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Keble College - Hilary 2012
Section VI: Condensed matter physics
Tutorial 1 - Solid state without the microscopic structure

Please leave your work in the Clarendon laboratory's 'J' pigeon hole by 5pm on Monday of 2nd week. Suggested reading: Hook & Hall 2.6, 3, 7.2.4; Kittel 5, 6; Ashcroft/Mermin 1, 2, 3.

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1   Technical preliminaries

> *During this course we will repeatedly invoke unrealistic boundary conditions and perform calculations using the density of states, which is strictly valid only for solids of infinite volume. Here we reflect on why we are able to use these to such great effect to describe real solids. It might seem abstract now, but as we will see, the physics keeps referring back to these concepts and it is important to confront them early on.*

1. (a) Imagine solving a partial differential equation (PDE), such as Newton's second law or the Schrödinger equation. What effect do boundary conditions have on the solutions to the PDE?

    (b) In this course, and in much of physics, we use the highly unrealistic periodic Born-von Karman (BvK) boundary conditions. Why does the particular choice of boundary conditions often not matter? Given this freedom, why might we choose BvK conditions?

    (c) Consider solutions to a PDE that depend on some parameter $\mathbf{k}$. In general, the boundary conditions will allow only some discrete set of $\mathbf{k}$-values. We will often make use of the replacement $Q = \sum_{\mathbf{k}} q(k) \to \int_0^\infty q(k)g(k)\mathrm{d}k$, where Q is some quantity of interest, e.g., heat capacity. Explain then what is meant by the *density of states $g(k)$*, why it use is helpful and when its use is valid.

    (d) Using similar arguments, explain how the density of states $g(\epsilon)$ relates to $g(k)$ for a particular $\epsilon(k)$.

    (e) Now, specialise to a d-dimensional system of length L in each dimension, use BvK boundary conditions, and consider wave-like solutions to the PDE that are of the form $\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}}$, as will be the case for free electrons and vibrations of atoms making up the lattice. Derive the allowed values of $\mathbf{k}$. Calculate $g(k)$ for $d = 1, 2$ and 3 dimensions. Include a factor of f due to additional degrees of freedom, e.g., spin or polarization.

    (f) Further specialise to free electron eigenfunctions, whose energy eigenvalues are given by $\epsilon = \hbar^2 k^2/2m$ and $f = 2$. Justify the form of ϵ, the value of f and calculate $g(\epsilon)$ for $d = 1, 2$ and 3 dimensions.

> *We considered wave-like solutions above, e.g., $\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}}$ and $\mathrm{e}^{\mathrm{i}(\mathbf{k}\cdot\mathbf{r}-\omega t)}$. Exactly the same allowed values of $\mathbf{k}$ are found for more general solutions of the form, e.g., $\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})$, where $u_{n\mathbf{k}}(\mathbf{r})$ is periodic in space; this will be vital for considering electrons in periodic potentials in tutorial 4. Your arguments for part (b) are strengthened by the following two points, which an enthusiastic or sceptical student could confirm: exactly the same $g(\epsilon)$ is found for free electrons using box boundary conditions, so no bulk system properties are affected by this change; also, considering more general system shapes, such as a parallelepiped, still results in the same $g(\epsilon)$ for a system of the same volume.*

2 Drude and Sommerfeld theories: the free electron model

Drude put forward one of the earliest models of electronic transport in metals, treating them like an ideal classical gas. While it makes several gross simplifications and fails to account for many experimental observations, it does predict the correct values of particular observables in some metals at certain temperatures. Perhaps more importantly, it gives us a basic theory to work with, which we will improve by adapting and removing various assumptions.

2. (a) *Basic assumptions* — What is Drude theory?

   (b) *Electrical conductivity* — The electronic current depends on the average *velocity* of electrons. Using this, derive an expression for the electrical conductivity σ in Drude theory, assuming a scattering time τ and a number density of conduction electrons n_c.

   (c) *The Hall effect* — Explain the Hall effect, define the Hall coefficient R_H and find the magnitude (and direction) of the Hall voltage V_H, according to Drude theory, for a rectangular rod of Na with cross-section 5mm × 5mm carrying 1 A through a perpendicular field of 1 T. The density of sodium is around $1\,\mathrm{gm/cm^3}$, it has an atomic mass of approximately 23 and a valence of one. What practical difficulties might there be in measuring the V_H and how might they be addressed?

