Problems for Solid State Physics
(3rd Year Course BVI)
Hilary Term 2013

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"Everything should be made as simple as possible, but no simpler."

— Frequently attributed to Albert Einstein

Actual quote:

"It can scarcely be denied that the supreme goal of all theory is to make the irreducible basic elements as simple and as few as possible without having to surrender the adequate representation of a single datum of experience"

— Albert Einstein, lecture delivered at Oxford 10 June 1933

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‡ Denotes crucial problems that you need to be able to do in your sleep.
* Denotes problems that are slightly harder.

Annotations of Homeworks 2013

-- including which topics are the most important to study for the exam!

Much of this problem set is standard exam material.

Problem Set 1

Einstein, Debye, Drude, and Free Electron Models

1.1. Einstein Solid

(a) **Classical Einstein Solid (or "Boltzmann" Solid):**
Consider a single harmonic oscillator in three dimensions with Hamiltonian

$$H = \frac{\mathbf{p}^2}{2m} + \frac{k}{2}\mathbf{x}^2$$

▷ Calculate the classical partition function

$$Z = \int \frac{\mathbf{dp}}{(2\pi\hbar)^3} \int \mathbf{dx}\, e^{-\beta H(\mathbf{p},\mathbf{x})}$$

Note: in this problem **p** and **x** are three dimensional vectors (they should appear bold to indicate this unless your printer is defective).

▷ Using the partition function, calculate the heat capacity $3k_B$.

▷ Conclude that if you can consider a solid to consist of N atoms all in harmonic wells, then the heat capacity should be $3Nk_B = 3R$, in agreement with the law of Dulong and Petit.

The classical calculation has never been on an exam (although it is examinable)

(b) **Quantum Einstein Solid:** Now consider the same Hamiltonian quantum mechanically.

▷ Calculate the quantum partition function

$$Z = \sum_j e^{-\beta E_j}$$

where the sum over j is a sum over all Eigenstates.

▷ Explain the relationship with Bose statistics.

▷ Find an expression for the heat capacity.

▷ Show that the high temperature limit agrees with the law of Dulong of Petit.

▷ Sketch the heat capacity as a function of temperature.

The quantum Einstein model could be on an exam (although it rarely is)

1.2. Debye Theory:

Debye theory is very frequently examined!

(a)‡ State the assumptions of the Debye model of heat capacity of a solid.

▷ Derive the Debye heat capacity as a function of temperature (you will have to leave the final result in terms of an integral that cannot be done analytically).

▷ From the final result, obtain the high and low temperature limits of the heat capacity analytically.

You may find the following integral to be useful
$\int_0^\infty dx \frac{x^3}{e^x-1} = \sum_{n=1}^\infty \int_0^\infty x^3 e^{-nx} = 6\sum_{n=1}^\infty \frac{1}{n^4} = \frac{\pi^4}{15}$
By integrating by parts this can also be written as $\int_0^\infty dx \frac{x^4 e^x}{(e^x-1)^2} = \frac{4\pi^4}{15}$

(b) The following table gives the heat capacity C for potassium iodide (KI) as a function of temperature.

T(K)	0.1	1.0	5	8	10	15	20
C (J K $^{-1}$ mol $^{-1}$)	8.5×10^{-7}	8.6×10^{-4}	1.2×10^{-1}	5.9×10^{-1}	1.1	2.8	6.3

▷ Discuss, with reference to the Debye theory, and make an estimate of the Debye temperature.

1.3. Drude Theory of Transport in Metals

Drude theory does show up on exams -- particularly in the context of semiconductors

(a) Assume a scattering time τ and use Drude theory to derive an expression for the conductivity of a metal.

(b) Define the resistivity matrix $\underset{\sim}{\rho}$ as $\vec{E} = \underset{\sim}{\rho}\vec{j}$.

▷ Use Drude theory to derive an expression for the matrix $\underset{\sim}{\rho}$ for a metal in a magnetic field. (You might find it convenient to assume $\vec{B}$ parallel to the $\hat{z}$ axis. The under-tilde notation means that the quantity $\underset{\sim}{\rho}$ is a matrix.)

▷ Invert this matrix to obtain an expression for the conductivity matrix $\underset{\sim}{\sigma}$.

(c) Define the Hall coefficient.

▷ Estimate the magnitude of the Hall voltage for a specimen of sodium in the form of a rod of rectangular cross section 5mm by 5mm carrying a current of 1A in a magnetic field of 1T. The density of sodium atoms is roughly 1 gram/cm^3, and sodium has atomic mass of roughly 23. You may assume that there is one free electron per sodium atom (Sodium has *valence* one).

▷ What practical difficulties would there be in measuring the Hall voltage and resistivity of such a specimen (and how might these difficulties be addressed).

(d) What properties of metals does Drude theory not explain well?

AC Drude theory is likely to be too hard for an exam

(e)* Consider now an applied AC field $\vec{E} \sim e^{i\omega t}$ which induces an AC current $\vec{j} \sim e^{i\omega t}$. Modify the above calculation (in the presence of a magnetic field) to obtain an expression for the complex AC conductivity matrix $\underset{\sim}{\sigma}(\omega)$. For simplicity in this case you may assume that the metal is very clean, meaning that $\tau \to \infty$, and you may assume that $\vec{E} \perp \vec{B}$. You might again find it convenient to assume $\vec{B}$ parallel to the $\hat{z}$ axis. (This problem might look hard, but if you think about it for a bit, it isn't really much harder than what you did above!)

▷ At what frequency is there a divergence in the conductivity?

▷ What does this divergence mean? (When τ is finite, the divergence is cut off).

▷ Explain how could one use this divergence (known as the cyclotron resonance) to measure the mass of the electron. (In fact, in real metals, the measured mass of the electron is generally not equal to the well known value $m_e = 9.1095 \times 10^{-31}$ kg. This is a result of *band structure* in metals, which we will explain later in the course.)

1.4. Fermi Surface in the Free Electron (Sommerfeld) Theory of Metals

This is very standard exam material

(a)‡ Explain what is meant by the Fermi energy, Fermi temperature and the Fermi surface of a metal.

(b)‡ Obtain an expression for the Fermi wavevector and the Fermi energy for a gas of electrons (in 3D).

▷ Show that the density of states at the Fermi surface, dN/dE_F can be written as $3N/2E_F$.

(c) Estimate the value of E_F for sodium [As above, the density of sodium atoms is roughly 1 gram/cm^3, and sodium has atomic mass of roughly 23. You may assume that there is one free electron per sodium atom (Sodium has *valence* one)]

(d) Now consider a two dimensional Fermi gas. Obtain an expression for the density of states at the Fermi surface.

1.5. Velocities in the Free Electron Theory

Also standard exam material

(a) Assuming that the free electron theory is applicable: show that the speed v_F of an electron at the Fermi surface of a metal is $v_F = \frac{\hbar}{m}(3\pi^2 n)^{1/3}$ where n is the density of electrons.

(b) Show that the mean drift speed v_d of an electron in an applied electric field E is $v_d = |\sigma E/(ne)|$, where σ is the electrical conductivity, and show that σ is given in terms of the mean free path λ of the electrons by $\sigma = ne^2\lambda/(mv_F)$.

(c) Assuming that the free electron theory is applicable to copper:

(i) calculate the values of both v_d and v_F for copper at 300K in an electric field of 1 V m^{-1} and comment on their relative magnitudes.

(ii) estimate λ for copper at 300K and comment upon its value compared to the mean spacing between the copper atoms.

Copper is monovalent, meaning there is one free electron per atom. The density of atoms in copper is $n = 8.45 \times 10^{28}$ m^{-3}. The conductivity of copper is $\sigma = 5.9 \times 10^7 \Omega^{-1}\text{m}^{-1}$ at 300K.

1.6. Physical Properties of the Free Electron Gas

Also standard exam question

In both (a) and (b) you may always assume that the temperature is much less than the Fermi temperature.

