

Condensed matter theory

Lecture notes and problem sets 2012/2013

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Recommended books and lecture notes:

- [AM] N. W. Ashcroft and N. D. Mermin, Solid State Physics.
[Mar] M. P. Marder, Condensed Matter Physics.
[AS] Andreas Schilling, lecture notes 2010/2011.

1 Introduction

1.1 Electrons in metals: methods and approximations

In solid state theory, one is interested in the physics of the interacting electrons and nuclei (the latter are usually ordered in a crystal). While the microscopic nature of interactions is known, finding the resulting effective behavior is a challenging task. Generally, the Hamiltonian of the system has the form

$$H = T_e + T_N + V_{ee} + V_{eN} + V_{NN}. \quad (1)$$

where T_e and T_N are the kinetic energies of the electrons and nuclei, and V_{ee} , V_{eN} , V_{NN} are the interactions (of which the strongest are the electrostatic Coulomb interactions, but spin-orbit interactions may also be relevant). Solving this complicated many-body problem exactly is impossible (even numerically), and various levels of approximations are used. We can mention several commonly used levels of approximations:

- **Drude theory of conductivity.** This approximation describes electrons *classically* and neglects the role of nuclei (except for impurities). See your course of General Physics and [AM] chapter 1.
- **Free-fermion approximation (Sommerfeld theory).** Treating electrons as free *quantum* particles (fermions). The periodic potential of nuclei is still neglected. See your course of Solid State Physics [AS] and [AM] chapter 2.
- **Band theory.** Quantum particles in a periodic potential of the nuclei. See your course of Solid State Physics [AS] and [AM] chapter 8.
- **Including electron-electron interactions.** Electron-electron interaction can be included at various levels of approximation: Hartree–Fock, random-phase-approximation (RPA), Landau Fermi liquid.

- **Numerical methods.** Interactions may be included more precisely with numerical methods: ab initio calculations, density functional theory.
- **Including electron-phonon interactions.** In some situations, these interactions may be important. For example, they provide an important mechanism of resistivity at high temperatures. They are also responsible for attraction between electrons leading to superconductivity.

In the first lecture, we briefly review the advantages and limitations of these methods and outline the program for the course.

1.1.1 Classical Drude theory

Ref: [AM] Chapter 1.

This is the simplest model of a metal (proposed by Drude in 1900). The electrons are treated as classical particles scattering randomly at impurities. Scattering on impurities is parameterized by the “relaxation time” τ (the time after which the electron randomly changes the direction of its motion). Then, from simple classical arguments (see your physics course) one finds the DC electrical conductivity

$$\sigma = \frac{ne^2\tau}{m}. \quad (2)$$

Here m is the electron mass and n is the density of electrons.

A similar calculation may be done for the thermal conductivity leading to

$$\kappa = \frac{1}{3}v^2\tau c_V, \quad (3)$$

where v^2 is the mean square electronic speed and c_V is the electronic specific heat. For the classical ideal gas model,

$$v^2 = \frac{3k_B T}{m}, \quad c_V = \frac{3}{2}nk_B, \quad (4)$$

leading to

$$\kappa = \frac{3nk_B^2\tau T}{2m} \quad (5)$$

and further to the “Wiedemann–Franz law” (with a wrong coefficient)

$$\frac{\kappa}{\sigma} = \frac{3}{2} \left(\frac{k_B}{e} \right)^2 T. \quad (6)$$

Experimentally, indeed, the ratio κ/σ is roughly proportional to T , but the proportionality coefficient is approximately two times larger (see Table 1.6 in [AM]). It turns out, however, that this qualitative agreement with experiment is due to a cancellation of two mistakes: both estimates in Eq. (4) are wrong, even though their product has a correct order of magnitude (see our discussion of the *quantum* theory in the next section).

Furthermore, the discrepancy with experiment is much larger if one considers the thermoelectric effect (the Seebeck effect: $\mathbf{E} = Q\nabla T$). In the Drude model, one finds for the thermoelectric coefficient

$$Q = -\frac{c_V}{3ne} = -\frac{k_B}{2e} = -0.43 \cdot 10^{-4} \text{volt/K}, \quad (7)$$

which is two orders of magnitude larger than the experimentally observed values.

One concludes that a *quantum* theory is needed for an accurate description of electrons in metals.

1.1.2 Sommerfeld theory of metals

Ref: [AM] Chapter 2.

