

Problems for Solid State Physics
(3rd year course B.VI)
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These problems are based substantially on those prepared and distributed by Prof S.H. Simon in Hilary Term 2015.

Suggested schedule:

- Problem Set 1: Hilary Term Week 3
- Problem Set 2: Hilary Term Week 5
- Problem Set 3: Hilary Term Week 7
- Problem Set 4: Hilary Term Vacation

‡ Denotes crucial problems that you need to be able to do in your sleep.

* Denotes problems that are slightly harder.

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

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

Note: in this problem \mathbf{p} and \mathbf{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.

(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.

1.2. Debye Theory

(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.

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

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

1.3. Drude Theory of Transport in Metals

(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 $\underline{\rho}$ as $\vec{E} = \underline{\rho}\vec{j}$.

▷ Use Drude theory to derive an expression for the matrix $\underline{\rho}$ 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 $\underline{\rho}$ is a matrix.)

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

(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 5 mm by 5 mm carrying a current of 1 A in a magnetic field of 1T orthogonal to the direction of the current. The density of sodium atoms is roughly 1 g/cm³, and sodium has atomic mass of roughly 23 u. 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?

(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 $\underline{\sigma}(\omega)$. For simplicity in this case you may assume that the metal is very clean, meaning that $\tau \rightarrow \infty$, 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

(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 g/cm³, and sodium has atomic mass of roughly 23 u. 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

(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 $v_F = \frac{\hbar}{m}(3\pi^2n)^{1/3}$ 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 300 K in an electric field of 1 V m^{-1} and comment on their relative magnitudes.

(ii) estimate λ for copper at 300 K 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 $n = 8.45 \times 10^{28} \text{ m}^{-3}$. The conductivity of copper is $\sigma = 5.9 \times 10^7 \text{ } \Omega^{-1}\text{m}^{-1}$ at 300 K.

1.6. Physical Properties of the Free Electron Gas

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 electrons in metals

(b)‡ Give a simple (not approximate) derivation of the Fermi gas prediction for magnetic susceptibility of the conduction electrons 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 those for 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 $\gamma = 2.08 \text{ mJ mol}^{-1} \text{ K}^{-2}$ and $\alpha = 2.6 \text{ mJ mol}^{-1} \text{ K}^{-4}$.

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

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

Problem Set 2

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

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 0.236 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 $n = 1, \dots, N$. For simplicity, let us assume this basis is orthonormal $\langle n|m\rangle = \delta_{n,m}$

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

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

where ϕ 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 known 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.)

(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

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

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

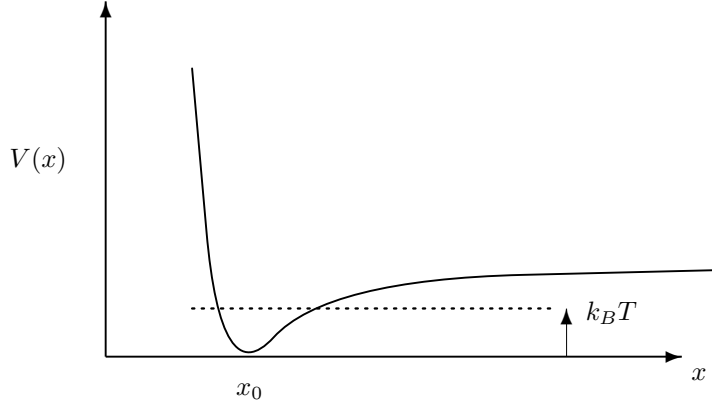
$$E = \epsilon + V_{\text{cross}} \pm |t|$$

▷ 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

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



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

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

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

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

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 .

2.4. Classical Model of Thermal Expansion

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

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

and let limits of integration go to $\pm\infty$.

▷ 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. 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.

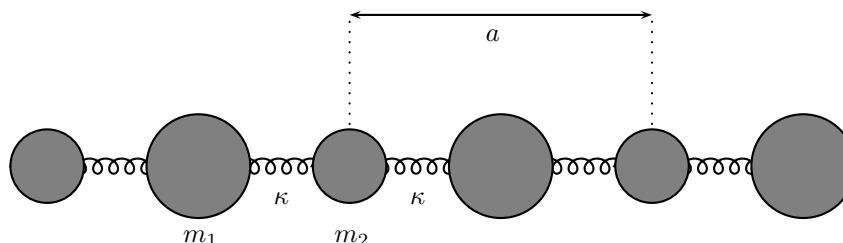
(e) Find the expression for $g(\omega)$, the density of states of modes per angular frequency.

▷ 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.

2.6. Normal modes of a One Dimensional Diatomic Chain



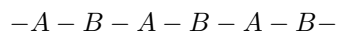
- (a) What is the difference between an acoustic mode and an optical mode?
- ▷ Describe how particles move in each case.
- (b) Derive the dispersion relation for the longitudinal oscillations of a one dimensional *diatomic* mass-and-spring crystal where the unit cell is of length a and each unit cell 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 $m_1 = m_2$?

2.7. One Dimensional Tight Binding Model

- (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 $n = 1 \dots N$ (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 $n = m \pm 1$.
- ▷ 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 2.5. above.)
 - ▷ 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?

- ▷ Estimate the heat capacity of the system at low temperature.
- ▷ What is the heat capacity if each atom is divalent? What about the spin susceptibility?

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



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 2.6. 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 $\epsilon_A = \epsilon_B$?