(a)‡ Give a simple but approximate derivation of the Fermi gas prediction for heat capacity of the conduction electron in metals

(b)‡ Give a simple (not approximate) derivation of the Fermi gas prediction for magnetic susceptibility of the conduction electron in metals. Here susceptibility is $\chi = dM/dH = \mu_0 dM/dB$ at small H and is meant to consider the magnetization of the electron spins only.

(c) How are the results of (a) and (b) different from that of a classical gas of electrons?

▷ What other properties of metals may be different from the classical prediction?

(d) The experimental heat capacity of potassium metal at low temperatures has the form:

$$C = (\gamma T + \alpha T^3)$$

where $\gamma = 2.08\text{mJ}\,\text{mol}^{-1}\,\text{K}^{-2}$ and $\alpha = 2.6\text{mJ}\,\text{mol}^{-1}\,\text{K}^{-4}$.

▷ Explain the origin of each of the two terms in this expression.

▷ Make an estimate of the Fermi energy for potassium metal.

Most of this problem set is examinable in principle, but many parts of it are unlikely to actually show up on the exam. Questions 2.7 and 2.8 are very crucial.

Problem Set 2

Chemical Bonding, Thermal Expansion, Normal Modes, Phonons in 1d

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Chemical bonding is mandated by the IOP as part of this course. It has never been examined on a condensed matter exam as far as I know. In principle it is examinable, but it seems unlikely.

Of these pieces probably knowing a bit about van der Waals is the most important.

2.1. Chemical Bonding

(a) Qualitatively describe five different types of chemical bonds and why they occur.

▷ Describe which combinations of what types of atoms are expected to form which types of bonds (make reference to location on the periodic table).

▷ Describe some of the qualitative properties of materials that have these types of bonds.

(Yes, you can just copy the table out of the notes, but the point of this exercise is to learn the information in the table!)

(b) Describe qualitatively the phenomenon of Van der Waals forces. Explain why the force is attractive and proportional to $1/R^7$ where R is the distance between two atoms.

(c) The ionization energy of a sodium (Na) atom is 5.14 eV. The electron affinity of a chlorine (Cl) atom is 3.62 eV. The bond length of a sodium-chloride *molecule* (i.e., one Na atom and one Cl atom) is .236 nm. Assuming the cohesive energy is purely Coulomb energy, calculate the total energy released when a Na atom and a Cl atom come together to form an NaCl molecule. The actual experimental value is 4.26 eV. Qualitatively account for the sign of your error.

2.2. Covalent Bonding in Detail*

(a) **Linear Combination of Atomic Orbitals (LCAO)** In class we considered two atoms each with a single atomic orbital. We called the orbital $|1\rangle$ around nucleus 1 and $|2\rangle$ around nucleus 2. More generally we may consider any set of wavefunctions $|n\rangle$ for $n = 1, \ldots, N$. For simplicity, let us assume this basis is orthonormal $\langle n|m\rangle = \delta_{n,m}$

Similar comment for covalent bonding. It is mandated by IOP but seems unlikely to be examined.

Let us write a trial wavefunction for our ground state as

$$|\Psi\rangle = \sum_n \phi_n |n\rangle$$

This is known as a linear combination of atomic orbitals (LCAO). We would like to find the lowest energy wavefunction we can construct in this form, that is the best approximation to the actual ground state wavefunction. (The more states we use in our basis, generally, the more accurate our results will be).

We claim that the the ground state is given by the solution of the effective Schroedinger equation

$$\mathcal{H}\,\boldsymbol{\phi} = E\,\boldsymbol{\phi} \tag{1}$$

where $\boldsymbol{\phi}$ is the vector of N coefficients ϕ_n, and $\mathcal{H}$ is the N by N matrix

$$\mathcal{H}_{n,m} = \langle n|H|m\rangle$$

with H the Hamiltonian of the full system we are considering.

To prove this, let us construct the energy

$$E = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}$$

▷ Show that minimizing this energy with respect to each ϕ_n gives the same eigenvalue equation, Eq. 1. (Caution: ϕ_n is generally complex! If you are not comfortable with complex differentiation, write everything in terms of real and imaginary parts of each ϕ_n). Similarly, the second eigenvalue of the effective Schroedinger equation will be an approximation to the first excited state of the system.

This technique is know as the molecular orbital approach, or the LCAO (linear combination of atomic orbitals) approach. It is used heavily in numerical simulation of molecules. However, more generally, one cannot assume that the basis set of orbitals is orthonormal. (See problem 6.5 from the book for handling the LCAO without this assumption.)

You probably have to know something about this for your atomic paper. Again, it seems unlikely to be examined in the condensed matter paper, although mandated by IOP.

(b) **Two-orbital covalent bond** Let us return to the case where there are only two orbitals in our basis. This pertains to a case where we have two identical nuclei and a single electron which will be shared between them to form a covalent bond. We write the full Hamiltonian as

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r} - \mathbf{R_1}) + V(\mathbf{r} - \mathbf{R_2}) = K + V_1 + V_2$$

where V is the Coulomb interaction between the electron and the nucleus, R_1 is the position of the first nucleus and R_2 is the position of the second nucleus. Let ϵ be the energy of the atomic orbital around one nucleus in the absence of the other. In other words

$$\begin{aligned} (K + V_1)|1\rangle &= \epsilon|1\rangle \\ (K + V_2)|2\rangle &= \epsilon|2\rangle \end{aligned}$$

Define also the cross-energy element

$$V_{cross} = \langle 1|V_2|1\rangle = \langle 2|V_1|2\rangle$$

and the hopping matrix element

$$t = -\langle 1|V_2|2\rangle = -\langle 1|V_1|2\rangle$$

These are not typos!

▷ Why can we write V_{cross} and t equivalently using either one of the expressions given on the right hand side?

▷ Show that the eigenvalues of our Schroedinger equation Eq. 1 are given by

$$E = \epsilon + V_{cross} \pm |t|$$

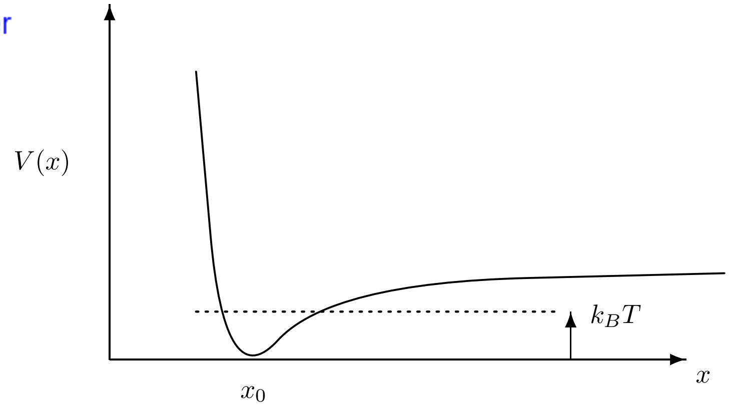
▷ Argue (perhaps using Gauss's law) that V_{cross} should roughly cancel the repulsion between nuclei, so that, in the lower eigenstate the total energy is indeed lower when the atoms are closer together.

▷ This approximation must fail when the atoms get sufficiently close. Why?

2.3. Potentials Between Atoms

Thermal expansion again is mandated by IOP. But it has never been examined.

As a model of thermal expansion, we study the distance between two nearest neighbor atoms in an anharmonic potential that looks roughly like this



where x is the distance between the two neighboring atoms. This potential can be expanded around its minimum as

$$V(x) = \frac{\kappa}{2}(x - x_0)^2 - \frac{\kappa_3}{3!}(x - x_0)^3 + \ldots \tag{2}$$

where the minimum is at position x_0 and $\kappa_3 > 0$. For small energies, we can truncate the series at the cubic term. (Note we are defining the energy at the bottom of the well to be zero here).

A very accurate approximate form for inter-atomic potentials (particularly for inert atoms such as helium or argon) is given by the so-called Lennard-Jones potential

Lennard-Jones potential did show up recently! Calculation of spring constants etc from the form of potential is useful to know.

$$V(x) = 4\epsilon\left[\left(\frac{\sigma}{x}\right)^{12} - \left(\frac{\sigma}{x}\right)^{6}\right] + \epsilon \tag{3}$$

where ϵ and σ are constants that depend on the particular atoms we are considering.

