Materials Science and Engineering
PhD Qualifying Exam

WRITTEN EXAM: Tuesday, May 22
9:00AM-1:00PM, 15 Saint Mary’s Street, Room 105

ORAL EXAM: Thursday, May 24 OR Friday, May 25
Time and location TBD

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 Question
• Intro to Solid State Physics (PY 543 Chandran) – OPEN BOOK (Ashcroft and Mermin/Solid State Physics; Steve Simon/Oxford Solid State Basics), NO LECTURE NOTES ALLOWED
• Electrical, Optical, Magnetic Properties of Matls (MS 577 Swan) – CLOSED BOOK. NOTES ALLOWED (one page, double-sided)

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 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: Polymers and Soft Materials (MS 504 Barbari) OPEN BOOK (Introduction to Polymers, 3rd edition, by Young and Lovell) AND one sheet of notes on only one side
• Problem 2: Computational Methods of Materials Science (MS 508, Coker) – CLOSED BOOK. NOTES ALLOWED (one page, double-sided).
• Problem 3: Physics of Semiconductor Materials (MS 574, Bellotti) – CLOSED BOOK. NOTES ALLOWED (one page, double-sided)
**Problem**

Graphene can be modeled by a single tight-binding orbital on each site of the honeycomb lattice. If we call the honeycomb sites \( \vec{r} \), and the corresponding orbital \( |\vec{r}\rangle \), the tight-binding Hamiltonian is:

\[
H_{TB} = -t \sum_{\langle \vec{r}, \vec{r}' \rangle} \langle \vec{r} | \vec{r}' \rangle + \langle \vec{r}' | \vec{r} \rangle
\]

where the sum is over nearest-neighbor bonds of the honeycomb lattice.

**Figure 1:** A: Honeycomb lattice. B: The construction of a carbon nanotube from a single graphene sheet. By rolling up the sheet along the wrapping vector \( \vec{C} \), that is, such that the origin (0,0) coincides with point \( \vec{C} \), a nanotube is formed. Wrapping vectors along the dotted lines lead to tubes that are zigzag or armchair. All other wrapping angles lead to chiral tubes whose wrapping angle is specified relative to the armchair direction by angle \( \phi \). Source: Nature 391, 6662, 59-62 (1998)

1. **(5 pts)** Draw a primitive unit cell of the honeycomb in Fig. 1(A). Identify the Bravais lattice type, a set of primitive lattice vectors, and an orbital basis within the primitive unit cell.

2. **(3 pts)** Write down the primitive lattice vectors of the reciprocal lattice, and draw the corresponding Brillouin zone (BZ).

3. **(2 pts)** At how many distinct points on the BZ boundary do two BZ boundaries meet? Draw these points on the BZ boundary.

4. **(12 pts)** Solve for the tight-binding band structure within the Brillouin zone. How many bands do you find?

5. **(3 pts)** In graphene, there is one valence electron per site of the honeycomb lattice. Describe which states in the band structure are filled, and which are empty (don’t forget spin!). Is graphene a metal or an insulator?

6. **(10 pts)** Carbon nanotubes can be thought of as graphene sheets wrapped up into a seamless cylinder. The wrapping vector, \( \vec{C} \), relates the points on the graphene lattice that are equivalent in the carbon nanotube. This wrapping vector makes an angle \( \phi \) with the armchair direction of the lattice (see Fig. 1(B)). Show that all nanotubes with \( \phi = 0 \) (the ‘armchair’ tubes) are metallic.
7. (3 pts) Argue that the electrical conductivity should be very sensitive to the angle $\phi$. This behavior is seen experimentally: Fig. 2 shows the current-voltage curves obtained by tunnelling spectroscopy on nanotubes with $\phi$ ranging from 0 to 30 degrees (the curves are offset vertically for clarity and the sign of $V_{\text{bias}}$ corresponds to that of the energy relative to the tube Fermi level). We see that the conductivity near zero bias is a non-monotonic function of the angle $\phi$.

