2022 Materials PhD Qual Exam
Whiteboard Notes

- Exam timeframe: 9:00am-1:00pm
    - a 1hour and a 15 minute time check will be given by the Exam Proctor
    - Calculators are permitted
    - No other smart devices are permitted (For example, cell phones are not
- permitted)
    - Only books and notes permitted as indicated on exam cover sheet
    - Exam Response Sheets
- All exam answers should be written on the response sheets provided.
- Handwriting should be clear and legible.
- Only write on one side of each exam response sheet. Exams may be scanned to the faculty for grading.
- If you run out of exam response sheets, there is white paper at the front of the room. Be sure your examinee number is on each page.
- Number the pages, by question (NOT by the entire exam). For example: Section 2, Problem 2, Page 1 of 4.
    - All exams and scratch paper must be given to the Exam Proctor at the end of the exam.
    - See the Exam Proctor if clarification is needed. The Exam Proctor will contact the faculty who will either come or send another faculty member to clarify.

Materials Science and Engineering
PhD Qualifying Exam

WRITTEN EXAM: **Tuesday, May 24**
                                      9:00AM-1:00PM, 15 Saint Mary's Street, Room 105

ORAL EXAM: **Thursday or Friday, May 26 or 27**
                                      Arranged, 15 Saint Mary's Street, Room 105, 121

General Instructions:
- Calculators are allowed.
- Only the books indicated will be allowed.

1) Please write your EXAM NUMBER on every sheet! Write clearly and legibly as the exam may be scanned to faculty for grading.

2) Complete the Required Sections as below:

Section I: Answer 1 Question
- Electrical, Optical, Magnetic Properties of Matls (MS 577 Swan) – CLOSED BOOK. NOTES ALLOWED (one page, double-sided)
- Intro to Solid State Physics (PY 543 Hu) - open book, notes allowed and a calculator

Section II: Answer 3 out of 4 questions
- **Problems 1 and/or 2:** Thermodynamics and Statistical Mechanics (MS 505, Pal) – OPEN NOTES (1 page, double sided) Bring a ruler and graphing Calculator or graphing paper to the exam.
- **Problems 3 and/or 4:** Kinetic Processes in Materials (MS 503, Basu) – CLOSED BOOK, NO NOTES. Equations and tables (if necessary) will be given in the question

Section III: Answer 1 Question
- **Problem 1:** Computational Methods of Materials Science (MS 508, Coker) – CLOSED BOOK. NOTES ALLOWED (one page, double-sided).
- **Problem 2:** Physics of Semiconductor Materials (MS 574, Bellotti) – CLOSED BOOK. NOTES ALLOWED (one page, double-sided
- **Problem 3:** Polymers & Soft Materials (MS 504 Kays) – OPEN NOTES (one page, double-sided, Chapters 6-7 (Hiemenz and Lodge, Polymer Chemistry 2nded.) and chapter 4 (Jones, Soft Condensed Matter)
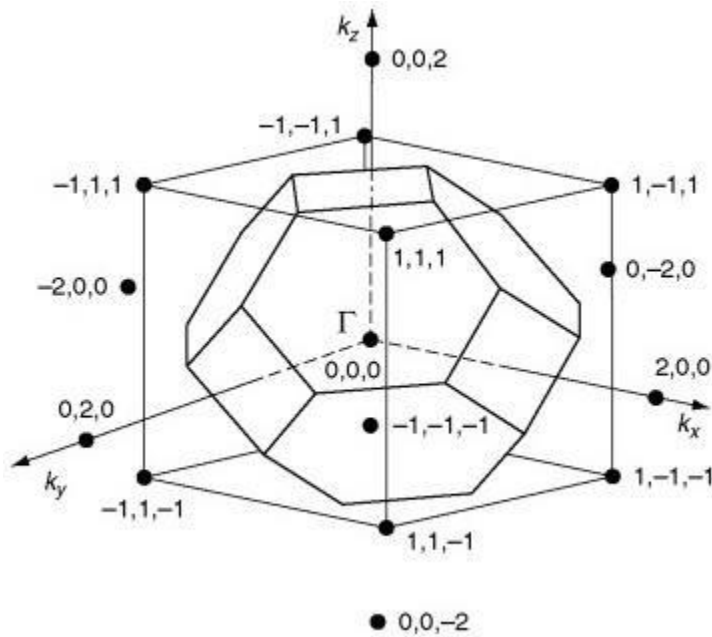
EC577/MS577

