

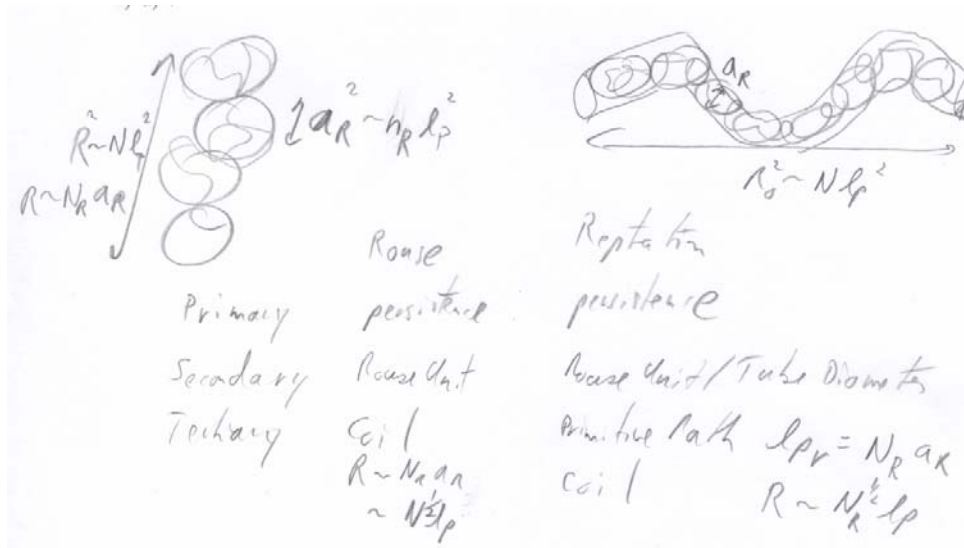
## 060215 Quiz 5 Morphology of Complex Materials

Long chain molecules display hierarchy in structure for solutions as well as in the melt. We have also seen that these molecules display hierarchy in dynamic response.

- 1)
  - a) Compare the hierarchy of a Rouse chain to the hierarchy of a reptating chain by sketching a model of the chain and explaining the different dynamic levels.
  - b) For each of the levels of dynamics you gave in part "a", explain using mostly words how the level would respond to random thermal vibrations.
  - c) Modulus,  $E$ , describes the static response of a system while viscosity,  $\eta$ , describes the dynamic response and the ratio of dynamic to static response yields a time constant,  $\tau \sim \eta/E$ . Explain how a similar approach is used for a Rouse unit of size  $a_R$  using the friction factor,  $\xi_R$ , and spring constant,  $k_R$ . Give the time constant for a single Rouse unit.
  - d) Make a table of powers of  $N$  for  $\tau$ ,  $D$ , and  $\eta$  for the Rouse model, the reptation model, the observed behavior of a dilute solution and of a high molecular weight polymer melt.
  - e) Explain in words the reason for the difference between melt and solution behavior in part "d".
  
- 2)
  - a) The structural hierarchy of a polymer chain in dilute solution can follow one of two models, explain briefly the difference between these two structural scaling models.
  - b) Are these models compatible with the Rouse model for dynamics?
  - c) Are these models compatible with the reptation model for dynamics?
  - d) How does the definition of the size of a Rouse unit,  $a_R$ , differ between the Rouse model and the Reptation model?
  - e) In your own words describe what you think would be the general consequence of using a self-avoiding walk in the Rouse model?
  
- 3)
  - a) The *fluctuation dissipation theorem* (FDT) is used to describe the relationship between the molecular response to *thermal fluctuations* (thermally driven motions that are proportional in magnitude to  $kT$ ) through the diffusion coefficient,  $D$ ; and the bulk relaxation as described by the viscosity,  $\eta$ , or friction factor,  $\xi$ . The FDT postulates that  $D \sim kT/\xi$ . Explain the main assumption involved in the *fluctuation dissipation theorem*.
  - b) For a random walk (in any dimension) the RMS distance traveled is proportional to the square root of time,  $\langle l^2 \rangle = D't$ , where  $D'$  is for diffusion along the primitive path. Show that the reptation time,  $\tau_d$  is proportional to  $N^3$  using the random walk law, the definition of the primitive path length  $l_{pr} \sim N$ , and the Rouse relationship that  $D_R \sim N^{-1}$ .
  - c) The reptation tube displays Gaussian scaling,  $\langle R^2 \rangle \sim N$ . Show that the coil diffusion coefficient for reptation follows  $1/N^2$  using the reptation time from part "b" and the distance  $\langle R^2 \rangle$ .
  - d) A protein is produced as a linear chain of amino acids residues that must undergo thermal diffusion to fold. How would you expect the time required to fold to differ for a chain in dilute solution versus a chain in a concentrated environment such as in a cell?
  - e) Reptation is capable of modeling the diffusion coefficient of polymers in the melt but can not fully describe the scaling of viscosity. Explain what might be missing from the dynamic hierarchy of the reptation model that could account for the discrepancy between the observed and predicted scaling of viscosity with molecular weight and explain why this wouldn't effect the diffusion prediction.