Source: Wildoer, Venema, Rinzler, Smalley & Dekker

Figure 2
Density of states $g(E)$ for an isotropic crystalline material where $g(E)dE$ is the number of energy states at energy $E$ in an energy slice $dE$ per volume, $L^d$, where $d$ is the dimension (i.e. the “volume” in 2 dimensions is $L^2$). Hint: $Ndk=NEDE$ ( $N_k, N_E$ number densities in $k$-space or $E$)

a. Draw the energy dispersion for a metal with energy dispersion $E(k) = \frac{\hbar^2 k^2}{2m^*}$. Show the correspondence between a $k$-state and an energy $E(k)$. How is the effective mass $m^*$ determined?

b. Show that $g(E) \propto (E)^{1/2}$ for a material with a dispersion $E(k) = \frac{\hbar^2 k^2}{2m^*}$ in 3 dimensions.

c. Show that $g(E)$ is constant for a material with a dispersion $E(k) = \frac{\hbar^2 k^2}{2m^*}$ in 2 dimensions.

d. Show that $g(E) \propto E$ for a material with linear dispersion $E(k) = \hbar v_F k$ in two dimensions where $v_F$ is a constant velocity. (This describes graphene).
Intentionally left blank. This is scratch paper provided by Prof. Swan for the MS 577 question. Formulas provided on the next page.
FORMULAS

**General:** De Broglie relation: \( p = \frac{h}{\lambda} = \hbar k \), wave vector \( k = \frac{2\pi}{\lambda} \)

**Total energy** \( U = \int \frac{d^3}{E} g(E) \cdot E \cdot \delta(E - nE) \cdot dE \) with DOS defines as \( g(E) \propto V \)

**Lattice vibrations:** Classical harmonic oscillator potential energy: \( U = \frac{1}{2} k \Delta x^2 \) \( k \) spring constant, force \( F = -\frac{dU}{dx} \) \( \) Frequency \( f = \frac{1}{T} \) \( T \)-period, \( \) Angular frequency \( \omega = 2\pi f = \frac{k}{\sqrt{m}} \)

**Harmonic Oscillator QM:** Quantized energy for harmonic vibrations \( E(\omega) = \hbar \omega(n + \frac{1}{2}) \), \( n \) - integer, \( \frac{1}{2} \hbar \omega \) -zero point energy. Phonon occupancy number \( n > \frac{1}{e^{\beta \hbar \omega / 2} - 1} \), \( \beta = \frac{1}{k_B T} \)

Density of states \( D(\omega) = \frac{dN}{d\omega} g(\omega) = \frac{dN}{dE} \) \( N \) - number of states with energy \( \leq \hbar \omega = E \)

Smallest volume in \( k \) space, periodic boundary condition: \( (\Delta k)^D = \left( \frac{2\pi}{L} \right)^D, D \)-dim

Heat capacity \( C = \frac{d< E >}{dt} \) \( (< E > \) expectation value of the energy, \( T \) Temperature),

Classical: \( C = 3Nk_B \) Debye: \( C = \frac{12\pi^4}{5} N k_B \left( \frac{T}{T_D} \right)^3 \) \( \omega_D^3 = 6\pi n^3 v^3 \) \( \omega = v_s k \) \( \) Einstein: \( \omega = \omega_0 \)

\( C = 3Nk_B(\beta \hbar \omega)^2 \frac{e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2} \) \( \) Thermal conductivity \( \kappa = \frac{1}{3} n C < v > \lambda, j_U = -\kappa \nabla T, \lambda = mf \)

path, \( n \) #density \( \) Lorenz number \( L = \frac{k}{\sigma T} \) \( \) Peltier coefficient \( P = \frac{j_U}{j_{Uq}} = -\frac{k_B T}{2q} \)

**Mechanical Properties:** Uniaxial stress: Young’s modulus \( Y: \sigma = YE, E = \frac{\Delta l}{l} \), Poisson ratio \( v \)

(length change perpendicular to stress) \( -\nu \varepsilon = \frac{\Delta l}{l} \) \( k = YA/L \) \( \) and \( Y = \frac{1}{a} U'' \) where \( U'' \) is the second derivative of the harmonic potential minimum (macro-microscopic connection)

Bulk modulus \( K = -\Delta p \frac{V}{V} \Delta p = \frac{\Delta F}{A} \) \( \sigma = \frac{\Delta F}{A} \) \( \sigma, Y, K \) in units of Pa

