.ntnu.edu.tw/ntnujava/viewtopic.php?t=41>

Simulation results where large (red) (M2) is a heavy particle and small (grey) (M1) are light gas atoms for instance, **Left:** Large (Red) is of comparable mass to small (grey) ( $M_2/M_1 = 5$ ), **Right:** Large (Red) is much heavier than Small (grey) ( $M_2/M_1 = 50$ ).

## Answers: 060331 Quiz 1 Polymer Properties

1)



- assume a lattice (x,y,z)
- assume a starting point (0,0,0)
- assume a step size  $l$
- assume restrictions on direction (along x-y-z only)
  - iii) and iv) lead to  $l_p$  the persistence length
- assume the nature of long range interactions (excluded volume or a phantom chain that can be passed through freely) Assume a chain that has NO LRI for Gaussian.
- you might want to list assumptions concerning branching and other things. (none for Gaussian)

c) The calculation of a melting point requires a detailed knowledge of the energetics of various rotational isomeric states for the chain. These can be compared with the available thermal energy ( $kT$ ) to see if the chain favors certain helical conformations associated with crystallization (planar zig-zag for polyethylene). A discrete transition can be determined in this way where planar zig-zag becomes favored over a more random conformation at a certain temperature,  $kT_m$ . At the melting point a crystal has the same free energy as a molten chain.

For a simulation similar energetic information might be used to choose bond rotations but the chain would be allowed to randomly probe free energy space by trial and error using the total chain conformational energy as a basis for skewing a random distribution such as would be used in a Monte-Carlo method (see web notes). At the melting point the average equilibrated volume of a chain shows a discrete transition from a low density to a higher density. Also, the simulation result should display long-range order associated with the crystalline lattice.

d) For a simulation the chain size is determined by application of a set of assumptions such as those listed in b) above repetitively. The chain size is the result of the repetitive calculation. A number of these calculations need to be averaged to obtain a reasonable answer.

For a model such as the random walk model an analytic function to predict average chain size is determined based on some assumptions and physics. The analytic function,  $R \sim N^{1/2} l_p$ , results in a direct value for the chain size.

e) The LRI simulation takes more time since it must check if the next step is excluded by the existing chain.

2) a) The Gaussian model assumes no long range interactions so the chain can pass directly through itself at long distances. The SAW model assumes total exclusion of the chain at long distances. This is the equivalent of a *hard core potential* in simulation literature.

b)  $R \sim N^{1/2} l_p$  Gaussian, Brownian, Random Walk  
 $R \sim N^{3/5} l_p$  SAW, Excluded volume, Good Solvent Scaling

c)  $R_{SAW}/R_{Gaussian} \sim N^{1/10} = (1e4)^{1/10} = 2.51$

d) A single simulation for a single chain is not sufficient since the results are a random sample of a wide variety of possible results. Any end-to-end distance from 0 to  $Nl$  is possible from a random simulation. On average the Gaussian simulation should follow Gaussian statistics except at very short lengths ( $N < 10$ ) where chain persistence comes into play.

e) As noted in class the nature of "random" differs from the perception of "random". An interesting example of this is in the random i-pod player. A number of purchasers have returned the random players for not being "random" because they sometimes play the same song twice. We expect clustering in a random process. Another analogy is to throw darts with a blind fold on. You would expect some to hit the bulls eye if you throw a sufficient number of darts.

3) a) There are many ways to describe persistence length. One way (the wikipedia way) is to consider the probability that a particle will continue traveling in a given direction. For the simulation on the left this probability is rather high. It is much lower for the simulation on the right. We can consider a correlation function as the dot product of two vectors for chain steps separated by  $n$  steps. The average of this dot product should be 0 for a random path. The average of the square of this dot product is a measure of path persistence.

$\langle \mathbf{r}(i) \cdot \mathbf{r}(j) \rangle = 0$  and  $\langle (\mathbf{r}(i) \cdot \mathbf{r}(j))^2 \rangle \sim l_p$ . There are many other ways to measure persistence.

b) Larger mass ratio results in a smaller persistence since the energy transferred in an elastic collision between a grey dot and the red is small and the motion of the large dot requires many collisions so shorter persistence results from a more jagged path.

c) The initial step length or lattice size and the probabilities for different directional motion as well as the lattice shape determine the persistence length.

d) No effect.

e) This is called self-similarity if it is true within a single object (fractal). Here it means that the solution for one random walk is the same except for scale as the solution for any other random walk. The value of  $M_2/M_1$  has no relevance except that it defines the scale of the walk, i.e. the persistence length.

## 060407 Quiz 2 Polymer Properties

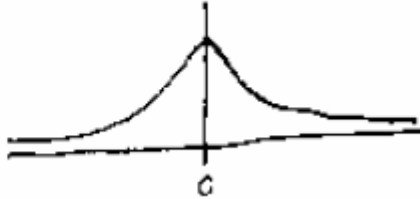
- 1) Polymers are best described by statistical features since they are disordered structures. For a system described by a large number of random events the Gaussian distribution is often used to approximate the average features.
  - a) Write the Gaussian distribution function for 1d and sketch the distribution curve (probability versus  $x$  or  $R$ ).
  - b) We mentioned in class that a Gaussian chain displays a mass-fractal dimension of 2 making it a 2d object. Is there a part of the Gaussian distribution function that indicates this dimensionality? If no explain why; if yes indicate which part.
  - c) Would the Gaussian distribution be appropriate for a self-avoiding walk? Explain how or why.
  - d) Would the Gaussian distribution be appropriate for a chain whose connectivity dimension,  $c$ , was 1.5 and whose minimum dimension,  $d_{\min}$  was 1.33?
  - e) Explain what  $c$  and  $d_{\min}$  are.
- 2) In class we mentioned *renormalization* of the Gaussian structure.
  - a) What does *normalization* mean? Think of a normalized distribution function and generalize the concept.
  - b) In your own words explain (or guess) what renormalization means.
  - c) In class we used the concept of renormalization to allow for an arbitrary (non-physical) value for the primary step length. Give an example of a situation where it would be useful to use a step length other than the physical persistence length.
  - d) Give an expression for the effect of  $z$ , the lattice coordination number on the persistence length.
  - e) Explain how the bond rotational-energy-map (energy versus rotation angle  $\psi$ ) from last week's quiz could be related to " $z$ ".
- 3) This week's graduate seminar speaker, V. Davis, mentioned that carbon nano-tubes can display a type of persistence length that is similar to persistence in polymers.
  - a) Is a carbon nano-tube's long-range conformation subject to thermal equilibrium if the chain is longer than a micron? Explain.
  - b) Is a CNT's short-range conformation subject to thermal equilibrium given the structure of a rolled graphitic sheet with basically a single planar bond conformation.
  - c) Give some problems you might expect from the application of the concept of a thermally equilibrated persistence length to CNT's.
  - d) V. Davis cooks her tubes with lithium to functionalize and compatibilize the tubes with polymers and solvents. Would you expect such treatment to affect the observed persistence length? How or why?
  - e) Polymers are commonly found at 100% concentration (a melt) while CNT's will form a useless clump at high concentrations. Explain this observation as best you can. (The word "entropy" may or may not be of use here.)

## ANSWERS: 060407 Quiz 2 Polymer Properties

1)

$$a) \quad P(x, \mu, \sigma) = \frac{1}{\sigma \sqrt{2\pi}} \exp\left[-\frac{1}{2} \frac{(x-\mu)^2}{\sigma^2}\right]$$

$$P(R, n, b) = \frac{1}{(2\pi n b^2)^{1/2}} \exp\left[-\frac{1}{2} \frac{R^2}{n b^2}\right]$$



- b) The standard deviation defines the second moment of size as  $nb^2$ . This defines a 2d object.
- c) No, a SAW is not a random structure. There is no simple distribution function to describe a SAW.
- d) While the fractal dimension of such a chain is 2 (because  $1.33 \times 1.5 = 2$ ) the chain does not follow the Gaussian probability function for the same reason that a disk ( $c=2$ ,  $d_{min}=1$ ) would not follow Gaussian statistics. A disk is not built from a random walk, nor is the chain of  $c = 1.5$  and  $d_{min} = 1.33$ .
- e)  $c$  is the connectivity dimension.  $c$  has a value of 1 for a linear chain and  $df$  for a regular object.  $c$  relates the minimum path,  $p$ , to the molecular weight  $z$  so  $p^c = z$ .  $d_{min}$  is the mass fractal dimension for a primitive path  $p$  in the structure so that  $p = R^{d_{min}}$ .

