

# Chapter 1

## Boltzmann Transport

### 1.1 References

- H. Smith and H. H. Jensen, *Transport Phenomena*
- N. W. Ashcroft and N. D. Mermin, *Solid State Physics*, chapter 13.
- P. L. Taylor and O. Heinonen, *Condensed Matter Physics*, chapter 8.
- J. M. Ziman, *Principles of the Theory of Solids*, chapter 7.

### 1.2 Introduction

Transport is the phenomenon of currents flowing in response to applied fields. By ‘current’ we generally mean an electrical current  $\mathbf{j}$ , or thermal current  $\mathbf{j}_q$ . By ‘applied field’ we generally mean an electric field  $\mathcal{E}$  or a temperature gradient  $\nabla T$ . The currents and fields are linearly related, and it will be our goal to calculate the coefficients (known as transport coefficients) of these linear relations. Implicit in our discussion is the assumption that we are always dealing with systems near equilibrium.

## 1.3 Boltzmann Equation in Solids

### 1.3.1 Semiclassical Dynamics and Distribution Functions

The semiclassical dynamics of a wavepacket in a solid are described by the equations

$$\frac{d\mathbf{r}}{dt} = \mathbf{v}_n(\mathbf{k}) = \frac{1}{\hbar} \frac{\partial \varepsilon_n(\mathbf{k})}{\partial \mathbf{k}} \quad (1.1)$$

$$\frac{d\mathbf{k}}{dt} = -\frac{e}{\hbar} \mathbf{E}(\mathbf{r}, t) - \frac{e}{\hbar c} \mathbf{v}_n(\mathbf{k}) \times \mathbf{B}(\mathbf{r}, t) . \quad (1.2)$$

Here,  $n$  is the band index and  $\varepsilon_n(\mathbf{k})$  is the dispersion relation for band  $n$ . The wavevector is  $\mathbf{k}$  ( $\hbar\mathbf{k}$  is the ‘crystal momentum’), and  $\varepsilon_n(\mathbf{k})$  is periodic under  $\mathbf{k} \rightarrow \mathbf{k} + \mathbf{G}$ , where  $\mathbf{G}$  is any reciprocal lattice vector. These formulae are valid only at sufficiently weak fields. They neglect, for example, Zener tunneling processes in which an electron may change its band index as it traverses the Brillouin zone. We also neglect the spin-orbit interaction in our discussion.

We are of course interested in more than just a single electron, hence to that end let us consider the distribution function  $f_n(\mathbf{r}, \mathbf{k}, t)$ , defined such that<sup>1</sup>

$$f_{n\sigma}(\mathbf{r}, \mathbf{k}, t) \frac{d^3r d^3k}{(2\pi)^3} \equiv \# \text{ of electrons of spin } \sigma \text{ in band } n \text{ with positions within } d^3r \text{ of } \mathbf{r} \text{ and wavevectors within } d^3k \text{ of } \mathbf{k} \text{ at time } t. \quad (1.3)$$

Note that the distribution function is dimensionless. By performing integrals over the distribution function, we can obtain various physical quantities. For example, the current density at  $\mathbf{r}$  is given by

$$\mathbf{j}(\mathbf{r}, t) = -e \sum_{n,\sigma} \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} f_{n\sigma}(\mathbf{r}, \mathbf{k}, t) \mathbf{v}_n(\mathbf{k}) . \quad (1.4)$$

The symbol  $\hat{\Omega}$  in the above formula is to remind us that the wavevector integral is performed only over the first Brillouin zone.

We now ask how the distribution functions  $f_{n\sigma}(\mathbf{r}, \mathbf{k}, t)$  evolve in time. To simplify matters, we will consider a single band and drop the indices  $n\sigma$ . It is clear that in the absence of collisions, the distribution function must satisfy the continuity equation,

$$\frac{\partial f}{\partial t} + \nabla \cdot (\mathbf{u}f) = 0 . \quad (1.5)$$

This is just the condition of number conservation for electrons. Take care to note that  $\nabla$  and  $\mathbf{u}$  are *six*-dimensional *phase space* vectors:

$$\mathbf{u} = (\dot{x}, \dot{y}, \dot{z}, \dot{k}_x, \dot{k}_y, \dot{k}_z) \quad (1.6)$$

$$\nabla = \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}, \frac{\partial}{\partial k_x}, \frac{\partial}{\partial k_y}, \frac{\partial}{\partial k_z} \right) . \quad (1.7)$$

<sup>1</sup>We will assume three space dimensions. The discussion may be generalized to quasi-two dimensional and quasi-one dimensional systems as well.

Now note that as a consequence of the dynamics (1.1,1.2) that  $\nabla \cdot \mathbf{u} = 0$ , *i.e.* phase space flow is *incompressible*, provided that  $\varepsilon(\mathbf{k})$  is a function of  $\mathbf{k}$  alone, and not of  $\mathbf{r}$ . Thus, in the absence of collisions, we have

$$\frac{\partial f}{\partial t} + \mathbf{u} \cdot \nabla f = 0. \quad (1.8)$$

The differential operator  $D_t \equiv \partial_t + \mathbf{u} \cdot \nabla$  is sometimes called the ‘convective derivative’.

*EXERCISE:* Show that  $\nabla \cdot \mathbf{u} = 0$ .

Next we must consider the effect of collisions, which are not accounted for by the semi-classical dynamics. In a collision process, an electron with wavevector  $\mathbf{k}$  and one with wavevector  $\mathbf{k}'$  can instantaneously convert into a pair with wavevectors  $\mathbf{k} + \mathbf{q}$  and  $\mathbf{k}' - \mathbf{q}$  (modulo a reciprocal lattice vector  $\mathbf{G}$ ), where  $\mathbf{q}$  is the wavevector transfer. Note that the total wavevector is preserved (mod  $\mathbf{G}$ ). This means that  $D_t f \neq 0$ . Rather, we should write

$$\frac{\partial f}{\partial t} + \dot{\mathbf{r}} \cdot \frac{\partial f}{\partial \mathbf{r}} + \dot{\mathbf{k}} \cdot \frac{\partial f}{\partial \mathbf{k}} = \left( \frac{\partial f}{\partial t} \right)_{\text{coll}} \equiv \mathcal{I}_{\mathbf{k}}\{f\} \quad (1.9)$$

where the right side is known as the *collision integral*. The collision integral is in general a *function* of  $\mathbf{r}$ ,  $\mathbf{k}$ , and  $t$  and a *functional* of the distribution  $f$ . As the  $\mathbf{k}$ -dependence is the most important for our concerns, we will write  $\mathcal{I}_{\mathbf{k}}$  in order to make this dependence explicit. Some examples should help clarify the situation.

First, let’s consider a very simple model of the collision integral,

$$\mathcal{I}_{\mathbf{k}}\{f\} = -\frac{f(\mathbf{r}, \mathbf{k}, t) - f^0(\mathbf{r}, \mathbf{k})}{\tau(\varepsilon(\mathbf{k}))}. \quad (1.10)$$

This model is known as the *relaxation time approximation*. Here,  $f^0(\mathbf{r}, \mathbf{k})$  is a static distribution function which describes a *local equilibrium* at  $\mathbf{r}$ . The quantity  $\tau(\varepsilon(\mathbf{k}))$  is the *relaxation time*, which we allow to be energy-dependent. Note that the collision integral indeed depends on the variables  $(\mathbf{r}, \mathbf{k}, t)$ , and has a particularly simple functional dependence on the distribution  $f$ .

A more sophisticated model might invoke Fermi’s golden rule, Consider elastic scattering from a static potential  $\mathcal{U}(\mathbf{r})$  which induces transitions between different momentum states. We can then write

$$\mathcal{I}_{\mathbf{k}}\{f\} = \frac{2\pi}{\hbar} \sum_{\mathbf{k}' \in \hat{\Omega}} |\langle \mathbf{k}' | \mathcal{U} | \mathbf{k} \rangle|^2 (f_{\mathbf{k}'} - f_{\mathbf{k}}) \delta(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'}) \quad (1.11)$$

$$= \frac{2\pi}{\hbar V} \int_{\hat{\Omega}} \frac{d^3 k'}{(2\pi)^3} |\hat{\mathcal{U}}(\mathbf{k} - \mathbf{k}')|^2 (f_{\mathbf{k}'} - f_{\mathbf{k}}) \delta(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'}) \quad (1.12)$$

where we abbreviate  $f_{\mathbf{k}} \equiv f(\mathbf{r}, \mathbf{k}, t)$ . In deriving the last line we’ve used plane wave wave-

functions<sup>2</sup>  $\psi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r})/\sqrt{V}$ , as well as the result

$$\sum_{\mathbf{k} \in \hat{\Omega}} A(\mathbf{k}) = V \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} A(\mathbf{k}) \quad (1.13)$$

for smooth functions  $A(\mathbf{k})$ . Note the factor of  $V^{-1}$  in front of the integral in eqn. 1.12. What this tells us is that for a bounded localized potential  $\mathcal{U}(\mathbf{r})$ , the contribution to the collision integral is inversely proportional to the size of the system. This makes sense because the number of electrons scales as  $V$  but the potential is only appreciable over a region of volume  $\propto V^0$ . Later on, we shall consider a finite density of scatterers, writing  $\mathcal{U}(\mathbf{r}) = \sum_{i=1}^{N_{\text{imp}}} U(\mathbf{r} - \mathbf{R}_i)$ , where the impurity density  $n_{\text{imp}} = N_{\text{imp}}/V$  is finite, scaling as  $V^0$ . In this case  $\hat{\mathcal{U}}(\mathbf{k} - \mathbf{k}')$  apparently scales as  $V$ , which would mean  $\mathcal{I}_{\mathbf{k}}\{f\}$  scales as  $V$ , which is unphysical. As we shall see, the random positioning of the impurities means that the  $\mathcal{O}(V^2)$  contribution to  $|\hat{\mathcal{U}}(\mathbf{k} - \mathbf{k}')|^2$  is *incoherent* and averages out to zero. The coherent piece scales as  $V$ , canceling the  $V$  in the denominator of eqn. 1.12, resulting in a finite value for the collision integral in the thermodynamic limit (*i.e.* neither infinite nor infinitesimal).

Later on we will discuss electron-phonon scattering, which is *inelastic*. An electron with wavevector  $\mathbf{k}'$  can scatter into a state with wavevector  $\mathbf{k} = \mathbf{k}' - \mathbf{q} \bmod \mathbf{G}$  by absorption of a phonon of wavevector  $\mathbf{q}$  or emission of a phonon of wavevector  $-\mathbf{q}$ . Similarly, an electron of wavevector  $\mathbf{k}$  can scatter into the state  $\mathbf{k}'$  by emission of a phonon of wavevector  $-\mathbf{q}$  or absorption of a phonon of wavevector  $\mathbf{q}$ . The matrix element for these processes depends on  $\mathbf{k}$ ,  $\mathbf{k}'$ , and the polarization index of the phonon. Overall, energy is conserved. These considerations lead us to the following collision integral:

$$\begin{aligned} \mathcal{I}_{\mathbf{k}}\{f, n\} = & \frac{2\pi}{\hbar V} \sum_{\mathbf{k}', \lambda} |g_{\lambda}(\mathbf{k}, \mathbf{k}')|^2 \left\{ (1 - f_{\mathbf{k}}) f_{\mathbf{k}'} (1 + n_{\mathbf{q}, \lambda}) \delta(\varepsilon_{\mathbf{k}} + \hbar\omega_{\mathbf{q}, \lambda} - \varepsilon_{\mathbf{k}'}) \right. \\ & + (1 - f_{\mathbf{k}}) f_{\mathbf{k}'} n_{-\mathbf{q}, \lambda} \delta(\varepsilon_{\mathbf{k}} - \hbar\omega_{-\mathbf{q}, \lambda} - \varepsilon_{\mathbf{k}'}) \\ & - f_{\mathbf{k}} (1 - f_{\mathbf{k}'}) (1 + n_{-\mathbf{q}, \lambda}) \delta(\varepsilon_{\mathbf{k}} - \hbar\omega_{-\mathbf{q}, \lambda} - \varepsilon_{\mathbf{k}'}) \\ & \left. - f_{\mathbf{k}} (1 - f_{\mathbf{k}'}) n_{\mathbf{q}, \lambda} \delta(\varepsilon_{\mathbf{k}} + \hbar\omega_{\mathbf{q}, \lambda} - \varepsilon_{\mathbf{k}'}) \right\} \delta_{\mathbf{q}, \mathbf{k}' - \mathbf{k} \bmod \mathbf{G}}, \quad (1.14) \end{aligned}$$

which is a functional of both the electron distribution  $f_{\mathbf{k}}$  as well as the phonon distribution  $n_{\mathbf{q}, \lambda}$ . The four terms inside the curly brackets correspond, respectively, to cases (a) through (d) in fig. 1.1.

While collisions will violate crystal momentum conservation, they do not violate conservation of particle number. Hence we should have<sup>3</sup>

$$\int d^3r \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} \mathcal{I}_{\mathbf{k}}\{f\} = 0. \quad (1.15)$$

<sup>2</sup>Rather than plane waves, we should use Bloch waves  $\psi_{n\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) u_{n\mathbf{k}}(\mathbf{r})$ , where cell function  $u_{n\mathbf{k}}(\mathbf{r})$  satisfies  $u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$ , where  $\mathbf{R}$  is any direct lattice vector. Plane waves do not contain the cell functions, although they do exhibit Bloch periodicity  $\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = \exp(i\mathbf{k} \cdot \mathbf{R}) \psi_{n\mathbf{k}}(\mathbf{r})$ .

<sup>3</sup>If collisions are purely local, then  $\int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} \mathcal{I}_{\mathbf{k}}\{f\} = 0$  at every point  $\mathbf{r}$  in space.

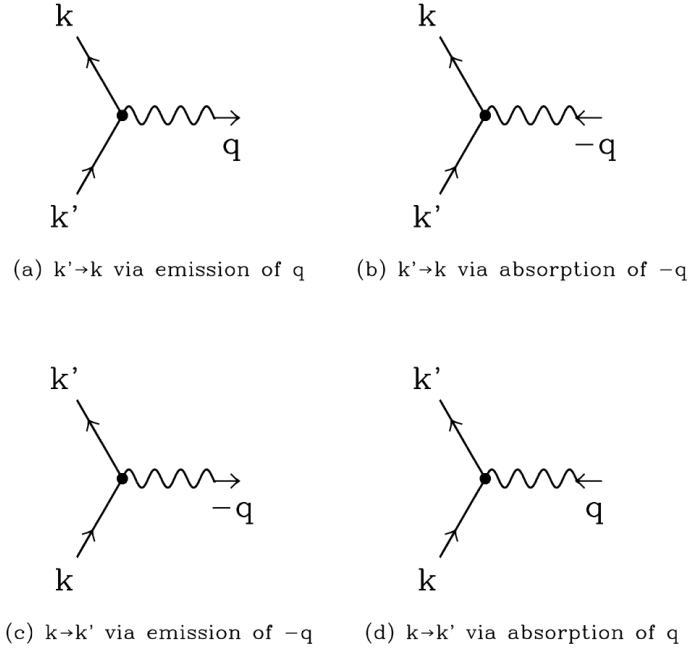


Figure 1.1: Electron-phonon vertices.

The total particle number,

$$N = \int_{\hat{\Omega}} d^3r \int \frac{d^3k}{(2\pi)^3} f(\mathbf{r}, \mathbf{k}, t) \quad (1.16)$$

is a *collisional invariant* - a quantity which is preserved in the collision process. Other collisional invariants include energy (when all sources are accounted for), spin (total spin), and crystal momentum (if there is no breaking of lattice translation symmetry)<sup>4</sup>. Consider a function  $F(\mathbf{r}, \mathbf{k})$  of position and wavevector. Its average value is

$$\bar{F}(t) = \int_{\hat{\Omega}} d^3r \int \frac{d^3k}{(2\pi)^3} F(\mathbf{r}, \mathbf{k}) f(\mathbf{r}, \mathbf{k}, t) . \quad (1.17)$$

Taking the time derivative,

$$\begin{aligned} \frac{d\bar{F}}{dt} &= \frac{\partial \bar{F}}{\partial t} = \int_{\hat{\Omega}} d^3r \int \frac{d^3k}{(2\pi)^3} F(\mathbf{r}, \mathbf{k}) \left\{ -\frac{\partial}{\partial \mathbf{r}} \cdot (\dot{\mathbf{r}} f) - \frac{\partial}{\partial \mathbf{k}} \cdot (\dot{\mathbf{k}} f) + \mathcal{I}_{\mathbf{k}}\{f\} \right\} \\ &= \int_{\hat{\Omega}} d^3r \int \frac{d^3k}{(2\pi)^3} \left\{ \left[ \frac{\partial F}{\partial \mathbf{r}} \cdot \frac{d\mathbf{r}}{dt} + \frac{\partial F}{\partial \mathbf{k}} \cdot \frac{d\mathbf{k}}{dt} \right] f + F \mathcal{I}_{\mathbf{k}}\{f\} \right\} . \end{aligned} \quad (1.18)$$

<sup>4</sup>Note that the relaxation time approximation violates all such conservation laws. Within the relaxation time approximation, there are no collisional invariants.

Hence, if  $F$  is preserved by the dynamics between collisions, then

$$\frac{d\bar{F}}{dt} = \int d^3r \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} F \mathcal{I}_{\mathbf{k}}\{f\}, \quad (1.19)$$

which says that  $\bar{F}(t)$  changes only as a result of collisions. If  $F$  is a collisional invariant, then  $\dot{\bar{F}} = 0$ . This is the case when  $F = 1$ , in which case  $\bar{F}$  is the total number of particles, or when  $F = \varepsilon(\mathbf{k})$ , in which case  $\bar{F}$  is the total energy.

### 1.3.2 Local Equilibrium

The equilibrium Fermi distribution,

$$f^0(\mathbf{k}) = \left\{ \exp\left(\frac{\varepsilon(\mathbf{k}) - \mu}{k_{\text{B}}T}\right) + 1 \right\}^{-1} \quad (1.20)$$

is a space-independent and time-independent solution to the Boltzmann equation. Since collisions act *locally* in space, they act on short time scales to establish a *local equilibrium* described by a distribution function

$$\boxed{f^0(\mathbf{r}, \mathbf{k}, t) = \left\{ \exp\left(\frac{\varepsilon(\mathbf{k}) - \mu(\mathbf{r}, t)}{k_{\text{B}}T(\mathbf{r}, t)}\right) + 1 \right\}^{-1}} \quad (1.21)$$

This is, however, not a solution to the full Boltzmann equation due to the ‘streaming terms’  $\dot{\mathbf{r}} \cdot \partial_{\mathbf{r}} + \dot{\mathbf{k}} \cdot \partial_{\mathbf{k}}$  in the convective derivative. These, though, act on longer time scales than those responsible for the establishment of local equilibrium. To obtain a solution, we write

$$f(\mathbf{r}, \mathbf{k}, t) = f^0(\mathbf{r}, \mathbf{k}, t) + \delta f(\mathbf{r}, \mathbf{k}, t) \quad (1.22)$$

and solve for the deviation  $\delta f(\mathbf{r}, \mathbf{k}, t)$ . We will assume  $\mu = \mu(\mathbf{r})$  and  $T = T(\mathbf{r})$  are time-independent. We first compute the differential of  $f^0$ ,

$$\begin{aligned} df^0 &= k_{\text{B}}T \frac{\partial f^0}{\partial \varepsilon} d\left(\frac{\varepsilon - \mu}{k_{\text{B}}T}\right) \\ &= k_{\text{B}}T \frac{\partial f^0}{\partial \varepsilon} \left\{ -\frac{d\mu}{k_{\text{B}}T} - \frac{(\varepsilon - \mu)dT}{k_{\text{B}}T^2} + \frac{d\varepsilon}{k_{\text{B}}T} \right\} \\ &= -\frac{\partial f^0}{\partial \varepsilon} \left\{ \frac{\partial \mu}{\partial \mathbf{r}} \cdot d\mathbf{r} + \frac{\varepsilon - \mu}{T} \frac{\partial T}{\partial \mathbf{r}} \cdot d\mathbf{r} - \frac{\partial \varepsilon}{\partial \mathbf{k}} \cdot d\mathbf{k} \right\}, \end{aligned} \quad (1.23)$$

from which we read off

$$\frac{\partial f^0}{\partial \mathbf{r}} = \left\{ \frac{\partial \mu}{\partial \mathbf{r}} + \frac{\varepsilon - \mu}{T} \frac{\partial T}{\partial \mathbf{r}} \right\} \left( -\frac{\partial f^0}{\partial \varepsilon} \right) \quad (1.24)$$

$$\frac{\partial f^0}{\partial \mathbf{k}} = \hbar \mathbf{v} \frac{\partial f^0}{\partial \varepsilon}. \quad (1.25)$$

We thereby obtain

$$\boxed{\frac{\partial \delta f}{\partial t} + \mathbf{v} \cdot \nabla \delta f - \frac{e}{\hbar} \left[ \mathbf{E} + \frac{1}{c} \mathbf{v} \times \mathbf{B} \right] \cdot \frac{\partial \delta f}{\partial \mathbf{k}} + \mathbf{v} \cdot \left[ e \mathcal{E} + \frac{\varepsilon - \mu}{T} \nabla T \right] \left( -\frac{\partial f^0}{\partial \varepsilon} \right) = \mathcal{I}_{\mathbf{k}} \{ f^0 + \delta f \}} \quad (1.26)$$

where  $\mathcal{E} = -\nabla(\phi - \mu/e)$  is the gradient of the ‘electrochemical potential’; we’ll henceforth refer to  $\mathcal{E}$  as the electric field. Eqn (1.26) is a nonlinear integrodifferential equation in  $\delta f$ , with the nonlinearity coming from the collision integral. (In some cases, such as impurity scattering, the collision integral may be a linear functional.) We will solve a *linearized* version of this equation, assuming the system is always close to a state of local equilibrium.

Note that the inhomogeneous term in (1.26) involves the electric field and the temperature gradient  $\nabla T$ . This means that  $\delta f$  is proportional to these quantities, and if they are small then  $\delta f$  is small. The gradient of  $\delta f$  is then of second order in smallness, since the external fields  $\phi - \mu/e$  and  $T$  are assumed to be slowly varying in space. To lowest order in smallness, then, we obtain the following *linearized Boltzmann equation*:

$$\boxed{\frac{\partial \delta f}{\partial t} - \frac{e}{\hbar c} \mathbf{v} \times \mathbf{B} \cdot \frac{\partial \delta f}{\partial \mathbf{k}} + \mathbf{v} \cdot \left[ e \mathcal{E} + \frac{\varepsilon - \mu}{T} \nabla T \right] \left( -\frac{\partial f^0}{\partial \varepsilon} \right) = \mathcal{L} \delta f} \quad (1.27)$$

where  $\mathcal{L} \delta f$  is the *linearized collision integral*;  $\mathcal{L}$  is a linear operator acting on  $\delta f$  (we suppress denoting the  $\mathbf{k}$  dependence of  $\mathcal{L}$ ). Note that we have not assumed that  $\mathbf{B}$  is small. Indeed later on we will derive expressions for high  $B$  transport coefficients.

## 1.4 Conductivity of Normal Metals

### 1.4.1 Relaxation Time Approximation

Consider a normal metal in the presence of an electric field  $\mathcal{E}$ . We’ll assume  $\mathbf{B} = 0$ ,  $\nabla T = 0$ , and also that  $\mathcal{E}$  is spatially uniform as well. This in turn guarantees that  $\delta f$  itself is spatially uniform. The Boltzmann equation then reduces to

$$\frac{\partial \delta f}{\partial t} - \frac{\partial f^0}{\partial \varepsilon} e \mathbf{v} \cdot \mathcal{E} = \mathcal{I}_{\mathbf{k}} \{ f^0 + \delta f \}. \quad (1.28)$$

We’ll solve this by adopting the relaxation time approximation for  $\mathcal{I}_{\mathbf{k}} \{ f \}$ :

$$\mathcal{I}_{\mathbf{k}} \{ f \} = -\frac{f - f^0}{\tau} = -\frac{\delta f}{\tau}, \quad (1.29)$$

where  $\tau$ , which may be  $\mathbf{k}$ -dependent, is the *relaxation time*. In the absence of any fields or temperature and electrochemical potential gradients, the Boltzmann equation becomes  $\dot{\delta f} = -\delta f/\tau$ , with the solution  $\delta f(t) = \delta f(0) \exp(-t/\tau)$ . The distribution thereby relaxes to the equilibrium one on the scale of  $\tau$ .

