Please read the exam through before starting. Clearly show all work in the space provided below each question. Feel free to use the additional pages at the end of this packet if necessary. Calculators and one double-sided 8 ½ x 11 page of notes are permitted. It is suggested that you outline the solution to your problem wherever possible. Partial credit will be given for answers that follow a logical thought process. Good luck!

RETURN THIS EXAM WITH YOUR EQUATION SHEET
AT THE END OF THE EXAM PERIOD

Name ______________________________________ (out of 15)

Question 1 ________________________________ (out of 20)

Question 2 ________________________________ (out of 20)

Question 3 ________________________________ (out of 20)

Question 4 ________________________________ (out of 20)

Question 5 ________________________________ (out of 25)

Total ____________________________________ (out of 100)
Problem 1 (15 points)

Ice cream shelf life is determined by the time it takes for the ice crystals to grow to a size where it is noticeable in your mouth. Inada et al (Chemical Engineering Science 61 (2006) 3149 – 3158) studied the coarsening of ice crystals in the presence of various additives. These additives were poly(vinyl alcohol) (PVA), antifreeze protein (AFP), NaCl, poly(ethylene glycol) (PEG), poly(vinyl pyrrolidone) (PVP), and poly(acrylic acid) (PAA). PVA and AFP showed a remarkable ability to preserve the crystal size on aging at 0°C. The investigators also noted that the presence of PVA and AFP appeared to affect the ice crystal shape as shown below in Figure 4.

What are PVA and AFP doing to preserve the crystal size? Why is it that this particular crystal shape is resistant to the forces of Ostwald ripening?
Fig. 3. Photographs of ice crystals in isothermal ice slurries with different additives (PVA, PEG, PVP, PAA, NaCl, and AFP type I) before preservation (left column) and after preservation (right column). Elapsed time is based on the time at which the test samples were made. (a) PVA, 11 min (b) PVA, 321 min (c) PEG, 7 min (d) PEG, 302 min (e) PVP, 9 min (f) PVP, 300 min (g) PAA, 8 min (h) PAA, 302 min (i) NaCl, 9 min (j) NaCl, 300 min (k) AFP type I, 9 min (l) AFP type I, 304 min.
Problem 1 cont.

Fig. 4. Photographs of ice crystals after about 600-min isothermal preservation with additive (a) PVA, 599 min or (b) AFP type I, 598 min.
Problem 2 (20 points)

Park et al (J. Mat. Sci 11, 1976) studied the initial stages of decomposition in the TiO$_2$-SnO$_2$ system, whose phase diagram is given below.

![Phase Diagram](image)

A single-phase solid sample of TiO$_2$-SnO$_2$ with 50/50 composition and another single-phase solid sample with 80% TiO$_2$ were annealed at 900°C. The microstructural evolutions for these alloy samples over different annealing times were observed with TEM (transmission electron microscopy).

a) Below is the microstructural evolution for a 50% TiO$_2$-SnO$_2$ sample. What is happening to this microstructure over time?
Figure 6: Microstructural evolution of the equimolar alloy decomposed at 900°C. The annealing times for (a) to (f) are 6, 15, 20, 60 and 450 min, and 127 h, respectively. All magnifications and orientations as for (a).
b) Given below are some microstructures for 80% TiO$_2$-SnO$_2$ samples annealed for 15 hours at 900$^\circ$ C. Phase separation in the 80% TiO$_2$ sample is only observed near the grain boundaries. Explain why this is different than what we see in part a.

c) Draw in the relevant features of the phase diagram that describe why the microstructures in a) and b) are different.
Problem 2 cont.

d) Can you think of a reason why the microstructure in part a) is so anisotropic? How would you modify the diagram in part c) to represent the different orientations of the precipitates?
Problem 3 (20 points)

The Czochralski method of growing silicon involves pulling a solid single crystal of silicon from a molten bath contained in a quartz (SiO$_2$) crucible. Processing takes place at elevated temperatures, resulting in oxygen from the crucible to be incorporated into the silicon crystal. Lowering the temperature of the as-produced silicon crystal to semiconductor processing temperatures results in a supersaturation of this incorporated oxygen. That is, more oxygen exists in the silicon beyond the solubility limit at that temperature, and exists in the form of oxide precipitates.

Kelton et al (J. Appl. Phys. 85(11), 1999) conducted experiments in which silicon ingots with different oxygen concentrations (low, med, high) were studied. Silicon wafers with medium oxygen concentration were annealed at 800$^\circ$C following pre-annealing treatments at 650$^\circ$C. All samples were further heat-treated at 1000$^\circ$C to grow the silicon dioxide precipitates so that they may be more easily observed. These precipitates were observed by etching a cross-section of the sample and counting the etch pits under a microscope.

The following graph shows oxygen precipitate density (number of precipitates/cm$^3$) as a function of annealing time at 800$^\circ$C for three different pre-annealing treatments (no pre-anneal, pre-anneal for 4 hours, and pre-anneal for 8 hours at 650$^\circ$C).