2) a) Normalization of a probability function means that you integrate the probability function from  $+\infty$  to  $-\infty$  and divide the function by this value so that the integral is set to 1. This means that the function represents the actual probability of an event happening rather than this probability times some constant. Normalization does not effect the shape or nature of a distribution function (unimodal, bimodal etc.), it only effects the absolute value of the function.

b) Renormalization means to change the base value of a structure, that is to use an arbitrary step length such as the statistical segment length. This is possible for a fractal structure where structural scaling is uniform across size scales (displaying self-similarity).

c) If we know the number of chemical units,  $N_{chem}$ , in a polymer (from synthesis) but do not know the number of persistence units, it is possible to measure the chain size,  $R$ , and to calculate an arbitrary statistical segment length,  $l_{ssl}$ , that is defined by  $l_{ssl} = R/\sqrt{N_{chem}}$ . This value can be used to calculate chain size,  $R$ , from  $N_{chem}$  for other similar polymers without knowledge of the persistence length or  $N_{per}$ .

d)  $l_{p,eff} = l_p (z/(z-2))^{1/2}$

e) More restrictions on bond rotation effectively decrease  $z$ . If the bonds were freely jointed  $z$  would be infinite.  $z$  is lower for a fixed bond angle and free rotation and lowest for constrained rotation about a fixed bond angle.

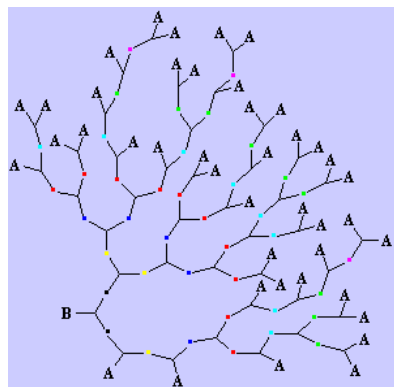
- 3) a) No. A micron scale object is not subject to thermal motion in the way that a polymer chain is. There is a fundamental difference between molecules (which hold  $kT$  energy) and macroscopic objects that do not. A CNT of such large size is not a molecule in this sense.
- b) No. There is little or no local flexibility in this structure. The persistence length observed for these structures is due to the modulus of an almost macroscopic object. The persistence is not derived from an energy map such as seen for bond rotation in polymers.
- c) One problem is Davis' somewhat naïve attempt to observe a "phase-diagram" for this system. Since the objects are not subject to thermal equilibration there is no reason to expect to observed thermodynamic behavior. The lack of thermal dependence to miscibility in this system indicates that is not a thermodynamic system but a macroscopic system. (There are many answers to this question.)
- d) The chemical modification of this system perturbs the conjugation of the carbon bonds and dramatically alters all properties of the tubes. The persistence length would probably decrease since the structure becomes much less rigid. Alternatively, steric interference of the alkyl side groups that are added could possibly increase persistence but this seems unlikely. Persistence would change and would probably decrease.
- e) A polymer chain explores the available conformational space and this exploration allows for a number of different states and a higher entropy. The nano-tubes do not display entropy since, they are too large to be subject to thermal equilibration and because they are so rigid that they display essentially only one state. This means that individual nanotubes, as macroscopic objects, do not display useful properties we associate with a single phase material.



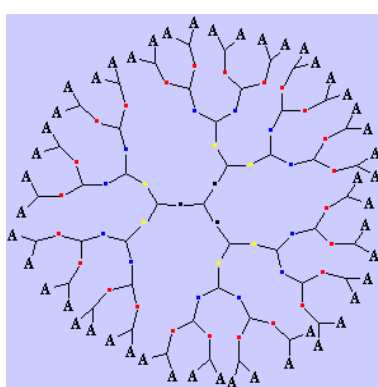
## 060414 Quiz 3 Polymer Properties

This week we considered measures of the overall coil size, mostly the hydrodynamic radius but also briefly the radius of gyration.

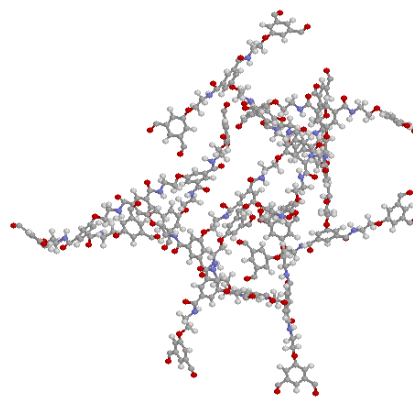
- 1) There seem to be a number of methods to measure size of a coil. Consider a hyperbranched polymer (or a dendrimer) such as shown in the figures below.



Hyperbranched



Dendrimer



Dendrimer

[www.ipfdd.de](http://www.ipfdd.de) and [www.ipf-analysis.de](http://www.ipf-analysis.de)

- a) If you could see these structures in a microscope how would you describe the size. Especially consider the structure in an equilibrated state such as the last image and subject to thermal motion (like a living, 'drunken', branched worm say).
- b) In class we discussed the root-mean-square end-to-end distance. What is the RMS end-to-end distance for these structures? Is it related to what you perceive as the size?
- c) Would you expect the RMS end-to-end distance to be larger or smaller for these objects compared to an unbranched polymer chain of similar molar mass?
- d) What problems might you expect in measuring the hydrodynamic radius for these structures?
- e) What problems would there be in measuring/interpreting the radius of gyration?
- 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.

3) The moment of inertia of an object is defined by  $I = \sum m_r (r - r_{COM})^2$  where the summation is over all points "r" in an object and  $r_{COM}$  is the center of mass defined by  $r_{COM} = \frac{\sum m_r r}{\sum m_r}$ , and  $m_r$  is the mass at point r. The torque,  $\tau$ , on an object resulting from an angular acceleration  $\alpha$  is given by  $\tau = I\alpha$ . The kinetic energy, K, of a rotating body is given by  $K = \frac{1}{2} I \omega^2$  where  $\omega$  is the angular velocity. For rotating bodies I serves the place of m for linear motion. (From Wikipedia).

- a) Compare the definition of the radius of gyration to the definition of the moment of inertia.
- b) How can scattering be used to measure the radius of gyration? (Give a universal equation.)
- c) How would you relate the end-to-end distance of a linear polymer chain to its moment of inertia? (just give an equation do not derive).
- d) What is the advantage of radius of gyration or moment of inertia over other measures of chain size such as the hydrodynamic radius or the end-to-end distance?
- e) It is natural to consider twice the radius to obtain size. In the case of radius of gyration, does it make sense to consider  $2 R_g$ ? (What meaning does  $2 I$  have?)

### ANSWERS: 060414 Quiz 3 Polymer Properties

1) a) The branched worm would be hard to describe in terms of size since it doesn't have a beginning or an end and because it displays many different sizes, in fact this is the definition of a fractal. We could compare two different objects of the same type (same  $d_f$ ,  $c$  and  $d_{min}$ ) and determine which is larger. This would be more difficult for objects of different dimensions. In the end, most people gravitate to the concept of the radius of an enclosing sphere which is basically the end to end distance of the minimum path,  $p$ , so  $l_p z^{1/df}$  would be a measure of this type.

b) The RMS end-to-end distance is the end to end distance of the minimum path,  $p$  as described in part a. This is  $l_p p^{1/d_{min}} = l_p z^{1/d_{min} c} = l_p z^{1/df}$ .

c) The RMS end-to-end distance would be larger for a linear chain.

d) Distortion of the structure under shear flow would be a problem. Also, if the structures are asymmetric the hydrodynamic radius could be inaccurate.

e) There would be no problem in measuring the radius of gyration but interpretation could be difficult if the extent of branching in the structure is not known.

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  $I(q,t) = \exp(-tq^2D)$  to yield  $D$ .

