

071116 Quiz 7 Morphology of Complex Materials

- 1) Polymers crystallize into thin lamellar sheets.
 - a) What are typical dimensions of these lamellar sheets?
 - b) How does the thickness of these sheets vary when crystals are grown from dilute solution, semi-dilute solution and from the melt?
 - c) Write an expression for the free energy of a sheet crystallized at a temperature T .
 - d) Apply an assumption of pseudo-equilibrium to obtain an expression for the lamellar thickness.
 - e) Explain the meaning of pseudo-equilibrium.

- 2) a) & b) Briefly describe several models for the lamellar interface
 - c) How would you expect these different models to effect the value of lamellar thickness.
 - d) Explain several problems involved in a polymer lamellar interface composed of extended chains.
 - e) Explain the term epitaxial crystallization and why it might be important to polymer lamellar crystals.

- 3) The equilibrium melting point is simple to determine in a metal or ceramic crystal.
 - a) Why is it more difficult to determine the equilibrium melting point for a polymer crystal.
 - b) Explain what occurs when a glass half full of ice and half full of water is brought to 0°C .
 - c) How can measurements of the lamellar thickness be used to determine the equilibrium melting point in polymers.
 - d) Explain the difficulty with this measurement.
 - e) Explain the Hoffman-Weeks approach to the determination of the melting point for polymer crystals.

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1) a) Thickness is typically 10 nm and lateral dimensions can be between 100 nm and 10 micron. This is similar to the aspect ratio for a sheet of paper.

b) The thickness depends only on the temperature and is identical for crystals grown under different conditions but at the same temperature.

$$c) \Delta G = V(\Delta H - T\Delta S) + 2\gamma S = V\Delta H\left(1 - \frac{T}{T_\infty}\right) + 2\gamma S$$

d) We assume that the free energy in (c) can be set to 0 and we solve for t using $V = St$. This yields,

$$t = \frac{2\gamma T_\infty}{\Delta H(T_\infty - T)}$$

e) Pseudo-equilibrium is not equilibrium since at equilibrium the crystal would be of infinite thickness. In application of pseudo-equilibrium we consider a free energy expression that includes terms that go to 0 at equilibrium such as the surface area. Then we calculate parameters associated with this pseudo (meaning false) equilibrium. This allows the calculation of parameters that are seen in kinetic processes associated with thermodynamic features.

2) a) b) Adjacent reentry is a model with the chains tightly knit in to the crystal; Switchboard model is with the chains more or less randomly reentering the crystal in what looks like an old time telephone switchboard; synoptic model involves interconnection between neighboring lamellae in what looks like nerve synapses. There are other models.

c) The nature of the interface could effect the surface energy term. Larger surface energy (associated with tighter chain reentry such as in adjacent reentry) is associated with larger lamellar thicknesses.

d) One problem with extended chains with no reentry is that the density difference between the crystal and amorphous can not be accommodated at the crystal interface. Also, if the chains extend directly from the crystal surface there isn't a real interface between crystalline and amorphous regions.

e) Epitaxial crystallization is the growth of a crystal on a seed. This can be homoepitaxy (on the same crystal) or heteroepitaxy on a seed crystal such as a low molecular weight organic crystal with similar crystallographic planes to a polymer crystal. We saw examples of homepitaxy in class where polypropylene seeded on its own lamellar crystals in solution growth. Epitaxy is also used to grow a silicon boule in semiconductor manufacturing.

3) a) There are three main reasons that it is difficult to determine the equilibrium melting point.

1) defects in the crystals; 2) kinetics of crystallization are very slow and 3) polymers form lamellar crystals with shifts in the melting point. Additionally, cold crystallization is a major problem in measuring thermal transitions in semi-crystalline polymers (crystallization while you heat from room temperature to the melting point).

b) At the equilibrium melting point the water will remain 50% crystalline but the water in ice will strive to reduce surface area by fusing crystals until you have one very large chunk of ice floating in water.

c) Using the Hoffman-Lauritzen equation we have $\frac{1}{t} = \left(\frac{\Delta H}{2\gamma T_\infty} \right) (T_\infty - T)$ so a plot of $1/t$ versus T

will yield T_{inf} .

d) The problem with this measurement is the determination of t from TEM or SAXS. In SAXS you determine L and DOC and get t from $L*DOC/100$ assuming a two phase model (too many assumptions) and using TEM it is difficult to distinguish projections to get a thickness.

e) Polymers crystallize with defects incorporated in the crystal so that the melting point is always higher than the crystallization temperature. A plot of T_m versus T_c yields T_{inf} at the high temperature extrapolation where $T_m = T_c$. This can be easily done in a DSC.