**Electrons:**

3D DOS: \( g(E) = \frac{3n}{2E_F} \left( \frac{E}{E_F} \right)^{1/2} \) \( \) heat capacity \( C = \frac{\pi^2}{3} \frac{3Nk_B}{2} \left( \frac{T}{T_F} \right) \)

Particle in a box energy \( E_j = \frac{\hbar^2 k_j^2}{2m} = \frac{\hbar^2 (2\pi)^2}{2m(2L)^2} j^2 \) \( j \) integer, \( L \) box size. occupancy \# \( f_{FD} = \left( e^{\beta \hbar \omega - E_F} + 1 \right)^{-1} \) \( \) eqn of motion \( \frac{d\mu}{dt} = \vec{F} - \frac{\mu}{\tau} \) \( \vec{F} = -e(\vec{E} + \vec{v} \times \vec{B}) \)

Drude conductivity \( \sigma = \frac{q^2 n e \tau}{m} \) \( \) Hall coefficient \( R_H = \frac{\partial \mu_x}{\partial B} = -\frac{1}{nq} \)

Fermi sphere, etc. \( N = 2 \sqrt{\frac{\pi}{(2\pi)^3}} \left( \frac{4\pi}{3} k_F^3 \right) \) \( \) Fermi wave vector \( k_F = \left( 3n\pi^2 \right)^{1/3} \) \( \) Fermi energy \( E_F = \frac{\hbar k_F^2}{2m} \) \( \) Fermi Temp \( E_F = k_B T_F \) \( \) Fermi velocity \( v_F = \frac{\hbar k_F}{m} \) Drift \( v_D = -\frac{q_\tau}{m} \frac{E}{E} \)

**Optical contribution:** Polarization \( P = q \chi \) \( \) Polarizability \( P = \varepsilon_0 \chi \chi \) \( n \) #density, 

Suscetibility \( \chi: \varepsilon_r = 1 + \chi \) \( \) Index of refraction \( N = n + iq = \sqrt{\varepsilon_r} \)

**Math**

Taylor expansion \( f(x) = \sum_{m=0}^{\infty} \frac{1}{m!} f^{(n)}(a)(x - a)^n \) where \( f^{(n)}(a) \) is the \( n \)th derivative at \( x=a \).

Expansion for small \( x \): \( e^x = 1 + x + \cdots \),
1a. A BU student wants to measure the standard free energy of formation of PdO. The student places PdO in the experimental apparatus pictured below. After evacuating the apparatus and closing all the valves, the student heats it to a specific temperature and observes the difference in height ($\Delta h$) of the two mercury columns of the manometer (see below). The student repeats this for another temperature and records $\Delta h$. The data is given below. Express the standard free energy of formation of PdO as a function of temperature. Assume negligible vapor pressure for Pd and PdO. (760 mm mercury = 1 atm.)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$\Delta h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>873 K</td>
<td>2.74 mm</td>
</tr>
<tr>
<td>1073 K</td>
<td>185.3 mm</td>
</tr>
</tbody>
</table>

1b. Find expressions for T, P, and the chemical potential, given that the internal energy $U$ (extensive property) is expressed as: $U = AS/(NV)$. Here, S is the entropy, N is the number of moles in the system, V is the Volume, and A is a constant. Derive the expressions for T, P and the chemical potential and show that they are intensive properties.

2. The stable form of chromium oxide (atomic weight 52) is bcc up to its melting point (2180 K). The stable form of nickel (atomic weight 58.7) is fcc up to its melting point (1728 K). The figure below shows the Gibbs energy change due to mixing for the bcc, fcc, and the liquid phases at 1200 K, 1550 K, 1650 K and 1800 K.