3) a) The radius of gyration squared is the moment of inertia divided by the total mass.

b) Measure  $I$  versus  $q = 4\pi/\lambda (\sin(\theta/2))$ , and fit with  $I(q) = G \exp(-q^2 R_g^2/3)$ .

c)  $\langle R^2 \rangle = R_g^2/6 = I/(6M)$  where  $M$  is the total mass of the sample.

d) The radius of gyration is not subject to distortion due to the application of force to the object. The radius of gyration has a strict mathematical definition for any object.

e) It does not make sense to consider  $2 R_g$  since the radius of gyration is not really a radius. For example, for a linear Gaussian chain we should consider  $\sqrt{6} R_g$  for the size of the object.  $2 R_g$  has no meaning.

### 060421 Quiz 4 Polymer Properties

- 1) Scattering of electromagnetic radiation is usually considered in terms of binary interference effects (*re-radiation from 2 points*) because the power of scattered radiation is less than 1% of the incident radiation and the probability of a scattering event from multiple sites would follow a power series in this fraction; so while binary power might be 0.1 % of the incident intensity; ternary (3 points) would display 0.0001 % of the incident intensity.
  - a) Explain why the binary scattered intensity might be related to the pairwise (binary) correlation function,  $g(\mathbf{r})$ .
  - b) Give a mathematical expression for the pairwise correlation function. (Define the del operator,  $\delta(x)$ .)
  - c) If you needed to consider ternary interactions (3 particles) guess how you would need to modify this function.
  - d) By writing the Fourier transform of  $g(\mathbf{r})$  in a series expansion of the  $\exp(-i \mathbf{q} \cdot \mathbf{r})$  term and using a double summation for binary interactions in the polymer chain, we were able to obtain Guinier's Law. Was the Gaussian structure of the coil considered in this derivation? Explain where it was used or why you think it was not used.
  - e) Sketch a plot of the Debye function for polymer coils and Guinier's law for the same coil in a log intensity versus log scattering vector plot. Does this plot agree with your assessment in part "d"?
- 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,  $p_B(R) = \exp(-G(R)/k_B T)$ , 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  $G = H - TS$ ).
- 3) In order to determine the effect of excluded volume on the chain end-to-end distance one of the methods of question "2" is modified following Flory and Krigbaum.
  - a) Explain which of the two methods of question "2a" can be used to obtain the end-to-end distance for an exclude-volume chain and why the other method can not be used.
  - b) What is the probability of excluding a single chain unit's volume,  $V_c$ , from a polymer coil?
  - c) What is the probability for a polymer chain to be excluded from all of the chains excluded volume?
  - d) Show how this can be combined with the Gaussian probability function and write an expression for the free energy of an excluded volume chain.
  - e) What can you say about the enthalpic part of the free energy for an isolated chain with excluded volume through a comparison of this new expression with the Boltzmann expression (this is somewhat of a trick question).

## ANSWERS: 060421 Quiz 4 Polymer Properties

1) a) The binary correlation function considers the probability that two points or chain units will be separated by a distance "r". If two points are separated by "r" then they can contribute to the observed binary interference at  $\mathbf{q} = 2\pi/\mathbf{r}$ , where q is the scattering vector  $q = (4\pi/\lambda) \sin\theta$  and  $\theta$  is the scattering angle.

b)

$$g(r) = \frac{1}{N} \sum_{n=1}^N g_n(r) = \frac{1}{N} \sum_{n=1}^N \sum_{m=1}^N \langle \delta(r - (R_m - R_n)) \rangle$$

where N is the number of steps in the chain and  $R_i$  are the chain step positions. The del operator equals 1 when the argument is 0 and equals 0 for all other situations.

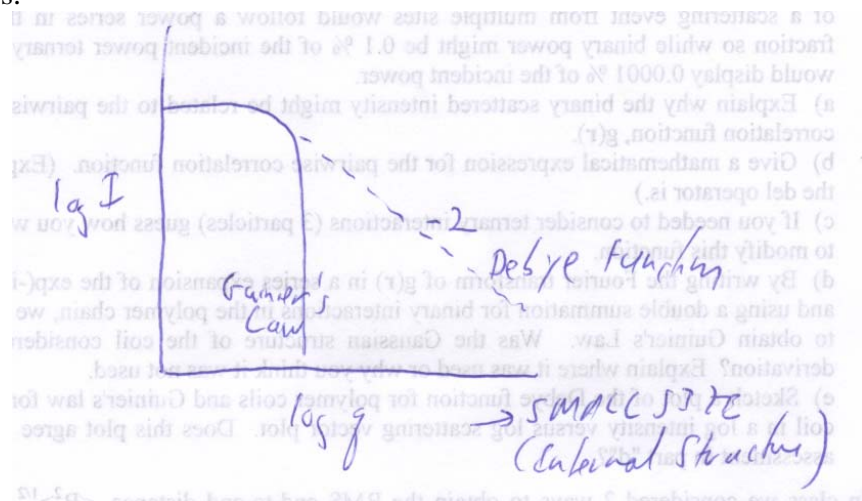
c) For ternary interactions this function would become fairly complicated, needing basically 3 distances,  $g(q,r,s)$  and three del-operators,

$$g(q,r,s) = \frac{1}{N} \sum_{n=1}^N \sum_{m=1}^N \sum_{o=1}^N \langle \delta(q - (R_m - R_n)) \rangle \langle \delta(r - (R_m - R_o)) \rangle \langle \delta(s - (R_n - R_o)) \rangle$$

There are other answers to this question.

d) It was not used since the Guinier function does not describe internal structure. The internal structure was not included since we did not use the Gaussian function to describe the position of the segments. This function would need to modify the summation of the position vectors using a Gaussian probability.

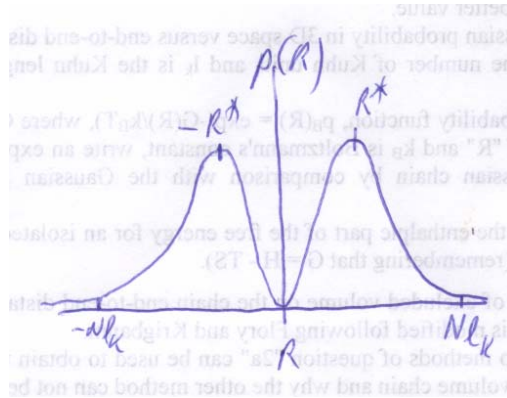
e) Yes it agrees.



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)  $3R^2/(2Nl_k^2) = 3R^2/(2R_0^2) = G(R)/k_B T$  so  $G(R) = 3k_B T R^2/(2R_0^2)$

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.

3) a) The derivative to obtain the most probable value is used since the integral for a modified Gaussian is not possible to solve using traditional methods.

b)  $(1 - V_c/R^3)$

c)  $(1 - V_c/R^3)^{N(N-1)/2}$

d)

$$p(R) = \exp\left[\frac{1}{2} N(N-1) \ln\left(1 - \frac{V_c}{R^3}\right)\right] = \exp\left(-\frac{N^2 V_c}{2R^3}\right)$$

$$W(R)dR = W_0(R)p(R)dR = kR^2 \exp\left(-\frac{3R^2}{2Nb^2} - \frac{N^2 V_c}{2R^3}\right)$$

$$G(R) = k_B T \left\{ \frac{3R^2}{2R_0^2} + N^2 V_c / (2R^3) \right\}$$

e) This expression also lacks an enthalpic term. An enthalpic term must involve  $V_c$  being a function of  $1/T$ .

## 060428 Quiz 5 Polymer Properties

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".