MSE QUALIFIER MAY 2022

Free electron bands empty lattice model in the reduced zone. Consider the free electron bands of an FCCcrystal in the empty lattice approximation. Calculate the bands along the ΓX direction (i.e. <100>

directions) in the reduced zone scheme for all allowed G vectors G_{hkl} up to $N = \sqrt{h^2 + k^2 + l^2} = 4$. Assume lattice is FCC with one atom per lattice point. Draw and label the bands with the relevant G vectors.

Introduction to Solid State Physics
PY 543 MSE Qualifying Exam

Thursday, May 24th 2022

Your signature: _____

1. You can use any textbooks and notes you want, but you should not discuss anything with other students, or with anyone else.

2. This exam contains 2 pages (including this cover page) and 1 problem.

3. Show all your work to receive full credit for each problem.

1 Sketch a rectangular lattice with $a_1/a_2 = 1/2$, where $a_1 = 1°A$, $a_2 = 2°A$

(a) (5 points) On your sketch indicate a pair of neighboring planes of each type:

$$(0\ 1);\ (1\ 2);\ (2\ 3);\ (1\ ^-2)$$

(b) (10 points) It can be shown that the spacing between adjacent planes indexed by (l,m) is given by:

$$\frac{1}{d} = \left(\frac{l^2}{a_1^2} + \frac{m^2}{a_2^2}\right)^{1/2}$$

Suppose we can do an x-ray diffraction experiment. The beam is incident on the crystal parallel to the a-axis. What will be the diffracting angles and wavelengths for the Bragg diffraction from the (1 1),(1 2) "planes"?

Note: If you don't have a calculator, then just leave the mathematical expressions without the final angles evaluated.

(c) (5 points) The cutoff wavelength (i.e., the shortest wavelength) of the x-ray produced with electrons can be evaluated from the electron energy. Suppose the energy of the electrons to generate the x-ray is 10 kV. What is the cutoff wavelength of x-rays? Note: If you don't have a calculator, then just leave the mathematical expression without the final result evaluated.

(d) (5 points) How will the cutoff wavelength of x-rays limit the detection of Bragg diffraction peaks?
If you have a calculator, compare your result of (b) with (c) to see which diffraction peak(s) will be observed.

If you don't have a calculator, describe the steps to determine which diffraction peals(s) will be observed.

Section II: Answer 3 out of 4 questions
Problems 1 and/or 2:

1.

In class, we derived the regular solution model for a binary A-B alloy. The free energy of mixing for the regular solution model is (expressed per mole):

$$\Delta G_{mix} = Z\omega X_A X_B + RT\left(X_A \ln X_A + X_B \ln X_B\right)$$

where

$$\omega = w_{AB} - \frac{1}{2}\left(w_{AA} + w_{BB}\right)$$

and Z = the coordination number of each atom in the crystal.

Assume $\omega = 630\frac{J}{mol}$ and $Z = 8$

(a) Calculate expression for the
    (i) enthalpy of mixing
    (ii) entropy of mixing
    (iii) the chemical potentials of A and B
    (iv) the activities of A and B

2.

The properties of mixing for a liquid A-B mixtures at a temperature of 1000 K are show below.

(a) Is the liquid A-B mixture an ideal solution? Briefly justify your answer.
(b) What is the vapor pressure of A in a mixture with 95% B?
(c) 1 mole of pure A liquid at $1000K$ is added to 1.5 moles of pure B liquid at $1000K$. How much heat needs to be extracted/added to keep the system at $1000K$?