a. Construct the common tangents at each temperature showing the phase boundaries. (10 points)
b. Determine the partial molar free energy change due to mixing of Cr and that of Ni in the fcc phase at 1550 K and 60% Ni. (5 points)
c. What is the activity of Cr and that of Ni in the fcc phase at 1550 K and 60% Ni? Specify the standard states for Cr and Ni. (5 points)
d. If the vapor pressure of pure Cr is $1.2 \times 10^{-6}$ atm at 1550 K, what is the vapor pressure of Cr over an alloy with 60% Ni and 40% Cr at 1550 K? (5 points)
e. Sketch the Cr-Ni phase diagram from the plots of the Gibbs energy change due to mixing at different temperatures. (15 points)
May 2018 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, \( R = 8.314 \text{ J/mole-K} \)
Avagadro's constant, \( N_A = 6.023 \times 10^{23} \text{ mole}^{-1} \)
Plank's constant, \( h = 6.626 \times 10^{-34} \text{ J-s} \)
Boltzman's constant, \( k = 1.381 \times 10^{-23} \text{ J/K} \)
Charge of an electron, \( e = -1.602 \times 10^{-19} \text{ Coulombs} \)

\[
c(x, t) = \frac{S}{\sqrt{4\pi Dt}} \exp(-x^2/4Dt), \quad c(x,t) = A + \text{Berf}(x/2\sqrt{Dt}),
\]

\[
c(x,t) = \frac{4c^0}{\pi} \sum_{j=0}^{\infty} \frac{1}{2j+1} \sin \left( \frac{(2j+1)\pi x}{l} \right) \exp \left( -\left( \frac{(2j+1)\pi}{l} \right)^2 Dt \right)
\]

\[
\bar{c}(t) = \frac{8c^0}{\pi^2} \sum_{j=0}^{\infty} \frac{1}{(2j+1)^2} \exp \left( -\left( \frac{2j+1}{l} \right)^2 Dt \right)
\]

\[
D(\text{vacancy mechanism}) = \gamma a^2 \nu_D \exp \left( -\frac{\Delta G_v}{RT} \right) \exp \left( -\frac{\Delta G_m^v}{RT} \right)
\]

\[
D(\text{interstitial mechanism}) = \gamma a^2 \nu_D \exp \left( -\frac{\Delta G_m^i}{RT} \right),
\]

\[
D(\text{self interstitial mechanism}) = \gamma a^2 \nu_D \exp \left( -\frac{\Delta G_m^v}{RT} \right) \exp \left( -\frac{\Delta G_m^v}{RT} \right),
\]

\[
\frac{\partial \Delta G}{\partial P} = \Delta V; \Delta V_m = 0.15 \Delta V_{\text{molar}}, \Delta V_v = 0.55 \Delta V_{\text{molar}}, \Delta V_{si} = -0.3 \Delta V_{\text{molar}}
\]

\[
pV = nRT
\]

\[
D_{\text{eff}} = \eta D_gb + (1-\eta) D_l
\]

\[
D_gb = D_gb^0 \exp \left( -\frac{\Delta G_m^{gb}}{RT} \right), \quad D_l = D_l^0 \exp \left( -\frac{\Delta G_m^{l}}{RT} \right)
\]

For chemical reaction: \( aA + bB = cC + dD \);

\[
\frac{d[C]}{dt} = -\frac{c}{a} \frac{d[A]}{dt}
\]

\[
\exp(-\Delta G^0/RT) = \exp(-\Delta g^0/kT) = (a_c)^c(a_d)^d(a_A)^{(a_d)}(a_B)^b
\]

Reaction rate = \( K_f[A]^a[B]^b - K_b[C]^c[D]^d \)
\[ \Delta G = V \Delta G_v + A \sigma \]

For an FCC unit cell, \( 4r = (2)^{1/2}a \)

**Prob. 3.** The oxide of cation ‘M’ is non-stoichiometric, with the formula \( \text{M}_{2+x}\text{O}_3 \).

i) What is the major point defect in this oxide?

ii) Is this an \( n \)- or \( p \)-type oxide?

iii) Will cation diffusion in this oxide be dominated by the vacancy mechanism or the self-interstitial mechanism?

iv) There is an ongoing debate about whether the effective charge of the major point defect in this oxide is +2 or +3. Assume that you are equipped to make precise measurements of anion and cation diffusivities in this oxide as a function of temperature and ambient oxygen partial pressure. Given this capability, describe in detail, including the defect formation reaction in both cases, how you would resolve this issue. State all the assumptions you make.

v) A requirement for a material to be used as an oxygen sensor is high oxygen diffusivity. Do you think that this oxide is a good candidate material for use in oxygen sensors? Explain your answer.