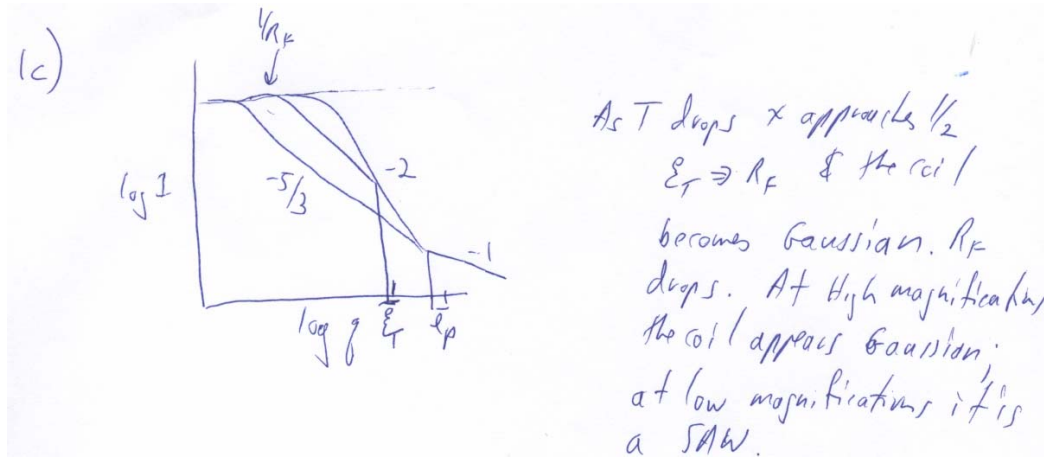
- 1)
  - a) Define a "blob".
  - b) Give the temperature dependence of the *thermal* blob for a polymer coil.
  - c) How can this temperature dependence describe structural changes that occur to a polymer in dilute solution? (Discuss these structural changes perhaps using scattering curves or using schematic 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?
- 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.
- 3) In addition to the thermal blob we began to discuss the concentration blob in class. The concentration blob involves a fundamental feature of interacting systems as their concentration is increased; termed "screening" by Debye in his book "Polar Molecules" (cited in his Nobel Prize).
  - a) Consider a human interaction such as a mother and child who are separated but enthalpically attracted in a large hall by the "*enthalpy of maternal instinct*". How will this interaction be effected if a large number of similar mothers and children are crowded into the same hall?
  - b) As the population density increases in the hall can you think of a characteristic distance or length-scale vital to the mother and child that changes with population density?
  - c) Last week's quiz considered pairwise interactions briefly. Explain how the concept of pairwise interactions might be important to the depiction of "screening" in question "a"? Comment on this.
  - d) In a crystal, enthalpic interactions are strong but screening of binary (pairwise) enthalpic interactions is not seen. Explain in your own words (guess) why this might be the case.
  - e) Consider a polymer solution. At what concentration would you expect the coils to just begin interpenetration? Write an expression for this concentration (mass/volume) using only the molar mass  $N$  and the coil size  $R_F$ .

### ANSWERS: 060428 Quiz 5 Polymer Properties

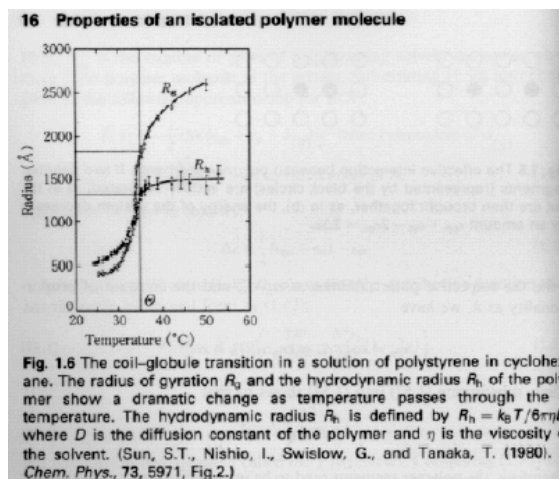
1) a) A blob is a size scale associated with a change in structural scaling. It is used to renormalize a chain structure.

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

c)



d)



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.

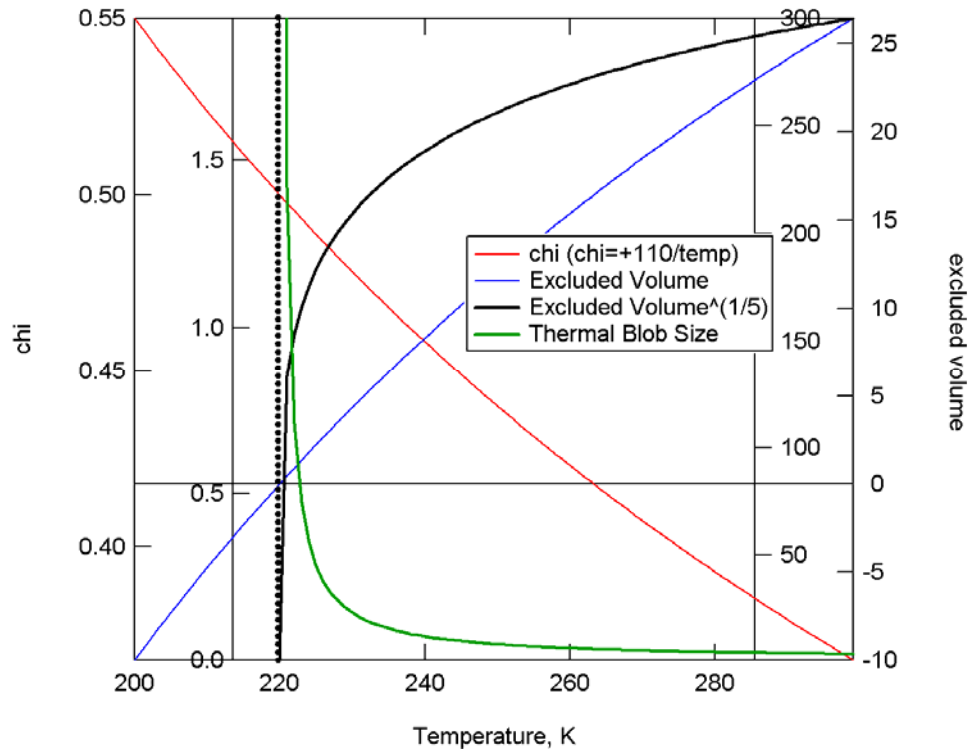
2) a) An ideal gas is composed of molecules of no volume so there is no excluded volume.

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 interaction 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  $V_0$ .

3) a) The interaction is effected in terms of the spatial distance over which it can have an effect. Crowding makes the attraction only effective at short distances. The higher the crowding the shorter the distance over which the attraction is functional. The strength of the attraction is not effected.

b) The length at which the child is first "lost" is analogous to the screening length. This length becomes smaller with higher concentration.

c) The pairwise distribution function considers the probability that given you are at one of a pair, what is the probability of finding the other of the pair at a distance "r". This function is plotted as a function of "r", the separation distance and it is a mean value over all beginning points and over all ending points a distance "r" away. Attractive interactions would lead to a shift of the pairwise distribution function to higher values at smaller "r". Screening would lead to a characteristic shift of this function, reducing the value especially at intermediate "r". No attraction would be seen beyond  $r = \text{the screening length}$ .

d) In a crystal the binary units are held in position enthalpically and are at closest approach. The presence of screening apparently relies on thermal Brownian motion of the binary pair.

e) The overlap concentration  $c^* = N/R_F^3$ .

### 060505 Quiz 6 Polymer Properties

- 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.
- 2) The size of a polymer coil decreases in concentration through the semi-dilute regime
  - a) What are the limits in size scaling with molar mass,  $N$  for this decrease?
  - b) At what concentration does the semi-dilute regime begin? How does this concentration change with the mass-fractal dimension of the chain?
  - c) How does the overlap concentration differ from the percolation threshold?
  - d) In the semi-dilute regime how does the concentration blob scale with concentration?
  - e) In the semi-dilute regime how does the coil size,  $R_F$ , scale with concentration?
- 3)
  - a) Make a rough sketch of an osmotic pressure instrument.
  - b) How can this instrument be compared with a container of gas?
  - c) How is the osmotic pressure,  $\pi$ , determined in this instrument?
  - d) In calculating the osmotic pressure what thermodynamic parameter is made equal between the parts of the instrument?
  - e) How is the Gibbs free energy calculated from the Flory-Huggins expression for the free energy of mixing of a polymer in solution?

## ANSWERS: 060505 Quiz 6 Polymer Properties

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  $(n/V) * (1/N)$ .

