**060313 Final Morphology of Complex Materials**
**(*There are 9 questions each with 5 parts.***
***The total exam is worth 300 points and each part of a question is worth ~6 points.*)**

**1** *Quiz 1 Question 1*) Explain how a protein displays structural hierarchy.

a) List 4 levels of structure for a protein
b) Describe each of these levels of structure
c) Explain what self-assembly means in the context of a protein.
d) How is structure related to function in a protein? (For example in a membrane protein.)
e) How could evolution act on the structural hierarchy of a protein?

**2** *Quiz 2 Question 2*) We considered circular dichroism as a method to monitor protein folding.

a) What is the difference between linearly-polarized and unpolarized light?
b) Explain how plane-polarized light can be produced from two circularly polarized beams.
c) For linearly polarized light explain the difference between absorption and refraction. (Absorption coefficient and the index of refraction).
d) For plane polarized light that is passed through a protein solution explain the state of polarization of the exiting light and explain why the exiting light has this state of polarization.
e) List 2 other methods that can be used to monitor protein folding.

**3** *Quiz 3 Question 2*) In class we compared protein and polymer hierarchies.

a) Polymers display short range and long range interactions. Explain what distinguishes short and long range interactions.
b) Give analogies in proteins for short and long range interactions in synthetic polymers.
c) If quaternary structure is view as a structure resulting from the interaction of multiple protein molecules, what topic in polymers relates to quarternary structure in proteins?
d) Explain why the average vector, $<\mathbf{r}_{i+1}>_{Gaussian} = 0$, reflecting the average direction and magnitude of a step from a fixed chain step, "i", for a Gaussian (random walk) chain; while $<\mathbf{r}_{i+1}>_{SRI}$ has a finite value, reflecting the average direction and magnirute of a step from a fixed chain step, "i", for a chain with short range interactions. How do short range interactions affect persistence length?
e) Explain how restrictions on bond rotation (rotational isomeric state theory) could lead to a larger persistence length in synthetic polymers (using your answer to part d).

**4** *Quiz 4 Question 3*) The concept of screening of interactions was developed by Debye for charged colloids. Debye developed the idea of a screening length that describes the distance over which interactions (such as static charge repulsion or attraction) are felt.

a) Does the screening length increase, decrease or not change with concentration? (Explain your answer with a brief description of the nature of screening).

b) In a polymer coil write chain scaling laws for sizes above and sizes below the screening length?

c) Does the screening length, $\xi$, depend on the molecular weight of the polymer, N? Explain your answer.

d) In the function $\xi = R_{F,SAW} (c/c^*)^P$ define the overlap concentration c* in terms of N, the number of persistence steps in a coil.

e) Using the function for $R_{F,SAW}$, from (*2a*); your answer to (*3c*); and your expression for c* in (*3d*), solve for P in the expression for $\xi$ in (*3d*).

**5** *Quiz 5 Question 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".

**6** *Quiz 6 Question 1*) We considered dynamics using two dynamic hierarchical models associated with dilute and concentrated conditions, the Rouse and the reptation models respectively. Polymer crystallization also seems to display differences associated with concentration that may be linked to the differences seen in dynamics.

a) Describe the structural hierarchy of polymer crystals grown from dilute conditions.

b) Describe the structural hierarchy of polymer crystals grown from the melt.

c) The micrographs below from Paul Ehrlich* in the 1990's shows polymer crystals grown in a semi-dilute solution. Comment on the hierarchy seen in these micrographs. How does it compare with "a" and "b" above?

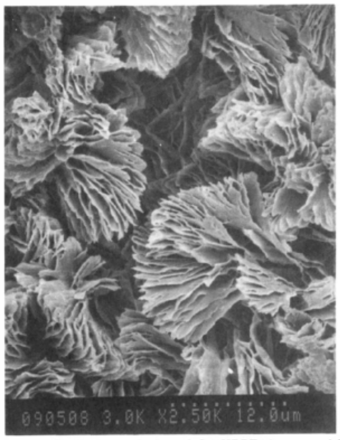


**Figure 1.** SEM micrograph of sample S-3, HDPE 1 (a commercial high density polyethylene with $\bar{M}_n$ = 7300 and $\bar{M}_w$ = 43 000) (rapid cooling).

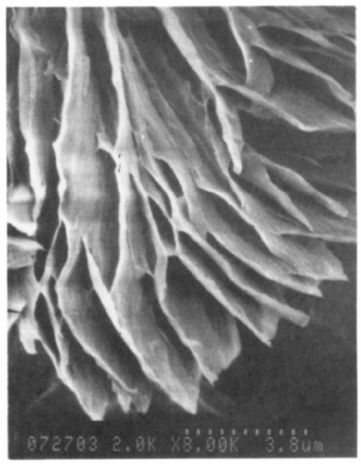


**Figure 2.** SEM micrograph of sample S-3, HDPE 1.

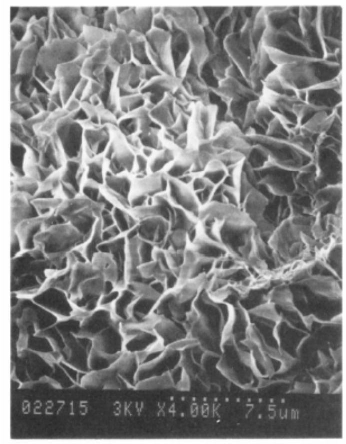


**Figure 4.** SEM micrograph of sample S-9, NBS 1475 (NIST standard reference linear polyethylene with $\bar{M}_n$ = 18 310 and $\bar{M}_w$ = 53 070; crystallized from a more concentrated solution).

d) How does the dynamics hierarchy for dilute, semi-dilute and concentrated govern the structural hierarchy seen in your answers a to d?

e) Explain how and why polymer spherulites differ from and how they are similar to dendrimers such as snow flakes.