Data:
   Vapor pressure of pure A at $1000K = 10^{-5}$ atm
   Vapor pressure of pure B at $1000K = 10^{-2}$ atm
   Heat capacity for all compositions of the liquid $= 30\frac{J}{mol-K}$
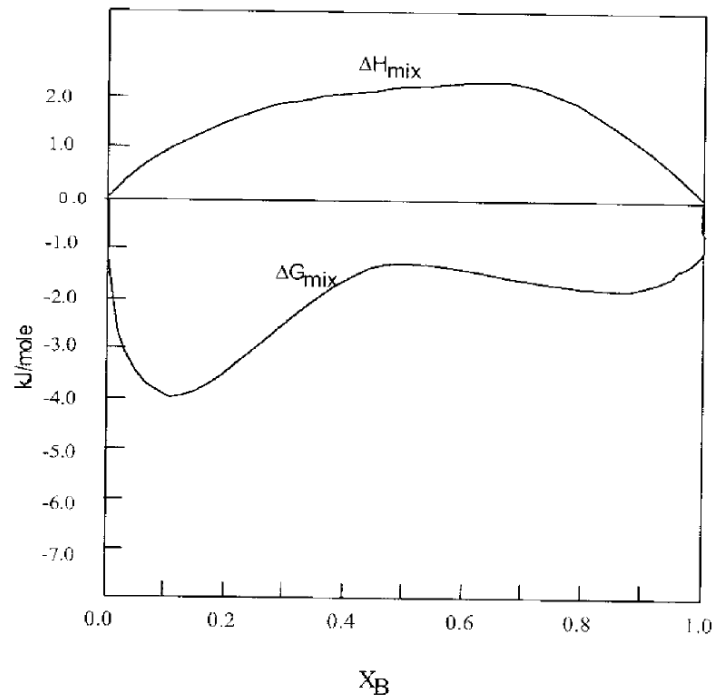
Problems 3 and/or 4:
May 2022 MSE Qualifier Questions: MS 503
Closed book, NO additional notes

Some physical constants and kinetic formulas that may or may not be relevant:

Gas constant, R = 8.314 J/mole-K

Avagadro's constant, N_{Av} = 6.023X10^{23} mole^{-1}

Plank's constant, h = 6.626X10^{-34} J-s

Boltzman's constant, k = 1.381X10^{-23} J/K

Charge of an electron, e = -1.602X10^{-19} Coulombs

$$D(\text{vacancy mechanism}) = ga^2 n_D p_v \exp\left(-\frac{DG_m^v}{RT}\right), p_v = exp\left(-\frac{\Delta G_v}{RT}\right), v_D = \frac{kT}{h}, \gamma = \frac{Z}{6}$$

$$D(\text{interstitial mechanism}) = ga^2 n_D \exp\left(-\frac{DG_m^i}{RT}\right),$$

$$D(self\ interstitial) = \gamma a^2 v_D\ exp\left(-\frac{\Delta G_{si}}{RT}\right) exp\left(-\frac{\Delta G_m^{si}}{RT}\right)$$

$$D_{gb} = D_{gb}^0 \exp\left(-\frac{DG_m^{gb}}{RT}\right), D_l = D_l^0 \exp\left(-\frac{DG_m^l}{RT}\right)$$

$$\text{For MO: } [V_M''][V_O^{\bullet\bullet}] = exp\left(-\frac{\Delta g_S}{kT}\right); \ [V_M''][M_i^{\bullet\bullet}] = exp\left(-\frac{\Delta g_F}{kT}\right)$$

$$\textit{For chemical reaction: } aA + bB = cC \textit{ with } \Delta G^0; K = exp\left(-\frac{\Delta G_0}{RT}\right) = \frac{(a_C)^c}{(a_A)^a(a_B)^b}$$

$$\frac{d[C]}{dt} = k_f\ [A]^{\propto}[B]^{\beta} - k_b\ [C]^{\gamma}; \quad \frac{d[C]}{dt} = -\frac{c}{a}\frac{d[A]}{dt}$$

$$\Delta G = V\Delta G_V + A\sigma$$

$$I = \frac{n_0 D_{int}}{\lambda^2}\ exp\left(-\frac{\Delta G^*}{kT}\right); \ U = \frac{D_{int}}{\lambda}; \ \Delta G_V = -\frac{L_V^f \Delta T}{T_M}; \ \Delta T = T_M - T$$

Problem 1.

a) The oxide MO is non-stoichiometric, with the M/O ratio less than 1. If the majority defects in MO is doubly charged, write **two** possible defect incorporation reactions. Which of these two is **probable**? Explain your reasons. Is the oxide *n*- or *p*-type?

b) Assume that during sintering of MO, both cation and anion species diffuse by the vacancy mechanism. Since both species need to diffuse, the **slowest** diffusing species would determine the rate-controlling step. In MO, do you expect anion or cation diffusion to be rate controlling? Explain your reasoning along with any assumptions you have made.

c) In order to reduce sintering time, you need to increase the kinetics of the rate-controlling step. Would you add small quantities of XO_2 or Y_2O to reduce sintering time? Write appropriate defect incorporation reactions to explain.

d) Would you increase or decrease the oxygen partial pressure in the sintering furnace to reduce the sintering time? **Explain why**.