In this theory, we treat electrons as a gaz of free fermions. The main results are:

1. Linear in T specific heat [note a huge difference from the classical result (4)].
2. The Drude expression (2) for the conductivity remains unchanged, as long as the motion of electrons is quasiclassical (i.e. the mean free path is much longer than the wave length), which is typically satisfied, and provided we can describe collisions by a single (independent of energy and momentum) relaxation time τ (which is a more subtle condition).
3. The expression (3) for the thermal conductivity remains valid, but the mean square velocity and the specific heat are given now by

$$v^2 = v_F^2 = \frac{2\varepsilon_F}{m}, \quad c_V = \frac{\pi^2 n k_B^2 T}{2\varepsilon_F}. \quad (8)$$

This results in a more accurate coefficient in the Wiedemann–Franz law:

$$\frac{\kappa}{\sigma} = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 T. \quad (9)$$

4. Thermopower: If we use the specific heat from Eq. (8) for calculating the thermopower, we get a reasonable estimate

$$Q = -\frac{\pi^2}{6} \frac{k_B}{e} \left(\frac{k_B T}{\varepsilon_F} \right), \quad (10)$$

which is smaller than in the classical Drude theory by a factor of about $(k_B T/\varepsilon_F)$ (two orders of magnitude at room temperature).

5. Spin susceptibility: The spin susceptibility is temperature independent at low temperatures (see, e.g. condensed-matter-physics course [AS]).

Overall, this approximation gives a good description of the quantum behavior of conduction electrons, but becomes inaccurate for properties depending on the geometry of the Fermi surface or on the interactions.

1.1.3 Band theory

As you have learned in previous physics courses, nuclei in solids form regular periodic patterns: crystals. You have discussed the symmetry properties and classification of crystal lattices in the course of condensed matter physics [AS].

The crystal lattice of nuclei produces a periodic potential for electrons. Single-particle quantum states in such potential are not localized, but are periodic in space: Bloch waves. Such states form bands.

This theory can explain:

1. Why some materials are metals and some insulators.
2. For metals, properties depending on the shape of the Fermi surface (de Haas–van Alphen effect, sign of the Hall coefficient, etc.)

In our lectures, we will discuss the role of the crystal symmetry in the band structure.

1.1.4 Including interactions: Hartree–Fock, Landau Fermi liquid, Density functional theory, etc.

All the methods discussed above treat electrons as non-interacting. For some physical effects, interactions *are* important.

In some situations, interactions may be taken into account analytically by renormalizing in some way the non-interacting model (Hartree–Fock, random-phase approximation, Landau Fermi Liquid theory). For more accurate estimates of the role of interactions on the electronic structure, one uses more sophisticated numerical methods (e.g., density functional theory).

In other situations, interactions lead to qualitatively new physics. One example, which we will discuss in our course: superconductivity (BCS theory). The BCS theory is a good textbook example, because a simple analytic theory exists. There are many other physical examples, where such a simple theory has not been yet developed (if it exists at all): high-temperature superconductivity, fractional quantum Hall effect, etc.

1.1.5 Estimating the importance of interactions

Consider a free electron gas of density n . A typical distance between electrons may be taken to be r_s , defined as the radius of the sphere whose volume equals the volume per one electron:

$$\frac{V}{N} = \frac{1}{n} = \frac{4\pi r_s^3}{3}, \quad r_s = \left(\frac{3}{4\pi n} \right)^{1/3} \quad (11)$$

It is also convenient to measure r_s in the units of the Bohr radius

$$a_0 = \frac{\hbar^2}{me^2} = 0.529\text{\AA} \quad (12)$$

The typical kinetic energy is of the order of the Fermi energy (below I do not keep track of numerical coefficients):

$$E_F \sim \frac{\hbar^2 k^2}{m} \sim \frac{\hbar^2}{r_s^2 m} \quad (13)$$

while the typical interaction energy is

$$E_C \sim \frac{e^2}{r_s} \quad (14)$$

The importance of interaction is determined by the ratio

$$\frac{E_C}{E_F} \sim \frac{me^2 r_s}{\hbar^2} = \frac{r_s}{a_0} \quad (15)$$

— i.e., the interaction is more important at *low* densities!

Moreover, it was predicted theoretically, that at very low densities the interactions become so strong that fermions crystallize at zero temperature (E. Wigner, 1934). Numerical studies suggest that such a crystallization occurs at $r_s/a_0 \sim 106$ in 3D and $r_s/a_0 \sim 31$ in 2D. For typical metals, r_s/a_0 is of the order 2–5.