▷ What is the meaning of the exponent 6 in the second term of this expression (i.e., why is the exponent necessarily chosen to be 6).

▷ By expanding Eq. 3 around its minimum, and comparing to Eq. 2, calculate the values of the coefficients x_0, κ, and κ_3 for the Lennard-Jones potential in terms of the constants ϵ and σ. We will need these results in exercise 2.5. below.

2.4. Classical Model of Thermal Expansion

Seems unlikely to show up on the exam.

In classical statistical mechanics, we write the expectation of x as

$$\langle x\rangle_\beta = \frac{\int dx\, x\, e^{-\beta V(x)}}{\int dx\, e^{-\beta V(x)}}$$

Although one cannot generally do such integrals for arbitrary potential $V(x)$ as in Eq. 2, one can expand the exponentials as

$$e^{-\beta V(x)} = e^{-\frac{\beta\kappa}{2}(x-x_0)^2}\left[1 + \frac{\beta\kappa_3}{6}(x - x_0)^3 + \ldots\right]$$

and let limits of integration go to ±∞

▷ Why is this expansion of the exponent and the extension of the limits of integration allowed?

▷ Use this expansion to derive $\langle x \rangle_\beta$ to lowest order in κ_3, and hence show that the coefficient of thermal expansion is

$$\alpha = \frac{1}{L}\frac{dL}{dT} \approx \frac{1}{x_0}\frac{d\langle x \rangle_\beta}{dT} = \frac{1}{x_0}\frac{k_B\,\kappa_3}{2\kappa^2}$$

with k_B Boltzmann's constant.

▷ In what temperature range is the above expansion valid?

▷ While this model of thermal expansion in a solid is valid if there are only two atoms, why is it invalid for the case of a many-atom chain? (Although actually it is not so bad as an approximation!)

2.5. Properties of Solid Argon

For argon, the Lennard-Jones constants ϵ and σ from Eq. 3 are given by ϵ = 10meV and σ = .34nm. You will need to use some of the results from exercise 2.3. above.

(a) *Sound*

Given that the atomic weight of argon is 39.9, estimate the sound wave velocity in solid argon. The actual value of the longitudinal velocity is about 1600 m/sec.

Figuring out the speed of sound from the interatomic potential would be good to know.

(b) *Thermal Expansion*

Using the results of exercise 2.4. Estimate the thermal expansion coefficient α of Argon. Note: *You can do this part even if you couldn't completely figure out exercise 2.4.!*

The actual thermal expansion coefficient of Argon is approximately $\alpha = 2 \times 10^{-3}$/K at about 80K. However at lower temperature α drops quickly. See exercise 8.4 from the book to see a more quantum treatment which explains this feature.

Thermal expansion is less likely to show up.

2.6. Classical Normal Modes to Quantum Eigenstates

In lecture we stated, without proof that a classical normal mode becomes a quantum eigenstate. Here we prove this fact for a simple diatomic molecule in a potential well.

Consider two particles, each of mass m in one dimension, connected by a spring (K), at the bottom of a potential well (with spring constant k). We write the potential energy as

$$U = \frac{k}{2}(x_1^2 + x_2^2) + \frac{K}{2}(x_1 - x_2)^2$$

▷ Write the classical equations of motion.

▷ Transform into relative $x_{rel} = (x_1 - x_2)$ and center of mass $x_{cm} = (x_1 + x_2)/2$ coordinates.

(a) Show that in these transformed coordinates, the system decouples, thus showing that the two normal modes have frequencies

$$\begin{aligned} \omega_{cm} &= \sqrt{k/m} \\ \omega_{rel} &= \sqrt{(k + 2K)/m} \end{aligned}$$

Note that since there are two initial degrees of freedom, there are two normal modes.

Now consider the quantum mechanical version of the same problem. The Hamiltonian is

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + U(x_1, x_2)$$

Although this is key to the idea of phonons being harmonic oscillators it is very unlikely that something of this sort would show up on an exam. Most examiners would say that this is too much of a quantum mechanics problem. I personally disagree with that since I think solid state IS quantum mechanics, but I am in the minority on this and I admit that this would be a very unlikely exam question.

▷ Again transform into relative and center of mass coordinates.

Define the corresponding momenta are given by $p_{rel} = (p_1 - p_2)/2$ and $p_{cm} = (p_1 + p_2)$.

(b) Show that $[p_\alpha, x_\gamma] = -i\hbar\delta_{\alpha,\gamma}$ where α and γ take the values cm or rel.

(c) In terms of these new coordinates show that the Hamiltonian decouples into two independent harmonic oscillators with the same eigenfrequencies ω_{cm} and ω_{rel}. Conclude that the spectrum of this system is

$$E_{n_{rel},n_{cm}} = \hbar\omega_{rel}(n_{rel} + \frac{1}{2}) + \hbar\omega_{cm}(n_{cm} + \frac{1}{2})$$

where n_{cm} and n_{rel} are nonnegative integers.

(d) At temperature T what is the expectation of the energy of this system?

In problem 9.7 of the book, the principle that normal modes become quantum eigenstates is proven in more generality.

THIS IS VERY VERY VERY VERY IMPORTANT.

KNOW THIS INSIDE AND OUT.

IT SHOWS UP ALMOST EVERY YEAR!!!!

2.7. **Normal Modes of a One Dimensional Monatomic Chain**

(a)‡ Explain what is meant by "normal mode" and by "phonon".

▷ Explain briefly why phonons obey Bose statistics.

(b)‡ Derive the dispersion relation for the longitudinal oscillations of a one dimensional mass-and-spring crystal with N identical atoms of mass m, lattice spacing a, and spring constant κ. (Motion of the masses is restricted to be in one dimension).

(c)‡ Show that the mode with wavevector k has the same pattern of mass displacements as the the mode with wavevector $k + 2\pi/a$. Hence show that the dispersion relation is periodic in reciprocal space (k-space).

▷ How many *different* normal modes are there.

(d)‡ Derive the phase and group velocities and sketch them as a function of k.

▷ What is the sound velocity?

▷ Show that the the sound velocity is also given by $v_s = \sqrt{\beta^{-1}/\rho}$ where ρ is the chain density and β is the compressibility.

(e) Find the expression for $g(\omega)$, the density of states of modes per angular frequency.

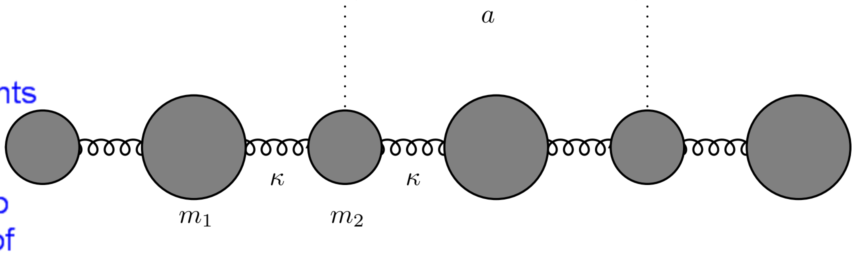
▷ Sketch $g(\omega)$.

(f) Write an expression for the heat capacity of this one dimensional chain. You will inevitably have an integral that you cannot do analytically.

(g) Show that at high temperature the law of Dulong-Petit (for one dimension) is recovered.

2.8. Normal modes of a One Dimensional Diatomic Chain

This is also very very important. You should know both the cases of alternating masses and alternating spring constants (we did the latter in lecture and it is in the book). You might want to try playing with variants of these problems as well.



Some sort of mass and spring problem shows up close to every year.

(a) What is the difference between an acoustic mode and an optical mode.

▷ Describe how particles move in each case.

(b) Derive the dispersion relation for the longitudinal oscillations of a one dimensional *diatomic* mass-and-spring crystal where the unit cell is of length a and each unit cell contains one atom of mass m_1 and one atom of mass m_2 connected together by springs with spring constant κ (all springs are the same, and motion of particles is in one dimension only).