Problem 2.

The newly discovered element, Bostonium is an FCC metal. There is some debate about the shape of the Bostonium nuclei during **homogeneous** nucleation on solidification. Researchers from Harvard claim that the nuclei are cubic in shape, bounded by 6 {100} surfaces. Researchers from MIT claim that they are tetrahedral in shape, bounded by 4 {111} surfaces. Both groups have submitted $500M proposals to study solidification of Bostonium to back up their respective claims.

a) You claim that having taken MS 503, you can use the 'broken bond model' to resolve this problem without spending any money. Which nuclei shape will be preferred? Show **ALL** calculations.

b) What would be the shape of the nuclei if the surface (interfacial) energy is isotropic (independent of orientation)? **Explain**.

DATA: For a tetrahedron of side 'a', total surface area = $\sqrt{3}\, a^2$, volume = $\dfrac{\sqrt{2}}{3}\, a^3$.

Section III: Answer 1 Question

- **Problem 1:** Computational Methods of Materials Science (MS 508, Coker) – CLOSED BOOK. NOTES ALLOWED (one page, double-sided).

Q1 The Helmholtz free energy is related to the canonical ensemble partition function according to the result $F(N,V,T) = -k_B T \ln Q_{NVT}$, where

$$Q_{NVT} = \frac{V^N}{\Lambda^{3N} N!} \int_0^1 \cdots \int_0^1 d\mathbf{s}^N e^{-\beta \mathcal{U}(\mathbf{s}^N; L)}$$

(1)

Here we have written the interaction potential $U(\mathbf{s}^N; L)$ in terms of the scaled coordinates of the N particles that are contained in a cubic region of volume $V = L^3$, and $\Lambda = (h^2/(2\pi m k_B T))^{1/2}$.

In class we showed that the partition function for the isothermal, isobaric ensemble, Q_{NPT}, is:

$$Q_{NPT} = \frac{\beta P}{\Lambda^{3N} N!} \int dV \; V^N e^{-\beta PV} \int_0^1 \cdots \int_0^1 d\mathbf{s}^N e^{-\beta \mathcal{U}(\mathbf{s}^N; L)}$$

(2)

(i) Obtain an expression for Q_{NPT} in terms of the Helmholtz free energy $F(N,V,T)$

(ii) Your result in (i) should contain an integral over volume and you can interpret it as the normalization constant for the probability distribution $P(V)$ for observing a system with volume V at an applied pressure P and temperature T. Use your result from (i) to obtain an expression for $P(V)$ in terms of $F(N,V,T)$.

(iii) The Virial estimator $P_{vir}(V)$ for the pressure of an N particle system with volume V at temperature T can be defined as

$$P_{vir}(V) = -\left(\frac{\partial F}{\partial V}\right)_{NT}$$

(3)

Use your results above to compute the average of the Virial estimator over your volume probability distribution

$$\langle P_{vir} \rangle = \int_0^\infty P_{vir}(V) \mathcal{P}(V) dV$$

(4)

and show how it is related to the applied pressure P. (Hint: You will need to use integration by parts to simplify your result.)