   (d) *Thermal conductivity* — Other properties of the free electron gas, e.g., the thermal conductivity κ, depend on the average *speed* of electrons or thermodynamic properties of the electron gas such as heat capacity. Using Drude theory, derive κ in terms of τ and n_c, using $\kappa = \frac{1}{3}c_v \langle v \rangle^2 \tau$ where c_v is the heat capacity per electron, and $\langle v \rangle$ is average speed of an electron. Hence find the Lorenz number $L = \kappa/\sigma T$ (this is the Wiedemann-Franz law).

   (e) *Failures* — When does the Drude theory fail badly?

In light of the development of quantum mechanics, Sommerfeld corrected a single but crucial aspect of Drude's theory. Instead of classical particles he treated the electrons as indistinguishable quantum mechanical particles obeying Fermi statistics. Hence the basis of the resulting Sommerfeld theory is the free Fermi gas, rather than the classical ideal gas considered by Drude. In Qu. 3, we look at the properties of the free Fermi gas in thermal equilibrium and the terminology describing it. We then look at which properties from Qu. 2 are updated in light of Sommerfeld's correction. Some relied on thermodynamic quantities of the electron gas, e.g. heat capacity, so in Qu. 4 we calculate thermodynamic quantities for the free Fermi gas. Others relied on the average speed of electrons in thermal equilibrium and so we examine the effect of Sommerfeld's correction on this in Qu. 5.

3. In the class we will discuss Hamiltonians describing electrons in a solid of the form $\mathcal{H} = \sum_j \mathcal{H}_{\mathrm{se}}(\mathbf{r}_j)$ where $\mathcal{H}_{\mathrm{se}}(\mathbf{r})$ is called the single electron Hamiltonian and the index j is summed over all electrons. We will find that, in the eigenstates of the total system, each electron is in an eigenstate of the single electron Hamiltonian, and the corresponding eigenvalue of the total system E is just the sum of the eigenvalues of the occupied single electron eigenstates $E = \sum_j \epsilon_j$. Since electrons are Fermions, the total eigenstates must by antisymmetric under exchange, the result of which is that no two electrons can be in the same single electron eigenstate (the Pauli exclusion principle).

   It follows that in the N electron ground state only the N single electron eigenstates with the lowest eigenvalues are occupied. In thermal equilibrium at some finite temperature $T = 1/k_B\beta$, the occupation of each of the eigenstates of the total system is weighted by the Boltzmann factor $\mathrm{e}^{-\beta E}$. From this it follows (with some algebra) that the occupation of a single electron eigenstate with eigenvalue ϵ is given by the Fermi distribution function

   $$n_F(\beta(\epsilon - \mu)) = \frac{1}{\mathrm{e}^{\beta(\epsilon-\mu)} + 1},$$

where the *chemical potential* is $\mu = \frac{\partial U}{\partial N}\big|_{V,S}$ and U is the expected total energy of the electrons.

For free electrons, $\mathcal{H}_{se}(\mathbf{r}) = -\frac{\hbar^2 \nabla^2}{2m}$, and choosing BvK boundary conditions results in single electron eigenfunctions of the unnormalised form $e^{i\mathbf{k}\cdot\mathbf{r}}$ with eigenvalues $\epsilon = \hbar^2 k^2/2m$, and a degeneracy $f = 2$ due to the electron's spin. Therefore we can use the values of $g(k)$ and $g(\epsilon)$ derived in Qu. 1 parts (e) and (f).

(a) *Zero temperature* — Referring to above, explain the terms *Fermi energy ϵ_F*, *Fermi temperature T_F* and *Fermi surface* in the context of a metal. Calculate the Fermi temperature of a metal with typical conduction electron number density $n_c = 10^{29}$ m^{-3}, hence demonstrate that typical temperatures of interest satisfy $T \ll T_F$.

(b) *Finite temperature* — Sketch the Fermi distribution function $n_F(\beta(\epsilon - \mu))$ at finite temperatures $T \ll T_F$. Define the chemical potential (give alternative definitions to the one above). Why are the chemical potential and the Fermi energy often used interchangeably when describing metals?