(c) Determine the frequencies of the acoustic and optical modes at $k = 0$ as well as at the Brillouin zone boundary.

▷ Determine the sound velocity and show that the group velocity is zero at the zone boundary.

▷ Show that the the sound velocity is also given by $v_s = \sqrt{\beta^{-1}/\rho}$ where ρ is the chain density and β is the compressibility.

(d) Sketch the dispersion in both reduced and extended zone scheme.

▷ If there are N unit cells, how many different normal modes are there?

▷ How many *branches* of excitations are there? (I.e., in reduced zone scheme, how many modes are there there at each k).

(e) What happens when $m_1 = m_2$?

2.9. One more problem

Problem 4.1. really belongs to this problem set, but this set is too long already, and some tutors felt it was too hard to discuss this material so early in the course, so I pushed this one to the beginning of problem set 4. If you have extra time, give it a shot.

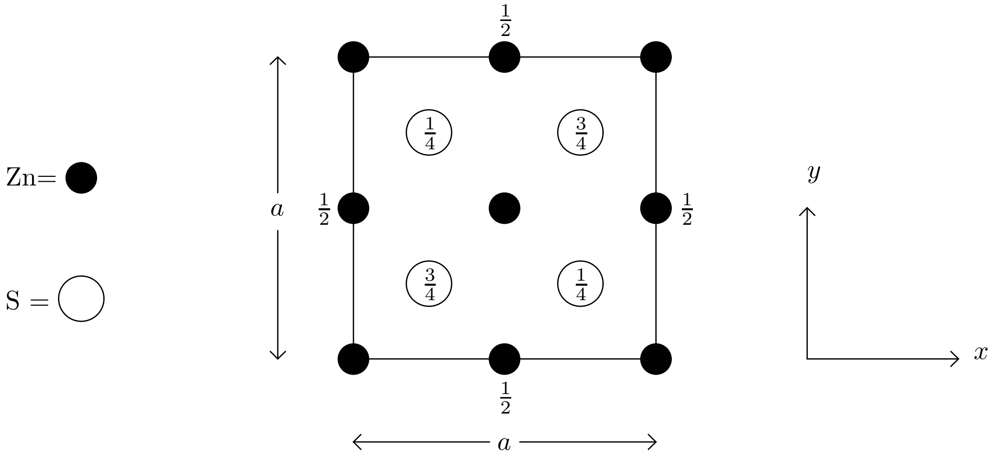
It is almost certain that there will be an exam question on crystal structure and/or diffraction/scattering.

Problem Set 3

Crystal Structure, Reciprocal Lattice, and Scattering

3.1. **Crystal Structure**

This should be very easy. It is a typical question and you should see it as free marks.



The diagram above shows a plan view of a structure of cubic ZnS (zinc blende) looking down the z axis. The numbers attached to some atoms represent the heights of the atoms above the $z = 0$ plane expressed as a fraction of the cube edge a. Unlabeled atoms are at $z = 0$ and $z = a$.

(a) What is the Bravais lattice type

(b) Describe the basis

(c) Given that $a = 0.541$ nm, calculate the nearest-neighbor Zn-Zn, Zn-S, and S-S distances.

(d) Copy the drawing above, and show the [210] direction and the set of (210) planes.

(e) Calculate the spacing between adjacent (210) planes.

3.2. **Directions and Spacings of Crystal Planes**

Also very standard exam question

▷ Explain briefly what is meant by the terms "Crystal Planes" and "Miller Indices."

▷ Show that the general direction $[hkl]$ in a cubic crystal is normal to the planes with Miller indices (hkl).

▷ Is the same true in general for an orthorhombic crystal?

▷ Show that the spacing d of the (hkl) set of planes in a cubic crystal with lattice parameter a is

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

▷ What is the generalization of this formula for an orthorhombic crystal?

3.3. ‡**Reciprocal Lattice**

Know this too!

(a) Define the term Reciprocal Lattice.

(b) Show that if a lattice in 3d has primitive lattice vectors $\mathbf{a_1}$, $\mathbf{a_2}$ and $\mathbf{a_3}$ then primitive lattice vectors for the reciprocal lattice can be taken as

$$\begin{aligned}\mathbf{b_1} &= 2\pi\frac{\mathbf{a_2}\times\mathbf{a_3}}{\mathbf{a_1}\cdot(\mathbf{a_2}\times\mathbf{a_3})} &(1)\\ \mathbf{b_2} &= 2\pi\frac{\mathbf{a_3}\times\mathbf{a_1}}{\mathbf{a_1}\cdot(\mathbf{a_2}\times\mathbf{a_3})} &(2)\\ \mathbf{b_3} &= 2\pi\frac{\mathbf{a_1}\times\mathbf{a_2}}{\mathbf{a_1}\cdot(\mathbf{a_2}\times\mathbf{a_3})} &(3)\end{aligned}$$

What is the proper formula in 2d?

(c) Define tetragonal and orthorhombic lattices. For an orthorhombic lattice, show that $|\mathbf{b_j}| = 2\pi/|\mathbf{a_j}|$. Hence, show that the length of the reciprocal lattice vector $\mathbf{G} = h\mathbf{b_1} + k\mathbf{b_2} + l\mathbf{b_3}$ is equal to $2\pi/d$, where d is the spacing of the (hkl) planes (see question 3.2.)

3.4. **Reciprocal Lattice and X-ray Scattering**

Know this!

A two-dimensional rectangular crystal has a unit cell with sides $a_1 = 0.468$ nm and $a_2 = 0.342$ nm. A collimated beam of monochromatic X-rays with wavelength 0.166 nm is used to examine the crystal.

(a) Draw to scale a diagram of the reciprocal lattice.

▷ Label the reciprocal lattice points for indices in the range $0 \le h \le 3$ and $0 \le k \le 3$.

(b) Calculate the magnitude of the wavevectors $\mathbf{k}$ and $\mathbf{k}'$ of the incident and reflected X-ray beams, and hence construct on your drawing the "scattering triangle" corresponding to the Laue condition $\Delta\mathbf{k} = \mathbf{G}$ for diffraction from the (210) planes. (the scattering triangle includes $\mathbf{k}$, $\mathbf{k}'$ and $\Delta\mathbf{k}$).

(c) Draw the first and second Brillouin zones using the Wigner-Seitz construction.

3.5. ‡ **X-ray scattering II**

Again, very standard exam question.

Know how to do this!

$BaTiO_3$ has a primitive cubic lattice and a basis with atoms having fractional coordinates

Ba	[0,0,0]		
Ti	$[\frac{1}{2},\frac{1}{2},\frac{1}{2}]$		
O	$[\frac{1}{2},\frac{1}{2},0]$,	$[\frac{1}{2},0,\frac{1}{2}]$,	$[0,\frac{1}{2},\frac{1}{2}]$

▷ Sketch the unit cell.

▷ Show that the X-ray structure factor for the $(00l)$ Bragg reflections is given by

$$S_{hkl} = f_{Ba} + (-1)^l f_{Ti} + \left[1 + 2(-1)^l\right] f_O \qquad (4)$$

where f_{Ba} is the atomic form factor for Ba, etc.

▷ Calculate the ratio I_{002}/I_{001}, where I_{hkl} is the intensity of the X-ray diffraction from the (hkl) planes. You may assume that the atomic form factor is proportional to atomic number (Z), and neglect its dependence on the scattering vector. [$Z_{\mathrm{Ba}} = 56$, $Z_{\mathrm{Ti}} = 22$, $Z_{\mathrm{O}} = 8$]

3.6. ‡ X-ray scattering and Systematic Absences

Very standard exam question!

(a) Explain what is meant by "Lattice Constant" for a cubic crystal structure.

(b) Explain why X-ray diffraction may be observed in first order from the (110) planes of a crystal with a body-centred cubic lattice, but not from the (110) planes of a crystal with a face-centred cubic lattice.

▷ Derive the general selection rules for which planes are observed in bcc and fcc lattices.