1.1.6 Plan of the course (approximate)

- **Lecture 1.** Specific heat and transport properties in the model of noninteracting fermions.
- **Lectures 2-3.** Electronic energy bands in crystals. Role of crystal symmetries. (Introduction to the theory of group representations.)
- **Lectures 4-5-6.** Interactions between electrons. Perturbative approach, Hartree–Fock, screening of interactions. (Second quantization and introduction to diagrammatic methods.)
- **Lecture 7.** Landau Fermi liquid theory.
- **Lecture 8.** Numerical approaches. Density functional theory. Local density approximation.
- **Lecture 9.** Phonons, electron-phonon interaction.
- **Lecture 10-11-12.** Attraction by exchanging phonons. BCS theory of superconductivity.

1.2 Specific heat and transport properties in the model of non-interacting fermions.

In this section, we derive the specific heat (8), the electrical conductivity (2), and the thermal conductivity (3) in the model of noninteracting fermions. We will present the calculations in a form suitable for both the Sommerfeld theory (spherical Fermi surface) and the band theory (for an arbitrary shape of the Fermi surface).

1.2.1 Specific heat

Ref: [AM] Chapter 2.

Specific heat is an *equilibrium* characteristic of a statistical system:

$$c_V = \frac{\partial \mathcal{E}}{\partial T}, \quad (16)$$

where \mathcal{E} is the energy at thermal equilibrium at a given temperature T . At equilibrium, every single-particle level (at a given energy E_i) can be treated independently: it is either empty or occupied, with the probabilities given by the Fermi–Dirac distribution:

$$p_0 = \frac{1}{1 + \exp[-(E_i - E_F)/T]}, \quad p_1 = n_F(E_i) = \frac{\exp[-(E_i - E_F)/T]}{1 + \exp[-(E_i - E_F)/T]}. \quad (17)$$

Then the total energy can be calculated as

$$\mathcal{E}(T) = \sum_i E_i n_F(E_i). \quad (18)$$

It only depends on the energy levels, but not on the properties of the eigenstates. Then it is convenient to introduce the *density of states* $\nu(E)$: the number of energy levels per unit of energy per unit of volume. Then the sum can be re-expressed as an integral

$$\mathcal{E}(T) = \int E n_F(E) \nu(E) dE \quad (19)$$

(energy per unit volume), and the specific heat then equals

$$c_V = \int E \frac{\partial}{\partial T} n_F(E) \nu(E) dE \quad (20)$$

Under the condition that the temperature is sufficiently low so that we can neglect the energy dependence of $\nu(E)$ in the corresponding energy window around the Fermi level, we can approximate

$$c_V = \nu(E_F) \int E \frac{\partial}{\partial T} n_F(E) dE. \quad (21)$$

After calculating the integral, one arrives at a general expression linear in T and in $\nu(E_F)$ (see Problem 1.1), which, in the case of the free fermion gas, further reduces to Eq. (8).

Note that this result for the specific heat (linear in T) is only relevant at very low temperatures, where c_V is dominated by electrons. At higher temperatures, the phonon contribution (proportional to T^3) comes in.

1.2.2 Electrical and thermal conductivities

Ref: [AM] Chapter 13.

Calculating electrical and thermal conductivities is a more complicated problem, even in a non-interacting model, since it requires taking into account a non-equilibrium distribution of electrons. We make two assumptions for our calculation:

- quasiclassical regime (mean free path of electrons is much larger than their wave length)

- relaxation-time approximation: relaxation processes lead to relaxation to a thermal equilibrium characterized by a single time scale τ (independent of the momentum and energy of the electron).

Under the quasiclassical assumption, we can describe the state of the electrons by the occupation number $n(k, r)$ as a function of *both* momentum and coordinate. Under the relaxation-time approximation, we can write the kinetic equation

$$\frac{\partial}{\partial t}n = -\frac{n - n_F}{\tau} - \mathbf{v} \frac{\partial}{\partial \mathbf{r}}n - e\mathbf{E} \frac{\partial}{\partial \mathbf{k}}n. \quad (22)$$

Here the first term describes the equilibration towards the Fermi–Dirac distribution (at a given temperature) n_F , the second term describes the ballistic transfer of the distribution function with the velocity $\mathbf{v}(k) = \partial E(k)/\partial k$ and the last term includes the acceleration of electrons by the electric field \mathbf{E} .