![Graph showing oxygen precipitate density](image)

a) Explain the trend in this graph. Why is the oxide precipitate density higher for samples that were pre-annealed at 650$^\circ$C for longer times?
The graph of oxide precipitate density vs. time at pre-annealing temperatures of 550°C and 650°C is given below.

b) The data appears to eventually grow linearly with time, as shown by the dashed lines. Why is it that the dashed lines intercept the x-axis at a non-zero time?

c) What does the slope of the linear part of the graph correspond to?
The change in oxide precipitate density with temperature following 32 hours of anneal for different initial oxygen concentrations is given in the graph below.

![Graph showing change in oxide precipitate density with temperature for different oxygen concentrations](image)

d) Why do these graphs go through a maximum?
Problem 3 cont.
Problem 4 (20 points)

Consider a faceted grain boundary between two grains of differing size.

a) How does the stress on a grain boundary vary with the Gibbs energy difference between two neighboring grains? If the grains are well annealed, what is the most common cause of the Gibbs energy difference between two grains?

b) How will the velocity vary with the stress if the grain boundary is atomically rough (accommodation coefficient equal to 1)?

c) Given what you know about solidification of faceted crystals, sketch in the graph below how the velocity of a faceted grain boundary will vary with Gibbs energy difference between the grains. Also show on the same graph your answer to part b.
d) Lee et al (Acta mater. 48 (2000) 3071-3080) studied grain growth behavior in nickel-based super alloys. They started with samples with microstructures shown below and then heat treated for various times at two temperatures (1200⁰ C and 1300⁰ C). The microstructures at 5 minutes for the two temperatures are also shown below. Several large grains are observed in the 1200⁰C sample. The grain size distributions as a function of time are also shown (note the scales on the y-axis). Note that the average grain size hardly changes between 5 and 10 minutes at 1200⁰C despite the fact that those few large grains are present in the 5-minute microstructure. The average grain size does, however, change between 5 and 10 minutes at 1300⁰ C. Finally, TEM micrographs of grain boundaries in samples annealed at 1200⁰ and 1300⁰ C are shown below. Explain why grains grow abnormally at 1200⁰ C in these nickel-based super alloys.

![Fig. 1. The initial optical microstructure of the specimen before the heat treatments.](image_url)
Grain size distribution as a function of time at 1200°C

Grain size distribution as a function of time at 1300°C

Fig. 5. The measured distributions of the equivalent sphere diameter of the grains in the specimens heat-treated at 1200°C for (a) 5 min, (b) 10 min, and (c) 2 h.

Fig. 6. The measured distributions of the equivalent sphere diameter of the grains in the specimens heat-treated at 1300°C for (a) 5 min, (b) 10 min, and (c) 2 h.

Fig. 9. The TEM micrographs of the grain boundaries in the specimens heat-treated for 10 min at (a) 1200°C and (b) 1300°C.
Problem 4 cont.
Problem 5 (25 points)

Zhai et al (Macromolecules 2005, 38, 1717-1722) studied ultra-thin PEO films. These films are so thin they are just one polymer molecule thick. The films were formed by drying a polymer-solvent solution on a substrate. The solvent evaporates to leave crystalline lamella islands on the substrate that change upon heating. The maximum length of the molecules in the fully extended form is \( L = l_m \cdot N \) = 31.6 nm where the repeating unit length is \( l_m = 0.2783 \) nm for PEO and the degree of polymerization is \( N = 114 \). Shown on the next page are atomic force microscopy (AFM) images of the films in their study. The precise AFM measurements show these lamellae to be initially 6.3 nm thick. They then either disappear or thicken in a step-wise fashion as the film is heated slowly from room temperature to 62°C.

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\begin{array}{c}
\text{PEO molecule with } N = 6
\end{array}
\]

a) What accounts for the step-wise change in thickness shown in the figure below?

b) What is the thermodynamic driving force for increasing the film thickness?

c) What other process is going on?
Figure 4. AFM height images showing the variations of PEO lamellar crystals with increasing temperature. The scale in z-direction is 40 nm for (a) to (h) and 100 nm for (i) to (l). The corresponding temperatures are 31 °C for (a), 35 °C for (b), 44 °C for (c), 48 °C for (d), 49 °C for (e), 51 °C for (f), 55 °C for (g), 56 °C for (h), 57 °C for (i), 60 °C for (j), 61 °C for (k), and 62 °C for (l). Arrows A to D point out the areas of which size and height were measured.
The same authors reported other results that indicate how the transition from one thickness to another occurs (Macromol. Chem. Phys. 2007, 208, 651-657). Shown below are further AFM images of the same PEO films above during the slow heating to higher temperature. It is observed that thicker regions first appear at the edge of thinner regions (see points A and B).

**d)** Explain what molecular event must happen for a thicker region to appear in the microstructure.

**e)** Why do you think these regions first appear at the edge of thinner regions?
Problem 5 cont.
Cont.