Writing  $\mathcal{E}(t) = \mathcal{E} e^{-i\omega t}$ , we solve

$$\frac{\partial \delta f(\mathbf{k}, t)}{\partial t} - e \mathbf{v}(\mathbf{k}) \cdot \mathcal{E} e^{-i\omega t} \frac{\partial f^0}{\partial \varepsilon} = -\frac{\delta f(\mathbf{k}, t)}{\tau(\varepsilon(\mathbf{k}))} \quad (1.30)$$

and obtain

$$\delta f(\mathbf{k}, t) = \frac{e \mathcal{E} \cdot \mathbf{v}(\mathbf{k}) \tau(\varepsilon(\mathbf{k}))}{1 - i\omega \tau(\varepsilon(\mathbf{k}))} \frac{\partial f^0}{\partial \varepsilon} e^{-i\omega t} . \quad (1.31)$$

The equilibrium distribution  $f^0(\mathbf{k})$  results in zero current, since  $f^0(-\mathbf{k}) = f^0(\mathbf{k})$ . Thus, the current density is given by the expression

$$\begin{aligned} j^\alpha(\mathbf{r}, t) &= -2e \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} \delta f v^\alpha \\ &= 2e^2 \mathcal{E}^\beta e^{-i\omega t} \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} \frac{\tau(\varepsilon(\mathbf{k})) v^\alpha(\mathbf{k}) v^\beta(\mathbf{k})}{1 - i\omega \tau(\varepsilon(\mathbf{k}))} \left( -\frac{\partial f^0}{\partial \varepsilon} \right) . \end{aligned} \quad (1.32)$$

In the above calculation, the factor of two arises from summing over spin polarizations. The conductivity tensor is defined by the linear relation  $j^\alpha(\omega) = \sigma_{\alpha\beta}(\omega) \mathcal{E}^\beta(\omega)$ . We have thus derived an expression for the conductivity tensor,

$$\boxed{\sigma_{\alpha\beta}(\omega) = 2e^2 \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} \frac{\tau(\varepsilon(\mathbf{k})) v^\alpha(\mathbf{k}) v^\beta(\mathbf{k})}{1 - i\omega \tau(\varepsilon(\mathbf{k}))} \left( -\frac{\partial f^0}{\partial \varepsilon} \right)} \quad (1.33)$$

Note that the conductivity is a property of the *Fermi surface*. For  $k_B T \ll \varepsilon_F$ , we have  $-\partial f^0/\partial \varepsilon \approx \delta(\varepsilon_F - \varepsilon(\mathbf{k}))$  and the above integral is over the Fermi surface alone. Explicitly, we change variables to energy  $\varepsilon$  and coordinates along a constant energy surface, writing

$$d^3k = \frac{d\varepsilon dS_\varepsilon}{|\partial \varepsilon / \partial \mathbf{k}|} = \frac{d\varepsilon dS_\varepsilon}{\hbar |\mathbf{v}|} , \quad (1.34)$$

where  $dS_\varepsilon$  is the differential area on the constant energy surface  $\varepsilon(\mathbf{k}) = \varepsilon$ , and  $\mathbf{v}(\mathbf{k}) = \hbar^{-1} \nabla_{\mathbf{k}} \varepsilon(\mathbf{k})$  is the velocity. For  $T \ll T_F$ , then,

$$\sigma_{\alpha\beta}(\omega) = \frac{e^2}{4\pi^3 \hbar} \frac{\tau(\varepsilon_F)}{1 - i\omega \tau(\varepsilon_F)} \int dS_F \frac{v^\alpha(\mathbf{k}) v^\beta(\mathbf{k})}{|\mathbf{v}(\mathbf{k})|} . \quad (1.35)$$

For free electrons in a parabolic band, we write  $\varepsilon(\mathbf{k}) = \hbar^2 \mathbf{k}^2 / 2m^*$ , so  $v^\alpha(\mathbf{k}) = \hbar \mathbf{k}^\alpha / m^*$ . To further simplify matters, let us assume that  $\tau$  is constant, or at least very slowly varying in the vicinity of the Fermi surface. We find

$$\sigma_{\alpha\beta}(\omega) = \delta_{\alpha\beta} \frac{2}{3m^*} \frac{e^2 \tau}{1 - i\omega \tau} \int d\varepsilon g(\varepsilon) \varepsilon \left( -\frac{\partial f^0}{\partial \varepsilon} \right) , \quad (1.36)$$

where  $g(\varepsilon)$  is the *density of states*,

$$g(\varepsilon) = 2 \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} \delta(\varepsilon - \varepsilon(\mathbf{k})) . \quad (1.37)$$



The (three-dimensional) parabolic band density of states is found to be

$$g(\varepsilon) = \frac{(2m^*)^{3/2}}{2\pi^2\hbar^3} \sqrt{\varepsilon} \Theta(\varepsilon), \quad (1.38)$$

where  $\Theta(x)$  is the step function. In fact, integrating (1.36) by parts, we only need to know about the  $\sqrt{\varepsilon}$  dependence in  $g(\varepsilon)$ , and not the details of its prefactor:

$$\begin{aligned} \int d\varepsilon \varepsilon g(\varepsilon) \left( -\frac{\partial f^0}{\partial \varepsilon} \right) &= \int d\varepsilon f^0(\varepsilon) \frac{\partial}{\partial \varepsilon} (\varepsilon g(\varepsilon)) \\ &= \frac{3}{2} \int d\varepsilon g(\varepsilon) f^0(\varepsilon) = \frac{3}{2} n, \end{aligned} \quad (1.39)$$

where  $n = N/V$  is the electron number density for the conduction band. The final result for the conductivity tensor is

$$\boxed{\sigma_{\alpha\beta}(\omega) = \frac{ne^2\tau}{m^*} \frac{\delta_{\alpha\beta}}{1 - i\omega\tau}} \quad (1.40)$$

This is called the *Drude model* of electrical conduction in metals. The dissipative part of the conductivity is  $\text{Re } \sigma$ . Writing  $\sigma_{\alpha\beta} = \sigma \delta_{\alpha\beta}$  and separating into real and imaginary parts  $\sigma = \sigma' + i\sigma''$ , we have

$$\sigma'(\omega) = \frac{ne^2\tau}{m^*} \frac{1}{1 + \omega^2\tau^2}. \quad (1.41)$$

The peak at  $\omega = 0$  is known as the *Drude peak*.

Here's an elementary derivation of this result. Let  $\mathbf{p}(t)$  be the momentum of an electron, and solve the equation of motion

$$\frac{d\mathbf{p}}{dt} = -\frac{\mathbf{p}}{\tau} - e\mathbf{E} e^{-i\omega t} \quad (1.42)$$

to obtain

$$\mathbf{p}(t) = -\frac{e\tau\mathbf{E}}{1 - i\omega\tau} e^{-i\omega t} + \left[ \mathbf{p}(0) + \frac{e\tau\mathbf{E}}{1 - i\omega\tau} \right] e^{-t/\tau}. \quad (1.43)$$

The second term above is a transient solution to the homogeneous equation  $\dot{\mathbf{p}} + \mathbf{p}/\tau = 0$ . At long times, then, the current  $\mathbf{j} = -ne\mathbf{p}/m^*$  is

$$\mathbf{j}(t) = \frac{ne^2\tau}{m^*(1 - i\omega\tau)} \mathbf{E} e^{-i\omega t}. \quad (1.44)$$

In the Boltzmann equation approach, however, we understand that  $n$  is the conduction electron density, which does not include contributions from filled bands.

In solids the effective mass  $m^*$  typically varies over a small range:  $m^* \approx (0.1 - 1) m_e$ . The two factors which principally determine the conductivity are then the carrier density  $n$  and the scattering time  $\tau$ . The *mobility*  $\mu$ , defined as the ratio  $\sigma(\omega = 0)/ne$ , is thus (roughly) independent of carrier density<sup>5</sup>. Since  $\mathbf{j} = -ne\mathbf{v} = \sigma\mathbf{E}$ , where  $\mathbf{v}$  is an average carrier velocity, we have  $\mathbf{v} = -\mu\mathbf{E}$ , and the mobility  $\mu = e\tau/m^*$  measures the ratio of the carrier velocity to the applied electric field.

<sup>5</sup>Inasmuch as both  $\tau$  and  $m^*$  can depend on the Fermi energy,  $\mu$  is not completely independent of carrier density.

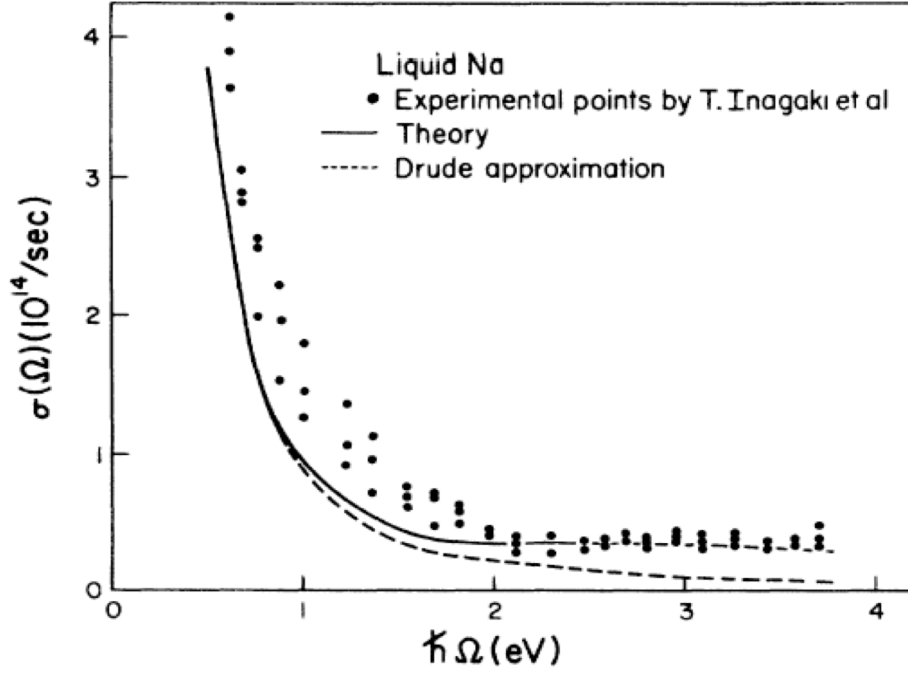


Figure 1.2: Frequency-dependent conductivity of liquid sodium by T. Inagaki *et al*, *Phys. Rev. B* **13**, 5610 (1976).

### 1.4.2 Optical Reflectivity of Metals and Semiconductors

What happens when an electromagnetic wave is incident on a metal? Inside the metal we have Maxwell's equations,

$$\nabla \times \mathbf{H} = \frac{4\pi}{c} \mathbf{j} + \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t} \quad \Longrightarrow \quad i\mathbf{k} \times \mathbf{B} = \left( \frac{4\pi\sigma}{c} - \frac{i\omega}{c} \right) \mathbf{E} \quad (1.45)$$

$$\nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} \quad \Longrightarrow \quad i\mathbf{k} \times \mathbf{E} = \frac{i\omega}{c} \mathbf{B} \quad (1.46)$$

$$\nabla \cdot \mathbf{E} = \nabla \cdot \mathbf{B} = 0 \quad \Longrightarrow \quad i\mathbf{k} \cdot \mathbf{E} = i\mathbf{k} \cdot \mathbf{B} = 0, \quad (1.47)$$

where we've assumed  $\mu = \epsilon = 1$  inside the metal, ignoring polarization due to virtual interband transitions (*i.e.* from core electrons). Hence,

$$\mathbf{k}^2 = \frac{\omega^2}{c^2} + \frac{4\pi i\omega}{c^2} \sigma(\omega) \quad (1.48)$$

$$= \frac{\omega^2}{c^2} + \frac{\omega_p^2}{c^2} \frac{i\omega\tau}{1 - i\omega\tau} \equiv \epsilon(\omega) \frac{\omega^2}{c^2}, \quad (1.49)$$

where  $\omega_p = \sqrt{4\pi n e^2 / m^*}$  is the *plasma frequency* for the conduction band. The dielectric function,

$$\epsilon(\omega) = 1 + \frac{4\pi i\sigma(\omega)}{\omega} = 1 + \frac{\omega_p^2}{\omega^2} \frac{i\omega\tau}{1 - i\omega\tau} \quad (1.50)$$

determines the complex refractive index,  $N(\omega) = \sqrt{\epsilon(\omega)}$ , leading to the electromagnetic dispersion relation  $k = N(\omega) \omega/c$ .

Consider a wave normally incident upon a metallic surface normal to  $\hat{z}$ . In the vacuum ( $z < 0$ ), we write

$$\mathbf{E}(\mathbf{r}, t) = E_1 \hat{\mathbf{x}} e^{i\omega z/c} e^{-i\omega t} + E_2 \hat{\mathbf{x}} e^{-i\omega z/c} e^{-i\omega t} \quad (1.51)$$

$$\mathbf{B}(\mathbf{r}, t) = \frac{c}{i\omega} \nabla \times \mathbf{E} = E_1 \hat{\mathbf{y}} e^{i\omega z/c} e^{-i\omega t} - E_2 \hat{\mathbf{y}} e^{-i\omega z/c} e^{-i\omega t} \quad (1.52)$$

while in the metal ( $z > 0$ ),

$$\mathbf{E}(\mathbf{r}, t) = E_3 \hat{\mathbf{x}} e^{iN\omega z/c} e^{-i\omega t} \quad (1.53)$$

$$\mathbf{B}(\mathbf{r}, t) = \frac{c}{i\omega} \nabla \times \mathbf{E} = N E_3 \hat{\mathbf{y}} e^{iN\omega z/c} e^{-i\omega t} \quad (1.54)$$

Continuity of  $\mathbf{E} \times \hat{\mathbf{n}}$  gives  $E_1 + E_2 = E_3$ . Continuity of  $\mathbf{H} \times \hat{\mathbf{n}}$  gives  $E_1 - E_2 = N E_3$ . Thus,

$$\frac{E_2}{E_1} = \frac{1 - N}{1 + N} \quad , \quad \frac{E_3}{E_1} = \frac{2}{1 + N} \quad (1.55)$$

and the reflection and transmission coefficients are

$$R(\omega) = \left| \frac{E_2}{E_1} \right|^2 = \left| \frac{1 - N(\omega)}{1 + N(\omega)} \right|^2 \quad (1.56)$$

$$T(\omega) = \left| \frac{E_3}{E_1} \right|^2 = \frac{4}{|1 + N(\omega)|^2} . \quad (1.57)$$

We've now solved the electromagnetic boundary value problem.

*Typical values* – For a metal with  $n = 10^{22} \text{ cm}^3$  and  $m^* = m_e$ , the plasma frequency is  $\omega_p = 5.7 \times 10^{15} \text{ s}^{-1}$ . The scattering time varies considerably as a function of temperature. In high purity copper at  $T = 4 \text{ K}$ ,  $\tau \approx 2 \times 10^{-9} \text{ s}$  and  $\omega_p \tau \approx 10^7$ . At  $T = 300 \text{ K}$ ,  $\tau \approx 2 \times 10^{-14} \text{ s}$  and  $\omega_p \tau \approx 100$ . In either case,  $\omega_p \tau \gg 1$ . There are then three regimes to consider.

- $\omega\tau \ll 1 \ll \omega_p\tau$ :

We may approximate  $1 - i\omega\tau \approx 1$ , hence

$$\begin{aligned} N^2(\omega) &= 1 + \frac{i\omega_p^2\tau}{\omega(1 - i\omega\tau)} \approx \frac{i\omega_p^2\tau}{\omega} \\ N(\omega) &\approx \frac{1 + i}{\sqrt{2}} \left( \frac{\omega_p^2\tau}{\omega} \right)^{1/2} \implies R \approx 1 - \frac{2\sqrt{2\omega\tau}}{\omega_p\tau} . \end{aligned} \quad (1.58)$$

Hence  $R \approx 1$  and the metal reflects.

- $1 \ll \omega\tau \ll \omega_p\tau$ :

In this regime,

$$N^2(\omega) \approx 1 - \frac{\omega_p^2}{\omega^2} + \frac{i\omega_p^2}{\omega^3\tau} \quad (1.59)$$

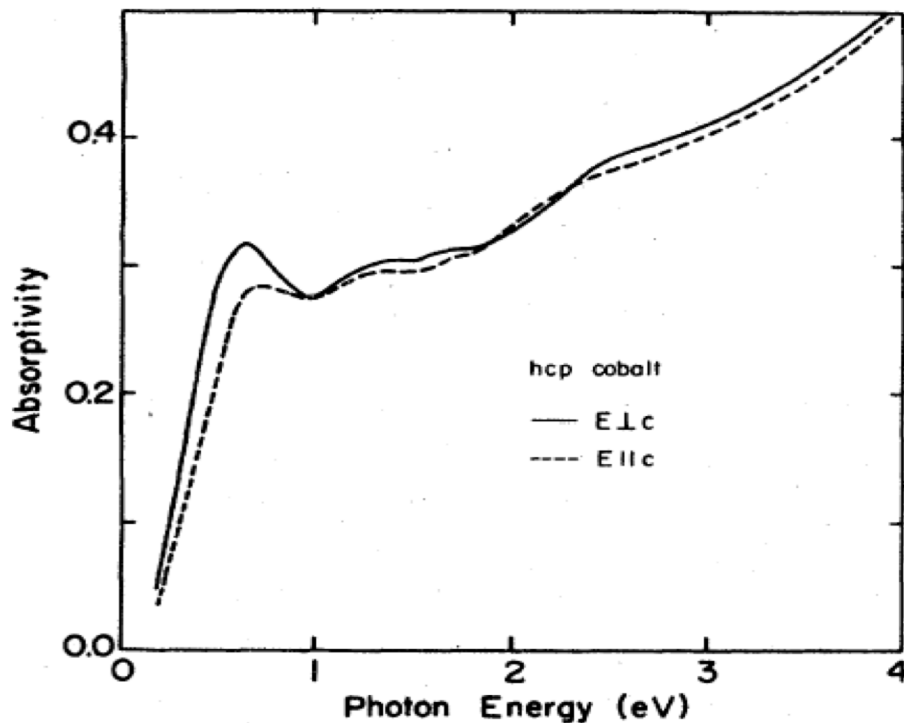


Figure 1.3: Frequency-dependent absorption of hcp cobalt by J. Weaver *et al.*, *Phys. Rev. B* **19**, 3850 (1979).

which is almost purely real and negative. Hence  $N$  is almost purely imaginary and  $R \approx 1$ . (To lowest nontrivial order,  $R = 1 - 2/\omega_p\tau$ .) Still high reflectivity.

- $1 \ll \omega_p\tau \ll \omega\tau$ :

Here we have

$$N^2(\omega) \approx 1 - \frac{\omega_p^2}{\omega^2} \implies R = \frac{\omega_p}{2\omega} \quad (1.60)$$

and  $R \ll 1$  – the metal is transparent at frequencies large compared to  $\omega_p$ .

### 1.4.3 Optical Conductivity of Semiconductors

In our analysis of the electrodynamics of metals, we assumed that the dielectric constant due to all the filled bands was simply  $\epsilon = 1$ . This is not quite right. We should instead have written

$$\mathbf{k}^2 = \epsilon_\infty \frac{\omega^2}{c^2} + \frac{4\pi i\omega\sigma(\omega)}{c^2} \quad (1.61)$$

$$\epsilon(\omega) = \epsilon_\infty \left\{ 1 + \frac{\omega_p^2}{\omega^2} \frac{i\omega\tau}{1 - i\omega\tau} \right\}, \quad (1.62)$$

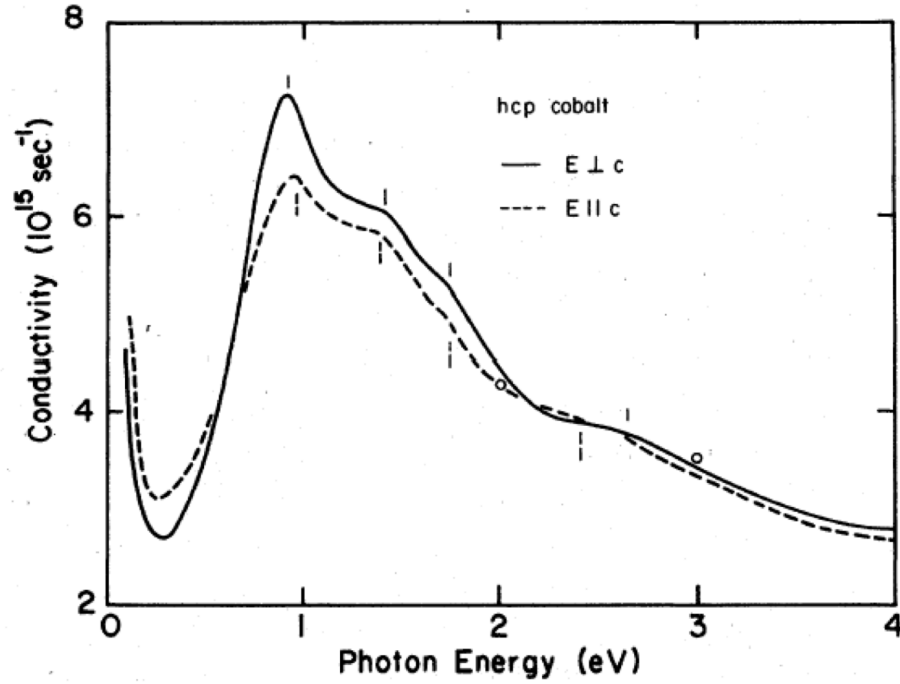


Figure 1.4: Frequency-dependent conductivity of hcp cobalt by J. Weaver *et al.*, *Phys. Rev. B* **19**, 3850 (1979). This curve is derived from the data of fig. 1.3 using a Kramers-Krönig transformation. A Drude peak is observed at low frequencies. At higher frequencies, interband effects dominate.

where  $\epsilon_\infty$  is the dielectric constant due to virtual transitions to fully occupied (*i.e.* core) and fully unoccupied bands, at a frequency small compared to the interband frequency. The plasma frequency is now defined as

$$\omega_p = \left( \frac{4\pi n e^2}{m^* \epsilon_\infty} \right)^{1/2} \quad (1.63)$$

where  $n$  is the conduction electron density. Note that  $\epsilon(\omega \rightarrow \infty) = \epsilon_\infty$ , although again this is only true for  $\omega$  smaller than the gap to neighboring bands. It turns out that for insulators one can write

$$\epsilon_\infty \simeq 1 + \frac{\omega_{pv}^2}{\omega_g^2} \quad (1.64)$$

where  $\omega_{pv} = \sqrt{4\pi n_v e^2 / m_e}$ , with  $n_v$  the number density of valence electrons, and  $\omega_g$  is the energy gap between valence and conduction bands. In semiconductors such as Si and Ge,  $\omega_g \sim 4$  eV, while  $\omega_{pv} \sim 16$  eV, hence  $\epsilon_\infty \sim 17$ , which is in rough agreement with the experimental values of  $\sim 12$  for Si and  $\sim 16$  for Ge. In metals, the band gaps generally are considerably larger.

There are some important differences to consider in comparing semiconductors and metals:

- The carrier density  $n$  typically is much smaller in semiconductors than in metals, ranging from  $n \sim 10^{16} \text{ cm}^{-3}$  in intrinsic (*i.e.* undoped, thermally excited at room temperature) materials to  $n \sim 10^{19} \text{ cm}^{-3}$  in doped materials.
- $\epsilon_\infty \approx 10 - 20$  and  $m^*/m_e \approx 0.1$ . The product  $\epsilon_\infty m^*$  thus differs only slightly from its free electron value.

Since  $n_{\text{semi}} \lesssim 10^{-4} n_{\text{metal}}$ , one has

$$\omega_p^{\text{semi}} \approx 10^{-2} \omega_p^{\text{metal}} \approx 10^{-14} \text{ s} . \quad (1.65)$$

In high purity semiconductors the mobility  $\mu = e\tau/m^* \gtrsim 10^5 \text{ cm}^2/\text{vs}$  the low temperature scattering time is typically  $\tau \approx 10^{-11} \text{ s}$ . Thus, for  $\omega \gtrsim 3 \times 10^{15} \text{ s}^{-1}$  in the optical range, we have  $\omega\tau \gg \omega_p\tau \gg 1$ , in which case  $N(\omega) \approx \sqrt{\epsilon_\infty}$  and the reflectivity is

$$R = \left| \frac{1 - \sqrt{\epsilon_\infty}}{1 + \sqrt{\epsilon_\infty}} \right|^2 . \quad (1.66)$$

Taking  $\epsilon_\infty = 10$ , one obtains  $R = 0.27$ , which is high enough so that polished Si wafers appear shiny.

