## 070418 Quiz 3 Properties

The figures below show typical leaf "*venation*" structure. Veins serve to transport liquids to and from the cells in the leaf as well as serving as a structural support for the leaf and as a toughing feature preventing the leaf from ripping. (http://en.wikipedia.org/wiki/Leaf)

 a) Which of the following structures has the highest and the lowest, d<sub>min</sub>; highest and lowest c and highest and lowest d<sub>f</sub>?



Explain your answer.

- 2) The Mark-Houwink Equation relates the intrinsic viscosity  $[\eta]$  to the molecular weight of a polymer,  $[\eta] = kM^a$ . We find that "*a*" has a theoretical value of 0.5 and 0.8 but that many polymers such as cellulose display values much higher than 0.8.
  - a) What is the intrinsic viscosity? (give an equation)
  - b) Describe how a value of 0.5 could be obtained
  - c) Describe how a value of 0.8 could be obtained

d) The intrinsic viscosity of a synthetic protein (polylysine) was measured for several molecular weights and it was found that  $[\eta]$  didn't depend on molecular weight and that k had a value of 2.9 when the volume fraction was used for the concentration in the equation of part (a). Were these experiments in error? (Explain your reasoning.)

- 3) Stokes Law explains the relationship between the friction factor, f, and the size of a particle, R<sub>H</sub>.
  - a) What is the friction factor?
  - b) Give Stokes Law.
  - c) Explain the functionality in  $R_H$  by an analysis of units.
  - d) For an ellipsoidal (hotdog) balloon would Stokes law be appropriate to describe the drag force as the balloon traveled through air?

- 4) Drag is considered a macroscopic phenomena while diffusion is considered a microscopic phenomena in that it involves atomic or molecular motion. The Fluctuation Dissipation Theorem, D = kT/f, relates the microscopic to the macroscopic by considering that fluctuations of concentration associated with diffusion (and driven by kT) are dissipated through macroscopic mechanisms, i.e. drag and the friction factor. Show that the units are correct for the above expression for the diffusion coefficient by
  - a) Calculating the units of D using Fick's First Law. (J is mass/(length<sup>2</sup> time)
  - b) Comparing these units with the units of kT/f (kT has units of energy or force \* distance).

c) If you considered  $R_H$  to be the end-to-end distance for a polymer chain which would have a larger diffusion coefficient, a Gaussian coil or a SAW coil?

d) Could you compare the diffusion coefficient of the two of part c with a rod following the same approach? Explain.

- 5) Dynamic light scattering (DLS) is used to measure the hydrodynamic radius.
  - a) Explain the DLS measurement by sketching the instrument and the resulting intensity versus time curve.
  - b) What is a Time Auto Correlation Function?
  - c) Estimate the time correlation function for the following pattern in time,



## ANSWERS: 070418 Quiz 3 Properties

1) a) highest d<sub>min</sub> is "vii Arcuate"; lowest is "vi Parallel" highest c is "ii Reticulate or could be iii, or viii.

highest d<sub>f</sub> is "ii Reticulate since it is the densest structure.

b) The most efficient liquid transport would be  $d_{min} = 1$  since this is the shortest path.

Structural support is best for higher d<sub>f</sub> since this provides a denser support structure.

toughness would improve with c since more branching will prevent tears from propagating.

2) a) The intrinsic viscosity describes the enhancement of the viscosity due to the presence of colloidal (suspended) particles at low dilution,

 $\eta = \eta_0 (1 + [\eta]\phi)$ 

b) For  $\phi = n/V$ , we have  $[\eta] = R^3/n$  for a Gaussian Chain  $R = n^{1/2} l_K$ , so  $[\eta] \sim n^{1/2}$ . c) For a SAW chain  $R = n^{3/5} l_K$ , so  $[\eta] \sim n^{4/5}$ .

d) The synthetic protein is in native state so  $R \sim n^{1/3}$  and  $[\eta] \sim n^0$ . For spheres Einstein found that  $\eta = \eta_0 (1 + 2.5c)$  where c is the volume fraction.

3) a) The friction factor, f, is a drag coefficient for a molecule defined by the relationship between the velocity, u, and the drag Force, F,

F = f u

b)  $f = 6 \pi R \eta_0$ 

c) The units of f are (Force time/length) from the equation of part (a). Newton's law of viscosity gives,  $\eta = \tau/\gamma'$  having units of Force Time/(Length)<sup>2</sup>. Using these units in the equation for Stokes Law we find that f can only depend linearly on R.

d) No because Stokes law is for a sphere.

4) a) J = -D dc/dx so the units of D are distance<sup>2</sup>/time.

b) f has units of F/u or Force time/distance and kT has units of Force distance so kT/f has units of distance<sup>2</sup>/time the same as (a).

c) f is linear in R<sub>H</sub> by Stokes Law so and R<sub>H</sub> is larger for a SAW compared to a Gaussian coil so D is lower for the SAW coil.

d) The assumptions in (c) are that the coils are spherical and non-draining. The would not hold for a rod and the diffusion coefficient would be much higher than predicted by the Stokes-Einstein approach.



5) a)

b) The time autocorrelation function calculates how correlated a signal is with itself in time. Take two points at t<sub>1</sub> and t<sub>2</sub> and multiply I. Fix  $\Delta t = |t_2-t_1|$  and average over all t<sub>1</sub>. This is the correlation function for  $\Delta t$ . Repeat this for all  $\Delta t$  to obtain the exponential decay function.

c) For the periodic function there is correlation at short  $\Delta t$  since two points within a pulse are correlated 100% and there are correlations at the period of pulse so the correlation function is a single pulse at the period of the pulses with a peak at low  $\Delta t$ .