**ANSWERS: 060215 Quiz 5 Morphology of Complex Materials**

1) a)



b) The persistence unit is rigid and does not respond to thermal vibrations.

The Rouse unit displays a decay (no momentum so no oscillation)

The Rouse coil displays a modal response like a guitar string with the majority of the response for the lowest order mode.

For reptation the Rouse units respond with the same decay but the chain relaxes with two time constants one along the primitive path (tube) that is a Rouse relaxation and a longer time lateral tube renewal.

c) The spring constant is defined using the rubber elasticity model, so  $k_R = 3kT/(n_R l_p^2)$ , and the friction factor is defined using Stokes Law,  $\xi_R = 6\pi a_R \eta_0 = 6\pi n_R^{1/2} l_p \eta_0$ . The Rouse unit displays an exponential decay with  $\tau \sim 2\pi n_R^{3/2} l_p^3 \eta_0 / (kT)$ .

d)	$\tau$	D	$\eta$
Rouse	$N^1$	$N^{-1}$	$N^1$
Reptation	$N^3$	$N^{-2}$	$N^3$
Dilute Soln.	$N^1$	$N^{-1}$	$N^1$
Melt	$N^{3.4}$	$N^{-2}$	$N^{3.4}$

e) Entanglements lead to the difference between melt and dilute solution dynamics. In the reptation model entanglements confine chain dynamics to a 1-d diffusion path along the primitive path created by a tube of entangling chains. It is assumed that the tube renewal time is much longer than the Rouse 1-d relaxation time for the chain to reptate through the primitive path.

2) a) Good solvent, self-avoiding walk with  $R \sim N^{3/5} l_p$  and the Gaussian, random walk or theta-state with  $R \sim N^{1/2} l_p$ .

b) The Gaussian model is compatible but the SAW model is not since the Rouse model assumes a Gaussian Rouse unit in terms of spring constant and friction factor (in that  $a_R$  follows Gaussian scaling).

c) The reptation model has similar restrictions to the Gaussian model since it is based on the Rouse model and since it is assumed that the tube/primitive path is a random walk.

d)  $a_R = n_R^{1/2} l_p$ . The only difference is that  $a_R$  is defined by the average distance between chains in the melt for the reptation model so it has a value that can be calculated and that is fixed for a system of a specific composition and temperature. The reptation model calculates  $a_R$  following Rouse theory but with a restriction on the value.

e) SAW would make the Rouse unit larger making the friction factor larger if it is assumed that the SAW coil is non-draining. The spring constant for a SAW would be smaller since the coil has lower entropy (fewer states). Then the time constant,  $\tau$ , from question (1c) for instance, would be larger. Overall the chain would be slower to relax and would have slower dynamics, higher viscosity, and a lower diffusion constant.

3) a) The main assumption in the FDT is that bulk relaxations such as seen in the viscosity are directly related to molecular relaxations such as seen in the diffusion coefficient. That is, the viscosity is directly related to the diffusion coefficient. The theorem implicitly assumes that there are no dynamic levels of hierarchy between the structure which is diffusing and the bulk melt.

b) 
$$\tau_d = \frac{l_{Pr}^2}{D'} \sim \frac{N^2}{N^{-1}} = N^3$$

c) 
$$D = \frac{R^2}{\tau_d} \sim \frac{N}{N^3} = N^{-2}$$

d) The relaxation time in dilute solution is proportional to  $N$  while in a concentrated solution it is proportional to  $N^3$  following the reptation model. The time required for protein folding should be proportional to the relaxation time so the time for folding should be much longer in the cell when compared to dilute solution. This effect should be greater for larger proteins.

e) The reptation model does not include long distance interactions and coupling between chain motion over a number of different chains (topologically tangled chains). These long distance tangles could give rise to a higher viscosity compared to the simple reptation model. Some authors have proposed that tube renewal could lead to the difference between the predicted  $N^3$  dependence of viscosity and the observed  $N^{3.4}$  dependence.

This doesn't effect the diffusion coefficient since diffusion is a local phenomena on the scale of a single chain while viscosity is a global phenomena that can sense larger scale dynamic levels.