#### 1.4.4 Optical Conductivity and the Fermi Surface

At high frequencies, when  $\omega\tau \gg 1$ , our expression for the conductivity, eqn. (1.33), yields

$$\sigma(\omega) = \frac{ie^2}{12\pi^3\hbar\omega} \int d\varepsilon \left( -\frac{\partial f^0}{\partial \varepsilon} \right) \int dS_\varepsilon |\mathbf{v}(\mathbf{k})| , \quad (1.67)$$

where we have presumed sufficient crystalline symmetry to guarantee that  $\sigma_{\alpha\beta} = \sigma \delta_{\alpha\beta}$  is diagonal. In the isotropic case, and at temperatures low compared with  $T_F$ , the integral over the Fermi surface gives  $4\pi k_F^2 v_F = 12\pi^3 \hbar n/m^*$ , whence  $\sigma = ine^2/m^*\omega$ , which is the large frequency limit of our previous result. For a general Fermi surface, we can define

$$\sigma(\omega \gg \tau^{-1}) \equiv \frac{ine^2}{m_{\text{opt}}\omega} \quad (1.68)$$

where the *optical mass*  $m_{\text{opt}}$  is given by

$$\frac{1}{m_{\text{opt}}} = \frac{1}{12\pi^3\hbar n} \int d\varepsilon \left( -\frac{\partial f^0}{\partial \varepsilon} \right) \int dS_\varepsilon |\mathbf{v}(\mathbf{k})| . \quad (1.69)$$

Note that at high frequencies  $\sigma(\omega)$  is purely imaginary. What does this mean? If

$$\mathcal{E}(t) = \mathcal{E} \cos(\omega t) = \frac{1}{2} \mathcal{E} (e^{-i\omega t} + e^{+i\omega t}) \quad (1.70)$$

then

$$\begin{aligned} \mathbf{j}(t) &= \frac{1}{2} \mathcal{E} \{ \sigma(\omega) e^{-i\omega t} + \sigma(-\omega) e^{+i\omega t} \} \\ &= \frac{ne^2}{m_{\text{opt}}\omega} \mathcal{E} \sin(\omega t) , \end{aligned} \quad (1.71)$$

where we have invoked  $\sigma(-\omega) = \sigma^*(\omega)$ . The current is therefore  $90^\circ$  out of phase with the voltage, and the average over a cycle  $\langle \mathbf{j}(t) \cdot \mathcal{E}(t) \rangle = 0$ . Recall that we found metals to be transparent for  $\omega \gg \omega_p \gg \tau^{-1}$ .

At zero temperature, the optical mass is given by

$$\frac{1}{m_{\text{opt}}} = \frac{1}{12\pi^3 \hbar n} \int dS_{\text{F}} |\mathbf{v}(\mathbf{k})| . \quad (1.72)$$

The density of states,  $g(\varepsilon_{\text{F}})$ , is

$$g(\varepsilon_{\text{F}}) = \frac{1}{4\pi^3 \hbar} \int dS_{\text{F}} |\mathbf{v}(\mathbf{k})|^{-1} , \quad (1.73)$$

from which one can define the thermodynamic effective mass  $m_{\text{th}}^*$ , appealing to the low temperature form of the specific heat,

$$c_V = \frac{\pi^2}{3} k_{\text{B}}^2 T g(\varepsilon_{\text{F}}) \equiv \frac{m_{\text{th}}^*}{m_{\text{e}}} c_V^0 , \quad (1.74)$$

where

$$c_V^0 \equiv \frac{m_{\text{e}} k_{\text{B}}^2 T}{3\hbar^2} (3\pi^2 n)^{1/3} \quad (1.75)$$

is the specific heat for a free electron gas of density  $n$ . Thus,

$$m_{\text{th}}^* = \frac{\hbar}{4\pi(3\pi^2 n)^{1/3}} \int dS_{\text{F}} |\mathbf{v}(\mathbf{k})|^{-1} \quad (1.76)$$

## 1.5 Calculation of the Scattering Time

### 1.5.1 Potential Scattering and Fermi's Golden Rule

Let us go beyond the relaxation time approximation and calculate the scattering time  $\tau$  from first principles. We will concern ourselves with scattering of electrons from crystalline impurities. We begin with Fermi's Golden Rule<sup>6</sup>,

$$\mathcal{I}_{\mathbf{k}}\{f\} = \frac{2\pi}{\hbar} \sum_{\mathbf{k}'} |\langle \mathbf{k}' | \mathcal{U} | \mathbf{k} \rangle|^2 (f_{\mathbf{k}'} - f_{\mathbf{k}}) \delta(\varepsilon(\mathbf{k}) - \varepsilon(\mathbf{k}')) , \quad (1.77)$$

---

<sup>6</sup>We'll treat the scattering of each spin species separately. We assume no spin-flip scattering takes place.

Metal	$m_{\text{opt}}^*/m_e$		$m_{\text{th}}^*/m_e$	
	thy	expt	thy	expt
Li	1.45	1.57	1.64	2.23
Na	1.00	1.13	1.00	1.27
K	1.02	1.16	1.07	1.26
Rb	1.08	1.16	1.18	1.36
Cs	1.29	1.19	1.75	1.79
Cu	-	-	1.46	1.38
Ag	-	-	1.00	1.00
Au	-	-	1.09	1.08

Table 1.1: Optical and thermodynamic effective masses of monovalent metals. (Taken from Smith and Jensen).

where  $\mathcal{U}(\mathbf{r})$  is a sum over individual impurity ion potentials,

$$\mathcal{U}(\mathbf{r}) = \sum_{j=1}^{N_{\text{imp}}} U(\mathbf{r} - \mathbf{R}_j) \quad (1.78)$$

$$|\langle \mathbf{k}' | \mathcal{U} | \mathbf{k} \rangle|^2 = V^{-2} |\hat{U}(\mathbf{k} - \mathbf{k}')|^2 \cdot \left| \sum_{j=1}^{N_{\text{imp}}} e^{i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{R}_j} \right|^2, \quad (1.79)$$

where  $V$  is the volume of the solid and

$$\hat{U}(\mathbf{q}) = \int d^3r U(\mathbf{r}) e^{-i\mathbf{q} \cdot \mathbf{r}} \quad (1.80)$$

is the Fourier transform of the impurity potential. Note that we are assuming a single species of impurities; the method can be generalized to account for different impurity species.

To make progress, we assume the impurity positions are random and uncorrelated, and we average over them. Using

$$\overline{\left| \sum_{j=1}^{N_{\text{imp}}} e^{i\mathbf{q} \cdot \mathbf{R}_j} \right|^2} = N_{\text{imp}} + N_{\text{imp}}(N_{\text{imp}} - 1) \delta_{\mathbf{q},0}, \quad (1.81)$$

we obtain

$$\overline{|\langle \mathbf{k}' | \mathcal{U} | \mathbf{k} \rangle|^2} = \frac{N_{\text{imp}}}{V^2} |\hat{U}(\mathbf{k} - \mathbf{k}')|^2 + \frac{N_{\text{imp}}(N_{\text{imp}} - 1)}{V^2} |\hat{U}(0)|^2 \delta_{\mathbf{k}\mathbf{k}'}. \quad (1.82)$$

*EXERCISE:* Verify eqn. (1.81).

We will neglect the second term in eqn. 1.82 arising from the spatial average ( $\mathbf{q} = 0$  Fourier component) of the potential. As we will see, in the end it will cancel out. Writing



$f = f^0 + \delta f$ , we have

$$\mathcal{I}_{\mathbf{k}}\{f\} = \frac{2\pi n_{\text{imp}}}{\hbar} \int_{\hat{\Omega}} \frac{d^3k'}{(2\pi)^3} |\hat{U}(\mathbf{k} - \mathbf{k}')|^2 \delta\left(\frac{\hbar^2 \mathbf{k}^2}{2m^*} - \frac{\hbar^2 \mathbf{k}'^2}{2m^*}\right) (\delta f_{\mathbf{k}'} - \delta f_{\mathbf{k}}), \quad (1.83)$$

where  $n_{\text{imp}} = N_{\text{imp}}/V$  is the number density of impurities. Note that we are assuming a parabolic band. We next make the *Ansatz*

$$\delta f_{\mathbf{k}} = \tau(\varepsilon(\mathbf{k})) e \mathcal{E} \cdot \mathbf{v}(\mathbf{k}) \left. \frac{\partial f^0}{\partial \varepsilon} \right|_{\varepsilon(\mathbf{k})} \quad (1.84)$$

and solve for  $\tau(\varepsilon(\mathbf{k}))$ . The (time-independent) Boltzmann equation is

$$\begin{aligned} -e \mathcal{E} \cdot \mathbf{v}(\mathbf{k}) \left. \frac{\partial f^0}{\partial \varepsilon} \right|_{\varepsilon(\mathbf{k})} &= \frac{2\pi}{\hbar} n_{\text{imp}} e \mathcal{E} \cdot \int_{\hat{\Omega}} \frac{d^3k'}{(2\pi)^3} |\hat{U}(\mathbf{k} - \mathbf{k}')|^2 \delta\left(\frac{\hbar^2 \mathbf{k}^2}{2m^*} - \frac{\hbar^2 \mathbf{k}'^2}{2m^*}\right) \\ &\times \left( \tau(\varepsilon(\mathbf{k}')) \mathbf{v}(\mathbf{k}') \left. \frac{\partial f^0}{\partial \varepsilon} \right|_{\varepsilon(\mathbf{k}')} - \tau(\varepsilon(\mathbf{k})) \mathbf{v}(\mathbf{k}) \left. \frac{\partial f^0}{\partial \varepsilon} \right|_{\varepsilon(\mathbf{k})} \right). \end{aligned} \quad (1.85)$$

Due to the isotropy of the problem, we must have  $\tau(\varepsilon(\mathbf{k}))$  is a function only of the magnitude of  $\mathbf{k}$ . We then obtain<sup>7</sup>

$$\frac{\hbar \mathbf{k}}{m^*} = \frac{n_{\text{imp}}}{4\pi^2 \hbar} \tau(\varepsilon(\mathbf{k})) \int_0^\infty dk' k'^2 \int d\hat{\mathbf{k}}' |\hat{U}(\mathbf{k} - \mathbf{k}')|^2 \frac{\delta(k - k')}{\hbar^2 k/m^*} \frac{\hbar}{m^*} (\mathbf{k} - \mathbf{k}'), \quad (1.86)$$

whence

$$\frac{1}{\tau(\varepsilon_{\text{F}})} = \frac{m^* k_{\text{F}} n_{\text{imp}}}{4\pi^2 \hbar^3} \int d\hat{\mathbf{k}}' |U(k_{\text{F}} \hat{\mathbf{k}} - k_{\text{F}} \hat{\mathbf{k}}')|^2 (1 - \hat{\mathbf{k}} \cdot \hat{\mathbf{k}}'). \quad (1.87)$$

If the impurity potential  $U(\mathbf{r})$  itself is isotropic, then its Fourier transform  $\hat{U}(\mathbf{q})$  is a function of  $q^2 = 4k_{\text{F}}^2 \sin^2 \frac{1}{2} \vartheta$  where  $\cos \vartheta = \hat{\mathbf{k}} \cdot \hat{\mathbf{k}}'$  and  $\mathbf{q} = \mathbf{k}' - \mathbf{k}$  is the transfer wavevector. Recalling the Born approximation for differential scattering cross section,

$$\sigma(\vartheta) = \left( \frac{m^*}{2\pi \hbar^2} \right)^2 |\hat{U}(\mathbf{k} - \mathbf{k}')|^2, \quad (1.88)$$

we may finally write

$$\boxed{\frac{1}{\tau(\varepsilon_{\text{F}})} = 2\pi n_{\text{imp}} v_{\text{F}} \int_0^\pi d\vartheta \sigma_{\text{F}}(\vartheta) (1 - \cos \vartheta) \sin \vartheta} \quad (1.89)$$

where  $v_{\text{F}} = \hbar k_{\text{F}}/m^*$  is the Fermi velocity<sup>8</sup>. The *mean free path* is defined by  $\ell = v_{\text{F}} \tau$ .

<sup>7</sup>We assume that the Fermi surface is contained within the first Brillouin zone.

<sup>8</sup>The subscript on  $\sigma_{\text{F}}(\vartheta)$  is to remind us that the cross section depends on  $k_{\text{F}}$  as well as  $\vartheta$ .

Notice the factor  $(1 - \cos \vartheta)$  in the integrand of (1.89). This tells us that forward scattering ( $\vartheta = 0$ ) doesn't contribute to the scattering rate, which justifies our neglect of the second term in eqn. (1.82). Why should  $\tau$  be utterly insensitive to forward scattering? Because  $\tau(\varepsilon_F)$  is the *transport lifetime*, and forward scattering does not degrade the current. Therefore,  $\sigma(\vartheta = 0)$  does not contribute to the 'transport scattering rate'  $\tau^{-1}(\varepsilon_F)$ . Oftentimes one sees reference in the literature to a 'single particle lifetime' as well, which is given by the same expression but without this factor:

$$\boxed{\left\{ \begin{array}{l} \tau_{\text{sp}}^{-1} \\ \tau_{\text{tr}}^{-1} \end{array} \right\} = 2\pi n_{\text{imp}} v_F \int_0^\pi d\vartheta \sigma_F(\vartheta) \left\{ \begin{array}{l} 1 \\ (1 - \cos \vartheta) \end{array} \right\} \sin \vartheta} \quad (1.90)$$

Note that  $\tau_{\text{sp}} = (n_{\text{imp}} v_F \sigma_{F,\text{tot}})^{-1}$ , where  $\sigma_{F,\text{tot}}$  is the total scattering cross section at energy  $\varepsilon_F$ , a formula familiar from elementary kinetic theory.

To derive the single particle lifetime, one can examine the linearized time-*dependent* Boltzmann equation with  $\mathcal{E} = 0$ ,

$$\frac{\partial \delta f_{\mathbf{k}}}{\partial t} = n_{\text{imp}} v_F \int d\hat{\mathbf{k}}' \sigma(\vartheta_{\mathbf{k}\mathbf{k}'}) (\delta f_{\mathbf{k}'} - \delta f_{\mathbf{k}}) , \quad (1.91)$$

where  $v = \hbar k/m^*$  is the velocity, and where the kernel is  $\vartheta_{\mathbf{k}\mathbf{k}'} = \cos^{-1}(\mathbf{k} \cdot \mathbf{k}')$ . We now expand in spherical harmonics, writing

$$\sigma(\vartheta_{\mathbf{k}\mathbf{k}'}) \equiv \sigma_{\text{tot}} \sum_{L,M} \nu_L Y_{LM}(\hat{\mathbf{k}}) Y_{LM}^*(\hat{\mathbf{k}}') , \quad (1.92)$$

where as before

$$\sigma_{\text{tot}} = 2\pi \int_0^\pi d\vartheta \sin \vartheta \sigma(\vartheta) . \quad (1.93)$$

Expanding

$$\delta f_{\mathbf{k}}(t) = \sum_{L,M} A_{LM}(t) Y_{LM}(\hat{\mathbf{k}}) , \quad (1.94)$$

the linearized Boltzmann equation simplifies to

$$\frac{\partial A_{LM}}{\partial t} + (1 - \nu_L) n_{\text{imp}} v_F \sigma_{\text{tot}} A_{LM} = 0 , \quad (1.95)$$

whence one obtains a hierarchy of relaxation rates,

$$\tau_L^{-1} = (1 - \nu_L) n_{\text{imp}} v_F \sigma_{\text{tot}} , \quad (1.96)$$

which depend only on the total angular momentum quantum number  $L$ . These rates describe the relaxation of nonuniform distributions, when  $\delta f_{\mathbf{k}}(t=0)$  is proportional to some spherical harmonic  $Y_{LM}(\mathbf{k})$ . Note that  $\tau_{L=0}^{-1} = 0$ , which reflects the fact that the total particle number is a collisional invariant. The single particle lifetime is identified as

$$\tau_{\text{sp}}^{-1} \equiv \tau_{L \rightarrow \infty}^{-1} = n_{\text{imp}} v_F \sigma_{\text{tot}} , \quad (1.97)$$

corresponding to a point distortion of the uniform distribution.

### 1.5.2 Screening and the Transport Lifetime

For a Coulomb impurity, with  $U(\mathbf{r}) = -Ze^2/r$  we have  $\hat{U}(\mathbf{q}) = -4\pi Ze^2/q^2$ . Consequently,

$$\sigma_{\text{F}}(\vartheta) = \left( \frac{Ze^2}{4\varepsilon_{\text{F}} \sin^2 \frac{1}{2}\vartheta} \right)^2, \quad (1.98)$$

and there is a strong divergence as  $\vartheta \rightarrow 0$ , with  $\sigma_{\text{F}}(\vartheta) \propto \vartheta^{-4}$ . The transport lifetime diverges logarithmically! What went wrong?

What went wrong is that we have failed to account for *screening*. Free charges will rearrange themselves so as to screen an impurity potential. At long range, the effective (screened) potential decays exponentially, rather than as  $1/r$ . The screened potential is of the Yukawa form, and its increase at low  $q$  is cut off on the scale of the inverse screening length  $\lambda^{-1}$ . There are two types of screening to consider:

- Thomas-Fermi Screening : This is the typical screening mechanism in metals. A weak local electrostatic potential  $\phi(\mathbf{r})$  will induce a change in the local electronic density according to  $\delta n(\mathbf{r}) = e\phi(\mathbf{r})g(\varepsilon_{\text{F}})$ , where  $g(\varepsilon_{\text{F}})$  is the density of states at the Fermi level. This charge imbalance is again related to  $\phi(\mathbf{r})$  through the Poisson equation. The result is a self-consistent equation for  $\phi(\mathbf{r})$ ,

$$\begin{aligned} \nabla^2 \phi &= 4\pi e \delta n \\ &= 4\pi e^2 g(\varepsilon_{\text{F}}) \phi \equiv \lambda_{\text{TF}}^{-2} \phi. \end{aligned} \quad (1.99)$$

The Thomas-Fermi screening length is  $\lambda_{\text{TF}} = (4\pi e^2 g(\varepsilon_{\text{F}}))^{-1/2}$ .

- Debye-Hückel Screening : This mechanism is typical of ionic solutions, although it may also be of relevance in solids with ultra-low Fermi energies. From classical statistical mechanics, the local variation in electron number density induced by a potential  $\phi(\mathbf{r})$  is

$$\delta n(\mathbf{r}) = n e^{e\phi(\mathbf{r})/k_{\text{B}}T} - n \approx \frac{ne\phi(\mathbf{r})}{k_{\text{B}}T}, \quad (1.100)$$

where we assume the potential is weak on the scale of  $k_{\text{B}}T/e$ . Poisson's equation now gives us

$$\begin{aligned} \nabla^2 \phi &= 4\pi e \delta n \\ &= \frac{4\pi ne^2}{k_{\text{B}}T} \phi \equiv \lambda_{\text{DH}}^{-2} \phi. \end{aligned} \quad (1.101)$$

A screened test charge  $Ze$  at the origin obeys

$$\nabla^2 \phi = \lambda^{-2} \phi - 4\pi Ze\delta(\mathbf{r}), \quad (1.102)$$

the solution of which is

$$U(\mathbf{r}) = -e\phi(\mathbf{r}) = -\frac{Ze^2}{r} e^{-r/\lambda} \implies \hat{U}(\mathbf{q}) = \frac{4\pi Ze^2}{\mathbf{q}^2 + \lambda^{-2}}. \quad (1.103)$$

The differential scattering cross section is now

$$\sigma_{\text{F}}(\vartheta) = \left( \frac{Ze^2}{4\epsilon_{\text{F}}} \cdot \frac{1}{\sin^2 \frac{1}{2}\vartheta + (2k_{\text{F}}\lambda)^{-2}} \right)^2 \quad (1.104)$$

and the divergence at small angle is cut off. The transport lifetime for screened Coulomb scattering is therefore given by

$$\begin{aligned} \frac{1}{\tau(\epsilon_{\text{F}})} &= 2\pi n_{\text{imp}} v_{\text{F}} \left( \frac{Ze^2}{4\epsilon_{\text{F}}} \right)^2 \int_0^{\pi} d\vartheta \sin \vartheta (1 - \cos \vartheta) \left( \frac{1}{\sin^2 \frac{1}{2}\vartheta + (2k_{\text{F}}\lambda)^{-2}} \right)^2 \\ &= 2\pi n_{\text{imp}} v_{\text{F}} \left( \frac{Ze^2}{2\epsilon_{\text{F}}} \right)^2 \left\{ \ln(1 + \pi\zeta) - \frac{\pi\zeta}{1 + \pi\zeta} \right\}, \end{aligned} \quad (1.105)$$

with

$$\zeta = \frac{4}{\pi} k_{\text{F}}^2 \lambda^2 = \frac{\hbar^2 k_{\text{F}}}{m^* e^2} = k_{\text{F}} a_{\text{B}}^*. \quad (1.106)$$

Here  $a_{\text{B}}^* = \epsilon_{\infty} \hbar^2 / m^* e^2$  is the effective Bohr radius (restoring the  $\epsilon_{\infty}$  factor). The resistivity is therefore given by

$$\rho = \frac{m^*}{ne^2\tau} = Z^2 \frac{h}{e^2} a_{\text{B}}^* \frac{n_{\text{imp}}}{n} F(k_{\text{F}} a_{\text{B}}^*), \quad (1.107)$$

where

$$F(\zeta) = \frac{1}{\zeta^3} \left\{ \ln(1 + \pi\zeta) - \frac{\pi\zeta}{1 + \pi\zeta} \right\}. \quad (1.108)$$

With  $h/e^2 = 25,813 \Omega$  and  $a_{\text{B}}^* \approx a_{\text{B}} = 0.529 \text{ \AA}$ , we have

$$\rho = 1.37 \times 10^{-4} \Omega \cdot \text{cm} \times Z^2 \frac{n_{\text{imp}}}{n} F(k_{\text{F}} a_{\text{B}}^*). \quad (1.109)$$

Impurity Ion	$\Delta\rho$ per % ( $\mu\Omega\text{-cm}$ )	Impurity Ion	$\Delta\rho$ per % ( $\mu\Omega\text{-cm}$ )
Be	0.64	Si	3.2
Mg	0.60	Ge	3.7
B	1.4	Sn	2.8
Al	1.2	As	6.5
In	1.2	Sb	5.4

Table 1.2: Residual resistivity of copper per percent impurity.

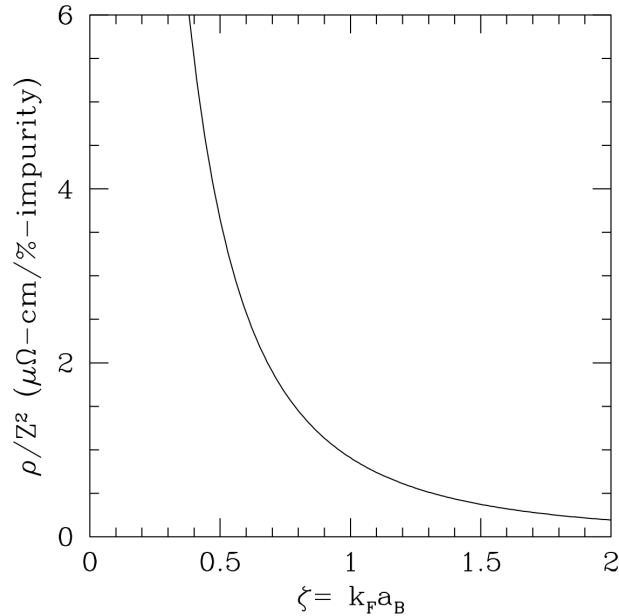


Figure 1.5: Residual resistivity per percent impurity.

## 1.6 Boltzmann Equation for Holes

### 1.6.1 Properties of Holes

Since filled bands carry no current, we have that the current density from band  $n$  is

$$\mathbf{j}_n(\mathbf{r}, t) = -2e \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} f_n(\mathbf{r}, \mathbf{k}, t) \mathbf{v}_n(\mathbf{k}) = +2e \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} \bar{f}_n(\mathbf{r}, \mathbf{k}, t) \mathbf{v}_n(\mathbf{k}), \quad (1.110)$$

where  $\bar{f} \equiv 1 - f$ . Thus, we can regard the current to be carried by fictitious particles of charge  $+e$  with a distribution  $\bar{f}(\mathbf{r}, \mathbf{k}, t)$ . These fictitious particles are called *holes*.

1. Under the influence of an applied electromagnetic field, the unoccupied levels of a band evolve as if they were occupied by real electrons of charge  $-e$ . That is, whether or not a state is occupied is irrelevant to the time evolution of that state, which is described by the semiclassical dynamics of eqs. (1.1, 1.2).
2. The current density due to a hole of wavevector  $\mathbf{k}$  is  $+e \mathbf{v}_n(\mathbf{k})/V$ .
3. The crystal momentum of a hole of wavevector  $\mathbf{k}$  is  $\mathbf{P} = -\hbar\mathbf{k}$ .
4. Any band can be described in terms of electrons or in terms of holes, but not both simultaneously. A “mixed” description is redundant at best, wrong at worst, and confusing always. However, it is often convenient to treat some bands within the electron picture and others within the hole picture.

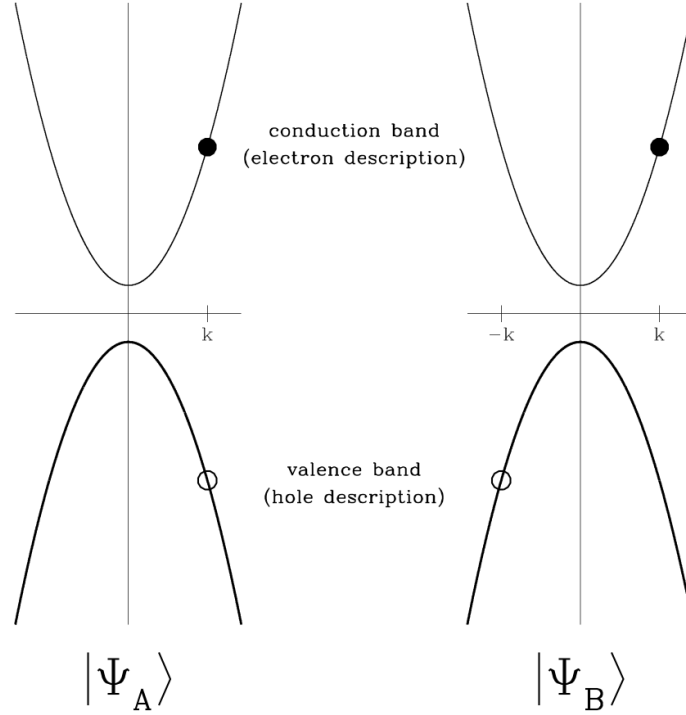


Figure 1.6: Two states:  $|\Psi_A\rangle = e_k^\dagger h_k^\dagger |0\rangle$  and  $|\Psi_B\rangle = e_k^\dagger h_{-k}^\dagger |0\rangle$ . Which state carries more current? What is the crystal momentum of each state?