**Prob. 4.** Studies have shown that in pure Ni, which has a FCC crystal structure, solid nuclei formed during solidification is in the shape of a tetrahedron, bounded by 4 equilateral triangles of side ‘\( s \)’ corresponding to \{111\} surfaces. For a tetrahedron of side \( s \), surface area of tetrahedron = \( \sqrt{3}s^2 \), and volume of tetrahedron = \( \frac{\sqrt{2}}{3} s^3 \).

i) Based on the broken bond model, calculate the surface energy (in J/m\(^2\)) of \{111\} surfaces in solid Ni. Assume that the surface energy is temperature independent. The latent heat of vaporization of solid Ni is 378 kJ/mole, and the lattice parameter of the FCC unit cell of Ni is 0.352 nm. Show all derivations and calculations.

ii) Show that if \( \Delta H_v \) and \( \Delta S_v \) are temperature independent, then \( \Delta G_v = \frac{-L_f \Delta T}{T_M} \), where \( L_f \) is the latent heat of fusion (in J/m\(^3\)), \( \Delta T \) is the undercooling and \( T_M \) is the melting temperature.

iii) If for Ni, the melting temperature is 1725K, the latent heat of fusion is 17.5 kJ/ mole, the molecular weight is 59 gm/mole, and the density is 8.9 gm/cm\(^3\); what is \( \Delta G_v \) at 20K undercooling?

iii) For a 20K undercooling, calculate \( \Delta G^* \) of a solid Ni nuclei. Show all derivations and calculations.
1. Polyisobutylene (PIB) is a versatile polymer that can be used in a wide variety of applications. It has a rubbery plateau over a wide temperature range. Unless stretched when processed, it is 100% amorphous.

(a) PIB is being considered for an application at –40°C in which it will be under a fixed strain. When tested at 25°C, it takes 0.1 h for the measured force to decrease to 10^4 dynes when elongated 50%. How long would it take at the use temperature of –40°C for the force to decrease to this value if exposed to the same strain and same initial stress? The T_g of PIB is –75°C. State any assumptions.

(b) PIB is soluble in cyclohexane with a χ parameter of 0.43. If 30% PIB is dissolved in this solvent, by volume, what is the vapor pressure of cyclohexane above the solution. The vapor pressure of pure cyclohexane is 100 mm Hg. State any assumptions.

(c) If copolymerized with isoprene (1,3-butadiene), which introduces a double bond into the backbone, PIB can be crosslinked into “butyl rubber”. If you want to synthesize a butyl rubber with a shear modulus of 5 x 10^6 dynes/cm^2 at 25°C, how much isoprene should be added, in mole percent. R = 8.314 x 10^7 dyne-cm/mole-K. The molecular weight of isoprene is 68. State any assumptions.

PIB Structure (molecular weight of repeat unit = 56):

![PIB Structure](image)
Q1 In class we showed that the density of free electron states (including spin) in 3d (number of states per unit energy) as a function of electron energy, is

$$\rho(E) = \frac{\Omega m}{\pi^2 \hbar^3} \sqrt{2mE}$$ (1)

where \(\Omega\) is the system volume. Let \(N\) be the total number of free electrons in the system so the electron density is \(n = N/\Omega\). Since the electrons are fermions there can only be one electron in each state so the energy of the highest occupied state (the Fermi energy, \(E_F\)) can be determined from the following relationship:

$$\int_0^{E_F} dE \rho(E) = N$$ (2)

(i) Use these results to obtain an expression for \(E_F\)
(ii) Use your results to derive an expression for the ground state energy of the \(N\) electron system in terms \(E_F\).
You have an a harmonic oscillator with $\alpha = (mk/h^2)^{1/4}$, where $k$ is the oscillator spring constant and $\omega = (k/m)^{1/2}$ the corresponding frequency. The eigenfunctions solution of the Schrödinger 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 polynomials is:

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

Based on the information you have, you are asked to construct a three-dimensional harmonic oscillator for which the first excited 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?
Discuss the roles of grain boundaries in each of the following aspects of the mechanical behavior of a material:

(a) hardening
(b) fracture toughness
(c) creep
(d) anisotropy

Your answer should be no more than ten sentences total.