(c) Show that these selection rules hold independent of what atoms are in the primitive unit cell, so long as the lattice is bcc or fcc respectively.

(d) A collimated beam of monochromatic X-rays of wavelength 0.162 nm is incident upon a powdered sample of the cubic metal palladium. Peaks in the scattered X-ray pattern are observed at angles of 42.3°, 49.2°, 72.2°, 87.4° and 92.3° from the direction of the incident beam.

All things you should know very well.

▷ Identify the lattice type

▷ Calculate the lattice constant.

▷ If you assume there is only a single atom in the basis, how well does this lattice constant agree with the known data that the density of palladium is 12023 kg m^{-3}? [Atomic mass of palladium = 106.4].

(e) How could you improve the precision with which the lattice constant is determined.

3.7. ‡ Neutron Scattering

You should know this. All of this is standard exam material.

(a) X-ray diffraction from sodium hydride (NaH) established that the Na atoms are arranged on a face-centred cubic lattice.

▷ Why is it difficult to locate the positions of the H atoms using X-rays?

The H atoms were thought to be displaced from the Na atoms either by $[\frac{1}{4}, \frac{1}{4}, \frac{1}{4}]$ or by $[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$, to form the ZnS (zincblende) structure or NaCl (sodium chloride) structure, respectively. To distinguish these models a neutron powder diffraction measurement was performed. The intensity of the Bragg peak indexed as (111) was found to be much larger than the intensity of the peak indexed as (200).

▷ Write down expressions for the structure factors S_{hkl} for neutron diffraction assuming NaH has

(i) the sodium chloride (NaCl) structure

(ii) the zinc blende (ZnS) structure.

▷ Hence, deduce which of the two structure models is correct for NaH. [Nuclear scattering length of Na $= 0.363 \times 10^5$nm; nuclear scattering length of H $= -0.374 \times 10^5$ nm]

(b) How does one produce monochromatic neutrons for use in neutron diffraction experiments?

▷ What are the main differences between neutrons and X-rays?

▷ Explain why (inelastic) neutron scattering is wells suited for observing phonons, but x-rays are not.

Most of this is standard exam material.

Problem Set 4

Tight Binding Chain, Band Structure, and Semiconductor Physics

4.1. One Dimensional Tight Binding Model

1d tight binding model has shown up on exams (albeit rarely)

This problem really belongs in problem set 2 due to its similarities with problems 2.7. and 2.8.. I recommend that you back up and review those problems before attempting this one. They are *extremely* similar to this.

(a) **Monatomic Solid:** Consider a one-dimensional tight binding model of electrons hopping between atoms. Let the distance between atoms be called a, and here let us label the atomic orbital on atom n as $|n\rangle$ for $n = 1 \ldots N$ (and you may assume periodic boundary conditions, and you may assume $\langle n|m\rangle = \delta_{nm}$). Suppose there is an on-site energy ϵ and a hopping matrix element $-t$. In other words, suppose $\langle n|H|m\rangle = \epsilon$ for $n = m$ and $\langle n|H|m\rangle = -t$ for $n = m \pm 1$.

The ideas of dispersions, and density of states you should know.

▷ Derive and sketch the dispersion curve for electrons. (Hint: Use the effective Schroedinger equations of problem 2.2.a. The resulting equation should look very similar to that of problem 2.7. above.)

Also effective mass you should know (comes back again in for semiconductors)

▷ How many different eigenstates are there in this system?

▷ What is the effective mass of the electron near the bottom of this band?

▷ What is the density of states?

▷ If each atom is monovalent (it donates a single electron) what is the density of states at the fermi surface?

Also know ideas about filling of bands and what makes a metal vs insulator.

▷ What then is the Pauli paramagentic (spin) susceptibility of the system? (See problem 1.6.).

▷ What is the spin susceptibility if each atom is divalent?

(b) **Diatomic Solid:** Now consider a model of a diatomic solid as such

$$-A - B - A - B - A - B-$$

The diatomic case has never shown up on an exam as far as I know.

I think it would be considered a fairly hard exam problem.

Suppose that the onsite energy of type A is different from the onsite energy of type B. I.e, $\langle n|H|n\rangle$ is ϵ_A for n being on a site of type A and is ϵ_B for n being on a site of type B. (All hopping matrix elements $-t$ are still identical to each other).

▷ Calculate the new dispersion relation. (This is extremely similar to problem 2.8. above. If you are stuck, try studying that problem again.)

▷ Sketch this dispersion relation in both the reduced and extended zone schemes.

▷ What happens in the "atomic" limit when t becomes very small.

▷ What is the effective mass of an electron near the bottom of the lower band?

▷ If each atom (of either type) is monovalent, is the system a metal or an insulator?

▷ What happens if $\epsilon_A = \epsilon_B$?

4.2. Number of States in the Brillouin Zone

A specimen in the form of a cube of side L has a primitive cubic lattice whose mutually orthogonal primitive lattice vectors have length a. Show that the number of different allowed $\vec{k}$-states within the first Brillouin zone equals the number of primitive unit cells forming the specimen (do not consider spin). One may assume periodic boundary conditions, although it is worth thinking about whether this still holds for hard-wall boundary conditions as well.

Worth knowing this

4.3. ‡Nearly Free Electron Model

A question tesing this shows up more than half the time.

You should be able to give both short and long answers to questions of this sort.

Consider an electron in a weak periodic potential in one dimension $V(x) = V(x+a)$. Write the periodic potential as

$$V(x) = \sum_G e^{iGx} V_G$$

where the sum is over the reciprocal lattice $G = 2\pi n/a$, and $V_G^* = V_{-G}$ assures that the potential $V(x)$ is real.

(a) Explain why for k near to a Brillouin zone boundary (such as k near π/a) the electron wavefunction should be taken to be

$$\psi = Ae^{ikx} + Be^{i(k+G)x} \tag{1}$$

where G is a reciprocal lattice vector such that $|k|$ is close to $|k+G|$.

(b) For an electron of mass m with k exactly at a zone boundary, use the above form of the wavefunction to show that the eigenenergies at this wavevector are

$$E = \frac{\hbar^2 k^2}{2m} + V_0 \pm |V_G|$$

where G is chosen so $|k| = |k+G|$.

▷ Give a qualitative explanation of why these two states are separated in energy by $2|V_G|$.

▷ Give a sketch (don't do a full calculation) of the energy as a function of k in both the extended and the reduced zone schemes.

Part c is rarely asked as it is more difficult.

(c) *Now consider k close to, but not exactly at, the zone boundary. Give an expression for the energy $E(k)$ correct to order $(\delta k)^2$ where δk is the wavevector difference of k to the zone boundary wavevector.

▷ Calculate the effective mass of an electron at this wavevector.

Part (d) is worth knowing.

(d) Consider a two dimensional square lattice with one divalent atom per unit cell. If the periodic potential is very very weak, you can consider the electrons to be free and to form a circular Fermi sea. Using the intuition from above (as well as the result of 4.2. above) sketch the Fermi surface for weak, medium, and strong periodic potentials.

▷ Roughly how strong should the periodic potential be for the system to be no longer a metal.

4.4. Band Theory

These are also standard exam questions.

(a) Give a brief description of the formation of electron bands in crystals including reference to the atomic structure of the constituent atoms.

(b) Explain the following:

(i) sodium, which has 2 atoms in a bcc (conventional cubic) unit cell, is a metal;

(ii) calcium, which has 4 atoms in a fcc (conventional cubic) unit cell, is a metal;

(iii) diamond, which has 8 atoms in a fcc (conventional cubic) unit cell with a basis, is an electrical insulator, whereas silicon and germanium, which have similar structures, are semiconductors.

▷ Why is diamond transparent?

More standard exam questions.

(c) A two-dimensional material has a square lattice with lattice constant a =0.3 nm. The dispersion relations for electron energies in the conduction and valence bands are given by

$$\begin{aligned}\epsilon_c(\mathbf{k}) &= 6 - 2(\cos k_x a + \cos k_y a)\\ \epsilon_v(\mathbf{k}) &= -2 + (\cos k_x a + \cos k_y a)\end{aligned}$$

where energies are given here in units of eV. Sketch ϵ_c and ϵ_v for the direction $k_x = k_y$.