It is instructive to consider the exercise of fig. 1.6. The two states to be analyzed are

$$|\Psi_A\rangle = \psi_{c,k}^\dagger \psi_{v,k} |\Psi_0\rangle = e_k^\dagger h_k^\dagger |0\rangle \quad (1.111)$$

$$|\Psi_B\rangle = \psi_{c,k}^\dagger \psi_{v,-k} |\Psi_0\rangle = e_k^\dagger h_{-k}^\dagger |0\rangle, \quad (1.112)$$

where  $e_k^\dagger \equiv \psi_{c,k}^\dagger$  is the creation operator for electrons in the conduction band, and  $h_k^\dagger \equiv \psi_{v,k}$  is the creation operator for holes (and hence the destruction operator for electrons) in the valence band. The state  $|\Psi_0\rangle$  has all states below the top of the valence band filled, and all states above the bottom of the conduction band empty. The state  $|0\rangle$  is the same state, but represented now as a *vacuum* for conduction electrons and valence *holes*. The current density in each state is given by  $j = e(v_h - v_e)/V$ , where  $V$  is the volume (*i.e.* length) of the system. The dispersions resemble  $\varepsilon_{c,v} \approx \pm \frac{1}{2}E_g \pm \hbar^2 k^2/2m^*$ , where  $E_g$  is the energy gap.

- State  $|\Psi_A\rangle$ :

The electron velocity is  $v_e = \hbar k/m^*$ ; the hole velocity is  $v_h = -\hbar k/m^*$ . Hence, the total current density is  $j \approx -2e\hbar k/m^*V$  and the total crystal momentum is  $P = p_e + p_h = \hbar k - \hbar k = 0$ .

- State  $|\Psi_B\rangle$ :

The electron velocity is  $v_e = \hbar k/m^*$ ; the hole velocity is  $v_h = -\hbar(-k)/m^*$ . The

total current density is  $j \approx 0$ , and the total crystal momentum is  $P = p_e + p_h = \hbar k - \hbar(-k) = 2\hbar k$ .

Consider next the dynamics of electrons near the bottom of the conduction band and holes near the top of the valence band. (We'll assume a 'direct gap', *i.e.* the conduction band minimum is located directly above the valence band maximum, which we take to be at the Brillouin zone center  $\mathbf{k} = 0$ , otherwise known as the  $\Gamma$  point.) Expanding the dispersions about their extrema,

$$\varepsilon_v(\mathbf{k}) = \varepsilon_0^v - \frac{1}{2}\hbar^2 m_{\alpha\beta}^v{}^{-1} k^\alpha k^\beta \quad (1.113)$$

$$\varepsilon_c(\mathbf{k}) = \varepsilon_0^c + \frac{1}{2}\hbar^2 m_{\alpha\beta}^c{}^{-1} k^\alpha k^\beta . \quad (1.114)$$

The velocity is

$$v^\alpha(\mathbf{k}) = \frac{1}{\hbar} \frac{\partial \varepsilon}{\partial k^\alpha} = \pm \hbar m_{\alpha\beta}^{-1} k^\beta , \quad (1.115)$$

where the + sign is used in conjunction with  $m^c$  and the – sign with  $m^v$ . We compute the acceleration  $\mathbf{a} = \dot{\mathbf{r}}$  via the chain rule,

$$\begin{aligned} a^\alpha &= \frac{\partial v^\alpha}{\partial k^\beta} \cdot \frac{dk^\beta}{dt} \\ &= \mp e m_{\alpha\beta}^{-1} \left[ E^\beta + \frac{1}{c} (\mathbf{v} \times \mathbf{B})^\beta \right] \end{aligned} \quad (1.116)$$

$$F^\alpha = m_{\alpha\beta} a^\beta = \mp e \left[ E^\beta + \frac{1}{c} (\mathbf{v} \times \mathbf{B})^\beta \right] . \quad (1.117)$$

Thus, the hole wavepacket accelerates as if it has charge  $+e$  but a *positive* effective mass.

Finally, what form does the Boltzmann equation take for holes? Starting with the Boltzmann equation for electrons,

$$\frac{\partial f}{\partial t} + \dot{\mathbf{r}} \cdot \frac{\partial f}{\partial \mathbf{r}} + \dot{\mathbf{k}} \cdot \frac{\partial f}{\partial \mathbf{k}} = \mathcal{I}_{\mathbf{k}}\{f\} , \quad (1.118)$$

we recast this in terms of the hole distribution  $\bar{f} = 1 - f$ , and obtain

$$\boxed{\frac{\partial \bar{f}}{\partial t} + \dot{\mathbf{r}} \cdot \frac{\partial \bar{f}}{\partial \mathbf{r}} + \dot{\mathbf{k}} \cdot \frac{\partial \bar{f}}{\partial \mathbf{k}} = -\mathcal{I}_{\mathbf{k}}\{1 - \bar{f}\}} \quad (1.119)$$

This then is the Boltzmann equation for the hole distribution  $\bar{f}$ . Recall that we can expand the collision integral functional as

$$\mathcal{I}_{\mathbf{k}}\{f^0 + \delta f\} = \mathcal{L} \delta f + \dots \quad (1.120)$$

where  $\mathcal{L}$  is a linear operator, and the higher order terms are formally of order  $(\delta f)^2$ . Note that the zeroth order term  $\mathcal{I}_{\mathbf{k}}\{f^0\}$  vanishes due to the fact that  $f^0$  represents a local equilibrium. Thus, writing  $\bar{f} = \bar{f}^0 + \delta \bar{f}$

$$-\mathcal{I}_{\mathbf{k}}\{1 - \bar{f}\} = -\mathcal{I}_{\mathbf{k}}\{1 - \bar{f}^0 - \delta \bar{f}\} = \mathcal{L} \delta \bar{f} + \dots \quad (1.121)$$

and the linearized collisionless Boltzmann equation for holes is

$$\boxed{\frac{\partial \delta \bar{f}}{\partial t} - \frac{e}{\hbar c} \mathbf{v} \times \mathbf{B} \cdot \frac{\partial \delta \bar{f}}{\partial \mathbf{k}} - \mathbf{v} \cdot \left[ e \mathbf{E} + \frac{\varepsilon - \mu}{T} \nabla T \right] \frac{\partial \bar{f}^0}{\partial \varepsilon} = \mathcal{L} \delta \bar{f}} \quad (1.122)$$

which is of precisely the same form as the electron case in eqn. (1.27). Note that the local equilibrium distribution for holes is given by

$$\boxed{\bar{f}^0(\mathbf{r}, \mathbf{k}, t) = \left\{ \exp \left( \frac{\mu(\mathbf{r}, t) - \varepsilon(\mathbf{k})}{k_B T(\mathbf{r}, t)} \right) + 1 \right\}^{-1}} \quad (1.123)$$

## 1.7 Magnetoresistance and Hall Effect

### 1.7.1 Boltzmann Theory for $\rho_{\alpha\beta}(\omega, B)$

In the presence of an external magnetic field  $\mathbf{B}$ , the linearized Boltzmann equation takes the form<sup>9</sup>

$$\frac{\partial \delta f}{\partial t} - e \mathbf{v} \cdot \mathbf{E} \frac{\partial f^0}{\partial \varepsilon} - \frac{e}{\hbar c} \mathbf{v} \times \mathbf{B} \cdot \frac{\partial \delta f}{\partial \mathbf{k}} = \mathcal{L} \delta f. \quad (1.124)$$

We will obtain an explicit solution within the relaxation time approximation  $\mathcal{L} \delta f = -\delta f/\tau$  and the effective mass approximation,

$$\varepsilon(\mathbf{k}) = \pm \frac{1}{2} \hbar^2 m_{\alpha\beta}^{-1} k^\alpha k^\beta \implies v^\alpha = \pm \hbar m_{\alpha\beta}^{-1} k^\beta, \quad (1.125)$$

where the top sign applies for electrons and the bottom sign for holes. With  $\mathbf{E}(t) = \mathbf{E} e^{-i\omega t}$ , we try a solution of the form

$$\delta f(\mathbf{k}, t) = \mathbf{k} \cdot \mathbf{A}(\varepsilon) e^{-i\omega t} \equiv \delta f(\mathbf{k}) e^{-i\omega t} \quad (1.126)$$

where  $\mathbf{A}(\varepsilon)$  is a vector function of  $\varepsilon$  to be determined. Each component  $A_\alpha$  is a function of  $\mathbf{k}$  through its dependence on  $\varepsilon = \varepsilon(\mathbf{k})$ . We now have

$$(\tau^{-1} - i\omega) k^\mu A^\mu - \frac{e}{\hbar c} \epsilon_{\alpha\beta\gamma} v^\alpha B^\beta \frac{\partial}{\partial k^\gamma} (k^\mu A^\mu) = e \mathbf{v} \cdot \mathbf{E} \frac{\partial f^0}{\partial \varepsilon}, \quad (1.127)$$

where  $\epsilon_{\alpha\beta\gamma}$  is the Levi-Civita tensor. Note that

$$\begin{aligned} \epsilon_{\alpha\beta\gamma} v^\alpha B^\beta \frac{\partial}{\partial k^\gamma} (k^\mu A^\mu) &= \epsilon_{\alpha\beta\gamma} v^\alpha B^\beta \left( A^\gamma + k^\mu \frac{\partial A^\mu}{\partial k^\gamma} \right) \\ &= \epsilon_{\alpha\beta\gamma} v^\alpha B^\beta \left( A^\gamma + \hbar k^\mu v^\gamma \frac{\partial A^\mu}{\partial \varepsilon} \right) \\ &= \epsilon_{\alpha\beta\gamma} v^\alpha B^\beta A^\gamma, \end{aligned} \quad (1.128)$$

<sup>9</sup>For holes, we replace  $f^0 \rightarrow \bar{f}^0$  and  $\delta f \rightarrow \delta \bar{f}$ .



owing to the asymmetry of the Levi-Civita tensor:  $\epsilon_{\alpha\beta\gamma} v^\alpha v^\gamma = 0$ . We now invoke the identity  $\hbar k^\alpha = \pm m_{\alpha\beta} v^\beta$  and match the coefficients of  $v^\alpha$  in each term of the Boltzmann equation. This yields,

$$\left[ (\tau^{-1} - i\omega) m_{\alpha\beta} \pm \frac{e}{c} \epsilon_{\alpha\beta\gamma} B^\gamma \right] A^\beta = \pm \hbar e \frac{\partial f^0}{\partial \varepsilon} \mathcal{E}^\alpha . \quad (1.129)$$

Defining

$$\Gamma_{\alpha\beta} \equiv (\tau^{-1} - i\omega) m_{\alpha\beta} \pm \frac{e}{c} \epsilon_{\alpha\beta\gamma} B^\gamma , \quad (1.130)$$

we obtain the solution

$$\delta f = \pm e v^\alpha m_{\alpha\beta} \Gamma_{\beta\gamma}^{-1} \mathcal{E}^\gamma \frac{\partial f^0}{\partial \varepsilon} . \quad (1.131)$$

From this, we can compute the current density and the conductivity tensor. The electrical current density is

$$\begin{aligned} j^\alpha &= \mp 2e \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} v^\alpha \delta f \\ &= +2e^2 \mathcal{E}^\gamma \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} v^\alpha v^\nu m_{\nu\beta} \Gamma_{\beta\gamma}^{-1}(\varepsilon) \left( -\frac{\partial f^0}{\partial \varepsilon} \right) , \end{aligned} \quad (1.132)$$

where we allow for an energy-dependent relaxation time  $\tau(\varepsilon)$ . Note that  $\Gamma_{\alpha\beta}(\varepsilon)$  is energy-dependent due to its dependence on  $\tau$ . The conductivity is then

$$\sigma_{\alpha\beta}(\omega, \mathbf{B}) = 2\hbar^2 e^2 m_{\alpha\mu}^{-1} \left\{ \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} k^\mu k^\nu \left( -\frac{\partial f^0}{\partial \varepsilon} \right) \Gamma_{\nu\beta}^{-1}(\varepsilon) \right\} \quad (1.133)$$

$$= \pm \frac{2}{3} e^2 \int_{-\infty}^{\infty} d\varepsilon \varepsilon g(\varepsilon) \Gamma_{\alpha\beta}^{-1}(\varepsilon) \left( -\frac{\partial f^0}{\partial \varepsilon} \right) , \quad (1.134)$$

where the chemical potential is measured with respect to the band edge. Thus,

$$\sigma_{\alpha\beta}(\omega, \mathbf{B}) = n e^2 \langle \Gamma_{\alpha\beta}^{-1} \rangle , \quad (1.135)$$

where averages denoted by angular brackets are defined by

$$\langle \Gamma_{\alpha\beta}^{-1} \rangle \equiv \frac{\int_{-\infty}^{\infty} d\varepsilon \varepsilon g(\varepsilon) \left( -\frac{\partial f^0}{\partial \varepsilon} \right) \Gamma_{\alpha\beta}^{-1}(\varepsilon)}{\int_{-\infty}^{\infty} d\varepsilon \varepsilon g(\varepsilon) \left( -\frac{\partial f^0}{\partial \varepsilon} \right)} . \quad (1.136)$$

The quantity  $n$  is the carrier density,

$$n = \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) \times \begin{cases} f^0(\varepsilon) & \text{(electrons)} \\ \{1 - f^0(\varepsilon)\} & \text{(holes)} \end{cases} \quad (1.137)$$

*EXERCISE:* Verify eqn. (1.134).

For the sake of simplicity, let us assume an energy-independent scattering time, or that the temperature is sufficiently low that only  $\tau(\varepsilon_F)$  matters, and we denote this scattering time simply by  $\tau$ . Putting this all together, then, we obtain

$$\sigma_{\alpha\beta} = ne^2 \Gamma_{\alpha\beta}^{-1} \quad (1.138)$$

$$\rho_{\alpha\beta} = \frac{1}{ne^2} \Gamma_{\alpha\beta} = \frac{1}{ne^2} \left[ (\tau^{-1} - i\omega) m_{\alpha\beta} \pm \frac{e}{c} \epsilon_{\alpha\beta\gamma} B^\gamma \right]. \quad (1.139)$$

We will assume that  $\mathbf{B}$  is directed along one of the principal axes of the effective mass tensor  $m_{\alpha\beta}$ , which we define to be  $\hat{\mathbf{x}}$ ,  $\hat{\mathbf{y}}$ , and  $\hat{\mathbf{z}}$ , in which case

$$\rho_{\alpha\beta}(\omega, B) = \frac{1}{ne^2} \begin{pmatrix} (\tau^{-1} - i\omega) m_x^* & \pm eB/c & 0 \\ \mp eB/c & (\tau^{-1} - i\omega) m_y^* & 0 \\ 0 & 0 & (\tau^{-1} - i\omega) m_z^* \end{pmatrix} \quad (1.140)$$

where  $m_{x,y,z}^*$  are the eigenvalues of  $m_{\alpha\beta}$  and  $\mathbf{B}$  lies along the eigenvector  $\hat{\mathbf{z}}$ .

Note that

$$\rho_{xx}(\omega, B) = \frac{m_x^*}{ne^2\tau} (1 - i\omega\tau) \quad (1.141)$$

is independent of  $B$ . Hence, the *magnetoresistance*,

$$\Delta\rho_{xx}(B) = \rho_{xx}(B) - \rho_{xx}(0) \quad (1.142)$$

vanishes:  $\Delta\rho_{xx}(B) = 0$ . While this is true for a single parabolic band, deviations from parabolicity and contributions from other bands can lead to a nonzero magnetoresistance.

The conductivity tensor  $\sigma_{\alpha\beta}$  is the matrix inverse of  $\rho_{\alpha\beta}$ . Using the familiar equality

$$\begin{pmatrix} a & b \\ c & d \end{pmatrix}^{-1} = \frac{1}{ad - bc} \begin{pmatrix} d & -b \\ -c & a \end{pmatrix}, \quad (1.143)$$

we obtain

$$\sigma_{\alpha\beta}(\omega, B) = ne^2\tau \begin{pmatrix} \frac{(1-i\omega\tau)/m_x^*}{(1-i\omega\tau)^2 + (\omega_c\tau)^2} & \mp \frac{\omega_c\tau/\sqrt{m_x^* m_y^*}}{(1-i\omega\tau)^2 + (\omega_c\tau)^2} & 0 \\ \pm \frac{\omega_c\tau/\sqrt{m_x^* m_y^*}}{(1-i\omega\tau)^2 + (\omega_c\tau)^2} & \frac{(1-i\omega\tau)/m_y^*}{(1-i\omega\tau)^2 + (\omega_c\tau)^2} & 0 \\ 0 & 0 & \frac{1}{(1-i\omega\tau)m_z^*} \end{pmatrix} \quad (1.144)$$

where

$$\omega_c \equiv \frac{eB}{m_\perp^* c}, \quad (1.145)$$

with  $m_{\perp}^* \equiv \sqrt{m_x^* m_y^*}$ , is the *cyclotron frequency*. Thus,

$$\sigma_{xx}(\omega, B) = \frac{ne^2\tau}{m_x^*} \frac{1 - i\omega\tau}{1 + (\omega_c^2 - \omega^2)\tau^2 - 2i\omega\tau} \quad (1.146)$$

$$\sigma_{zz}(\omega, B) = \frac{ne^2\tau}{m_z^*} \frac{1}{1 - i\omega\tau}. \quad (1.147)$$

Note that  $\sigma_{xx,yy}$  are field-dependent, unlike the corresponding components of the resistivity tensor.

### 1.7.2 Cyclotron Resonance in Semiconductors

A typical value for the effective mass in semiconductors is  $m^* \sim 0.1 m_e$ . From

$$\frac{e}{m_e c} = 1.75 \times 10^7 \text{ Hz/G}, \quad (1.148)$$

we find that  $eB/m^*c = 1.75 \times 10^{11}$  Hz in a field of  $B = 1$  kG. In metals, the disorder is such that even at low temperatures  $\omega_c\tau$  typically is small. In semiconductors, however, the smallness of  $m^*$  and the relatively high purity (sometimes spectacularly so) mean that  $\omega_c\tau$  can get as large as  $10^3$  at modest fields. This allows for a measurement of the effective mass tensor using the technique of *cyclotron resonance*.

The absorption of electromagnetic radiation is proportional to the dissipative (*i.e.* real) part of the diagonal elements of  $\sigma_{\alpha\beta}(\omega)$ , which is given by

$$\sigma'_{xx}(\omega, B) = \frac{ne^2\tau}{m_x^*} \frac{1 + (\lambda^2 + 1)s^2}{1 + 2(\lambda^2 + 1)s^2 + (\lambda^2 - 1)^2s^4}, \quad (1.149)$$

where  $\lambda = B/B_{\omega}$ , with  $B_{\omega} = m_{\perp}^* c \omega / e$ , and  $s = \omega\tau$ . For fixed  $\omega$ , the conductivity  $\sigma'_{xx}(B)$  is then peaked at  $B = B^*$ . When  $\omega\tau \gg 1$  and  $\omega_c\tau \gg 1$ ,  $B^*$  approaches  $B_{\omega}$ , where  $\sigma'_{xx}(\omega, B_{\omega}) = ne^2\tau/2m_x^*$ . By measuring  $B_{\omega}$  one can extract the quantity  $m_{\perp}^* = eB_{\omega}/\omega c$ . Varying the direction of the magnetic field, the entire effective mass tensor may be determined.

For finite  $\omega\tau$ , we can differentiate the above expression to obtain the location of the cyclotron resonance peak. One finds  $B = (1 + \alpha)^{1/2} B_{\omega}$ , with

$$\begin{aligned} \alpha &= \frac{-(2s^2 + 1) + \sqrt{(2s^2 + 1)^2 - 1}}{s^2} \\ &= -\frac{1}{4s^4} + \frac{1}{8s^6} + \mathcal{O}(s^{-8}). \end{aligned} \quad (1.150)$$

As depicted in fig. 1.7, the resonance peak shifts to the left of  $B_{\omega}$  for finite values of  $\omega\tau$ . The peak collapses to  $B = 0$  when  $\omega\tau \leq 1/\sqrt{3} = 0.577$ .

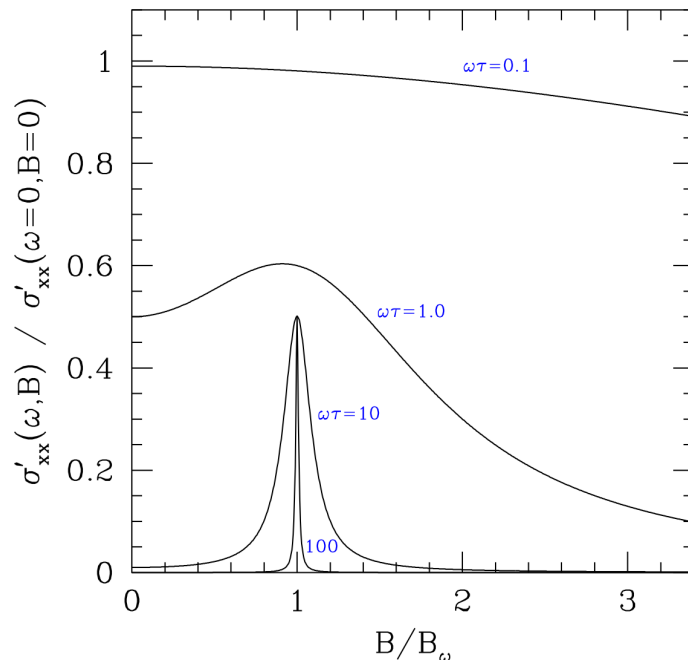


Figure 1.7: Theoretical cyclotron resonance peaks as a function of  $B/B_\omega$  for different values of  $\omega\tau$ .

### 1.7.3 Magnetoresistance: Two-Band Model

For a semiconductor with both electrons and holes present – a situation not uncommon to metals either (*e.g.* Aluminum) – each band contributes to the conductivity. The individual band conductivities are *additive* because the electron and hole conduction processes occur *in parallel*, exactly as we would deduce from eqn. (1.4). Thus,

$$\sigma_{\alpha\beta}(\omega) = \sum_n \sigma_{\alpha\beta}^{(n)}(\omega) , \quad (1.151)$$

where  $\sigma_{\alpha\beta}^{(n)}$  is the conductivity tensor for band  $n$ , which may be computed in either the electron or hole picture (whichever is more convenient). We assume here that the two distributions  $\delta f_c$  and  $\delta f_v$  evolve according to independent linearized Boltzmann equations, *i.e.* there is no interband scattering to account for.

The resistivity tensor of each band,  $\rho_{\alpha\beta}^{(n)}$  exhibits no magnetoresistance, as we have found. However, if two bands are present, the total resistivity tensor  $\rho$  is obtained from  $\rho^{-1} = \rho_c^{-1} + \rho_v^{-1}$ , and

$$\rho = (\rho_c^{-1} + \rho_v^{-1})^{-1} \quad (1.152)$$

will in general exhibit the phenomenon of magnetoresistance.