- **Problem 2:** Physics of Semiconductor Materials (MS 574, Bellotti) – CLOSED BOOK. NOTES ALLOWED (one page, double-sided)

You have an a harmonic oscillator with $\alpha = (mk/\hbar^2)^{1/4}$, where k is the oscillator spring constant and $\omega = (k/m)^{1/2}$ the corresponding frequency. The eigenfunctions solution of the Schroedinger equation are given by:

$$\psi_n(x) = \left(\frac{\alpha}{\sqrt{\pi}\,2^n\,n!}\right)^{1/2} e^{-\frac{\alpha^2\,x^2}{2}} H_n(\alpha\,x)$$

and the corresponding generating function of the Hermite polynomia is:

$$H_n(\xi) = (-1)^n\,e^{\xi^2}\,\frac{d^n\,e^{-\xi^2}}{d\xi^n}$$

– Based on the information you have, you are asked to construct a three-dimensional harmonic oscillator for which the first excite state is doubly degenerate. What parameter do you use/change to construct the 3D Hamiltonian? Write the complete expressions of the eigenvalues and the first three eigenfunctions of the three-dimensional oscillator and explicitly determine the degeneracies. – Subsequently you are asked to measure the energy of your system. After an infinite number of tests you obtain that the measured value is 50% of the time the ground state, 40% the first excited state, and 10% the second excited state. Write an explicit expression for the state function.

– What is the corresponding expectation value of the energy?

- **Problem 3:** Polymers & Soft Materials (MS 504 Kays) – OPEN NOTES (one page, double-sided, Chapters 6-7 (Hiemenz and Lodge, Polymer Chemistry 2nded.) and chapter 4 (Jones, Soft Condensed Matter)

1) Polyethylenimine (PEI, right) is a common biomedical polymer used in the delivery of DNA or RNA to cells. Use the data plots to answer the following questions. Additional info: MW of nitrogen is 14Da, C-C bond length is 0.154 nm, and C-N is 0.147nm
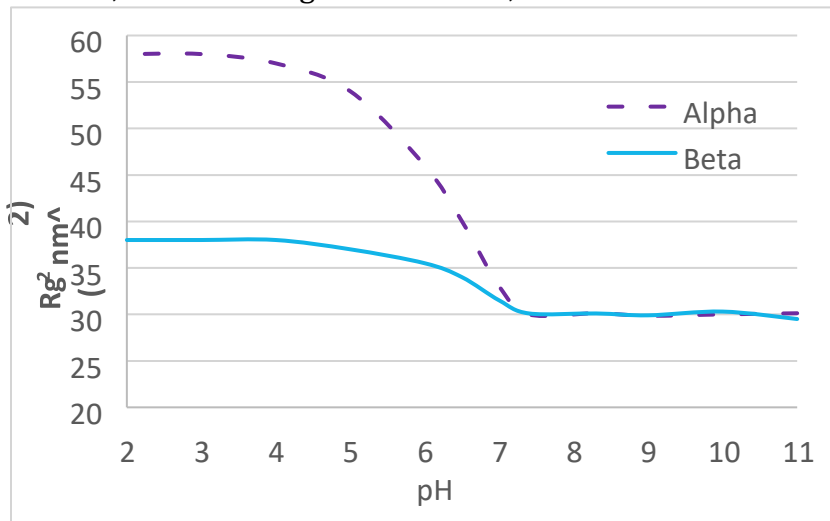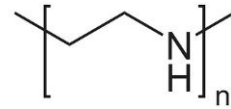

a. Explain why the R_g^2 changes with pH

b. Which region of the plot should you select to calculate the Flory characteristic ratio $(C)_\infty$, particularly if you are interested in linking C to trans/gauche content$_\infty$ of the polymer in its **native/molten** state? Circle the region, and **please explain** briefly why you selected that region.

c. Assuming the purple dotted line in the plot above was from 43 kDa PEI, please calculate the Cinf from the data. You may approximate the Rg^2 value from the plot, and if a calculator is not allowed, you may give your answer in terms of l.

d. One of these samples is in 5mM NaCl and the other is in 100mM NaCl. Which data plot corresponds to? Briefly how you know.