(c) *At the Fermi surface* — Show that $g(\epsilon_F) = 3N_c/2\epsilon_F$ and the speed of an electron at the Fermi surface is $v_F = \frac{\hbar}{m}(3\pi^2 n_c)^{1/3}$, where $N_c = n_c V$ is the total number of conduction electrons and V is the volume of the system. For temperatures $T \ll T_F$ we will find that many metallic properties depend only on the values quantities take at the Fermi surface and as a result these expressions will be of use in the next two questions.

A large part of the success of the Sommerfeld theory lies in its correction of Drude theory's predictions of electronic contributions to thermodynamic quantities. Here we consider two examples.

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4. (a) *Heat capacity* — Derive the Sommerfeld prediction for the heat capacity of conduction electrons in metals.

(b) *Pauli susceptibility* — Derive the Sommerfeld prediction for the Pauli paramagnetic susceptibility of conduction electrons in metals ($\chi = \mu_0 \frac{dM}{dB}\big|_{V,T}$ as $B \to 0$, where M is the magnetisation and B is the magnetic B-field).

(c) *"Frozen" Fermi sea* — How do the values of the heat capacity and susceptibility compare to those derived classically? [Note: Drude was working before the discovery of electron spin, but assuming two possible values of spin, each adding $\pm\mu_B B$ to the energy of an electron in a magnetic field, the classically derived susceptibility is $\chi = \frac{n_c \mu_0 \mu_B^2}{k_B T}$.] What is the cause of the discrepancy?

Fermi statistics cause the velocity distribution of free electrons in thermal equilibrium to be drastically changed from the classical result, for $T \ll T_F$. As a result, we must correct quantities derived in Drude theory that depend on the average speed of electrons in thermal equilibrium (but not those that only depend on the average velocity). The average speed has no effect on the current and so the electronic conductivity σ and the Hall effect remain unchanged in the Sommerfeld approach. Fortuitously, the thermal conductivity κ (and so L) is also largely unaffected due to cancelling corrections to the average velocity and heat capacity. The mean free path, on the other hand, does change.

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5. (a) *Average speed* — Argue that the typical speeds of electrons in a metal are of order v_F for temperatures $T \ll T_F$. Show that v_F is of the order of $\sqrt{T_F/T}$ times larger than the speeds expected by kinetic theory.

(b) *Mean free path* — The Drude result for σ you derived in Qu. 2(b) remains valid in the Sommerfeld approach. Show that for the same σ (and hence τ) the Sommerfeld theory predicts a mean free path λ that is roughly $\sqrt{T_F/T}$ larger than Drude theory.

(c) *Thermal conductivity* — Use answers to Qus. 4(a) and 5(a) to calculate κ in the Sommerfeld picture, confirming its flukey (for Drude) similarity to the Drude result of Qu. 2(d).

(d) *Example* — Assuming Sommerfeld theory, calculate v_F (typical *speed*), the average electron drift speed v_d (magnitude of average *velocity*), and λ for a copper specimen in an electric field of $1\,\mathrm{Vm^{-1}}$. Assume copper is monovalent, with an atomic number density $n = 8.45 \times 10^{28}\,\mathrm{m^{-3}}$ and a conductivity $\sigma = 5.9 \times 10^7\,\Omega^{-1}\mathrm{m^{-1}}$. Comment on the relative values of v_d and v_F, and the length of λ in comparison to the atomic spacing.

The astute student might be uneasy about how, given the uncertainty principle, we can use a model of an electron with a well defined momentum and position, as we have implicitly done above. This semiclassical approach is discussed in Chapter 2 of Ashcroft and Mermin. Essentially, it is possible for the uncertainty Δk to be much smaller than k_F so long as an electron's wavepacket is delocalised over many atoms, as occurs in metals. The results for electronic transport properties hold provided electric or magnetic field fields vary slowly over this distance and the mean free path λ is much greater than the spacing between atoms, as found above.

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3 Lattice vibrations

The Drude-Sommerfeld theory considers aspects of a solid arising from conduction electrons. It describes ions (atomic nuclei together with their core electrons) as stationary positive charges. However, to explain several key thermodynamic quantities of solids, e.g. heat capacity, we must include the motional degrees of freedom of these atoms. For small displacements from their equilibrium positions the N atoms move in harmonic potentials. As a result their collective vibrations can be represented by several harmonic oscillators (this will be the focus of the third tutorial). The number of these harmonic oscillators must be N in order to keep the number of motional degrees of freedom the same. The exact contribution of atoms will then depend on the exact distribution of the frequencies of these harmonic oscillators. Various approximation exists that capture the behaviour of the heat capacity for different crystal structures and temperatures. We consider three below, those due to Dulong and Petit, Einstein and Debye, saving a discussion of their validity and justification for the third tutorial.