**Lamellar Structure and Organization in Polyethylene Gels Crystallized from Supercritical Solution in Propane.* Bush PJ, Pradhan D, Ehrlich P *Macromolecules* **24** 1439-1440 (1991).

**7** *Quiz 6 Question 2*) The base structure seen in polymer crystals is a lamellar crystal.

a) Obtain the Hoffman expression for lamellar thickness using the expression for the difference in the Gibbs free energy between the crystal and melt.

b) Use the Hoffman expression to explain why polymer crystals are nanometer-sized crystals.

c) Does the Hoffman expression work for the polymers shown in the Ehrlich micrographs above? Explain.

d) Why are polymer crystals asymmetric (why is the lateral size larger than the thickness)?

e) What governs the lateral size of polymer lamellae? (Define the Keith-Padden $\delta$-parameter.)

**8** *Quiz 7 Question 1*) In class we discussed the source of the bell shaped curve of growth rate versus temperature.

a) Explain in words why a maximum in growth rate, G, is observed in temperature, T.

b) Write expressions for two rate constants $k_d$ and $k_g$.

c) Derive a rate limiting function $G \sim 1/(1/k_d + 1/k_g)$ using the chemical kinetics model from class.

d) What are the two temperature limits for polymers in the growth rate curve?

e) Would you expect spherulites to follow such a bell shaped growth rate curve?

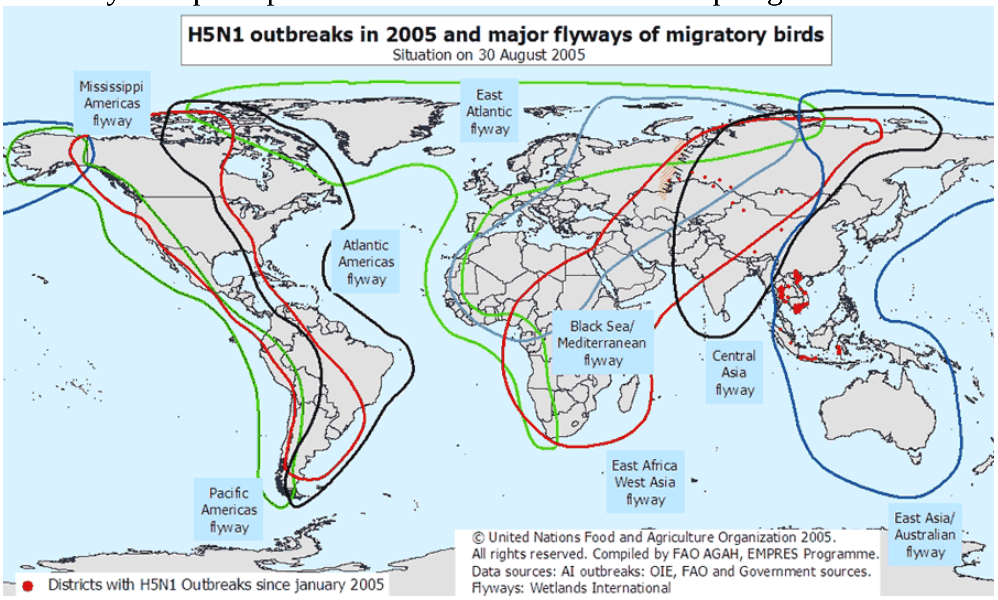


Figure 1. Migratory flight paths.

**9** *Quiz 8 Question 1*)

Above is a map of migration routes for birds which can carry the dreaded bird flu pandemic. Public Health scientists worry most about locations in central China since they connect with most of the world in a single year. The human population is like a supersaturated phase which can be nucleated (infected) at random locations along these flyways almost instantaneously (spontaneous nucleation). The World Health Organization has information concerning the fraction of the overall population infected as a function of time from hospital records, $\phi_{inf}$. By constant monitoring it is possible to know the exact time of mutation of a human virulent strain ($t_0$ for "*nucleation*").

Assuming constant infection rate in terms of distance per time, dr/dt, from a "*nucleation*" site and complete infection of a region after an infection front passes through, derive an expression for $\phi_{inf}$ as a function of time that relies on the geometry of spreading by:

a) Writing the Poisson distribution and explain the use of this distribution for this situation.

b) Writing an expression for the average number of infection fronts that have passed through a random point at time t, <F> if infection spreads in 2d rings at a rate of dr/dt.

c) Using the expression from "b" to write an expression for the expected behavior of $\phi_{inf}$ with time.

d) If it is observed that $\phi_{inf}$ follows (1 - exp(-kt)) where t is time and k is a constant, what can be said about the transmission of the flu (perhaps along trade routes)? What is *k*?

e) Could sporatic nucleation explain the behavior seen in part "d"? How or Why?