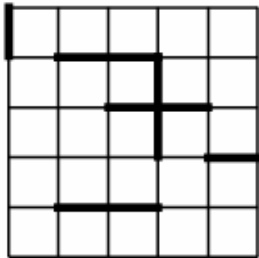
d) The polymer chain has essentially a fixed internal concentration because it is connected together. For this reason, the dilute condition is already quite high in local concentration compared to a gas and we observed non-ideal behavior with an expanded coil structure. At high concentration these effects are screened due to interpenetration of the coils above  $(n/V)^*$ .

e)  $A_2 = (1/2 - \chi)$

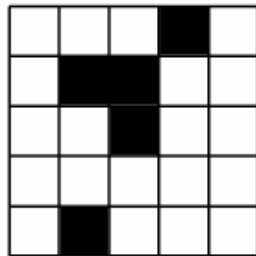
2) a) In dilute conditions  $R_F \sim N^{3/5}$  while in concentrated conditions  $R_F \sim N^{1/2}$ .

b) At the overlap concentration,  $c^* = N/R_F^3 \sim N/N^{3/df} = N^{1-3/df}$ .

c) The percolation threshold and overlap concentration have some similarities in that both are related to a system change on increasing concentration that involve interaction of units. The percolation threshold is the concentration where a path across the system is first formed. Usually the percolation threshold is a statistically average value. Values for percolation threshold are shown below for various lattices that are randomly filled.



*bond percolation*



*site percolation*

From (<http://mathworld.wolfram.com/BondPercolation.html>)

The critical fraction of lattice points that must be filled to create a continuous path of nearest neighbors from one side to another. The following table is taken from Stauffer and Aharony (1992, p. 17). Entries indicated with an asterisk (\*) have known exact solutions.

lattice	$p_c$ (site percolation)	$p_c$ (bond percolation)
cubic (body-centered)	0.246	0.1803
cubic (face-centered)	0.198	0.119
cubic (simple)	0.3116	0.2488
diamond	0.43	0.388
honeycomb	0.6962	0.65271*
4-hypercubic	0.197	0.1601
5-hypercubic	0.141	0.1182
6-hypercubic	0.107	0.0942
7-hypercubic	0.089	0.0787
square	0.592746	0.50000*
triangular	0.50000*	0.34729*

Exactly known values include

$$p_c \text{ (square bond)} = \frac{1}{2} \quad (1)$$

$$p_c \text{ (triangular site)} = \frac{1}{2} \quad (2)$$

$$p_c \text{ (triangular bond)} = 2 \sin\left(\frac{\pi}{18}\right) \quad (3)$$

$$p_c \text{ (honeycomb bond)} = 1 - 2 \sin\left(\frac{\pi}{18}\right). \quad (4)$$

Determining an exact expression for other percolation thresholds, including of the square site percolation, remains an open problem.

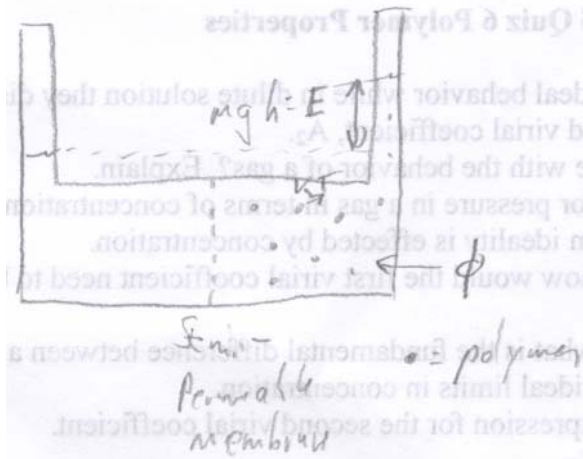
From (<http://mathworld.wolfram.com/PercolationThreshold.html>)

The overlap concentration is for objects that have an "internal" concentration so specifically mass fractal objects like polymers. The overlap concentration is the concentration where the system has the same concentration as the object and at this is seen as the concentration where significant interpenetration of the objects can occur. For our purposes the object is a polymer coil. Such objects can also percolate at a **much lower** concentration. For instance, for a Gaussian coil percolation can occur when  $c \sim 1/N$  while overlap occurs when  $c \sim 1/N^{1/2}$ .

d)  $\xi_c \sim R_{F0}(c/c^*)^{-3/4}$

e)  $R_F \sim R_{F0} (c/c^*)^{-1/8}$

3) a)



- b) In the right hand chamber in part "a" the polymer chains move thermally with  $kT$  energy so they act like gas molecules in terms of the pressure generated in the system.
- c) It is the pressure difference between the two cells.
- d) The chemical potential of the solvent is made equal and the osmotic pressure is solved for using the Flory-Huggins expression for the Helmholtz free energy per lattice site per  $kT$ . The chemical potential of the solvent is the derivative of the Gibbs free energy with respect to the number of moles of solvent holding all other parameters constant.
- e) The Flory expression,

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

is per lattice site and is per  $kT$  so the Helmholtz free energy for the system of size  $\Omega$ , is,

$$F(\phi) = kT \Omega f(\phi).$$

The Gibbs free energy,  $G$ , can be obtained from  $F$  using  $G = F + PV$ , where  $P$  is  $P + \pi$  for the right side of the Pfeffer Cell shown in part "a" and  $P$  is  $P$  for the left side.

## 060512 Quiz 7 Polymer Properties

This week we covered the concentration dependencies of the osmotic pressure of a polymer solution using the concentration blob model and the Flory-Huggins (F-H) equation for polymer solutions and blends.

1) Last weeks quiz discussed an analogy between a gas in a container and the Pfeffer cell for measurement of osmotic pressure.

a) Consider a lattice with two types of gas atoms, A and B of identical size that are randomly arranged. Wikipedia describes the entropy of mixing by:

We can use [Boltzmann's equation](#) for the entropy change as applied to the *mixing* process

$$\Delta S_m = k_B \ln \Omega$$

where  $k_B$  is [Boltzmann's constant](#). We then calculate the number of ways  $\Omega$  of arranging  $N_1$  molecules of component 1 and  $N_2$  molecules of component 2 on a lattice, where

$$N = N_1 + N_2$$

is the total number of molecules, and therefore the number of lattice sites. Calculating the number of [permutations](#) of  $N$  objects, correcting for the fact that  $N_1$  of them are *identical* to one another, and likewise for  $N_2$ ,

$$\Omega = N! / N_1! N_2!$$

After applying [Stirling's approximation](#), the result is

$$\Delta S_m = -k_B [N_1 \ln(N_1/N) + N_2 \ln(N_2/N)]$$

### Sterling's Approximation

$$\ln n! \cong n \ln n - n$$

Explain the connection or disagreement with the F-H Equation for an ideal gas ( $N = 1$ ).

b) How does this expression differ from the expression for a polymer solution. Explain the reasoning for this difference.

c) Add to this expression a term representing the average enthalpic interaction per lattice site per kT.

d) From the discussion of chain overlap we know that there is a finite limit to dilution for a polymer coil. Comment on how this might effect the phase diagram and implementation of the F-H equation.

e) What is the critical value of  $\chi$ ,  $\chi_c$ , for the gas and for the polymer solution? Explain the difference.

2) a) Plot the Flory-Huggins equation for the gas mixture of question "1a" 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".
- 3) a) In models and simulations of polymer mixing the critical  $\chi$  is calculated from  $N \chi_c = 2$ , show how this can be obtained from the F-H equation.
- b) In class we observed the phase separation of PVME (polyvinylmethylether) in water when the solution was heated. If we consider  $N$  in the Flory-Huggins equation to be the number of thermal blobs in a chain how would changes in the size of thermal blobs with temperature effect miscibility? Could this explain the observation of an LCST in this system (phase separation on heating)?
- c) If we do not invoke the thermal blob, how can the Flory-Huggins equation be modified to allow for the observed LCST behavior?
- d) Would it be possible to have both an LSCT and an UCST in the same polymer blend according to your answer to "c"?
- e) Explain what happens to thermodynamic fluctuations at the critical point.

## ANSWERS: 060512 Quiz 7 Polymer Properties

1a)  $S/(NkT) = \phi_A \ln \phi_A + (1-\phi_A) \ln(1-\phi_A)$

The two equations are identical

b) The polymer term is divided by the chain molecular weight  $z$ . The number of ways to arrange the units remains random since the chain is Gaussian but the number of molecules is reduced by  $z$ .