Explicitly, then, let us consider a model with isotropic and nondegenerate conduction band

minimum and valence band maximum. Taking  $\mathbf{B} = B\hat{z}$ , we have

$$\rho_c = \frac{(1 - i\omega\tau_c)m_c}{n_c e^2 \tau_c} \mathbb{I} + \frac{B}{n_c e c} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} \alpha_c & \beta_c & 0 \\ -\beta_c & \alpha_c & 0 \\ 0 & 0 & \alpha_c \end{pmatrix} \quad (1.153)$$

$$\rho_v = \frac{(1 - i\omega\tau_v)m_v}{n_v e^2 \tau_v} \mathbb{I} - \frac{B}{n_v e c} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} \alpha_v & -\beta_v & 0 \\ \beta_v & \alpha_v & 0 \\ 0 & 0 & \alpha_v \end{pmatrix}, \quad (1.154)$$

where

$$\alpha_c = \frac{(1 - i\omega\tau_c)m_c}{n_c e^2 \tau_c} \quad \beta_c = \frac{B}{n_c e c} \quad (1.155)$$

$$\alpha_v = \frac{(1 - i\omega\tau_v)m_v}{n_v e^2 \tau_v} \quad \beta_v = \frac{B}{n_v e c}, \quad (1.156)$$

we obtain for the upper left  $2 \times 2$  block of  $\rho$ :

$$\rho_{\perp} = \left[ \left( \frac{\alpha_v}{\alpha_v^2 + \beta_v^2} + \frac{\alpha_c}{\alpha_c^2 + \beta_c^2} \right)^2 + \left( \frac{\beta_v}{\alpha_v^2 + \beta_v^2} + \frac{\beta_c}{\alpha_c^2 + \beta_c^2} \right)^2 \right]^{-1} \\ \times \begin{pmatrix} \frac{\alpha_v}{\alpha_v^2 + \beta_v^2} + \frac{\alpha_c}{\alpha_c^2 + \beta_c^2} & \frac{\beta_v}{\alpha_v^2 + \beta_v^2} + \frac{\beta_c}{\alpha_c^2 + \beta_c^2} \\ -\frac{\beta_v}{\alpha_v^2 + \beta_v^2} - \frac{\beta_c}{\alpha_c^2 + \beta_c^2} & \frac{\alpha_v}{\alpha_v^2 + \beta_v^2} + \frac{\alpha_c}{\alpha_c^2 + \beta_c^2} \end{pmatrix}, \quad (1.157)$$

from which we compute the magnetoresistance

$$\boxed{\frac{\rho_{xx}(B) - \rho_{xx}(0)}{\rho_{xx}(0)} = \frac{\sigma_c \sigma_v \left( \frac{\sigma_c}{n_c e c} - \frac{\sigma_v}{n_v e c} \right)^2 B^2}{(\sigma_c + \sigma_v)^2 + (\sigma_c \sigma_v)^2 \left( \frac{1}{n_c e c} + \frac{1}{n_v e c} \right)^2 B^2}} \quad (1.158)$$

where

$$\sigma_c = \alpha_c^{-1} = \frac{n_c e^2 \tau_c}{m_c} \cdot \frac{1}{1 - i\omega\tau_c} \quad (1.159)$$

$$\sigma_v = \alpha_v^{-1} = \frac{n_v e^2 \tau_v}{m_v} \cdot \frac{1}{1 - i\omega\tau_v}. \quad (1.160)$$

Note that the magnetoresistance is *positive* within the two band model, and that it *saturates* in the high field limit:

$$\frac{\rho_{xx}(B \rightarrow \infty) - \rho_{xx}(0)}{\rho_{xx}(0)} = \frac{\sigma_c \sigma_v \left( \frac{\sigma_c}{n_c e c} - \frac{\sigma_v}{n_v e c} \right)^2}{(\sigma_c \sigma_v)^2 \left( \frac{1}{n_c e c} + \frac{1}{n_v e c} \right)^2}. \quad (1.161)$$

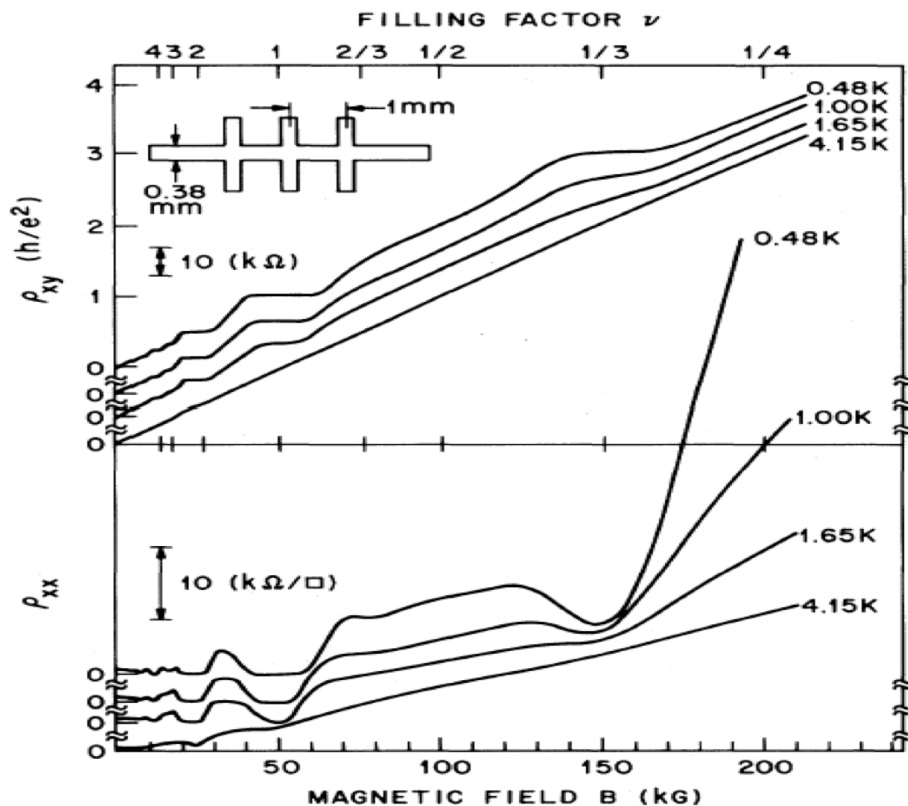


Figure 1.8: Nobel Prize winning magnetotransport data in a clean two-dimensional electron gas at a GaAs-AlGaAs inversion layer, from D. C. Tsui, H. L. Störmer, and A. C. Gossard, *Phys. Rev. Lett.* **48**, 1559 (1982).  $\rho_{xy}$  and  $\rho_{xx}$  are shown *versus* magnetic field for a set of four temperatures. The Landau level filling factor is  $\nu = nhc/eB$ . At  $T = 4.2$  K, the Hall resistivity obeys  $\rho_{xy} = B/nec$  ( $n = 1.3 \times 10^{11} \text{ cm}^{-2}$ ). At lower temperatures, quantized plateaus appear in  $\rho_{xy}(B)$  in units of  $h/e^2$ .

The longitudinal resistivity is found to be

$$\rho_{zz} = (\sigma_c + \sigma_v)^{-1} \quad (1.162)$$

and is independent of  $B$ .

In an intrinsic semiconductor,  $n_c = n_v \propto \exp(-E_g/2k_B T)$ , and  $\Delta\rho_{xx}(B)/\rho_{xx}(0)$  is finite even as  $T \rightarrow 0$ . In the extrinsic (*i.e.* doped) case, one of the densities (say,  $n_c$  in a p-type material) vanishes much more rapidly than the other, and the magnetoresistance vanishes with the ratio  $n_c/n_v$ .

### 1.7.4 Hall Effect in High Fields

In the high field limit, one may neglect the collision integral entirely, and write (at  $\omega = 0$ )

$$-e \mathbf{v} \cdot \boldsymbol{\mathcal{E}} \frac{\partial f^0}{\partial \varepsilon} - \frac{e}{\hbar c} \mathbf{v} \times \mathbf{B} \cdot \frac{\partial \delta f}{d\mathbf{k}} = 0 . \quad (1.163)$$

We'll consider the case of electrons, and take  $\boldsymbol{\mathcal{E}} = \mathcal{E} \hat{\mathbf{y}}$  and  $\mathbf{B} = B \hat{\mathbf{z}}$ , in which case the solution is

$$\delta f = \frac{\hbar c \mathcal{E}}{B} k_x \frac{\partial f^0}{\partial \varepsilon} . \quad (1.164)$$

Note that  $k_x$  is not a smooth single-valued function over the Brillouin-zone due to Bloch periodicity. This treatment, then, will make sense only if the derivative  $\partial f^0 / \partial \varepsilon$  confines  $\mathbf{k}$  to a closed orbit within the first Brillouin zone. In this case, we have

$$j_x = 2ec \frac{\mathcal{E}}{B} \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} k_x \frac{\partial \varepsilon}{\partial k_x} \frac{\partial f^0}{\partial \varepsilon} \quad (1.165)$$

$$= 2ec \frac{\mathcal{E}}{B} \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} k_x \frac{\partial f^0}{\partial k_x} . \quad (1.166)$$

Now we may integrate by parts, if we assume that  $f^0$  vanishes on the boundary of the Brillouin zone. We obtain

$$j_x = -\frac{2ec\mathcal{E}}{B} \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} f^0 = -\frac{nec}{B} \mathcal{E} . \quad (1.167)$$

We conclude that

$$\sigma_{xy} = -\sigma_{yx} = -\frac{nec}{B} , \quad (1.168)$$

*independent* of the details of the band structure. “Open orbits” – trajectories along Fermi surfaces which cross Brillouin zone boundaries and return in another zone – post a subtler problem, and generally lead to a finite, *non-saturating* magnetoresistance.

For holes, we have  $\bar{f}^0 = 1 - f^0$  and

$$j_x = -\frac{2ec\mathcal{E}}{B} \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} k_x \frac{\partial \bar{f}^0}{\partial k_x} = +\frac{nec}{B} \mathcal{E} \quad (1.169)$$

and  $\sigma_{xy} = +nec/B$ , where  $n$  is the hole density.

We define the *Hall coefficient*  $R_H = -\rho_{xy}/B$  and the *Hall number*

$$z_H \equiv -\frac{1}{n_{\text{ion}} ec R_H} , \quad (1.170)$$

where  $n_{\text{ion}}$  is the ion density. For high fields, the off-diagonal elements of both  $\rho_{\alpha\beta}$  and  $\sigma_{\alpha\beta}$  are negligible, and  $\rho_{xy} = -\sigma_{xy}$ . Hence  $R_H = \mp 1/nec$ , and  $z_H = \pm n/n_{\text{ion}}$ . The high

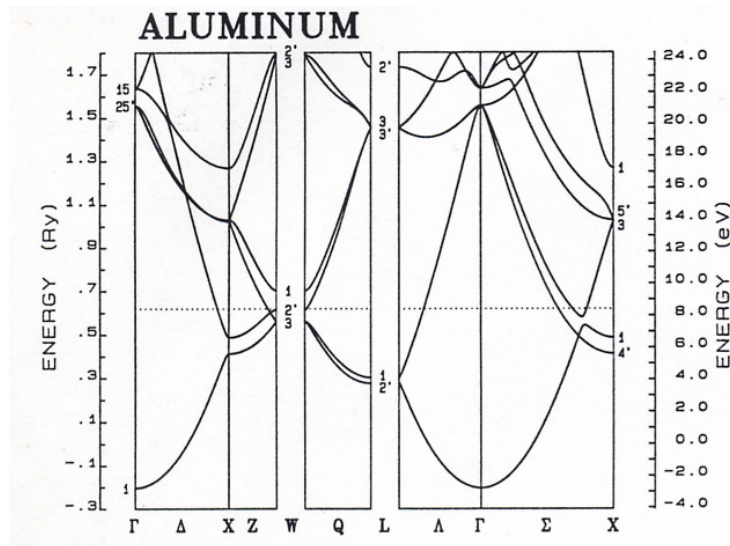


Figure 1.9: Energy bands in aluminum.

field Hall coefficient is used to determine both the carrier density as well as the sign of the charge carriers;  $z_H$  is a measure of valency.

In Al, the high field Hall coefficient saturates at  $z_H = -1$ . Why is  $z_H$  negative? As it turns out, aluminum has both electron and hole bands. Its valence is 3; two electrons go into a filled band, leaving one valence electron to split between the electron and hole bands. Thus  $n = 3n_{\text{ion}}$ . The Hall conductivity is

$$\sigma_{xy} = (n_h - n_e) ec/B . \quad (1.171)$$

The difference  $n_h - n_e$  is determined by the following argument. The *electron* density in the hole band is  $n'_e = 2n_{\text{ion}} - n_h$ , *i.e.* the total density of levels in the band (two states per unit cell) minus the number of empty levels in which there are holes. Thus,

$$n_h - n_e = 2n_{\text{ion}} - (n_e + n'_e) = n_{\text{ion}} , \quad (1.172)$$

where we've invoked  $n_e + n'_e = n_{\text{ion}}$ , since precisely one electron from each ion is shared between the two partially filled bands. Thus,  $\sigma_{xy} = n_{\text{ion}} ec/B = nec/3B$  and  $z_H = -1$ . At lower fields,  $z_H = +3$  is observed, which is what one would expect from the free electron model. Interband scattering, which is suppressed at high fields, leads to this result.



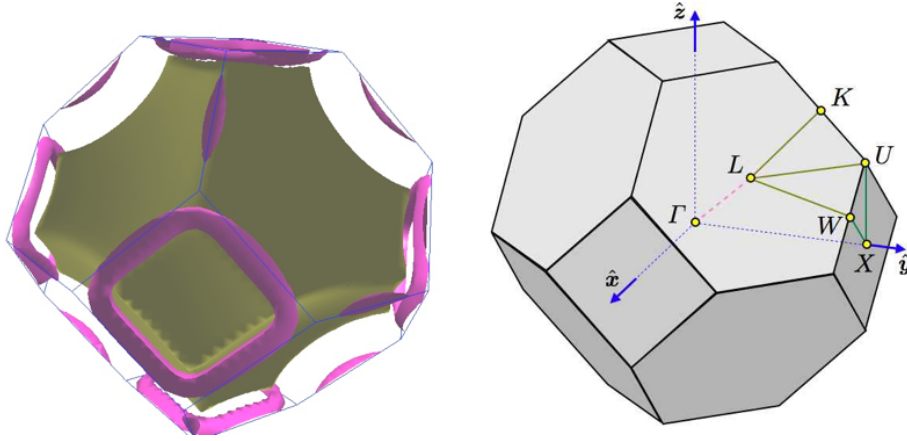


Figure 1.10: Fermi surfaces for electron (pink) and hole (gold) bands in Aluminum.

## 1.8 Thermal Transport

### 1.8.1 Boltzmann Theory

Consider a small region of solid with a fixed volume  $\Delta V$ . The first law of thermodynamics applied to this region gives  $T\Delta S = \Delta E - \mu\Delta N$ . Dividing by  $\Delta V$  gives

$$dq \equiv T ds = d\varepsilon - \mu dn , \quad (1.173)$$

where  $s$  is the entropy density,  $\varepsilon$  is energy density, and  $n$  the number density. This can be directly recast as the following relation among current densities:

$$\mathbf{j}_q = T\mathbf{j}_s = \mathbf{j}_\varepsilon - \mu \mathbf{j}_n , \quad (1.174)$$

where  $\mathbf{j}_n = \mathbf{j}/(-e)$  is the number current density,  $\mathbf{j}_\varepsilon$  is the energy current density,

$$\mathbf{j}_\varepsilon = 2 \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} \varepsilon \mathbf{v} \delta f , \quad (1.175)$$

and  $\mathbf{j}_s$  is the entropy current density. Accordingly, the thermal (heat) current density  $\mathbf{j}_q$  is defined as

$$\mathbf{j}_q \equiv T\mathbf{j}_s = \mathbf{j}_\varepsilon + \frac{\mu}{e} \mathbf{j} \quad (1.176)$$

$$= 2 \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} (\varepsilon - \mu) \mathbf{v} \delta f . \quad (1.177)$$

In the presence of a time-independent temperature gradient and electric field, linearized Boltzmann equation in the relaxation time approximation has the solution

$$\delta f = -\tau(\varepsilon) \mathbf{v} \cdot \left( e\mathcal{E} + \frac{\varepsilon - \mu}{T} \nabla T \right) \left( -\frac{\partial f^0}{\partial \varepsilon} \right) . \quad (1.178)$$

We now consider both the electrical current  $\mathbf{j}$  as well as the thermal current density  $\mathbf{j}_q$ . One readily obtains

$$\mathbf{j} = -2e \int_{\hat{\Omega}} \frac{d^3\mathbf{k}}{(2\pi)^3} \mathbf{v} \delta f \equiv L_{11} \boldsymbol{\mathcal{E}} - L_{12} \nabla T \quad (1.179)$$

$$\mathbf{j}_q = 2 \int_{\hat{\Omega}} \frac{d^3\mathbf{k}}{(2\pi)^3} (\varepsilon - \mu) \mathbf{v} \delta f \equiv L_{21} \boldsymbol{\mathcal{E}} - L_{22} \nabla T \quad (1.180)$$

where the *transport coefficients*  $L^{11}$  etc. are matrices:

$$L_{11}^{\alpha\beta} = \frac{e^2}{4\pi^3\hbar} \int d\varepsilon \tau(\varepsilon) \left( -\frac{\partial f^0}{\partial \varepsilon} \right) \int dS_\varepsilon \frac{v^\alpha v^\beta}{|\mathbf{v}|} \quad (1.181)$$

$$L_{21}^{\alpha\beta} = TL_{12}^{\alpha\beta} = -\frac{e}{4\pi^3\hbar} \int d\varepsilon \tau(\varepsilon) (\varepsilon - \mu) \left( -\frac{\partial f^0}{\partial \varepsilon} \right) \int dS_\varepsilon \frac{v^\alpha v^\beta}{|\mathbf{v}|} \quad (1.182)$$

$$L_{22}^{\alpha\beta} = \frac{1}{4\pi^3\hbar T} \int d\varepsilon \tau(\varepsilon) (\varepsilon - \mu)^2 \left( -\frac{\partial f^0}{\partial \varepsilon} \right) \int dS_\varepsilon \frac{v^\alpha v^\beta}{|\mathbf{v}|} . \quad (1.183)$$

If we define the hierarchy of integral expressions

$$\mathcal{J}_n^{\alpha\beta} \equiv \frac{1}{4\pi^3\hbar} \int d\varepsilon \tau(\varepsilon) (\varepsilon - \mu)^n \left( -\frac{\partial f^0}{\partial \varepsilon} \right) \int dS_\varepsilon \frac{v^\alpha v^\beta}{|\mathbf{v}|} \quad (1.184)$$

then we may write

$$L_{11}^{\alpha\beta} = e^2 \mathcal{J}_0^{\alpha\beta} \quad L_{21}^{\alpha\beta} = TL_{12}^{\alpha\beta} = -e \mathcal{J}_1^{\alpha\beta} \quad L_{22}^{\alpha\beta} = \frac{1}{T} \mathcal{J}_2^{\alpha\beta} . \quad (1.185)$$

The linear relations in eqn. (1.180) may be recast in the following form:

$$\boldsymbol{\mathcal{E}} = \rho \mathbf{j} + Q \nabla T \quad (1.186)$$

$$\mathbf{j}_q = \Gamma \mathbf{j} - \kappa \nabla T , \quad (1.187)$$

where the matrices  $\rho$ ,  $Q$ ,  $\Gamma$ , and  $\kappa$  are given by

$$\rho = L_{11}^{-1} \quad Q = L_{11}^{-1} L_{12} \quad (1.188)$$

$$\Gamma = L_{21} L_{11}^{-1} \quad \kappa = L_{22} - L_{21} L_{11}^{-1} L_{12} , \quad (1.189)$$

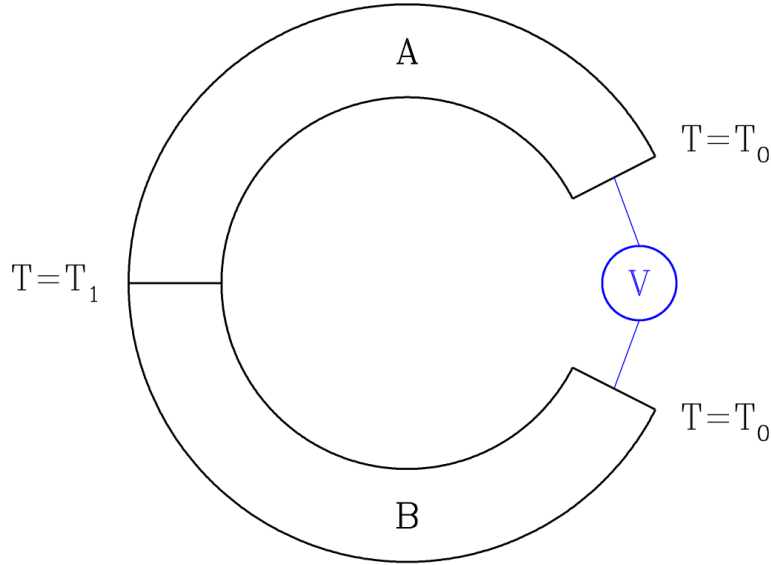
or, in terms of the  $\mathcal{J}_n$ ,

$$\rho = \frac{1}{e^2} \mathcal{J}_0^{-1} \quad Q = -\frac{1}{eT} \mathcal{J}_0^{-1} \mathcal{J}_1 \quad (1.190)$$

$$\Gamma = -\frac{1}{e} \mathcal{J}_1 \mathcal{J}_0^{-1} \quad \kappa = \frac{1}{T} \left( \mathcal{J}_2 - \mathcal{J}_1 \mathcal{J}_0^{-1} \mathcal{J}_1 \right) , \quad (1.191)$$

The names and physical interpretation of these four transport coefficients is as follows:

- $\rho$  is the *resistivity*:  $\boldsymbol{\mathcal{E}} = \rho \mathbf{j}$  under the condition of zero thermal gradient (*i.e.*  $\nabla T = 0$ ).



$$V = (Q_B - Q_A)(T_1 - T_0)$$

Figure 1.11: A thermocouple is a junction formed of two dissimilar metals. With no electrical current passing, an electric field is generated in the presence of a temperature gradient, resulting in a voltage  $V = V_A - V_B$ .

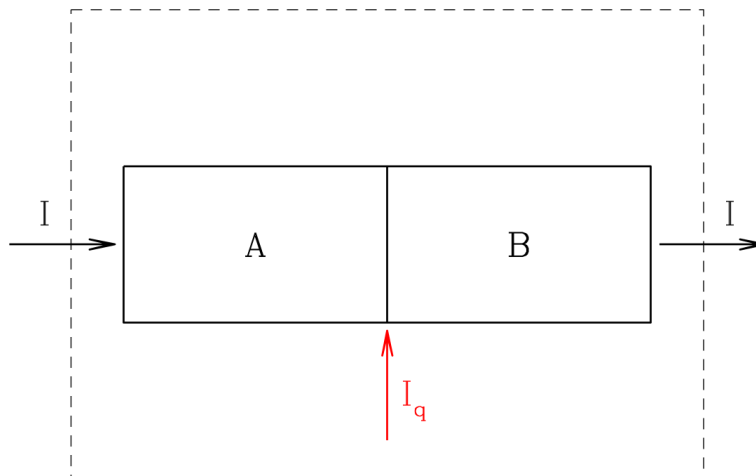
- $Q$  is the *thermopower*:  $\mathcal{E} = Q\nabla T$  under the condition of zero electrical current (*i.e.*  $\mathbf{j} = 0$ ).  $Q$  is also called the *Seebeck coefficient*.
- $\Pi$  is the *Peltier coefficient*:  $\mathbf{j}_q = \Pi\mathbf{j}$  when  $\nabla T = 0$ .
- $\kappa$  is the *thermal conductivity*:  $\mathbf{j}_q = -\kappa\nabla T$  when  $\mathbf{j} = 0$ .

One practical way to measure the thermopower is to form a junction between two dissimilar metals, A and B. The junction is held at temperature  $T_1$  and the other ends of the metals are held at temperature  $T_0$ . One then measures a voltage difference between the free ends of the metals – this is known as the Seebeck effect. Integrating the electric field from the free end of A to the free end of B gives

$$V_A - V_B = - \int_A^B \mathcal{E} \cdot d\mathbf{l} = (Q_B - Q_A)(T_1 - T_0). \quad (1.192)$$

What one measures here is really the difference in thermopowers of the two metals. For an absolute measurement of  $Q_A$ , replace B by a superconductor ( $Q = 0$  for a superconductor). A device which converts a temperature gradient into an emf is known as a *thermocouple*.

The Peltier effect has practical applications in refrigeration technology. Suppose an electrical current  $I$  is passed through a junction between two dissimilar metals, A and B. Due to



$$I_q = (\Pi_B - \Pi_A) \cdot I$$

Figure 1.12: A sketch of a Peltier effect refrigerator. An electrical current  $I$  is passed through a junction between two dissimilar metals. If the dotted line represents the boundary of a thermally well-insulated body, then the body cools when  $\Pi_B > \Pi_A$ , in order to maintain a heat current balance at the junction.

the difference in Peltier coefficients, there will be a net heat current into the junction of  $W = (\Pi_A - \Pi_B) I$ . Note that this is proportional to  $I$ , rather than the familiar  $I^2$  result from Joule heating. The sign of  $W$  depends on the direction of the current. If a second junction is added, to make an ABA configuration, then heat absorbed at the first junction will be liberated at the second.<sup>10</sup>

### 1.8.2 The Heat Equation

We begin with the continuity equations for charge density  $\rho$  and energy density  $\varepsilon$ :

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} = 0 \quad (1.193)$$

$$\frac{\partial \varepsilon}{\partial t} + \nabla \cdot \mathbf{j}_\varepsilon = \mathbf{j} \cdot \mathbf{E} , \quad (1.194)$$

<sup>10</sup>To create a refrigerator, stick the cold junction inside a thermally insulated box and the hot junction outside the box.

where  $\mathbf{E}$  is the electric field<sup>11</sup>. Now we invoke local thermodynamic equilibrium and write

$$\begin{aligned}\frac{\partial \varepsilon}{\partial t} &= \frac{\partial \varepsilon}{\partial n} \frac{\partial n}{\partial t} + \frac{\partial \varepsilon}{\partial T} \frac{\partial T}{\partial t} \\ &= -\frac{\mu}{e} \frac{\partial \rho}{\partial t} + c_V \frac{\partial T}{\partial t},\end{aligned}\tag{1.195}$$

where  $n$  is the electron *number density* ( $n = -\rho/e$ ) and  $c_V$  is the specific heat. We may now write

$$\begin{aligned}c_V \frac{\partial T}{\partial t} &= \frac{\partial \varepsilon}{\partial t} + \frac{\mu}{e} \frac{\partial \rho}{\partial t} \\ &= \mathbf{j} \cdot \mathbf{E} - \nabla \cdot \mathbf{j}_\varepsilon - \frac{\mu}{e} \nabla \cdot \mathbf{j} \\ &= \mathbf{j} \cdot \boldsymbol{\mathcal{E}} - \nabla \cdot \mathbf{j}_q.\end{aligned}\tag{1.196}$$

Invoking  $\mathbf{j}_q = \nabla T - \kappa \nabla T$ , we see that if there is no electrical current ( $\mathbf{j} = 0$ ), we obtain the *heat equation*

$$c_V \frac{\partial T}{\partial t} = \kappa_{\alpha\beta} \frac{\partial^2 T}{\partial x^\alpha \partial x^\beta}.\tag{1.197}$$

This results in a time scale  $\tau_T$  for temperature diffusion  $\tau_T = \mathcal{C}L^2 c_V / \kappa$ , where  $L$  is a typical length scale and  $\mathcal{C}$  is a numerical constant. For a cube of size  $L$  subjected to a sudden external temperature change,  $L$  is the side length and  $\mathcal{C} = 1/3\pi^2$  (solve by separation of variables).