e. In the plot below, MW vs Ree^2 data is gathered and plotted, along with a linear fit as dotted lines.
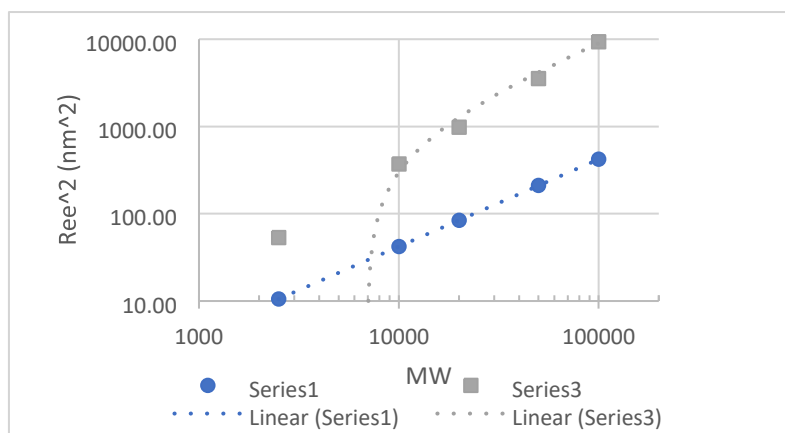
These two plots represent data gathered at either pH 9 or pH 4. Please explain which is which, and compare/contrast the data with Kuhn's model (ie, universal freely jointed chain)

2) Pure 50kDa polyisoprene (PI) in hexanes has G** values that are ~100 times higher than it's G* values at frequencies below 10^3 Hz. However, if sulfur is added at high temperatures to polyisoprene and then cooled, the resulting material yields opposite results, with G* being nearly 500x higher than G** at all frequencies. Additionally, this material doesn't dissolve in hexanes!

   a. Explain the rheological results above, as well as why the post-sulfur PI doesn't dissolve in solvents

   b. If the frequency of the rheology measurement is above 10^3, the G* of pure PI exceeds the measured G**, even when in a solvent. Please explain why.

3) PEGylated phospholipids (DSPE-PEG copolymer) were some of the first FDA approved nanomaterials, due to their ability to form micelles and sequester hydrophobic drugs (such as doxorubicin, in Doxil). which would have a lower CMC, $DSPE2_{0k}$-PEG_{5k}, or $DSPE_{10k}$-PEG_{10k}? Explain your answer in 2 sentences or less.

4) The data on the right, which I have taken from a trashy paper in a noname jouirnal, was collected on NPs coated with a small molecule charged ligand in varying pH solutions, with the blue plot corresponding to the left axis (zeta potential) and the red plot the right axis (particle size). Size was measured by DLS.
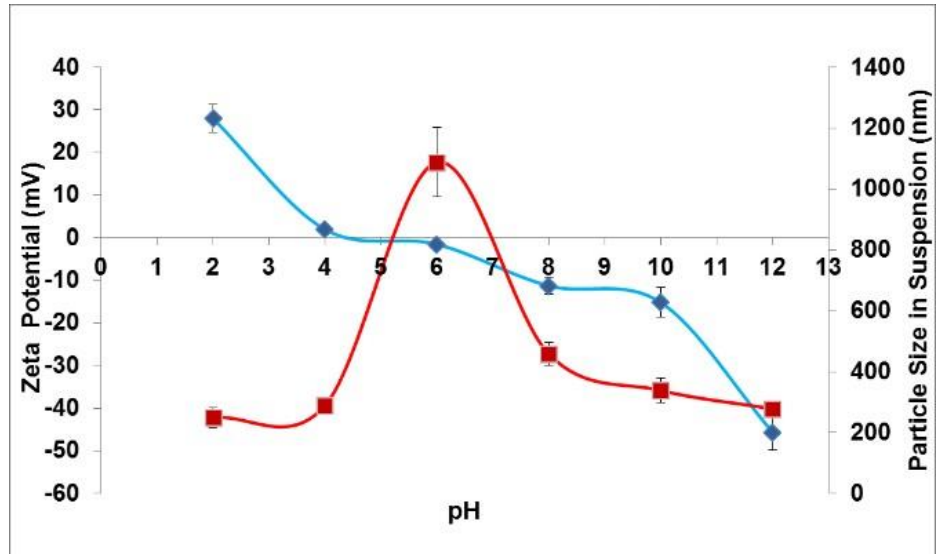
a. Explain why size is the largest at pH 6. Interpret what is happening to your colloid under that condition.

b. Bonus question: what is the name of the point where the zeta potential = 0 on this plot, and what does that indicate about your ligand?

c. The ligand is now attached to a polymer chain, such that the charged part sticks on the outermost part of the NP, while the polymer forms a brush coating and is anchored to the surface of the hard NP core.
Please redraw how size would change with varying pH. Explain using the concepts from class.