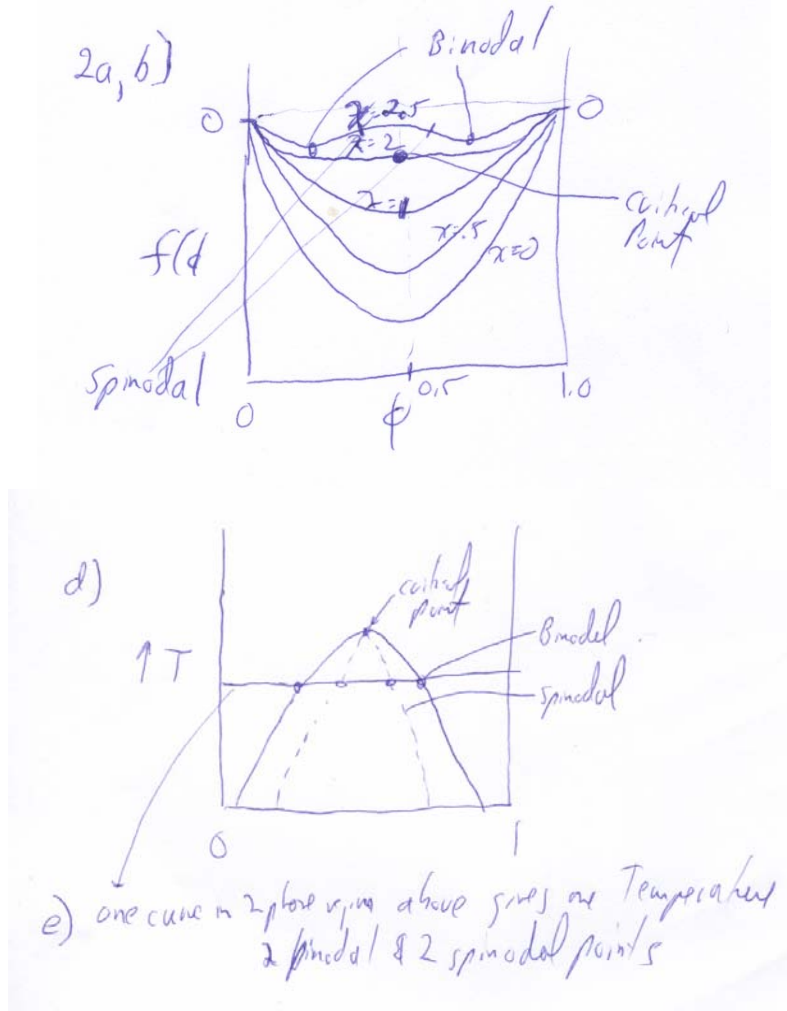
c)  $S/(NkT) = (\phi_A \ln \phi_A)/z + (1-\phi_A) \ln(1-\phi_A) + \phi_A(1-\phi_A)\chi$

d) F-H assumes that infinite dilution is possible. This is not true at very low number fractions. The free energy plot will show a horizontal tail at the polymer end of the curve.

e) For the gas  $\chi_c = 2$  while for the solution  $\chi_c = 1/2$ . This is because the second derivative using the critical volume fraction from the third derivative yields,

$$\chi_c = \frac{1}{2} \left( \frac{1}{\sqrt{N_A}} + \frac{1}{\sqrt{N_B}} \right)^2 \quad \text{which when } N_A = N_B = 1 \text{ yields } 2 \text{ and when } N_A \gg 1 \text{ yields } 1/2.$$

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 fluctuations dissipate due to a weak increase in free energy but large fluctuations decay into phase separation with a net lowering of the free energy.

3) a) We consider a symmetric blend of two polymers. Then the F-H free energy of mixing is given by,

$$f_{\text{FH}}(\phi) = \frac{\phi \ln \phi}{N} + \frac{(1-\phi) \ln (1-\phi)}{N} + \phi(1-\phi)\chi$$

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

$$N \frac{df(\phi)}{d\phi} = \ln \phi + (-\ln(1-\phi) - 1) + N\chi - 2\phi N\chi$$

$$N \frac{d^2f(\phi)}{d\phi^2} = \frac{1}{\phi} + \frac{1}{(1-\phi)} - 2N\chi$$

$$N \frac{d^3f(\phi)}{d\phi^3} = \frac{-2}{\phi^2} + \frac{2}{(1-\phi)^2}$$

$$\text{from } \frac{d^3f(\phi)}{d\phi^3} = 0 \text{ we get } \phi_c = 0.5$$

$$\text{using this in } \frac{d^2f(\phi)}{d\phi^2} = 0 \text{ we get } 4 = 2N\chi_c$$

$$\text{or } \boxed{\chi_c N = 2}$$

b)  $N_T = N/n_T = N(1 - 2\chi)^2$  as temperature rises  $N_T$  drops and the entropy for the system drops reducing miscibility.

c) Traditionally, we redefine  $\chi$  as  $\chi = A - B/T$  where  $A$  is the noncombinatorial entropy and  $B$  is the conventional enthalpic part of  $\chi$ .

d) It would require higher order terms in  $(1/T)$  such as  $\chi = A - B/T + C/T^2$ . Such systems have been observed (see book by Olabisi on polymer blends).

e) At the critical point the free energy as a function of composition is essentially flat meaning that there is no penalty to but also no gain from large composition fluctuations on large scales. The fluctuations are random and not really governed by thermodynamics. Since there is no driving force for these fluctuations the kinetics (rate of composition fluctuation) becomes slow (critical slowing down). Basically the system becomes unpredictable near the critical point.

## 060519 Quiz 8 Polymer Properties

- 1) Suppose that Flory had taken the simple route of substituting  $\phi/N$  for  $\phi$ 's in the gas equation rather than substituting only the lead terms to the natural logs.
  - a) Calculate the critical interaction parameter for a symmetric blend using this substitution.
  - b) Compare your result with the critical interaction parameter found for the Flory-Huggins equation for a symmetric blend of two polymers.
  - c) What can you say about the reasonableness of the critical temperature,  $T_c$ , you would obtain for a degree of polymerization of  $N = 1000$ ?
  - d) Using the normal Flory-Huggins equation, consider the dilute limit for a polymer solution, that is concentrations below  $\phi^*$ . What term in this equation would you modify to be a constant (that being  $\phi^*$ ) for this regime? Explain your answer.
  - e) How would such a modification affect the binodal? (Remember that for our purposes, the binodal is defined by  $df(\phi)/d\phi = 0$ )
  
- 2) This week we discussed the random phase approximation (RPA) for polymer blends.
  - a) What is the meaning of the term  $\phi_{k,A}$  in the RPA discussion?
  - b) A *constitutive equation* is an empirical (not derived) equation that relates a *perturbation* (such as stress,  $\sigma$ ) to a *response* (such as strain,  $\epsilon$ ) through a *constitutive parameter* (such as the compliance,  $J$ ). Give a linear constitutive equation relating  $\phi_k$  to the external field  $\psi_k$ .
  - c) The scattering intensity  $I(k)$  ( $k$  is  $q/2\pi$ ) is proportional to the mean square fluctuation  $\langle \phi_k^2 \rangle$  of composition (or contrast) in a thermally equilibrated, single phase system. If the external field is related to the free energy at wavenumber  $k$  by  $\psi_k = dG_k/d\phi_k$ , and using the constitutive equation of part "b" for  $\phi_k$ , show how  $G_k$  is related to the susceptibility,  $\alpha_k^0$ .
  - d) If the average free energy  $\langle G_k \rangle$  in a thermally equilibrated system is  $kT$ , give a relationship between  $\alpha_k^0$  and  $\langle \phi_k^2 \rangle$  and hence (from part "c")  $I(k)$ .
  - e) Comment on the importance of the "field" from your expression for free energy  $G_k$ , and mean square fluctuation,  $\langle \phi_k^2 \rangle$ .
  
- 3) In class we considered fluctuations in composition as the mechanism to determine thermodynamic stability of a system.
  - a) Explain why the binodal regime is a meta-stable regime using this approach.
  - b) In the RPA approach we talk about a fluctuation at wavenumber  $k$ ,  $\phi_k$ , while in your answer to "a" you talk about a fluctuation of arbitrary size. Explain how a real space observation of composition fluctuations at various distances can be converted to fluctuations at wavenumbers " $k$ ",  $\phi_k$ , using a Fourier transform.
  - c) If the susceptibility for an isolated A chain is  $\alpha_k^{AA}$  and for an isolated B chain is  $\alpha_k^{BB}$ , write expressions for  $\phi_{k,A} = \phi_k$  and  $\phi_{k,B} = -\phi_k$  using the internal field  $\psi_k$ .
  - d) Use the two expressions from part "c" and the expression from question 2 part "b" to obtain the RPA equation for an athermal system.
  - e) Write the RPA equation for a thermal system (with  $\chi$ ).