### 1.8.3 Calculation of Transport Coefficients

We will henceforth assume that sufficient crystalline symmetry exists (*e.g.* cubic symmetry) to render all the transport coefficients multiples of the identity matrix. Under such conditions, we may write  $\mathcal{J}_n^{\alpha\beta} = \mathcal{J}_n \delta_{\alpha\beta}$  with

$$\mathcal{J}_n = \frac{1}{12\pi^3 \hbar} \int d\varepsilon \tau(\varepsilon) (\varepsilon - \mu)^n \left( -\frac{\partial f^0}{\partial \varepsilon} \right) \int dS_\varepsilon |\mathbf{v}|.\tag{1.198}$$

The low-temperature behavior is extracted using the Sommerfeld expansion,

$$\mathcal{I} \equiv \int_{-\infty}^{\infty} d\varepsilon H(\varepsilon) \left( -\frac{\partial f^0}{\partial \varepsilon} \right) = \pi \mathcal{D} \operatorname{csc}(\pi \mathcal{D}) H(\varepsilon) \Big|_{\varepsilon=\mu}\tag{1.199}$$

$$= H(\mu) + \frac{\pi^2}{6} (k_B T)^2 H''(\mu) + \dots\tag{1.200}$$

where  $\mathcal{D} \equiv k_B T \frac{\partial}{\partial \varepsilon}$  is a dimensionless differential operator.<sup>12</sup>

<sup>11</sup>Note that it is  $\mathbf{E} \cdot \mathbf{j}$  and *not*  $\boldsymbol{\mathcal{E}} \cdot \mathbf{j}$  which is the source term in the energy continuity equation.

<sup>12</sup>Remember that physically the fixed quantities are temperature and total carrier number density (or charge density, in the case of electron and hole bands), and *not* temperature and chemical potential. An equation of state relating  $n$ ,  $\mu$ , and  $T$  is then inverted to obtain  $\mu(n, T)$ , so that all results ultimately may be expressed in terms of  $n$  and  $T$ .

To quickly derive the Sommerfeld expansion, note that

$$\left(-\frac{\partial f^0}{\partial \varepsilon}\right) = \frac{1}{k_B T} \frac{1}{[e^{(\varepsilon-\mu)/k_B T} + 1][e^{(\mu-\varepsilon)/k_B T} + 1]}, \quad (1.201)$$

hence, changing variables to  $x \equiv (\varepsilon - \mu)/k_B T$ ,

$$\begin{aligned} \mathcal{I} &= \int_{-\infty}^{\infty} dx \frac{H(\mu + x k_B T)}{(e^x + 1)(e^{-x} + 1)} = \int_{-\infty}^{\infty} dx \frac{e^{x\mathcal{D}}}{(e^x + 1)(e^{-x} + 1)} H(\varepsilon) \Big|_{\varepsilon=\mu} \\ &= 2\pi i \sum_{n=0}^{\infty} \text{Res} \left[ \frac{e^{x\mathcal{D}}}{(e^x + 1)(e^{-x} + 1)} \right]_{x=(2n+1)i\pi} H(\varepsilon) \Big|_{\varepsilon=\mu}, \end{aligned} \quad (1.202)$$

where we treat  $\mathcal{D}$  as if it were  $c$ -number even though it is a differential operator. We have also closed the integration contour along a half-circle of infinite radius, enclosing poles in the upper half plane at  $x = (2n + 1)i\pi$  for all nonnegative integers  $n$ . To compute the residue, set  $x = (2n + 1)i\pi + \epsilon$ , and examine

$$\begin{aligned} \frac{e^{(2n+1)i\pi\mathcal{D}} e^{\epsilon\mathcal{D}}}{(1 - e^\epsilon)(1 - e^{-\epsilon})} &= -\frac{1 + \epsilon\mathcal{D} + \frac{1}{2}\epsilon^2\mathcal{D}^2 + \dots}{\epsilon^2 + \frac{1}{12}\epsilon^4 + \dots} \cdot e^{(2n+1)i\pi\mathcal{D}} \\ &= \left\{ -\frac{1}{\epsilon^2} - \frac{\mathcal{D}}{\epsilon} + \left(\frac{1}{12} - \frac{1}{2}\mathcal{D}^2\right) + \mathcal{O}(\epsilon) \right\} e^{(2n+1)i\pi\mathcal{D}}. \end{aligned} \quad (1.203)$$

We conclude that the residue is  $-\mathcal{D} e^{(2n+1)i\pi\mathcal{D}}$ . Therefore,

$$\begin{aligned} \mathcal{I} &= -2\pi i \mathcal{D} \sum_{n=0}^{\infty} e^{(2n+1)i\pi\mathcal{D}} H(\varepsilon) \Big|_{\varepsilon=\mu} \\ &= \pi \mathcal{D} \csc(\pi\mathcal{D}) H(\varepsilon) \Big|_{\varepsilon=\mu}, \end{aligned} \quad (1.204)$$

which is what we set out to show.

Let us now perform some explicit calculations in the case of a parabolic band with an energy-independent scattering time  $\tau$ . In this case, one readily finds

$$\mathcal{J}_n = \frac{\sigma_0}{e^2} \mu^{-3/2} \pi \mathcal{D} \csc \pi \mathcal{D} \varepsilon^{3/2} (\varepsilon - \mu)^n \Big|_{\varepsilon=\mu}, \quad (1.205)$$

where  $\sigma_0 = ne^2\tau/m^*$ . Thus,

$$\mathcal{J}_0 = \frac{\sigma_0}{e^2} \left[ 1 + \frac{\pi^2}{8} \frac{(k_B T)^2}{\mu^2} + \dots \right] \quad (1.206)$$

$$\mathcal{J}_1 = \frac{\sigma_0}{e^2} \frac{\pi^2}{2} \frac{(k_B T)^2}{\mu} + \dots \quad (1.207)$$

$$\mathcal{J}_2 = \frac{\sigma_0}{e^2} \frac{\pi^2}{3} (k_B T)^2 + \dots, \quad (1.208)$$

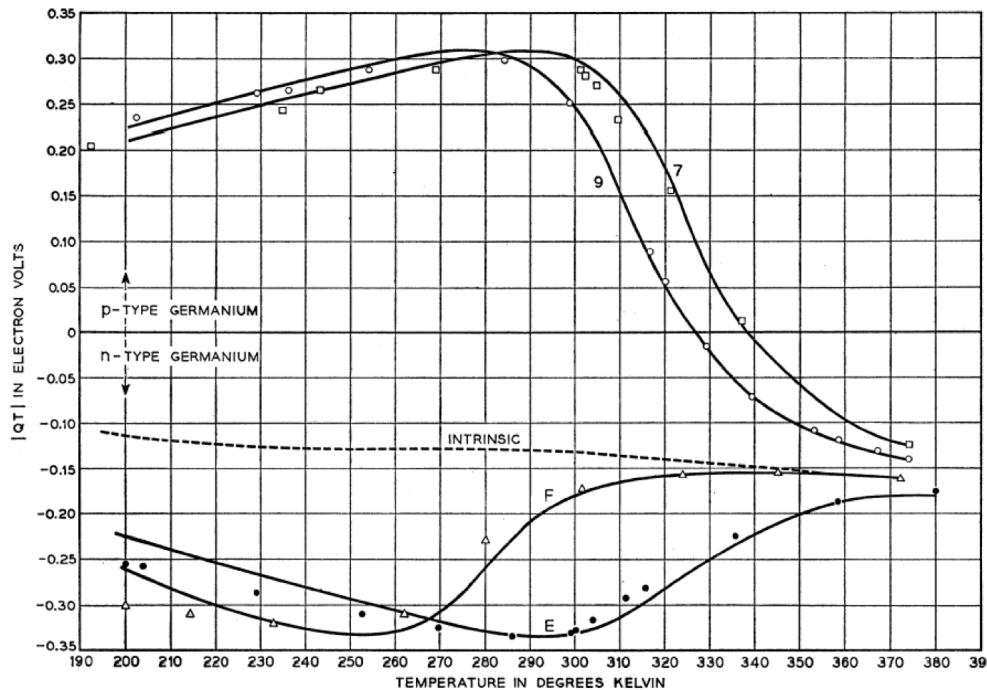


Figure 1.13:  $QT$  product for  $p$ -type and  $n$ -type Ge, from T. H. Geballe and J. W. Hull, *Phys. Rev.* **94**, 1134 (1954). Samples 7, 9, E, and F are distinguished by different doping properties, or by their resistivities at  $T = 300$  K:  $21.5 \Omega\text{-cm}$  (7),  $34.5 \Omega\text{-cm}$  (9),  $18.5 \Omega\text{-cm}$  (E), and  $46.0 \Omega\text{-cm}$  (F).

from which we obtain the low- $T$  results  $\rho = \sigma_0^{-1}$ ,

$$Q = -\frac{\pi^2}{2} \frac{k_B^2 T}{e \varepsilon_F} \quad \kappa = \frac{\pi^2}{3} \frac{n\tau}{m^*} k_B^2 T, \quad (1.209)$$

and of course  $\Pi = TQ$ . The predicted universal ratio

$$\frac{\kappa}{\sigma T} = \frac{\pi^2}{3} (k_B/e)^2 = 2.45 \times 10^{-8} \text{ V}^2 \text{ K}^{-2}, \quad (1.210)$$

is known as the *Wiedemann-Franz law*. Note also that our result for the thermopower is unambiguously negative. In actuality, several nearly free electron metals have positive low-temperature thermopowers (Cs and Li, for example). What went wrong? We have neglected electron-phonon scattering!

#### 1.8.4 Onsager Relations

Transport phenomena are described in general by a set of linear relations,

$$J_i = L_{ik} F_k, \quad (1.211)$$

where the  $\{F_k\}$  are *generalized forces* and the  $\{J_i\}$  are *generalized currents*. Moreover, to each force  $F_i$  corresponds a unique conjugate current  $J_i$ , such that the rate of internal entropy production is

$$\dot{S} = \sum_i F_i J_i \quad \Longrightarrow \quad F_i = \frac{\partial \dot{S}}{\partial J_i} . \quad (1.212)$$

The Onsager relations (also known as *Onsager reciprocity*) states that

$$L_{ik}(\mathbf{B}) = \eta_i \eta_k L_{ki}(-\mathbf{B}) , \quad (1.213)$$

where  $\eta_i$  describes the parity of  $J_i$  under time reversal:

$$\mathcal{T} J_i = \eta_i J_i . \quad (1.214)$$

We shall not prove the Onsager relations.

The Onsager relations have some remarkable consequences. For example, they require, for  $\mathbf{B} = 0$ , that the thermal conductivity tensor  $\kappa_{ij}$  of any crystal must be symmetric, independent of the crystal structure. In general, this result does not follow from considerations of crystalline symmetry. It also requires that for every ‘off-diagonal’ transport phenomenon, *e.g.* the Seebeck effect, there exists a distinct corresponding phenomenon, *e.g.* the Peltier effect.

For the transport coefficients studied, Onsager reciprocity means that in the presence of an external magnetic field,

$$\rho_{\alpha\beta}(\mathbf{B}) = \rho_{\beta\alpha}(-\mathbf{B}) \quad (1.215)$$

$$\kappa_{\alpha\beta}(\mathbf{B}) = \kappa_{\beta\alpha}(-\mathbf{B}) \quad (1.216)$$

$$\Pi_{\alpha\beta}(\mathbf{B}) = T Q_{\beta\alpha}(-\mathbf{B}) . \quad (1.217)$$

Let’s consider an isotropic system in a weak magnetic field, and expand the transport coefficients to first order in  $\mathbf{B}$ :

$$\rho_{\alpha\beta}(\mathbf{B}) = \rho \delta_{\alpha\beta} + \nu \epsilon_{\alpha\beta\gamma} B^\gamma \quad (1.218)$$

$$\kappa_{\alpha\beta}(\mathbf{B}) = \kappa \delta_{\alpha\beta} + \varpi \epsilon_{\alpha\beta\gamma} B^\gamma \quad (1.219)$$

$$Q_{\alpha\beta}(\mathbf{B}) = Q \delta_{\alpha\beta} + \zeta \epsilon_{\alpha\beta\gamma} B^\gamma \quad (1.220)$$

$$\Pi_{\alpha\beta}(\mathbf{B}) = \Pi \delta_{\alpha\beta} + \theta \epsilon_{\alpha\beta\gamma} B^\gamma . \quad (1.221)$$

Onsager reciprocity requires  $\Pi = T Q$  and  $\theta = T \zeta$ . We can now write

$$\mathcal{E} = \rho \mathbf{j} + \nu \mathbf{j} \times \mathbf{B} + Q \nabla T + \zeta \nabla T \times \mathbf{B} \quad (1.222)$$

$$\mathbf{j}_q = \Pi \mathbf{j} + \theta \mathbf{j} \times \mathbf{B} - \kappa \nabla T - \varpi \nabla T \times \mathbf{B} . \quad (1.223)$$

There are several new phenomena lurking!

- Hall Effect ( $\frac{\partial T}{\partial x} = \frac{\partial T}{\partial y} = j_y = 0$ )

An electrical current  $\mathbf{j} = j_x \hat{\mathbf{x}}$  and a field  $\mathbf{B} = B_z \hat{\mathbf{z}}$  yield an electric field  $\mathcal{E}$ . The Hall coefficient is  $R_H = \mathcal{E}_y / j_x B_z = -\nu$ .



- Etingshausen Effect ( $\frac{\partial T}{\partial x} = j_y = j_{q,y} = 0$ )  
An electrical current  $\mathbf{j} = j_x \hat{\mathbf{x}}$  and a field  $\mathbf{B} = B_z \hat{\mathbf{z}}$  yield a temperature gradient  $\frac{\partial T}{\partial y}$ . The Etingshausen coefficient is  $P = \frac{\partial T}{\partial y} / j_x B_z = -\theta/\kappa$ .
- Nernst Effect ( $j_x = j_y = \frac{\partial T}{\partial y} = 0$ )  
A temperature gradient  $\nabla T = \frac{\partial T}{\partial x} \hat{\mathbf{x}}$  and a field  $\mathbf{B} = B_z \hat{\mathbf{z}}$  yield an electric field  $\mathcal{E}$ . The Nernst coefficient is  $\Lambda = \mathcal{E}_y / \frac{\partial T}{\partial x} B_z = -\zeta$ .
- Righi-Leduc Effect ( $j_x = j_y = \mathcal{E}_y = 0$ )  
A temperature gradient  $\nabla T = \frac{\partial T}{\partial x} \hat{\mathbf{x}}$  and a field  $\mathbf{B} = B_z \hat{\mathbf{z}}$  yield an orthogonal temperature gradient  $\frac{\partial T}{\partial y}$ . The Righi-Leduc coefficient is  $\mathcal{L} = \frac{\partial T}{\partial y} / \frac{\partial T}{\partial x} B_z = \zeta/Q$ .

## 1.9 Electron-Phonon Scattering

### 1.9.1 Introductory Remarks

We begin our discussion by recalling some elementary facts about phonons in solids:

- In a crystal with  $r$  atoms per unit cell, there are  $3(r-1)$  optical modes and 3 acoustic modes, the latter guaranteed by the breaking of the three generators of space translations. We write the phonon dispersion as  $\omega = \omega_\lambda(\mathbf{q})$ , where  $\lambda \in \{1, \dots, 3r\}$  labels the phonon branch, and  $\mathbf{q} \in \hat{\Omega}$ . If  $j$  labels an acoustic mode,  $\omega_j(\mathbf{q}) = c_j(\hat{\mathbf{q}})q$  as  $\mathbf{q} \rightarrow 0$ .
- Phonons are bosonic particles with zero chemical potential. The equilibrium phonon distribution is

$$n_{\mathbf{q}\lambda}^0 = \frac{1}{\exp(\hbar\omega_\lambda(\mathbf{q})/k_B T) - 1} . \quad (1.224)$$

- The maximum phonon frequency is roughly given by the Debye frequency  $\omega_D$ . The Debye temperature  $\Theta_D = \hbar\omega_D \sim 100 \text{ K} - 1000 \text{ K}$  in most solids.

At high temperatures, equipartition gives  $\langle(\delta\mathbf{R}_i)^2\rangle \propto k_B T$ , hence the effective scattering cross-section  $\sigma_{\text{tot}}$  increases as  $T$ , and  $\tau \gtrsim 1/n_{\text{ion}} v_F \sigma_{\text{tot}} \propto T^{-1}$ . From  $\rho = m^*/ne^2\tau$ , then, we deduce that the high temperature resistivity should be linear in temperature due to phonon scattering:  $\rho(T) \propto T$ . Of course, when the mean free path  $\ell = v_F\tau$  becomes as small as the Fermi wavelength  $\lambda_F$ , the entire notion of coherent quasiparticle transport becomes problematic, and rather than continuing to grow we expect that the resistivity should saturate:  $\rho(T \rightarrow \infty) \approx h/k_F e^2$ , known as the *Ioffe-Regel limit*. For  $k_F = 10^8 \text{ cm}^{-1}$ , this takes the value  $260 \mu\Omega \text{ cm}$ .

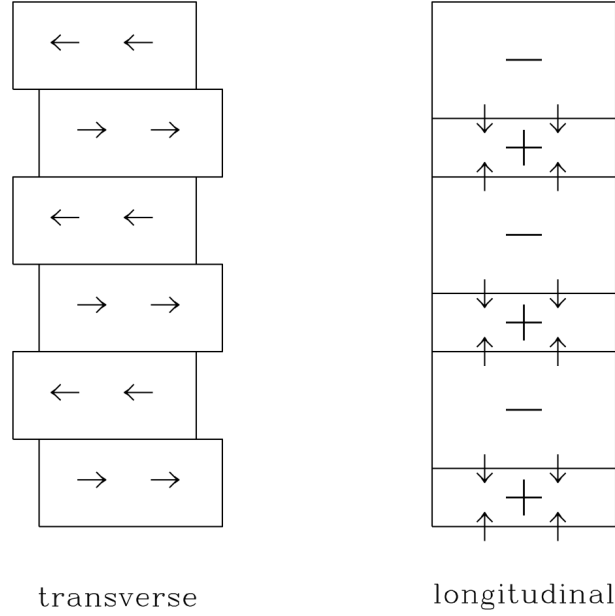


Figure 1.14: Transverse and longitudinal phonon polarizations. Transverse phonons do not result in charge accumulation. Longitudinal phonons create local charge buildup and therefore couple to electronic excitations via the Coulomb interaction.

### 1.9.2 Electron-Phonon Interaction

Let  $\mathbf{R}_i = \mathbf{R}_i^0 + \delta\mathbf{R}_i$  denote the position of the  $i^{\text{th}}$  ion, and let  $U(\mathbf{r}) = -Ze^2 \exp(-r/\lambda_{\text{TF}})/r$  be the electron-ion interaction. Expanding in terms of the ionic displacements  $\delta\mathbf{R}_i$ ,

$$\mathcal{H}_{\text{el-ion}} = \sum_i U(\mathbf{r} - \mathbf{R}_i^0) - \sum_i \delta\mathbf{R}_i \cdot \nabla U(\mathbf{r} - \mathbf{R}_i^0), \quad (1.225)$$

where  $i$  runs from 1 to  $N_{\text{ion}}$ <sup>13</sup>. The deviation  $\delta\mathbf{R}_i$  may be expanded in terms of the vibrational normal modes of the lattice, *i.e.* the phonons, as

$$\delta\mathbf{R}_i^\alpha = \frac{1}{\sqrt{N_{\text{ion}}}} \sum_{\mathbf{q}\lambda} \left( \frac{\hbar}{2\omega_\lambda(\mathbf{q})} \right)^{1/2} \hat{\mathbf{e}}_\lambda^\alpha(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{R}_i^0} (a_{\mathbf{q}\lambda} + a_{-\mathbf{q}\lambda}^\dagger). \quad (1.226)$$

The phonon polarization vectors satisfy  $\hat{\mathbf{e}}_\lambda(\mathbf{q}) = \hat{\mathbf{e}}_\lambda^*(-\mathbf{q})$  as well as the generalized orthonormality relations

$$\sum_\alpha \hat{\mathbf{e}}_\lambda^\alpha(\mathbf{q}) \hat{\mathbf{e}}_{\lambda'}^\alpha(-\mathbf{q}) = M^{-1} \delta_{\lambda\lambda'}, \quad (1.227)$$

$$\sum_\lambda \hat{\mathbf{e}}_\lambda^\alpha(\mathbf{q}) \hat{\mathbf{e}}_\lambda^\beta(-\mathbf{q}) = M^{-1} \delta_{\alpha\beta}, \quad (1.228)$$

<sup>13</sup>We assume a Bravais lattice, for simplicity.

where  $M$  is the ionic mass. The number of unit cells in the crystal is  $N_{\text{ion}} = V/\Omega$ , where  $\Omega$  is the Wigner-Seitz cell volume. Again, we approximate Bloch states by plane waves  $\psi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r})/\sqrt{V}$ , in which case

$$\langle \mathbf{k}' | \nabla U(\mathbf{r} - \mathbf{R}_i^0) | \mathbf{k} \rangle = -\frac{i}{V} e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{R}_i^0} \frac{4\pi Z e^2 (\mathbf{k} - \mathbf{k}')}{(\mathbf{k} - \mathbf{k}')^2 + \lambda_{\text{TF}}^{-2}}. \quad (1.229)$$

The sum over lattice sites gives

$$\sum_{i=1}^{N_{\text{ion}}} e^{i(\mathbf{k}-\mathbf{k}'+\mathbf{q}) \cdot \mathbf{R}_i^0} = N_{\text{ion}} \delta_{\mathbf{k}', \mathbf{k}+\mathbf{q} \bmod \mathbf{G}}, \quad (1.230)$$

so that

$$\mathcal{H}_{\text{el-ph}} = \frac{1}{\sqrt{V}} \sum_{\substack{\mathbf{k}, \mathbf{k}' \\ \mathbf{q} \in \mathbf{G}}} g_{\lambda}(\mathbf{k}, \mathbf{k}') (a_{\mathbf{q}\lambda}^{\dagger} + a_{-\mathbf{q}\lambda}) \psi_{\mathbf{k}\sigma}^{\dagger} \psi_{\mathbf{k}'\sigma} \delta_{\mathbf{k}', \mathbf{k}+\mathbf{q}+\mathbf{G}} \quad (1.231)$$

with

$$g_{\lambda}(\mathbf{k}, \mathbf{k} + \mathbf{q} + \mathbf{G}) = -i \left( \frac{\hbar}{2\Omega \omega_{\lambda}(\mathbf{q})} \right)^{1/2} \frac{4\pi Z e^2}{(\mathbf{q} + \mathbf{G})^2 + \lambda_{\text{TF}}^{-2}} (\mathbf{q} + \mathbf{G}) \cdot \hat{\mathbf{e}}_{\lambda}^*(\mathbf{q}). \quad (1.232)$$

In an isotropic solid<sup>14</sup> ('jellium'), the phonon polarization at wavevector  $\mathbf{q}$  either is parallel to  $\mathbf{q}$  (longitudinal waves), or perpendicular to  $\mathbf{q}$  (transverse waves). We see that only longitudinal waves couple to the electrons. This is because transverse waves do not result in any local accumulation of charge density, and it is to the charge density that electrons couple, via the Coulomb interaction.