▷ Indicate the value and position of the minimum band gap.

▷ Show that close to the conduction and valence band edges, contours of constant energy are circles in k-space and..

▷ .. determine the effective masses of both the electrons and the holes.

▷ Sketch the density of states as a function of energy for the whole of both the conduction and the valence band.

(d) Using tight-binding theory, explain where the above dispersion relations come from.

4.5. Law of Mass Action and Doping of Semiconductors

Very common exam question. (I think this showed up last year!)

(a) Assume that the band gap energy E_g is much greater than the temperature $k_b T$. Show that in a pure semiconductor at a fixed T, the product of the number of electrons (n) and the number of holes (p) depends only on the density of states in the conduction band and the density of states in the valence band (through their effective masses), and on the band gap energy.

▷ Derive expressions for n for p and for the product np. You may need to use the integral $\int_0^\infty dx x^{1/2} e^{-x} = \sqrt{\pi}/2$.

(b) The band gaps of Silicon and Germanium are 1.1 eV and 0.75 eV respectively. You may assume the effective masses for Silicon and Germanium are isotropic, roughly the same, and are roughly .5 of the bare electron mass for both electrons and holes. (Actually the effective masses are not quite the same, and furthermore the effective masses are both rather anisotropic.. but we are just making a rough estimates here).

▷ Estimate the conduction electron concentration for intrinsic (undoped) Silicon at room temperature.

▷ Make a rough estimate of the maximum concentration of ionized impurities that will still allow for this "intrinsic" behavior.

▷ Estimate the conduction electron concentration for Germanium at room temperature.

(c) The graph in Figure 1 shows the relationship between charge-carrier concentration for a certain n-doped semiconductor.

▷ Estimate the bandgap for the semiconductor and the concentration of donor ions.

▷ Describe in detail an experimental method by which this data could have been measured and suggest possible sources of experimental error.

4.6. More about Semiconductors

(a) In semiconductor physics what is meant by a hole and why is it useful?

(b) An electron near the top of the valence band in a semiconductor has energy

$$E = -10^{-37}|\vec{k}|^2$$

where E is in Joules and k is in m^{-1}. An electron is removed from a state $\vec{k} = 2 \times 10^8 \mathrm{m}^{-1}\hat{x}$ where $\hat{x}$ is the unit vector in the x-direction. For a hole, calculate (and give the sign of!)

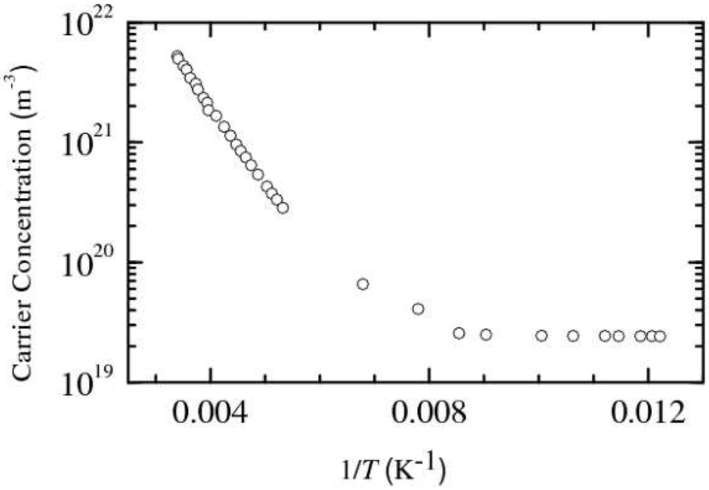


FIG. 1: Figure for Problem 4.5.

(i) the effective mass

(ii) the energy

(iii) the momentum

(iv) the velocity.

Yes, know all of these. And appropriate signs for holes.

(v) If there is a density $p = 10^5 m^{-3}$ of such holes all having almost exactly this same momentum, calculate the current density and its sign.

(c)Show that the chemical potential in an intrinsic semiconductor lies in the middle of the gap at low temperature.

▷ Explain how the chemical potential varies with temperature if the semiconductor is doped with (i) donors (ii) acceptors.

(d) A direct gap semiconductor is doped to produce a density of 10^{23} electrons/m^3. Calculate the hole density at room temperature given that the gap is 1.0 eV, and the effective mass of carries in the conduction and valence band are 0.25 and 0.4 electron masses respectively. Hint: use the result of problem 4.5..a.

This is also standard exam material.

Magnetism of some form shows up frequently. Although many aspects of magnetism are rarely examined.

Problem Set 5

Magnetism and Mean Field Theory

5.1. ‡ **General Magnetism**

Part (a) you should know.

Also (b). Although Ferrimagnetism does not tend to show up.

Hund's rules are newly examinable this year. Worth knowing.

(a) Explain qualitatively why some atoms are paramagnetic and others are diamagnetic with reference to the electronic structure of these materials.

(b) Define the terms Ferromagnetism, Antiferromagnetism, Ferrimagnetism, and Itinerant Ferromagnetism.

▷ Write down an example of a Hamiltonian which would have each one of these as its ground state.

(c) Use Hund's rules and the Aufbau principle to determine L, S, and J for the following isolated atoms:

(i) Sulfer (S) atomic number = 16

(ii) Vanadium (V), atomic number = 23

(iii) Zirconium (Zr), atomic number = 40

(iv) Xenon (Xe), atomic number = 54

(v) Dysprosium (Dy), atomic number =66

5.2. ‡ **Para and Diamagnetism**

Both curie paramag and larmor diamag do show up on exams.

Make sure you know how to derive both of these results.

Manganese (Mn, atomic number=25) forms an atomic vapor at 2000K with vapor pressure 10^5 Pa. You can consider this vapor to be an ideal gas.

(a) Determine L, S, and J for an isolated manganese atom. Determine the paramagnetic contribution to the (Curie) susceptibility of this gas at 2000K.

(b) In addition to the Curie susceptibility, the manganese atom will also have some diamagnetic susceptibility due to its filled core orbitals. Determine the Larmor diamagnetism of the gas at 2000K. You may assume the atomic radius of an Mn atom is one angstrom.

Make sure you know the derivations of all the formulas you use!

5.3. ‡ **Weiss Mean Field Theory of the Ferromagnet** Consider the spin-1/2, ferromagnetic Heisenberg Hamiltonian on the cubic lattice

Mean field theory is probably the most common question on magnetism.

Make sure you understand how to do this!

(And how to generalize to spin S=1, etc)

$$\mathcal{H} = -\frac{J}{2}\sum_{<i,j>} \mathbf{S_i}\cdot\mathbf{S_j} + g\mu_B\mathbf{B}\sum_i \mathbf{S_i} \tag{1}$$

Here, $J > 0$, with the sum indicated with $< i, j >$ means summing over i and j being neighboring sites of the cubic lattice, and $\mathbf{B}$ is the externally applied magnetic field, which we will assume is in the $\hat{z}$ direction for simplicity. The factor of 1/2 out front is included so that each pair of spins is counted only once. Each site i is assumed to have a spin $\mathbf{S_i}$ of spin $S = 1/2$. Here μ_B is the conventional Bohr magneton defined to be positive. The fact that the final term has a + sign out front is from the fact that the electron charge is negative, therefore the magnetic moment opposes the spin direction. If one were to assume that these were nuclear spins the sign would be reversed (and the magnitude would be much smaller due to the larger nuclear mass).

(a) Focus your attention on one particular spin $\mathbf{S_i}$, and write down an effective Hamiltonian for this spin, treating all other variables $\mathbf{S_j}$ with $j \neq i$ as expectations $\langle \mathbf{S_j} \rangle$ rather than operators.

(b) Calculate $\langle \mathbf{S_i} \rangle$ in terms of the temperature and the fixed variables $\langle \mathbf{S_j} \rangle$ to obtain a mean-field self-consistency equation.