**ANSWERS: 060519 Quiz 8 Polymer Properties**

$$1) a) \quad f(\phi) = \frac{\phi}{N} \ln \frac{\phi}{N} + \frac{(1-\phi)}{N} \ln \left( \frac{1-\phi}{N} \right) + \frac{\phi}{N} \frac{(1-\phi)}{N} \chi$$

$$Nf(\phi) = \phi \ln \frac{\phi}{N} + (1-\phi) \ln \left( \frac{1-\phi}{N} \right) + \frac{\phi(1-\phi)}{N} \chi$$

$$N \frac{df(\phi)}{d\phi} = \ln \frac{\phi}{N} + N - \ln \frac{(1-\phi)}{N} - N + \frac{\chi}{N} - 2 \frac{\phi\chi}{N}$$

$$N \frac{d^2f(\phi)}{d\phi^2} = \frac{N}{\phi} + \frac{N}{(1-\phi)} - \frac{2\chi}{N}$$

$$N \frac{d^3f(\phi)}{d\phi^3} = -\frac{2N}{\phi^2} + \frac{2N}{(1-\phi)^2} \quad \phi_c^2 = -(1-\phi_c)^2$$

$$= -1 + 2\phi_c - \phi_c^2$$

$$0 = -1 + 2\phi_c$$

$$\boxed{\phi_c = \frac{1}{2}} \checkmark$$

use in 2nd derivative

$$2N + 2N - \frac{2\chi_c}{N} = 0$$

$$4N^2 = 2\chi_c$$

$$\boxed{\chi_c = 2N^2}$$

$$b) \quad \chi_c N = 2$$

$\chi_{c, FH}$  is much smaller  $\sim 10^{-3}$  to  $10^{-4}$   
spank

This is expected from measurements

using the simple substitution

$$\chi_c \sim 10^6 \text{ or } 10^8 \quad \text{Far too large for reality (9 orders)}$$

$$c) \quad \chi = \frac{z \Delta \epsilon}{kT}$$

$$T_c \sim \frac{1}{\chi_c}$$

$T_c$  would be almost absolute 0 for any polymer so we would never see phase separation. This does not make sense.

d) Normal Flory-Huggins

$$f(\phi) = \frac{\phi}{N} \ln \phi + (1-\phi) \ln(1-\phi) + \phi(1-\phi)\chi$$

$$\frac{df(\phi)}{d\phi} = \frac{\ln \phi}{N} + \frac{1}{N} - \ln(1-\phi) - 1 + \chi - 2\phi\chi$$

Deriv of Normal  
Binodal  
( $\chi_{bin} = 0$ )

modified

$$f_n(\phi) = \frac{\phi}{N} \ln \phi^* + (1-\phi) \ln(1-\phi) + \phi(1-\phi)\chi$$

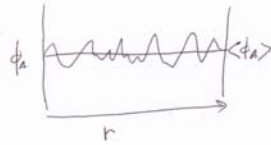
$$\frac{df(\phi)}{d\phi} = \frac{\ln \phi^*}{N} - \ln(1-\phi) - 1 + \chi - 2\phi\chi$$

Only slightly different from unmodified

e)

would have No effect at large "N"

2) a)

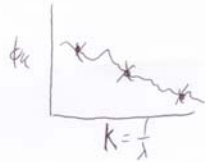
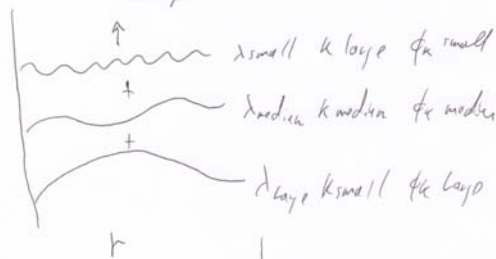


Composition in space "r" fluctuates about the mean value  $\langle \phi_A \rangle$ . We consider only the deviations

$$\phi_{Ar} = \phi_A - \langle \phi_A \rangle \text{ which is associated with } kT.$$

The noise pattern can be Fourier Decomposed into series of cosine waves of amplitude  $\phi_k$

$$\text{where } k = \frac{1}{\text{wavelength}}$$



b)

$$\phi_k = \alpha_k^0 \psi_k \quad \alpha_k^0 \equiv \text{susceptibility}$$

c)

$$dG_k = \psi_k d\phi_k$$

$$\psi_k = \frac{\phi_k}{\alpha_k^0}$$

$$\int dG_k = G_k = \int \frac{\phi_k d\phi_k}{\alpha_k^0} = \frac{\phi_k^2}{2\alpha_k^0}$$

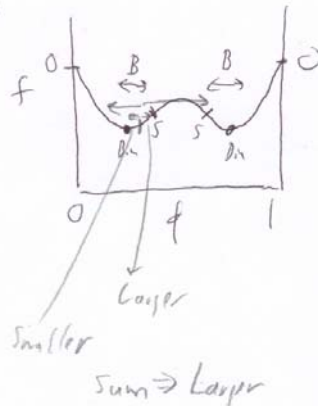
$$d) \quad \langle G_k \rangle = \frac{\langle \phi_k^2 \rangle}{2\alpha_k} = kT$$

$$\text{so } \boxed{\langle \phi_k^2 \rangle = 2\alpha_k kT}$$

e) Field,  $\psi_k$ , has no influence to  $G_k$  or to  $\langle \phi_k^2 \rangle$

The assumption of a "mean field" is needed only for the math trick to get the answers.

3) a)



Indicate broad regions where fluctuation in  $\phi$  of small magnitude leads to a higher net  $f$  while a fluctuation of large magnitude leads to a lower net  $f$ .

b) see "2a" answer

$$c) \quad \phi_{KA} = \alpha_K^{AA} (\psi_K + \underline{\psi}_K)$$

$$\phi_{KB} = \alpha_K^{BB} (\psi_K)$$

$$d) \quad \alpha_K^{AA} (\psi_K + \underline{\psi}_K) = -\alpha_K^{BB} (\underline{\psi}_K)$$

Solve for  $\underline{\psi}_K$

$$\underline{\psi}_K = \frac{-\alpha_K^{AA}}{(\alpha_K^{AA} + \alpha_K^{BB})} \psi_K$$

$$\phi_K = \frac{\alpha_K^{AA} \alpha_K^{BB}}{\alpha_K^{AA} + \alpha_K^{BB}} \psi_K = \alpha_K^0 \psi_K$$

So

$$\alpha_K^0 = \frac{\alpha_K^{AA} \alpha_K^{BB}}{\alpha_K^{AA} + \alpha_K^{BB}}$$

&

$$\frac{1}{\alpha_K^0} = \frac{1}{\alpha_K^{AA}} + \frac{1}{\alpha_K^{BB}}$$

$$e) \quad \frac{1}{\alpha_K} = \frac{1}{\alpha_K^{AA}} + \frac{1}{\alpha_K^{BB}} - \frac{2 \times kT}{V_C \epsilon_0}$$

## 060526 Quiz 9 Polymer Properties

This week we considered the basic approach to describe mechanical dynamics in polymers which includes the concepts of *anelasticity* and *linear response*.