Restricting our attention to the longitudinal phonon, we have  $\hat{\mathbf{e}}_{\text{L}}(\mathbf{q}) = \hat{\mathbf{q}}/\sqrt{M}$  and hence, for small  $\mathbf{q} = \mathbf{k}' - \mathbf{k}$ ,

$$g_{\text{L}}(\mathbf{k}, \mathbf{k} + \mathbf{q}) = -i \left( \frac{\hbar}{2M\Omega} \right)^{1/2} \frac{4\pi Z e^2}{q^2 + \lambda_{\text{TF}}^{-2}} c_{\text{L}}^{-1/2} q^{1/2}, \quad (1.233)$$

where  $c_{\text{L}}$  is the longitudinal phonon velocity. Thus, for small  $\mathbf{q}$  we have that the electron-longitudinal phonon coupling  $g_{\text{L}}(\mathbf{k}, \mathbf{k} + \mathbf{q}) \equiv g_{\mathbf{q}}$  satisfies

$$|g_{\mathbf{q}}|^2 = \lambda_{\text{el-ph}} \cdot \frac{\hbar c_{\text{L}} q}{g(\varepsilon_{\text{F}})}, \quad (1.234)$$

where  $g(\varepsilon_{\text{F}})$  is the electronic density of states, and where the dimensionless *electron-phonon coupling constant* is

$$\lambda_{\text{el-ph}} = \frac{Z^2}{2M c_{\text{L}}^2 \Omega g(\varepsilon_{\text{F}})} = \frac{2Z}{3} \frac{m^*}{M} \left( \frac{\varepsilon_{\text{F}}}{k_{\text{B}} \Theta_{\text{s}}} \right)^2, \quad (1.235)$$

with  $\Theta_{\text{s}} \equiv \hbar c_{\text{L}} k_{\text{F}}/k_{\text{B}}$ . Table 1.3 lists  $\Theta_{\text{s}}$ , the Debye temperature  $\Theta_{\text{D}}$ , and the electron-phonon coupling  $\lambda_{\text{el-ph}}$  for various metals.

**EXERCISE:** Derive eqn. (1.235).

<sup>14</sup>The jellium model ignores  $\mathbf{G} \neq 0$  *Umklapp* processes.

Metal	$\Theta_s$	$\Theta_D$	$\lambda_{\text{el-ph}}$	Metal	$\Theta_s$	$\Theta_D$	$\lambda_{\text{el-ph}}$
Na	220	150	0.47	Au	310	170	0.08
K	150	100	0.25	Be	1940	1000	0.59
Cu	490	315	0.16	Al	910	394	0.90
Ag	340	215	0.12	In	300	129	1.05

Table 1.3: Electron-phonon interaction parameters for some metals. Temperatures are in Kelvins.

### 1.9.3 Boltzmann Equation for Electron-Phonon Scattering

Earlier we had quoted the result for the electron-phonon collision integral,

$$\begin{aligned}
\mathcal{I}_{\mathbf{k}}\{f, n\} = & \frac{2\pi}{\hbar V} \sum_{\mathbf{k}', \lambda} |g_{\lambda}(\mathbf{k}, \mathbf{k}')|^2 \left\{ (1 - f_{\mathbf{k}}) f_{\mathbf{k}'} (1 + n_{q, \lambda}) \delta(\varepsilon_{\mathbf{k}} + \hbar\omega_{q\lambda} - \varepsilon_{\mathbf{k}'}) \right. \\
& + (1 - f_{\mathbf{k}}) f_{\mathbf{k}'} n_{-q\lambda} \delta(\varepsilon_{\mathbf{k}} - \hbar\omega_{-q\lambda} - \varepsilon_{\mathbf{k}'}) \\
& - f_{\mathbf{k}} (1 - f_{\mathbf{k}'}) (1 + n_{-q\lambda}) \delta(\varepsilon_{\mathbf{k}} - \hbar\omega_{-q\lambda} - \varepsilon_{\mathbf{k}'}) \\
& \left. - f_{\mathbf{k}} (1 - f_{\mathbf{k}'}) n_{q\lambda} \delta(\varepsilon_{\mathbf{k}} + \hbar\omega_{q\lambda} - \varepsilon_{\mathbf{k}'}) \right\} \delta_{\mathbf{q}, \mathbf{k}' - \mathbf{k} \bmod \mathbf{G}}.
\end{aligned} \tag{1.236}$$

The four terms inside the curly brackets correspond, respectively, to cases (a) through (d) in fig. 1.1. The  $(1 + n)$  factors in the phonon emission terms arise from both spontaneous as well as stimulated emission processes. There is no spontaneous absorption.

*EXERCISE:* Verify that in equilibrium  $\mathcal{I}_{\mathbf{k}}\{f^0, n^0\} = 0$ .

In principle we should also write down a Boltzmann equation for the phonon distribution  $n_{q\lambda}$  and solve the two coupled sets of equations. The electronic contribution to the phonon collision integral is written as  $\mathcal{J}_{q\lambda}\{f, n\}$ , with

$$\begin{aligned}
\mathcal{J}_{q\lambda}\{f, n\} \equiv \left( \frac{\partial n_{q\lambda}}{\partial t} \right)_{\text{coll}} = & \frac{4\pi}{\hbar V} |g_{q\lambda}|^2 \sum_{\mathbf{k} \in \hat{\Omega}} \left\{ (1 + n_{q\lambda}) f_{\mathbf{k}+q} (1 - f_{\mathbf{k}}) \right. \\
& \left. - n_{q\lambda} f_{\mathbf{k}} (1 - f_{\mathbf{k}+q}) \right\} \times \delta(\varepsilon_{\mathbf{k}+q} - \varepsilon_{\mathbf{k}} - \hbar\omega_{q\lambda}).
\end{aligned} \tag{1.237}$$

Here, we will assume that the phonons are always in equilibrium, and take  $n_{q\lambda} = n_{q\lambda}^0$ . Phonon equilibrium can be achieved via anharmonic effects (*i.e.* phonon-phonon scattering), or by scattering of phonons from impurities or crystalline defects. At low temperatures,

$$\frac{1}{\tau(\omega)} = \begin{cases} A\omega^2 & \text{impurity scattering} \\ B\omega^2 T^3 & \text{anharmonic phonon scattering} \\ C/L & \text{boundary scattering } (L = \text{crystal size}) \end{cases} \tag{1.238}$$

where  $A$ ,  $B$ , and  $C$  are constants.

We now linearize  $\mathcal{I}_{\mathbf{k}}\{f\}$ , and obtain

$$\begin{aligned} \mathcal{L} \delta f = \frac{2\pi}{\hbar V} \sum_{q\lambda} |g_{q\lambda}|^2 \left\{ \left[ (1 - f_{\mathbf{k}}^0 + n_{q\lambda}^0) \delta f_{\mathbf{k}+\mathbf{q}} - (f_{\mathbf{k}+\mathbf{q}}^0 + n_{q\lambda}^0) \delta f_{\mathbf{k}} \right] \delta(\varepsilon_{\mathbf{k}+\mathbf{q}} - \varepsilon_{\mathbf{k}} - \hbar\omega_{q\lambda}) \right. \\ \left. - \left[ (1 - f_{\mathbf{k}+\mathbf{q}}^0 + n_{-q\lambda}^0) \delta f_{\mathbf{k}} - (f_{\mathbf{k}}^0 + n_{-q\lambda}^0) \delta f_{\mathbf{k}+\mathbf{q}} \right] \delta(\varepsilon_{\mathbf{k}+\mathbf{q}} - \varepsilon_{\mathbf{k}} + \hbar\omega_{-q\lambda}) \right\}. \end{aligned} \quad (1.239)$$

This integral operator must be inverted in order to solve for  $\delta f_{\mathbf{k}}$  in

$$\mathcal{L} \delta f = e \mathbf{v} \cdot \boldsymbol{\mathcal{E}} \left( -\frac{\partial f^0}{\partial \varepsilon} \right). \quad (1.240)$$

Unfortunately, the inversion is analytically intractable – there is no simple solution of the form  $\delta f_{\mathbf{k}} = e \tau_{\mathbf{k}} \mathbf{v}_{\mathbf{k}} \cdot \boldsymbol{\mathcal{E}} (\partial f^0 / \partial \varepsilon)$  as there was in the case of isotropic impurity scattering. However, we can still identify the coefficient of  $-\delta f_{\mathbf{k}}$  in  $\mathcal{L} \delta f$  as the scattering rate  $\tau_{\mathbf{k}}^{-1}$ . As before,  $\tau_{\mathbf{k}}$  in fact is a function of the energy  $\varepsilon(\mathbf{k})$ :

$$\begin{aligned} \frac{1}{\tau(\varepsilon)} = \frac{1}{4\pi^2 \hbar^2} \int d\varepsilon' \int dS_{\varepsilon'} \frac{|g_{\mathbf{k}'-\mathbf{k}}|^2}{|\mathbf{v}_{\mathbf{k}'}|} \left\{ [f^0(\varepsilon') + n_{\mathbf{k}'-\mathbf{k}}^0] \delta(\varepsilon' - \varepsilon - \hbar\omega_{\mathbf{k}'-\mathbf{k}}) \right. \\ \left. + [1 + f^0(\varepsilon') + n_{\mathbf{k}-\mathbf{k}'}^0] \delta(\varepsilon' - \varepsilon + \hbar\omega_{\mathbf{k}-\mathbf{k}'}) \right\} \end{aligned} \quad (1.241)$$

In an isotropic system,  $\tau(\varepsilon(\mathbf{k}))$  is independent of  $\hat{\mathbf{k}}$ . This means we can take  $\mathbf{k} = \sqrt{2m^*\varepsilon/\hbar^2} \hat{\mathbf{z}}$  in performing the above integral.

It is convenient to define the dimensionless function

$$\alpha^2 F(\omega) \equiv \frac{1}{8\pi^3 \hbar^2} \int dS_{\varepsilon'} \frac{|g_{\mathbf{k}'-\mathbf{k}}|^2}{|\mathbf{v}_{\mathbf{k}'}|} \delta(\omega - \omega_{\mathbf{k}'-\mathbf{k}}). \quad (1.242)$$

For parabolic bands, one obtains

$$\begin{aligned} \alpha^2 F(\omega) &= \frac{1}{8\pi^3 \hbar^2} \frac{\lambda_{\text{el-ph}} \hbar\omega}{m^* k_{\text{F}} / \pi^2 \hbar^2} \frac{m^*}{\hbar k_{\text{F}}} k_{\text{F}}^2 \int d\hat{\mathbf{k}}' \delta(\omega - c_{\text{L}} k_{\text{F}} |\hat{\mathbf{k}}' - \hat{\mathbf{z}}|) \\ &= \lambda_{\text{el-ph}} \left( \frac{\hbar\omega}{k_{\text{B}} \Theta_{\text{s}}} \right)^2 \Theta(2k_{\text{B}} \Theta_{\text{s}} - \hbar\omega). \end{aligned} \quad (1.243)$$

The scattering rate is given in terms of  $\alpha^2 F(\omega)$  as

$$\frac{1}{\tau(\varepsilon)} = 2\pi \int_0^{\infty} d\omega \alpha^2 F(\omega) \left\{ f^0(\varepsilon + \hbar\omega) - f^0(\varepsilon - \hbar\omega) + 2n^0(\omega) + 1 \right\}. \quad (1.244)$$

At  $T = 0$  we have  $f^0(\varepsilon) = \Theta(\varepsilon_{\text{F}} - \varepsilon)$  and  $n^0(\omega) = 0$ , whence

$$\begin{aligned} \frac{1}{\tau(\varepsilon)} &= 2\pi \int_0^{\infty} d\omega \alpha^2 F(\omega) \left\{ \Theta(\varepsilon_{\text{F}} - \varepsilon - \hbar\omega) - \Theta(\varepsilon_{\text{F}} - \varepsilon + \hbar\omega) + 1 \right\} \\ &= \begin{cases} \frac{\lambda_{\text{el-ph}}}{12} \frac{2\pi}{\hbar} \cdot \frac{|\varepsilon - \varepsilon_{\text{F}}|^3}{(k_{\text{B}} \Theta_{\text{s}})^2} & \text{if } |\varepsilon - \varepsilon_{\text{F}}| < 2k_{\text{B}} \Theta_{\text{s}} \\ \frac{2\lambda_{\text{el-ph}}}{3} \frac{2\pi}{\hbar} \cdot (k_{\text{B}} \Theta_{\text{s}}) & \text{it } |\varepsilon - \varepsilon_{\text{F}}| > 2k_{\text{B}} \Theta_{\text{s}}. \end{cases} \end{aligned} \quad (1.245)$$

Note that  $\tau(\varepsilon_F) = \infty$ , unlike the case of impurity scattering. This is because at  $T = 0$  there are no phonons! For  $T \neq 0$ , the divergence is cut off, and one obtains

$$\frac{1}{\tau(\mu)} = \frac{2\pi\lambda_{\text{el-ph}}}{\hbar} \frac{k_B T^3}{\Theta_s^2} G\left(\frac{2\Theta_s}{T}\right) \quad (1.246)$$

$$G(y) = \int_0^y dx \frac{x^2}{2\sinh x} = \begin{cases} \frac{7}{4}\zeta(3) & \text{if } y = \infty \\ \frac{1}{4}y & \text{if } y \ll 1, \end{cases} \quad (1.247)$$

and so

$$\frac{1}{\tau(\mu)} = \begin{cases} \frac{7\pi\zeta(3)}{2\hbar} \frac{k_B T^3}{\Theta_s^2} \lambda_{\text{el-ph}} & \text{if } T \ll \Theta_s \\ \frac{2\pi}{\hbar} k_B T \lambda_{\text{el-ph}} & \text{if } T \gg \Theta_s \end{cases} \quad (1.248)$$

This calculation predicts that  $\tau \propto T^{-3}$  at low temperatures. This is correct if  $\tau$  is the *thermal lifetime*. However, a more sophisticated calculation shows that the *transport lifetime* behaves as  $\tau_{\text{tr}} \propto T^{-5}$  at low  $T$ . The origin of the discrepancy is our neglect of the  $(1 - \cos \vartheta)$  factor present in the average of the momentum relaxation time. At low  $T$ , there is only small angle scattering from the phonons, and  $\langle \vartheta^2 \rangle \propto \langle \mathbf{q}^2/k_F^2 \rangle \propto T^2$ . The Wiedemann-Franz law,  $\tau_\sigma = \tau_\kappa$ , is valid for  $k_B T \gtrsim \hbar c_L k_F$ , as well as at low  $T$  in isotropic systems, where impurity scattering is the dominant mechanism. It fails at intermediate temperatures.

## 1.10 Stuff You Should Know About Phonons

Crystalline solids support propagating waves called *phonons*, which are quantized vibrations of the lattice. Recall that the quantum mechanical Hamiltonian for a single harmonic oscillator,  $\hat{H} = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 q^2$ , may be written as  $\hat{H} = \hbar\omega_0(a^\dagger a + \frac{1}{2})$ , where  $a$  and  $a^\dagger$  are ‘ladder operators’ satisfying commutation relations  $[a, a^\dagger] = 1$ .

### 1.10.1 One-dimensional chain

Consider the linear chain of masses and springs depicted in fig. 1.15. We assume that our system consists of  $N$  mass points on a large ring of circumference  $L$ . In equilibrium, the masses are spaced evenly by a distance  $b = L/N$ . That is,  $x_n^0 = nb$  is the equilibrium position of particle  $n$ . We define  $u_n = x_n - x_n^0$  to be the difference between the position of mass  $n$  and The Hamiltonian is then

$$\begin{aligned} \hat{H} &= \sum_n \left[ \frac{p_n^2}{2m} + \frac{1}{2}\kappa(x_{n+1} - x_n - a)^2 \right] \\ &= \sum_n \left[ \frac{p_n^2}{2m} + \frac{1}{2}\kappa(u_{n+1} - u_n)^2 \right] + \frac{1}{2}N\kappa(b - a)^2, \end{aligned} \quad (1.249)$$

where  $a$  is the unstretched length of each spring,  $m$  is the mass of each mass point,  $\kappa$  is the force constant of each spring, and  $N$  is the total number of mass points. If  $b \neq a$  the springs are under tension in equilibrium, but as we see this only leads to an additive constant in the Hamiltonian, and hence does not enter the equations of motion.

The classical equations of motion are

$$\dot{u}_n = \frac{\partial \hat{H}}{\partial p_n} = \frac{p_n}{m} \quad (1.250)$$

$$\dot{p}_n = -\frac{\partial \hat{H}}{\partial u_n} = \kappa (u_{n+1} + u_{n-1} - 2u_n) . \quad (1.251)$$

Taking the time derivative of the first equation and substituting into the second yields

$$\ddot{u}_n = \frac{\kappa}{m} (u_{n+1} + u_{n-1} - 2u_n) . \quad (1.252)$$

We now write

$$u_n = \frac{1}{\sqrt{N}} \sum_k \tilde{u}_k e^{ikna} , \quad (1.253)$$

where periodicity  $u_{N+n} = u_n$  requires that the  $k$  values are quantized so that  $e^{ikNa} = 1$ , *i.e.*  $k = 2\pi j/Na$  where  $j \in \{0, 1, \dots, N-1\}$ . The inverse of this discrete Fourier transform is

$$\tilde{u}_k = \frac{1}{\sqrt{N}} \sum_n u_n e^{-ikna} . \quad (1.254)$$

Note that  $\tilde{u}_k$  is in general complex, but that  $\tilde{u}_k^* = \tilde{u}_{-k}$ . In terms of the  $\tilde{u}_k$ , the equations of motion take the form

$$\ddot{\tilde{u}}_k = -\frac{2\kappa}{m} (1 - \cos(ka)) \tilde{u}_k \equiv -\omega_k^2 \tilde{u}_k . \quad (1.255)$$

Thus, each  $\tilde{u}_k$  is a normal mode, and the normal mode frequencies are

$$\omega_k = 2 \sqrt{\frac{\kappa}{m}} \left| \sin\left(\frac{1}{2}ka\right) \right| . \quad (1.256)$$

The density of states for this band of phonon excitations is

$$\begin{aligned} g(\varepsilon) &= \int_{-\pi/a}^{\pi/a} \frac{dk}{2\pi} \delta(\varepsilon - \hbar\omega_k) \\ &= \frac{2}{\pi a} (J^2 - \varepsilon^2)^{-1/2} \Theta(\varepsilon) \Theta(J - \varepsilon) , \end{aligned} \quad (1.257)$$

where  $J = 2\hbar\sqrt{\kappa/m}$  is the phonon bandwidth. The step functions require  $0 \leq \varepsilon \leq J$ ; outside this range there are no phonon energy levels and the density of states accordingly vanishes.

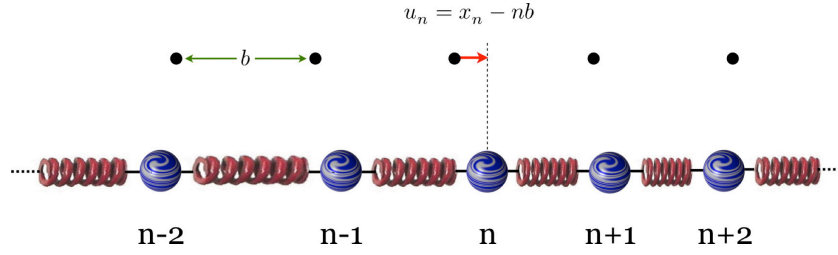


Figure 1.15: A linear chain of masses and springs. The black circles represent the equilibrium positions of the masses. The displacement of mass  $n$  relative to its equilibrium value is  $u_n$ .

The entire theory can be quantized, taking  $[p_n, u_{n'}] = -i\hbar\delta_{nn'}$ . We then define

$$p_n = \frac{1}{\sqrt{N}} \sum_k \tilde{p}_k e^{ikna} \quad , \quad \tilde{p}_k = \frac{1}{\sqrt{N}} \sum_n p_n e^{-ikna} \quad , \quad (1.258)$$

in which case  $[\tilde{p}_k, \tilde{u}_{k'}] = -i\hbar\delta_{kk'}$ . Note that  $\tilde{u}_k^\dagger = \tilde{u}_{-k}$  and  $\tilde{p}_k^\dagger = \tilde{p}_{-k}$ . We then define the ladder operator

$$a_k = \left( \frac{1}{2m\hbar\omega_k} \right)^{1/2} \tilde{p}_k - i \left( \frac{m\omega_k}{2\hbar} \right)^{1/2} \tilde{u}_k \quad (1.259)$$

and its Hermitean conjugate  $a_k^\dagger$ , in terms of which the Hamiltonian is

$$\hat{H} = \sum_k \hbar\omega_k \left( a_k^\dagger a_k + \frac{1}{2} \right) \quad , \quad (1.260)$$

which is a sum over independent harmonic oscillator modes. Note that the sum over  $k$  is restricted to an interval of width  $2\pi$ , e.g.  $k \in [-\frac{\pi}{a}, \frac{\pi}{a}]$ , which is the *first Brillouin zone* for the one-dimensional chain structure. The state at wavevector  $k + \frac{2\pi}{a}$  is identical to that at  $k$ , as we see from eqn. 1.254.

### 1.10.2 General theory of lattice vibrations

The most general model of a harmonic solid is described by a Hamiltonian of the form

$$\hat{H} = \sum_{\mathbf{R}, i} \frac{\mathbf{p}_i^2(\mathbf{R})}{2M_i} + \frac{1}{2} \sum_{i, j} \sum_{\alpha, \beta} \sum_{\mathbf{R}, \mathbf{R}'} u_i^\alpha(\mathbf{R}) \Phi_{ij}^{\alpha\beta}(\mathbf{R} - \mathbf{R}') u_j^\beta(\mathbf{R}') \quad , \quad (1.261)$$

where the *dynamical matrix* is

$$\Phi_{ij}^{\alpha\beta}(\mathbf{R} - \mathbf{R}') = \frac{\partial^2 U}{\partial u_i^\alpha(\mathbf{R}) \partial u_j^\beta(\mathbf{R}')} \quad , \quad (1.262)$$

where  $U$  is the potential energy of interaction among all the atoms. Here we have simply expanded the potential to second order in the local displacements  $u_i^\alpha(\mathbf{R})$ . The lattice sites  $\mathbf{R}$  are elements of a *Bravais lattice*. The indices  $i$  and  $j$  specify *basis elements* with respect to



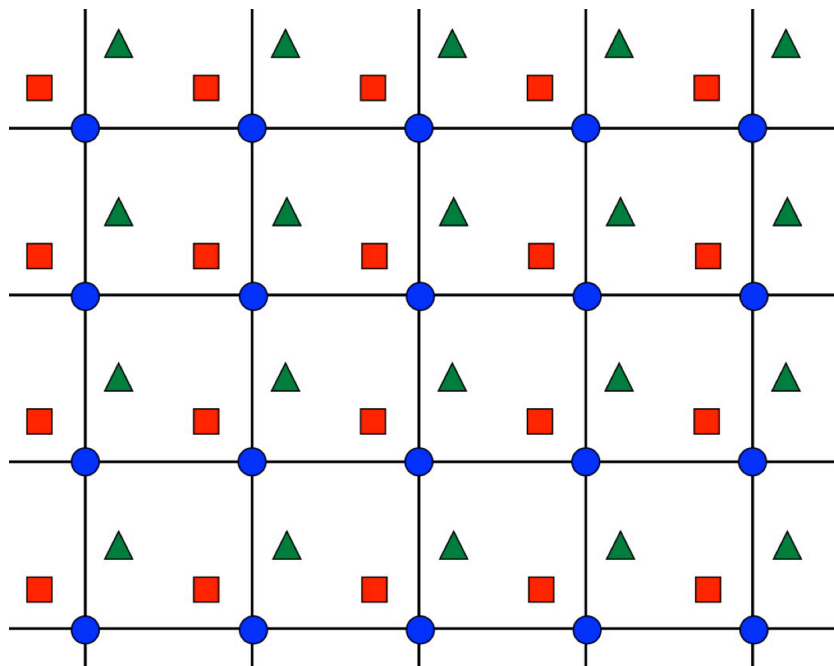


Figure 1.16: A crystal structure with an underlying square Bravais lattice and a three element basis.

this lattice, and the indices  $\alpha$  and  $\beta$  range over  $\{1, \dots, d\}$ , the number of possible directions in space. The subject of crystallography is beyond the scope of these notes, but, very briefly, a Bravais lattice in  $d$  dimensions is specified by a set of  $d$  linearly independent *primitive direct lattice vectors*  $\mathbf{a}_l$ , such that any point in the Bravais lattice may be written as a sum over the primitive vectors with integer coefficients:  $\mathbf{R} = \sum_{l=1}^d n_l \mathbf{a}_l$ . The set of all such vectors  $\{\mathbf{R}\}$  is called the *direct lattice*. The direct lattice is closed under the operation of vector addition: if  $\mathbf{R}$  and  $\mathbf{R}'$  are points in a Bravais lattice, then so is  $\mathbf{R} + \mathbf{R}'$ .

A crystal is a periodic arrangement of lattice sites. The fundamental repeating unit is called the *unit cell*. Not every crystal is a Bravais lattice, however. Indeed, Bravais lattices are special crystals in which there is only one atom per unit cell. Consider, for example, the structure in fig. 1.16. The blue dots form a square Bravais lattice with primitive direct lattice vectors  $\mathbf{a}_1 = a \hat{\mathbf{x}}$  and  $\mathbf{a}_2 = a \hat{\mathbf{y}}$ , where  $a$  is the *lattice constant*, which is the distance between any neighboring pair of blue dots. The red squares and green triangles, along with the blue dots, form a *basis* for the crystal structure which label each *sublattice*. Our crystal in fig. 1.16 is formally classified as a *square Bravais lattice with a three element basis*. To specify an arbitrary site in the crystal, we must specify both a direct lattice vector  $\mathbf{R}$  as well as a basis index  $j \in \{1, \dots, r\}$ , so that the location is  $\mathbf{R} + \boldsymbol{\eta}_j$ . The vectors  $\{\boldsymbol{\eta}_j\}$  are the *basis vectors* for our crystal structure. We see that a general crystal structure consists of a repeating unit, known as a *unit cell*. The centers (or corners, if one prefers) of the unit cells form a Bravais lattice. Within a given unit cell, the individual sublattice sites are located at positions  $\boldsymbol{\eta}_j$  with respect to the unit cell position  $\mathbf{R}$ .