We can compute the response of the electric current \mathbf{j} to the electric field \mathbf{E} by assuming a homogeneous non-equilibrium distribution $n = n_F + \delta n$. To the leading order, we can solve for δn :

$$\delta n = -\tau e\mathbf{E}\mathbf{v} \frac{\partial}{\partial E}n_F, \quad (23)$$

while the current is given by

$$\mathbf{j} = e \int \frac{d^3k}{(2\pi)^3} \mathbf{v} \delta n. \quad (24)$$

This immediately leads to the expression for the tensor of electrical conductivity (defined as $\mathbf{j}_\alpha = \sigma_{\alpha\beta}\mathbf{E}_\beta$):

$$\sigma_{\alpha\beta} = -e^2\tau \int \frac{d^3k}{(2\pi)^3} v_\alpha v_\beta \frac{\partial}{\partial E}n_F. \quad (25)$$

Note that this expression, at low temperature, only weakly depends on temperature and is determined only by the energy dispersion in the vicinity of the Fermi surface. For the quadratic spectrum, it reduces to the Drude expression (2) (see Problem 1.2).

In a similar way, one can calculate the thermal conductivity. The delicate point here is that the thermal conductivity is defined as the energy flow under the condition of the *zero electric current*. This condition can be taken into account, to the leading order, if we compute the energy current as

$$\mathbf{j}_E = \int \frac{d^3k}{(2\pi)^3} (E - E_F)\mathbf{v}\delta n. \quad (26)$$

The out-of-equilibrium part of the distribution function δn can be computed from Eq. (22) with $\partial n/\partial t = 0$, $\mathbf{E} = 0$, and $\partial n/\partial \mathbf{r} = (\nabla T)\partial n_F/\partial T$. As a result, we find for the tensor of thermal conductivity (defined as $(\mathbf{j}_E)_\alpha = -\kappa_{\alpha\beta}(\nabla T)_\beta$):

$$\kappa_{\alpha\beta} = \tau \int \frac{d^3k}{(2\pi)^3} v_\alpha v_\beta (E - E_F) \frac{\partial}{\partial T}n_F. \quad (27)$$

This expression has a structure similar to Eq. (25). At low temperature, both expressions are proportional to the integral over the Fermi surface:

$$\int dS \frac{v_\alpha v_\beta}{v} \quad (28)$$

(see Problem 1.2), and their ratio obeys the Wiedemann–Franz law (9).

In reality, the Wiedemann–Franz law is not always obeyed. The main limitation comes from the relaxation-time approximation. The validity of this approximation depends on the mechanism of relaxation and on the temperature (which determines the typical energy range of electrons). For elastic scattering on impurities, in isotropic systems, the relaxation-time approximation can be rigorously derived (we will not do it in our lectures, see [AM] Chapter 16). For electron-electron scattering, it is applicable only qualitatively. For electron-phonon scattering, it is invalid at low temperatures, but works at high temperatures. As a result, the Wiedemann–Franz law is often applicable at high temperatures (room temperature and above) and at very low temperatures, but does not apply in the intermediate temperature range. For illustration, see Table 1.6 in [AM]. For more details on the applicability of the relaxation-time approximation, see, e.g., the book by A. A. Abrikosov “Fundamentals of the Theory of Metals”.

Problem Set 1

Problem 1.1.

(a) Complete the derivation (21). Verify that for the Sommerfeld model (free fermions), the result reduces to the expression (8).

(b) For copper, compare the experimentally measured electronic specific heat with the free-fermion expression (8). Experimental data are available, e.g., in the papers

- D. W. Osborne, H. E. Flotow, and F. Schreiner, *Rev. Sci. Instrum.* **38**, 159 (1967).
- M. Hurley and B. C. Gerstein, *J. Chem. Thermodynamics* **6**, 787 (1974).

(remember that you need the low-temperature limit for comparison)

Problem 1.2

(a) Show that both expressions (25) and (27) are proportional to the integral over the Fermi surface

$$\int dS \frac{v_\alpha v_\beta}{v}.$$

(b) Calculate the coefficients and demonstrate the Wiedemann–Franz law (9).

(c) In the model of free fermions (Sommerfeld theory), show that the results for σ and κ reduce to Eqs. (2) and (3), respectively.

(d) Find in the literature the electrical conductivity of copper at room temperature. Within the free-fermion theory, estimate (by the order of magnitude) the relaxation time τ and the mean free path $l = \tau v_F$. How does it compare with the lattice constant? Is the quasiclassical approximation justified?