- 1) Mechanics is based on constitutive equations and constitutive constants. A constitutive equation is generally empirical, meaning that it *has no theoretical basis* and *merely describes a series of observations*. You should be able to recognize a constitutive equation and to realize that there is no deeper understanding involved than the description of a simple response to a perturbation. (*In a sense constitutive equations are just a language to describe observations*. To quote [Oliver Heaviside](#), "Why should I refuse a good dinner simply because I don't understand the digestive processes involved?") Constitutive equations form the basis of engineering and technology.
  - a) We can write that the response  $x(t)$  to a constant field,  $\psi_0$ , is given by  $x(t) = \psi_0 \mu(t)$  in a impulse experiment. Is this a constitutive equation? Explain.
  - b) For an ideal gas we know that  $PV = nRT$ . Is this a constitutive equation? Explain.
  - c) Bragg's law states that  $d = 2\pi/q$ , is this a constitutive equation?
  - d) When you turn the steering wheel on your car, the car turns in proportion and in the direction you turn in a one-to-one relationship in the limits of the play in the wheel and the fully turned steering. Is this relationship a constitutive relationship? Explain.
  - e) Newton's law of viscosity states that the shear stress on a fluid is proportional to the rate of strain (or velocity gradient). If a fluid obeys this proportionality what could we say concerning the molecular make-up of the material? What structural model does this law rely on?
- 2) In polymer mechanical dynamics we consider three main categories of deformation.
  - a) List these three categories and explain briefly what is involved.
  - b) Consider an analogous electrical system such as a dielectric subjected to an electric field resulting in a polarization of the material. Explain the three analogous types of perturbation in part "a" for an electrical system.
  - c) For a tensile creep measurement sketch a plot of the time dependent strain for a Newtonian fluid, a Hookean elastic and an anelastic material such as the "Silly Putty" shown in class.
  - d) The decay of the anelastic component of an anelastic material in creep follows  $(1 - \exp(-t/\tau))$ . Explain what  $\tau$  is and how it might be related to material properties.
  - e) Any dynamic process involves a frequency,  $\omega_0$ , or strain rate  $d\gamma/dt$ . For instance the vibrations of a rocket engine are high frequency while mechanical strains on a rocket casing could also be of extremely low frequency due to wind shear for instance. How could this impact the design of an elastomeric rocket engine seal? (Use " $\tau$ " in your answer.)

- 3) Linear response theory is based on two main principles, *Causality* and *Superposition*.  
 a) Explain how causality and superposition are involved in the following function,

$$x(t) = \int_{\psi(t=-\infty)}^{\psi(t=t)} \alpha(t-t') d\psi(t')$$

where  $\alpha(t)$  is the susceptibility.

- b) Explain how causality and superposition are involved in the following function,

$$\psi(t) = \int_{x(t=-\infty)}^{x(t=t)} a(t-t') dx(t')$$

where  $a(t)$  is the time dependent modulus.

- c) What is the "response function",  $\mu(t)$ ?  
 d) Write a constitutive equation for the strain  $x(t)$  as a function of stress  $\psi(t)$  using this function.  
 e) Give a sketch of the response function as a function of time for a damped harmonic oscillator (like a bell), a Hookean elastic, a Newtonian fluid and an anelastic material (polymer like "Silly Putty").



## ANSWERS: 060526 Quiz 9 Polymer Properties

- 1) a) This is a constitutive equation with the response function as a constitutive function. (It is possibly a non-linear constitutive equation.)
- b) The ideal gas law is not a constitutive equation. There is no constitutive constant and it is an exact function that can be proved from basic concepts.
- c) Bragg's law is not a constitutive equation. It is an exact function that can be proven to describe wave interference.
- d) Yes, we rely on a constitutive relationship to drive a car.
- e) A constitutive equation like Newton's viscosity law does not indicate anything concerning the make-up of the material, for instance sand grains will obey Newton's viscosity law even though they are composed of macroscopic particles rather than molecules. No structural model is implied by this law.

- 2) a) Creep where a constant stress is applied and the strain is followed as a function of time. Stress relaxation where a constant strain is applied and the decay of stress in time is followed. Dynamic mechanical test where an oscillating strain with a fixed strain amplitude is applied and the stress is followed as a function of time.
- b) Creep would be analogous to a constant field applied to a dielectric, dielectric relaxation. Stress relaxation would be analogous to the decay of polarization with release of an electric field. DMA would be analogous to dynamic dielectric measurements. Also, DMA could be analogous to the interaction of electromagnetic radiation (light) with a material that scatters or diffracts since electromagnetic radiation consists of an oscillating electric field (coupled to an oscillating magnetic field).
- c)

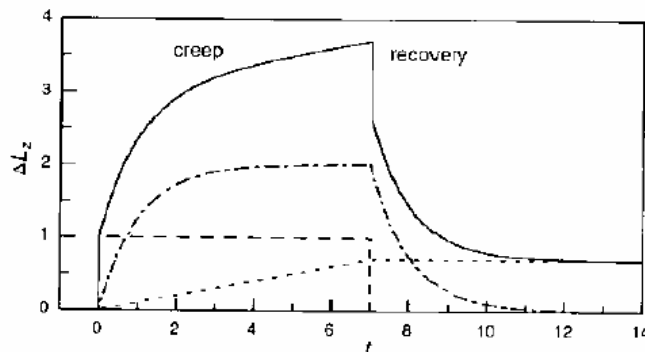


Fig. 5.1. Creep curve of a polymer sample under tension (schematic). The elongation  $\Delta L_z$  induced by a constant force applied at zero time is set up by a superposition of an instantaneous elastic response (*dashed line*), a retarded anelastic part (*dash-dot line*) and viscous flow (*dotted line*). An irreversible elongation is retained after an unloading and the completion of the recovery process

- d)  $\tau$  is the relaxation time. It corresponds with approximately the time for the material to relax 1/3 of the total anelastic strain that will be recovered after infinite time.  $\tau$  should be compared with the time of the process such as the strain rate or frequency. For the rubber balls in class,  $\tau$  was near the "bounce time" for the dead ball and was a much longer time for the bouncy ball.
- e) When a polymer component is expected to have constant properties across a wide range of temperature or frequency problems will be encountered. This was the case, for example, with

the first space shuttle disaster where seals that were suitable at 40 C turned to glass at 32 C during launch allowing for a blow-by and destruction of the crew and the 30 billion dollar space craft. The destruction was determined to be due to an engineering miscalculation involving the behavior of  $\tau$  by a congressional commission.

3) a) Casuality basically means that there is a constitutive equation that applies chronologically with the perturbation followed by the response. Superposition means that events sum in time modified by some type of memory function. In this case the memory function is the time dependent susceptibility, the perturbation is the stress and the response is the strain. A sequence of stress steps of infinitely small size are summed and weighted by the susceptibility to yield the strain at time "t".

b) For the equation for the time dependent stress in a stress relaxation measurement steps of strain are integrated using the time dependent modulus as a weighting factor.

c)  $\mu(t) = d\alpha/dt$ . It is the response to a impulse stress. The response function is also the memory function for stress in time,

$$x(t) = \int_{(t=-\infty)}^{(t=t)} \mu(t-t') \nu(t') dt'$$

d) See above.

e)

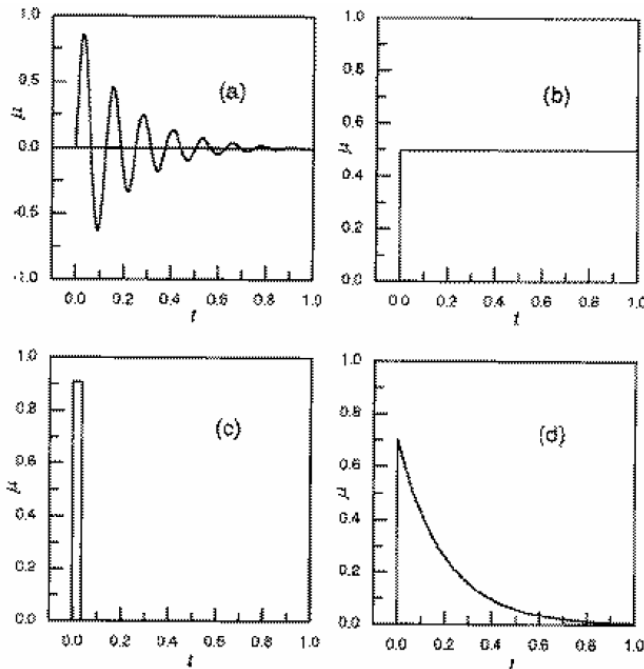


Fig. 5.4. Primary response function of a damped harmonic oscillator (a), a perfectly viscous body (b), a Hookean solid (c), a simple relaxatory system (d)

For Silly Putty, the response would be partly "d" above but with a small spike like "c" and a partial permanent deformation like "b".