▷ Write the magnetization $M = |\mathbf{M}|$ in terms of $\langle \mathbf{S} \rangle$ and the density of spins.

(c) At high temperature, find the susceptibility $\chi = dM/dH = \mu_0 dM/dB$ in this approximation.

(d) Find the critical temperature in this approximation.

▷ Write the susceptibility in terms of this critical temperature.

(e) Show graphically that in zero external field ($\mathbf{B} = 0$), below the critical temperature, there are solutions of the self consistency equation with $M \neq 0$.

(f) Repeat parts (a)-(d) but now assuming there is an $S = 1$ spin on each site (meaning that S_z takes the values $-1, 0, +1$).

5.4. Bragg-Williams Approximation

Bragg-Williams has never been on an exam.

This problem provides a different approach to obtaining the Weiss mean-field equations. For simplicity we will again assume spin 1/2 variables on each site.

Assume there are N lattice sites in the system. Let the average spin value be $\langle S_i \rangle = s$. Thus the probability the probability of a spin being an up spin is $P_\uparrow = 1/2 + s$ whereas the probability of any spin being a down spin is $P_\downarrow = 1/2 - s$. The total number of up spins or down spins is then $NP_\uparrow$ and $NP_\downarrow$ respectively where there are N total lattice sites in the system.

(a) Consider first a case where sites do not interact with each other. In the micro-canonical ensemble, we can count the number of configurations (microstates) which have the given number of spin ups and spin downs (determined by s). Using $S = k_b \ln \Omega$ calculate the entropy of the system in the large N limit.

(b) Assuming all sites have independent probabilities $P_\uparrow$ and $P_\downarrow$ of pointing up and down respectively, calculate the probability that two neighboring sites will point in the same direction and the probability that two neighboring sites will point in opposite directions.

▷ Use this result to calculate an approximation to the expectation of the Hamiltonian. Note: This is not an exact result, as in reality, sites that are next to each other will have a tendency to have the same spin because that will lower their energies, but we have ignored this effect here.

(c) Putting together the results of (a) and (b) above, derive the approximation to the free energy

$$F = E - TS = Nk_bT\left[(\frac{1}{2}+s)\log(\frac{1}{2}+s) + (\frac{1}{2}-s)\log(\frac{1}{2}-s)\right] + g\mu_B B_z N s - JNZs^2/2$$

where Z is the number of neighbors each spin has, and we have assumed the external field to be in the $\hat{z}$ direction. (Again we assume the spin is electron spin so that the the energy of a spin interacting with the external field is $+g\mu_b \vec{B}\cdot\vec{S}$.)

(d) Extremize this expression with respect to the variable s to obtain the same mean field equations as above.

▷ Below the critical temperature note that there are three solutions of the mean field equations.

▷ By examining the second derivative of F with respect to s, show that the $s = 0$ solution is actually a maximum of the free energy rather than a minimum.

▷ Sketch $F(s)$ both above and below the critical temperature for $B = 0$. At nonzero B?

5.5. Mean Field Theory for the Antiferromagnet

This HAS been examined before.

For this exercise we use the Molecular Field (Weiss Mean Field) approximation for the spin-1/2 *Antiferromagnetic* model on a 3 dimensional cubic lattice. The full Hamiltonian is exactly that of Eq. 1 above, except that now we have $J < 0$, so neighboring spins want to point in opposite directions. (Compared to a Ferromagnet where $J > 0$ and neighboring spins want to point in the same direction). For simplicity let us assume that the external field points in the $\hat{z}$ direction.

At mean field level, the ordered ground state of this Hamiltonian will have alternating spins pointing up and down respectively. Let us call the sublattices of alternating sites, sublattice A and sublattice B respectively (i.e, A sites have lattice coordinates (i, j, k) with $i + j + k$ odd whereas B sites have lattice coordinates with $i + j + k$ even).

In Mean field theory the interaction between neighboring spins is replaced by an interaction with an average spin. Let $s_A = \langle S^z \rangle_A$ be the average value of the spins on sub-lattice A, and $s_B = \langle S^z \rangle_B$ be the average value of the spins on sub-lattice B. (We assume that these are also oriented in the $\pm\hat{z}$ direction).

(a) Write the mean field Hamiltonian for a single site on sublattice A and the mean field Hamiltonian for a single site on sublattice B.

(b) Derive the mean-field self consistency equations

$$\begin{aligned} s_A &= \frac{1}{2}\tanh(\beta[JZs_B - g\mu_B B]/2) \\ s_B &= \frac{1}{2}\tanh(\beta[JZs_A - g\mu_B B]/2) \end{aligned}$$

with $\beta = 1/(k_b T)$. Recall that $J < 0$.

(c) Let $B = 0$. Reduce the two self-consistency equations to a single self consistency equation. (Hint: Use symmetry to simplify! Try plotting s_A versus s_B).

(d) Assume $s_{A,B}$ are small near the critical point and expand the self consistency equations. Derive the critical temperature T_c below which the system is antiferromagnetic (i.e., $s_{A,B}$ become nonzero).

(e) How does one detect antiferromagnetism experimentally?

(f) In this mean-field approximation, the magnetic susceptibility can be written as

$$\chi = -(N/2) g\mu_0\mu_B \lim_{B\to 0} \frac{\partial(s_A + s_B)}{\partial B}$$

(why the factor of 1/2 out front?).

▷ Derive this susceptibility for $T > T_c$ and write it in terms of T_c.

▷ Compare your result with the analogous result for a ferromagnet. (Problem 5.3.). In fact, it was this type of measurement that first suggested the existence of antiferromagnets!

But part g would be considered too hard

(g)* For $T < T_c$ show that

$$\chi = \frac{(N/4)\mu_0(g\mu_b)^2(1 - (2s)^2)}{k_b T + k_b T_c(1 - (2s)^2)}$$

with s the staggered moment (ie, $s(T) = |s_A(T)| = |s_B(T)|$).

▷ Compare this low T result with that of part f.

▷ Give a sketch of the susceptibility at all T.

5.6. Ground States

Not clear if this is examinable... it probably should be

But I don't think it ever has been.

Consider the spin-1 Heisenberg Hamiltonian from Problem 5.3.. Let us take **B** to be in the $-\hat{z}$ direction, and assume a cubic lattice.

It will be useful to remember that

$$\mathbf{S_i} \cdot \mathbf{S_j} = \frac{1}{2}(S_i^+ S_j^- + S_i^- S_j^+) + S_i^z S_j^z$$

(a) For $J > 0$, i.e., for the case of a ferromagnet, intuition tells us that the ground state of this Hamiltonian should simply have all spins aligned. Consider such a state. Show that this is an eigenstate of the Hamiltonian Eq. 1 and find its energy.

(b) For $J < 0$, the case of an antiferromagnet, one might expect that, at least for $\mathbf{B} = 0$ the state where spins on alternating sites point in opposite directions might be an eigenstate. Unfortunately, this is not precisely true. Consider such a state of the system.

▷ Show that the state in question is not an eigenstate of the Hamiltonian.

Although the intuition of alternating spins on alternating sites is not perfect, it becomes reasonable for systems with large spins S. For smaller spins (like spin 1/2) one needs to consider these so-called "quantum fluctuations". (We will not do that here).

5.7. Itinerant Ferromagnetism

It is worth knowing (at least qualitatively) what Itinerant Ferromagnetism is.

In principle this sort of thing is examinable.

In practice I'd be very surprised if it showed up.

A calculation like this would be considered much too hard I think.

(a.i) Review 1: For a three dimensional tight binding model on a cubic lattice, calculate the effective mass in terms of the hopping matrix element t between nearest neighbors and the lattice constant a.

(a.ii) Review 2: Assuming the density n of electrons in this tight binding band is very low, one can view the electrons as being free electrons with this effective mass m^*. For a system of spin polarized electrons show that the total energy per unit volume (at zero temperature) is given by

$$E/V = nE_{min} + Cn^{5/3}$$

where E_{min} is the energy of the bottom of the band.

▷ Calculate the constant C.