6. *Dulong and Petit* — The partition function of a classical harmonic oscillator is given by

$$\mathcal{Z} \propto \int \int \mathrm{e}^{-\beta \mathcal{H}} \mathrm{d}\mathbf{x} \mathrm{d}\mathbf{p},$$

with

$$\mathcal{H} = \frac{p^2}{2m} + \frac{m\omega^2 x^2}{2}.$$

Calculate the heat capacity, $C = \frac{\partial U}{\partial T}$, with $U = -\frac{\partial \ln \mathcal{Z}}{\partial \beta}$. How does this depend on temperature? This is an example of the *equipartition theorem* in classical statistical mechanics. Considering all N oscillators to be classical gives the law of *Dulong and Petit*.

7. *Einstein* — What are the energy eigenvalues E_j of a quantum system with the same Hamiltonian $\mathcal{H}$? Evaluate the partition function,

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

and hence calculate the heat capacity. Evaluate the high and low temperature limits, and compare the latter to what was found for a classical oscillator. Considering all N oscillators to be quantum oscillators each with the same frequency ω is the *Einstein* treatment.

8. *Debye* — The Debye model again approximates the atomic vibrations by N quantum mechanical oscillators. The frequencies of these oscillators are however not assumed to be the same. The modes are assumed to be labelled by some continuous parameter $\mathbf{k}$ and, in the simplest case, have frequencies $\omega(k) \propto k$. The magnitudes k are distributed according to some density $g(k) \propto k^{d-1}$ up to some maximum wavevector k_{max}, which determines N. [Note: We'll justify this in tutorial 3.]

    Derive the high and low temperature limits for the heat capacity in $d = 3$ dimensions (the high temperature limit should be no surprise by now). It might be useful to use

    $$4 \int_0^\infty \frac{x^3}{(\mathrm{e}^x - 1)} \mathrm{d}x = \int_0^\infty \frac{x^4 \mathrm{e}^x}{(\mathrm{e}^x - 1)^2} \mathrm{d}x = \frac{4\pi^4}{15}.$$

    In the third tutorial we will find that the collective vibrations of the atoms are indeed well described by N harmonic oscillator modes. However, only for the lowest frequency modes does the linear relation $\omega(k) \propto k$ hold. Why, for the lowest temperatures, does the heat capacity still satisfy the Debye expression?

9. Briefly compare the predictions of the Debye, Einstein, and Dulong and Petit models for heat capacity.

4   Final thought - contributions to the heat capacity

10. The experimental heat capacity of potassium at low temperatures has the form

    $$C = (2.08T + 2.6T^3)\mathrm{mJ}\,\mathrm{mol}^{-1}\mathrm{K}^{-1},$$

    where T is in Kelvin. Explain the origin of both terms in this expression, and estimate both the Fermi energy and the Debye temperature.

    So, the heat capacities of solids at low temperatures is explained by considering only excitations that extend to zero energy, e.g. excitations of electrons across the Fermi sphere (Sommerfeld theory) and the excitations of collective atomic vibrations (Debye theory). Why don't other excitations contribute to the heat capacity, e.g. higher frequency modes of oscillations, excitations of the internal states of nuclei or core electrons? [Hint: Classically, we would expect every single degree of freedom to contribute $k_B/2$. In your answer to the question above, explain what exactly it is about quantum systems that prevents some degrees of freedom from contributing to the heat capacity. It may help to think about how the heat capacity of a quantum harmonic oscillator depends on its frequency ω.]

In this tutorial we have treated two aspects of solid state physics, conduction electrons and atomic motion, in a basic manner. We treated electrons as moving independently in a periodic box, and represented atomic motion by multiple harmonic oscillators, without justifying the frequencies of these oscillators. In the next few weeks we will consider more sophisticated treatments of the electrons, allowing us to explain why some solids are insulators and others are metals or semiconductors (tutorial 4 and 5), and justify the frequencies of the oscillators representing atomic motion (tutorial 3). All of this will rest upon the periodicity of the atoms forming the solid, and is best described using the concept of a lattice, which is the focus of tutorial 2.