

071026 Quiz 5 Morphology of Complex Materials

- 1) The Rouse model involves a hierarchical view of the dynamics of a chain that looks very familiar to someone who has just considered the sub-secondary structures associated with thermodynamic equilibrium (i.e. blobs).
 - a) Is the Rouse model an equilibrium model?
 - b) How is the spring constant, used in the Rouse model, related to the tensile blob?
 - c) Could the Rouse unit be observed through rheology?
 - d) What is the difference between the friction factor and the viscosity as well as the spring constant and the modulus?

- 2)
 - a) Write an expression for a force balance between kinetic and potential forces in the Rouse chain.
 - b) When we consider a force balance for a pendulum we write an expression for a force balance that includes momentum (ma) as well a viscous dissipation and storage of potential energy (like a spring). Why is there no acceleration term in the force balance of part a? How would the response change with a momentum term.
 - c) Explain why discrete values are needed for the phase lag term δ in order to develop the Rouse model.
 - d) Why is a cyclic chain model used in polymer physics and in simulations to simplify macromolecular problems?
 - e) Explain the difference in relaxation time between the Rouse theory for a cyclic and for a linear chain.
 - f) We usually only consider the lowest order Rouse mode ($m = 1$) because this relaxation can be shown to account for 87% of the energy dispersed across the polymer chain spectrum. Is this mode the longest or shortest Rouse relaxation time.
 - g) Would you expect the shortest relaxation time to depend on the Rouse unit more than the longest relaxation time?
 - h) Give the molecular weight dependence of viscosity predicted by the Rouse theory and explain how this relationship relates to the theory.

- 3) Many researchers including 2 new professors in Chemistry and several in Environmental Health at UC are interested in simulating the dynamics of protein folding involve the transition from an unfolded chain to the native state. To date no one has been successful in simulating folding for a moderately complicated protein.
 - a) Comment on the appropriateness of using the Rouse model to approximate early stages of protein folding by listing the assumptions inherent in the Rouse approach.
 - b) List the special conditions that distinguish a folding protein from a synthetic polymer in solution.
 - c) Judge if the assumptions are appropriate for the conditions of protein folding at an early stage.

ANSWERS: 071026 Quiz 5 Morphology of Complex Materials

1) a) No, the Rouse model describes dynamics.

b)

$$F = \left(\frac{2kT}{nl^2} \right) R = k_{spr} R$$

we say $nl^2 \sim \zeta_p \sim \lambda$ $\zeta_p \sim \frac{kT}{F}$

c) No, the Rouse unit is a mathematical tool used to calculate the dynamic response of the chain. The Rouse unit does not exist.

d) We use friction factor for molecules and objects that do not have a cross sectional area. The friction factor relates drag force to velocity while the viscosity relates stress (force/area) to strain rate (velocity gradient). Similarly the spring constant relates force to distance while the modulus relates stress (force/area) to strain (change in distance by initial distance).

2)

$$2 \text{ a) } \quad \zeta_R \frac{dz_e}{dt} = b_R (z_{e+1} + z_{e-1} - 2z_e)$$

$$F_{vis} = F_{spr}$$

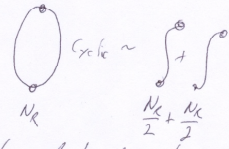
b) The mass of a rouse unit is extremely small and the momentum term is ignored. If the momentum term were included the rouse units would oscillate rather than just showing a decay towards the equilibrium position. This oscillation would complicate the behavior of the chain.

c) Discrete values of the phase lag allow the consideration of modes of vibration for the Rouse chain. With modes we can consider the distribution of energy among modes and find that most energy is stored in the lowest order mode. This allows a discrete value for the Rouse relaxation time as well as allowing us to ignore the Rouse unit that becomes important for high order modes.

d) Cyclics are used because all chain units are identical for a cyclic. There is no end effect for cyclics.

e)

$$e) \quad \zeta_{cyclic} = \frac{2\eta m}{N_R}$$

$$\zeta_{linear} = \frac{\pi \eta m}{(N_R/2)}$$


Cyclic behavior like a chain of $\frac{1}{2}$ the number of units.

f) $m = 1$ is the longest Rouse relaxation time.

g) The shortest relaxation time depends strongly on local structure.

h)

h)
$$\zeta_R = \frac{(\xi_R d_R^2) R_0^4}{3kT \pi^2}$$

For ζ_R to not depend on the size of the Rouse unit $\xi_R \sim d_R^2 \sim \frac{\eta}{\rho R}$

$\xi_R \sim \eta$ when the chain is freely draining. # of units in a Rouse segment.

Similarly $\eta \sim M'$

3) a) Assumptions of Rouse Model:

- i) Gaussian chain
- ii) Free draining chain
- iii) Friction factor follows Stokes law, this assumes domains are spheres and velocity is slow.
- iv) We ignore momentum, that is we assume the mass is small.

Gaussian chain is a bad assumption for a polyelectrolyte in a good solvent (water).

Free draining is a poor assumption for a protein where some residual folding exists and water is probably trapped sterically and by ionic association with the chain.

The Rouse units are probably not spherical especially if they are free draining.

The momentum assumption is probably pretty good. That is, the mass of a subunit of a chain is small.

b) Mainly the protein chain displays hydrophobic regions that initiate chain folding as well as ionic and disulfide interactions that drive folding enthalpically. These effects are not seen in the Rouse model.

c) As a crude approximation the Rouse model might add some information that could be useful in studies of protein folding. The disparity between the actual situation and the assumptions needs to be carefully considered.