(b) Let the density of spin-up electrons be $n_\uparrow$ and the density of spin-down electrons be $n_\downarrow$ we can write these as

$$n_\uparrow = (n/2)(1+\alpha) \quad (2)$$
$$n_\downarrow = (n/2)(1-\alpha) \quad (3)$$

where the total net magnetization of the system is given by

$$M = -\mu_b n \alpha$$

Using the result of part (a), fixing the total density of electrons in the system n,

▷ calculate the total energy of the system per unit volume as a function of α.

▷ Expand your result to fourth order in α.

▷ Show that $\alpha = 0$ gives the lowest possible energy.

▷ Argue that this remains true to all orders in α

(c) Now consider adding a Hubbard interaction term

$$H_{hubbard} = U \sum_i N^i_\uparrow N^i_\downarrow$$

with $U \geq 0$ where N^i_σ is the number of electrons of spin σ on site i.

Calculate the expectation value of this interaction term given that the up and down electrons form fermi seas with densities $n_\uparrow$ and $n_\downarrow$ as given by Eqns. 2 and 3 above.

▷ Write this energy in terms of α.

(d) Adding together the kinetic energy calculated in part b with the interaction energy calculated in part c, determine the value of U for which it is favorable for α to become nonzero.

▷ For values of U not too much bigger than this value, calculate the magnetization as a function of U.

▷ Explain why this calculation is only an approximation.

(e) Consider now a two dimensional tight binding model on a square lattice with a Hubbard interaction. How does this alter the result of part (d)?

5.8. Antiferromagnetism in the Hubbard Model

Similar comment about antiferromagnetism. Probably this is considered too hard to show up on an exam.

Consider a tight binding model with hopping t and a strong Hubbard interaction.

$$H_{hubbard} = U \sum_i N^i_\uparrow N^i_\downarrow$$

(a) If there is one electron per site, if the interaction term U is very strong, explain qualitatively why the system must be an insulator.

(b) On a square lattice, with one electron per site, and large U, use second order perturbation theory to determine the energy difference between the ferromagnetic state and the antiferromagnetic state. Which one is lower energy?

Almost all of these are acceptable as exam questions - except where noted

Some Revision Problems

6.1. **Debye Theory**

Use the Debye approximation to determine the specific heat of a two dimensional solid as a function of temperature. State your assumptions. You will need to leave your answer in terms of an integral that generally one cannot do. At high T, show the specific heat goes to a constant and find that constant. At low T, show that $C_v = KT^n$ Find n. Find K in terms of a definite integral. If you are brave you can try to evaluate the integral, but you will need to leave your result in terms of the Riemann zeta function $\zeta(s) = \sum_{n=1}^{\infty} n^{-s}$.

6.2. **Debye Theory II**

Physicists should be good at making educated guesses: Guess the element with the highest Debye temperature. The lowest? You might not guess the ones with the absolutely highest or lowest temperatures, but you should be able to get close.

6.3. **Free Electron Theory**

(a) Explain what is meant by the Fermi energy, Fermi temperature and the Fermi surface of a metal.

(b) Show that the kinetic energy of a free electron gas in 3D is $(3/5)NE_F$ where E_F is the fermi energy.

(c) Consider a two dimensional electron gas. Derive an expression for the density of states.

(d) is probably too hard for an exam

(d) *Calculate the specific heat at low temperature of this two dimensional electron gas. The following integral may be useful:

$$\int_{-\infty}^{\infty} dx \frac{x^2 e^x}{(e^x+1)^2} = \frac{\pi^2}{3}$$

6.4. **Vibrations I**

(a) Consider a 1 dimensional mass and spring model of a crystal. Write down the dispersion curve $\omega(k)$ for this model (this should be easy by this time). Now write an expression for the specific heat of this 1 dimensional chain. You will inevitably have an integral that you cannot do.

(b)* However, you can expand exponentials for high temperature to obtain a high temperature approximation. It should be obvious that the high temperature limit should give heat capacity $C = k_B$ per atom (the law of Dulong-Petit in one dimension). By expanding to next nontrivial order, show that

$$C/N = k_B(1 - A/T^2 + \ldots)$$

where

$$A = \frac{\hbar^2 k}{6m}$$

where m is the atomic mass and k is the spring constant.

6.5. **Vibrations II** Consider a 1 dimensional spring and mass model of a crystal. Generalize this model to include springs not only between neighbors but also between second nearest neighbors. Let the spring constant between neighbors be called κ_1 and the spring constant between second neighbors be called κ_2. Let the mass of each atom be M.

(a) Calculate the dispersion curve $\omega(k)$ for this model.

(b) Determine the sound wave velocity, Show the group velocity vanishes at the Brillouin zone boundary.

6.6. **Reciprocal Lattice**

Show that the reciprocal lattice of a FCC (face-centered-cubic) lattice is a BCC (body-centered-cubic) lattice. Correspondingly show that the reciprocal lattice of a BCC lattice is an FCC lattice. If an FCC lattice has conventional unit cell with lattice constant a, what is the lattice constant for the conventional unit cell of the reciprocal BCC lattice?

Consider now an orthorhombic face-centered lattice with conventional lattice constants a_1, a_2, a_3. What it the reciprocal lattice now?

6.7. **Scattering**

The Bragg angles of a certain reflection from copper is 47.75° at 20°C but is 46.60° at 1000°C. What is the coefficient of linear expansion of copper? (Note: the Bragg angle θ is half of the measured diffraction (deflection) angle 2θ).

6.8. **More scattering**

KCl and KBr are alkali-halides with the same crystal structure as NaCl: fcc cubic with Na at (0,0,0) and Cl at (1/2,1/2,1/2). KBr shows X-ray diffraction peaks from planes (111) (200) (220) (311) (222) (400)(331)(420), but KCl shows peaks only at (200)(220)(222)(400)(420). Why might this be true?

6.9. **Semiconductors**

Describe experiments to determine the following properties of a semiconductor sample: (i) sign of the majority carrier, (ii) carrier concentration (assume that one carrier type is dominant), (iii) band gap, (iv) effective mass (v) mobility of the majority carrier.

6.10. **More Semiconductors**

Outline the absorption properties of a semiconductor and how these are related to the band gap. Explain the significance of the distinction between a direct and an indirect semiconductor. What region of the optical spectrum would be being studied for a typical semiconducting crystal?

6.11. **Yet More Semiconductors**

Outline a model with which you could estimate the energy of electron states introduced by donor atoms into an n-type semiconductor. Write down an expression for this energy, explaining why the energy levels are very close to the conduction band edge.

6.12. **Magnetism**

Explain briefly the origin of diamagnetism and paramagnetism in atoms.

Consider a crystal of volume V composed of N identical atoms. Each atom has spin 1/2 and $g = 2$. Assume neighboring atoms do not interact, derive an expression for the paramagnetic susceptibility as a function of temperature in the high temperature limit. How would your answer be different if each atom had spin 1?

Explain how this system might be used to make a refrigerator. In reality what limits how well this works?

Quenching would not be asked I would think.

Discuss what is meant by "quenching" of orbital angular momentum and its consequences for paramagnetism.

6.13. **Mean field theory**

(a) β-Brass is an alloy containing equal numbers of of Cu and Zn atoms. Above a temperature of 730K, the atoms are arranged randomly on a body centered cubic lattice. Below 730K, the lattice becomes simple cubic with Cu atoms largely on the (0,0,0) position and the Zn atoms largely at the (1/2,1/2,1/2) position in the unit cell. The energy of the crystal depends on the occupancy of the sites and is given by

$$E = \frac{1}{2} \sum_{\langle i,j \rangle} J \sigma_i \sigma_j$$

where $\sigma_i = +1$ if the site is occupied by a Cu atom and $\sigma_i = -1$ if the site is occupied by a Zn atom and $J > 0$. Here the sum is restricted to nearest neighbors. Using mean field approximation show that

$$\langle |\sigma| \rangle = \tanh(\beta z J \langle |\sigma| \rangle)$$

what is z ? (b) Estimate the magnitude of J (c) Explain, in detail, how this ordering could be observed.