Upon diagonalization, the Hamiltonian of eqn. 1.261 takes the form

$$\hat{H} = \sum_{\mathbf{k}, a} \hbar \omega_a(\mathbf{k}) \left( A_a^\dagger(\mathbf{k}) A_a(\mathbf{k}) + \frac{1}{2} \right), \quad (1.263)$$

where

$$[A_a(\mathbf{k}), A_b^\dagger(\mathbf{k}')] = \delta_{ab} \delta_{\mathbf{k}\mathbf{k}'} . \quad (1.264)$$

The eigenfrequencies are solutions to the eigenvalue equation

$$\sum_{j, \beta} \tilde{\Phi}_{ij}^{\alpha\beta}(\mathbf{k}) \mathbf{e}_{j\beta}^{(a)}(\mathbf{k}) = M_i \omega_a^2(\mathbf{k}) \mathbf{e}_{i\alpha}^{(a)}(\mathbf{k}), \quad (1.265)$$

where

$$\tilde{\Phi}_{ij}^{\alpha\beta}(\mathbf{k}) = \sum_{\mathbf{R}} \Phi_{ij}^{\alpha\beta}(\mathbf{R}) e^{-i\mathbf{k}\cdot\mathbf{R}} . \quad (1.266)$$

Here,  $\mathbf{k}$  lies within the first *Brillouin zone*, which is the unit cell of the *reciprocal lattice* of points  $\mathbf{G}$  satisfying  $e^{i\mathbf{G}\cdot\mathbf{R}} = 1$  for all  $\mathbf{G}$  and  $\mathbf{R}$ . The reciprocal lattice is also a Bravais lattice, with primitive reciprocal lattice vectors  $\mathbf{b}_l$ , such that any point on the reciprocal lattice may be written  $\mathbf{G} = \sum_{l=1}^d m_l \mathbf{b}_l$ . One also has that  $\mathbf{a}_l \cdot \mathbf{b}_{l'} = 2\pi\delta_{ll'}$ . The index  $a$  ranges from 1 to  $d \cdot r$  and labels the *mode* of oscillation at wavevector  $\mathbf{k}$ . The vector  $\mathbf{e}_{i\alpha}^{(a)}(\mathbf{k})$  is the *polarization vector* for the  $a^{\text{th}}$  phonon branch. In solids of high symmetry, phonon modes can be classified as longitudinal or transverse excitations.

### 1.10.3 Example: phonons in the HCP structure

The HCP structure is represented as an underlying simple hexagonal lattice with a two-element basis:

$$\mathbf{a}_1 = a \hat{\mathbf{x}} \quad , \quad \mathbf{a}_2 = \frac{1}{2}a \hat{\mathbf{x}} + \frac{\sqrt{3}}{2}a \hat{\mathbf{y}} \quad , \quad \mathbf{a}_3 = \sqrt{\frac{8}{3}}a \hat{\mathbf{z}} . \quad (1.267)$$

Bravais lattice sites are of the form  $\mathbf{R} = l\mathbf{a}_1 + m\mathbf{a}_2 + n\mathbf{a}_3$ . The A sublattice occupies the sites  $\{\mathbf{R}\}$ , while the B sublattice occupies the sites  $\{\mathbf{R} + \boldsymbol{\delta}\}$ , where

$$\boldsymbol{\delta} = \frac{1}{2}a \hat{\mathbf{x}} + \frac{1}{2\sqrt{3}}a \hat{\mathbf{y}} + \sqrt{\frac{2}{3}}a \hat{\mathbf{z}} . \quad (1.268)$$

The nearest neighbor separation is  $|\mathbf{a}_1| = |\mathbf{a}_2| = |\boldsymbol{\delta}| = a$ . Note that  $\mathbf{R}$  can be used to label the unit cells, *i.e.* each unit cell is labeled by the coordinates of its constituent A sublattice site.

#### Classical energy

The classical energy for the system is the potential energy of the fixed lattice, given by

$$\frac{U_0}{N} = \sum_{\mathbf{R}} \left[ v(\mathbf{R}) (1 - \delta_{\mathbf{R},0}) + v(\mathbf{R} + \boldsymbol{\delta}) \right], \quad (1.269)$$

where  $v(\mathbf{r})$  is the interatomic potential.

### Dynamical matrix

When phonon fluctuations are included, the positions of the A and B sublattice sites are written

$$\begin{aligned}\mathbf{R} &\longrightarrow \mathbf{R} + \mathbf{u}_A(\mathbf{R}) \\ \mathbf{R} + \boldsymbol{\delta} &\longrightarrow \mathbf{R} + \boldsymbol{\delta} + \mathbf{u}_B(\mathbf{R}) .\end{aligned}\quad (1.270)$$

Then the potential energy is

$$\begin{aligned}U = U_0 + \sum_{\mathbf{R}} \left( \mathbf{u}_A(\mathbf{R}) \cdot \mathbf{F}_A(\mathbf{R}) + \mathbf{u}_B(\mathbf{R}) \cdot \mathbf{F}_B(\mathbf{R}) \right) \\ + \frac{1}{2} \sum_{\mathbf{R}, \mathbf{R}'} \sum_{j, j'} \sum_{\alpha, \alpha'} \Phi_{jj'}^{\alpha\alpha'}(\mathbf{R} - \mathbf{R}') u_j^\alpha(\mathbf{R}) u_{j'}^{\alpha'}(\mathbf{R}') + \mathcal{O}(u^3) ,\end{aligned}\quad (1.271)$$

where

$$\Phi_{jj'}^{\alpha\alpha'}(\mathbf{R} - \mathbf{R}') = \frac{\partial^2 U}{\partial u_j^\alpha(\mathbf{R}) \partial u_{j'}^{\alpha'}(\mathbf{R}')} .\quad (1.272)$$

Here  $\{\alpha, \alpha'\}$  are spatial indices  $(x, y, z)$ , and  $\{j, j'\}$  are sublattice indices (A, B).

It is convenient to Fourier transform, with

$$\begin{aligned}u_A^\alpha(\mathbf{R}) &= \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} \hat{u}_A^\alpha(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{R}} \\ u_B^\alpha(\mathbf{R}) &= \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} \hat{u}_B^\alpha(\mathbf{k}) e^{i\mathbf{k}\cdot(\mathbf{R}+\boldsymbol{\delta})} ,\end{aligned}\quad (1.273)$$

where  $N$  is the total number of unit cells. Then

$$U = U_0 + \sum_{\mathbf{k}} \sum_j \hat{\mathbf{u}}_j(\mathbf{k}) \cdot \hat{\mathbf{F}}_j(-\mathbf{k}) + \frac{1}{2} \sum_{\mathbf{k}} \sum_{j, j'} \sum_{\alpha, \alpha'} \hat{\Phi}_{jj'}^{\alpha\alpha'}(\mathbf{k}) \hat{u}_j^\alpha(\mathbf{k}) \hat{u}_{j'}^{\alpha'}(-\mathbf{k}) + \mathcal{O}(u^3) ,\quad (1.274)$$

where the dynamical matrix is

$$\hat{\Phi}_{jj'}^{\alpha\alpha'}(\mathbf{k}) = \begin{pmatrix} \hat{\Phi}_{11}^{\alpha\alpha'}(\mathbf{k}) & \hat{\Phi}_{12}^{\alpha\alpha'}(\mathbf{k}) \\ \hat{\Phi}_{21}^{\alpha\alpha'}(\mathbf{k}) & \hat{\Phi}_{11}^{\alpha\alpha'}(\mathbf{k}) \end{pmatrix} .\quad (1.275)$$

where

$$\begin{aligned}\hat{\Phi}_{11}^{\alpha\beta}(\mathbf{k}) &= \sum_{\mathbf{R}}' (1 - \cos \mathbf{k} \cdot \mathbf{R}) \frac{\partial^2 v(\mathbf{R})}{\partial R^\alpha \partial R^\beta} + \sum_{\mathbf{R}} \partial_\alpha \partial_\beta v(\mathbf{R} + \boldsymbol{\delta}) \\ \hat{\Phi}_{12}^{\alpha\beta}(\mathbf{k}) &= - \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot(\mathbf{R}+\boldsymbol{\delta})} \frac{\partial^2 v(\mathbf{R} + \boldsymbol{\delta})}{\partial R^\alpha \partial R^\beta}\end{aligned}\quad (1.276)$$

Note that  $\hat{\Phi}_{21}^{\alpha\beta}(\mathbf{k}) = [\hat{\Phi}_{12}^{\alpha\beta}(\mathbf{k})]^*$ . Note also that if  $v(\mathbf{R}) = v(R)$  is a central potential, then

$$\frac{\partial^2 v(R)}{\partial R^\alpha \partial R^\beta} = (\delta^{\alpha\beta} - \hat{R}^\alpha \hat{R}^\beta) \frac{v'(R)}{R} + \hat{R}^\alpha \hat{R}^\beta v''(R) ,\quad (1.277)$$

where  $\hat{R}^\alpha = R^\alpha / |\mathbf{R}|$ .

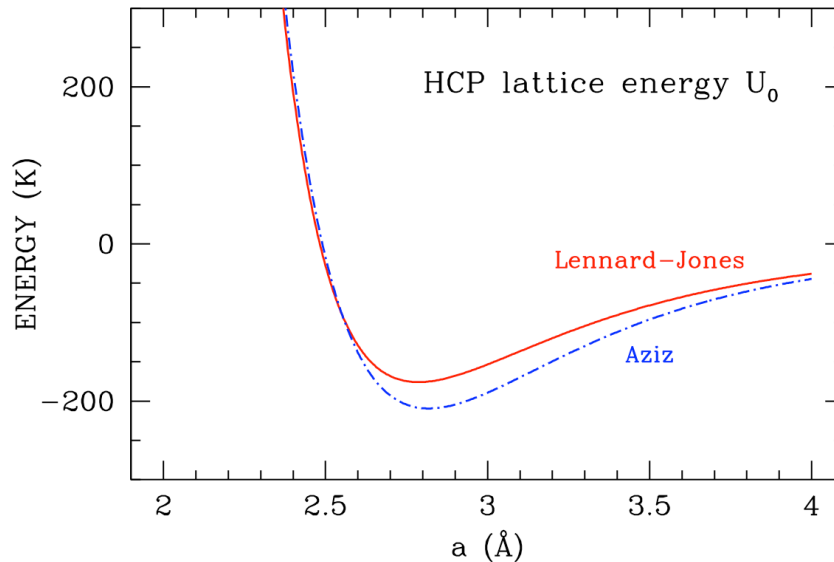


Figure 1.17: Classical lattice energy for hcp  ${}^4\text{He}$  as a function of nearest neighbor separation  $a$  for the Lennard-Jones potential (red) and the Aziz potential (blue).

### Lennard-Jones potential

The Lennard-Jones potential is given by

$$v(r) = 4\varepsilon_0 \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad (1.278)$$

where

$$\varepsilon_0 = 10.22 \text{ K} \quad , \quad \sigma = 2.556 \text{ \AA} . \quad (1.279)$$

### Aziz potential

The Aziz potential is given by

$$v(r) = \varepsilon_0 \left\{ A e^{-\alpha r/b} - \left[ C_6 \left( \frac{b}{r} \right)^6 + C_8 \left( \frac{b}{r} \right)^8 + C_{10} \left( \frac{b}{r} \right)^{10} \right] F(r) \right\} , \quad (1.280)$$

where

$$F(r) = \begin{cases} e^{-\left(\frac{Db}{r}-1\right)^2} & \text{if } r \leq Db \\ 1 & \text{if } r > Db \end{cases} , \quad (1.281)$$

with

$$\varepsilon = 10.8 \text{ K} \quad , \quad b = 2.9763 \text{ \AA} \quad , \quad A = 5.448504 \times 10^5 \quad , \quad \alpha = 13.353384 \quad (1.282)$$

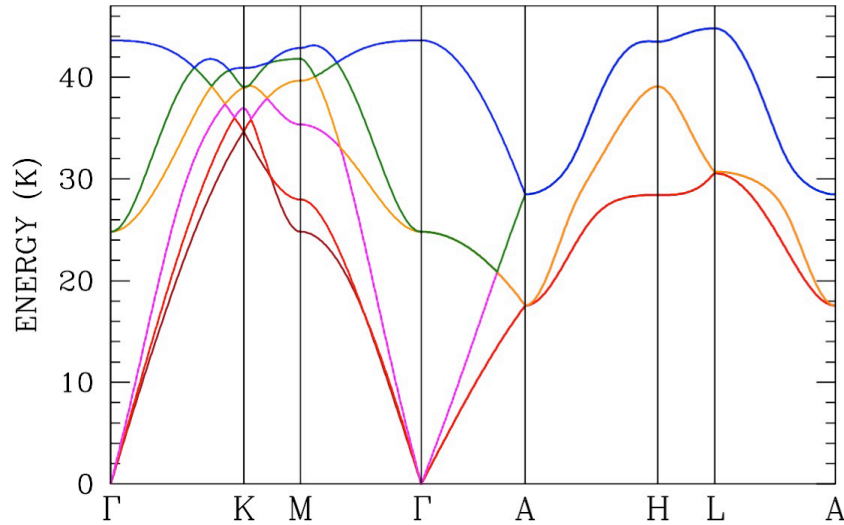


Figure 1.18: Phonon dispersions along high-symmetry directions in the Brillouin zone for hcp  ${}^4\text{He}$  at molar volume  $v_0 = 12 \text{ cm}^3/\text{mol}$ , using the Lennard-Jones potential.

and

$$C_6 = 1.37732412 \quad , \quad C_8 = 0.4253785 \quad , \quad C_{10} = 0.171800 \quad , \quad D = 1.231314 \quad . \quad (1.283)$$

The mass of the helium-4 atom is  $m = 6.65 \times 10^{-24} \text{ g}$ .

#### 1.10.4 Phonon density of states

For a crystalline lattice with an  $r$ -element basis, there are then  $d \cdot r$  phonon modes for each wavevector  $\mathbf{k}$  lying in the first Brillouin zone. If we impose periodic boundary conditions, then the  $\mathbf{k}$  points within the first Brillouin zone are themselves quantized, as in the  $d = 1$  case where we found  $k = 2\pi n/N$ . There are  $N$  distinct  $\mathbf{k}$  points in the first Brillouin zone – one for every direct lattice site. The total number of modes is then  $d \cdot r \cdot N$ , which is the total number of translational degrees of freedom in our system:  $rN$  total atoms ( $N$  unit cells each with an  $r$  atom basis) each free to vibrate in  $d$  dimensions. Of the  $d \cdot r$  branches of phonon excitations,  $d$  of them will be *acoustic modes* whose frequency vanishes as  $\mathbf{k} \rightarrow 0$ . The remaining  $d(r - 1)$  branches are *optical modes* and oscillate at finite frequencies. Basically, in an acoustic mode, for  $\mathbf{k}$  close to the (Brillouin) zone center  $\mathbf{k} = 0$ , all the atoms in each unit cell move together in the same direction at any moment of time. In an optical mode, the different basis atoms move in different directions.

There is no number conservation law for phonons – they may be freely created or destroyed in anharmonic processes, where two photons with wavevectors  $\mathbf{k}$  and  $\mathbf{q}$  can combine into a single phonon with wavevector  $\mathbf{k} + \mathbf{q}$ , and *vice versa*. Therefore the chemical potential for

phonons is  $\mu = 0$ . We define the density of states  $g_a(\omega)$  for the  $a^{\text{th}}$  phonon mode as

$$g_a(\omega) = \frac{1}{N} \sum_{\mathbf{k}} \delta(\omega - \omega_a(\mathbf{k})) = \mathcal{V}_0 \int_{\text{BZ}} \frac{d^d \mathbf{k}}{(2\pi)^d} \delta(\omega - \omega_a(\mathbf{k})) , \quad (1.284)$$

where  $N$  is the number of unit cells,  $\mathcal{V}_0$  is the unit cell volume of the direct lattice, and the  $\mathbf{k}$  sum and integral are over the first Brillouin zone only. Note that  $\omega$  here has dimensions of frequency. The functions  $g_a(\omega)$  is normalized to unity:

$$\int_0^{\infty} d\omega g_a(\omega) = 1 . \quad (1.285)$$

The total phonon density of states per unit cell is given by<sup>15</sup>

$$g(\omega) = \sum_{a=1}^{dr} g_a(\omega) . \quad (1.286)$$

The grand potential for the phonon gas is

$$\begin{aligned} \Omega(T, V) &= -k_{\text{B}} T \ln \prod_{\mathbf{k}, a} \sum_{n_a(\mathbf{k})=0}^{\infty} e^{-\beta \hbar \omega_a(\mathbf{k}) (n_a(\mathbf{k}) + \frac{1}{2})} \\ &= k_{\text{B}} T \sum_{\mathbf{k}, a} \ln \left[ 2 \sinh \left( \frac{\hbar \omega_a(\mathbf{k})}{2k_{\text{B}} T} \right) \right] \\ &= N k_{\text{B}} T \int_0^{\infty} d\omega g(\omega) \ln \left[ 2 \sinh \left( \frac{\hbar \omega}{2k_{\text{B}} T} \right) \right] . \end{aligned} \quad (1.287)$$

Note that  $V = N\mathcal{V}_0$  since there are  $N$  unit cells, each of volume  $\mathcal{V}_0$ . The entropy is given by  $S = -(\frac{\partial \Omega}{\partial T})_V$  and thus the heat capacity is

$$C_V = -T \frac{\partial^2 \Omega}{\partial T^2} = N k_{\text{B}} \int_0^{\infty} d\omega g(\omega) \left( \frac{\hbar \omega}{2k_{\text{B}} T} \right)^2 \text{csch}^2 \left( \frac{\hbar \omega}{2k_{\text{B}} T} \right) \quad (1.288)$$

Note that as  $T \rightarrow \infty$  we have  $\text{csch}(\frac{\hbar \omega}{2k_{\text{B}} T}) \rightarrow \frac{2k_{\text{B}} T}{\hbar \omega}$ , and therefore

$$\lim_{T \rightarrow \infty} C_V(T) = N k_{\text{B}} \int_0^{\infty} d\omega g(\omega) = rdNk_{\text{B}} . \quad (1.289)$$

This is the classical Dulong-Petit limit of  $\frac{1}{2}k_{\text{B}}$  per quadratic degree of freedom; there are  $rN$  atoms moving in  $d$  dimensions, hence  $d \cdot rN$  positions and an equal number of momenta, resulting in a high temperature limit of  $C_V = rdNk_{\text{B}}$ .

<sup>15</sup>Note the dimensions of  $g(\omega)$  are (frequency)<sup>-1</sup>. By contrast, the dimensions of  $g(\varepsilon)$  in eqn. ?? are (energy)<sup>-1</sup> · (volume)<sup>-1</sup>. The difference lies in the a factor of  $\mathcal{V}_0 \cdot \hbar$ , where  $\mathcal{V}_0$  is the unit cell volume.

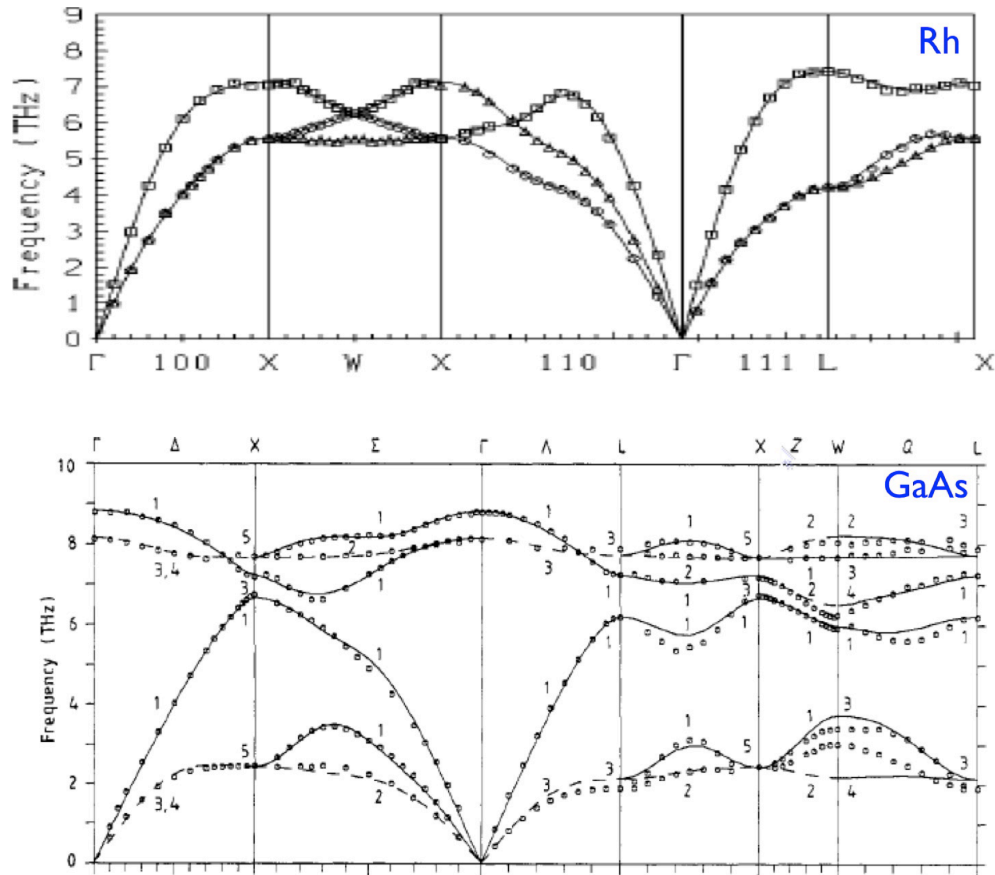


Figure 1.19: Upper panel: phonon spectrum in elemental rhodium (Rh) at  $T = 297$  K measured by high precision inelastic neutron scattering (INS) by A. Eichler *et al.*, *Phys. Rev. B* **57**, 324 (1998). Note the three acoustic branches and no optical branches, corresponding to  $d = 3$  and  $r = 1$ . Lower panel: phonon spectrum in gallium arsenide (GaAs) at  $T = 12$  K, comparing theoretical lattice-dynamical calculations with INS results of D. Strauch and B. Dorner, *J. Phys.: Condens. Matter* **2**, 1457 (1990). Note the three acoustic branches and three optical branches, corresponding to  $d = 3$  and  $r = 2$ . The Greek letters along the  $x$ -axis indicate points of high symmetry in the Brillouin zone.

### 1.10.5 Einstein and Debye models

Historically, two models of lattice vibrations have received wide attention. First is the so-called *Einstein model*, in which there is no dispersion to the individual phonon modes. We approximate  $g_a(\omega) \approx \delta(\omega - \omega_a)$ , in which case

$$C_V(T) = Nk_B \sum_a \left( \frac{\hbar\omega_a}{2k_B T} \right)^2 \operatorname{csch}^2 \left( \frac{\hbar\omega_a}{2k_B T} \right). \quad (1.290)$$

At low temperatures, the contribution from each branch vanishes exponentially, since  $\operatorname{csch}^2 \left( \frac{\hbar\omega_a}{2k_B T} \right) \simeq 4e^{-\hbar\omega_a/k_B T} \rightarrow 0$ . Real solids don't behave this way.

A more realistic model, due to Debye, accounts for the low-lying acoustic phonon branches. Since the acoustic phonon dispersion vanishes linearly with  $|\mathbf{k}|$  as  $\mathbf{k} \rightarrow 0$ , there is no temperature at which the acoustic phonons ‘freeze out’ exponentially, as in the case of Einstein phonons. Indeed, the Einstein model is appropriate in describing the  $d(r-1)$  optical phonon branches, though it fails miserably for the acoustic branches.

In the vicinity of the zone center  $\mathbf{k} = 0$  (also called  $\Gamma$  in crystallographic notation) the  $d$  acoustic modes obey a linear dispersion, with  $\omega_a(\mathbf{k}) = c_a(\hat{\mathbf{k}})k$ . This results in an acoustic phonon density of states in  $d = 3$  dimensions of

$$\begin{aligned}\tilde{g}(\omega) &= \frac{\mathcal{V}_0 \omega^2}{2\pi^2} \sum_a \int \frac{d\hat{\mathbf{k}}}{4\pi} \frac{1}{c_a^3(\hat{\mathbf{k}})} \Theta(\omega_D - \omega) \\ &= \frac{3\mathcal{V}_0}{2\pi^2 \bar{c}^3} \omega^2 \Theta(\omega_D - \omega),\end{aligned}\tag{1.291}$$

where  $\bar{c}$  is an average acoustic phonon velocity (*i.e.* speed of sound) defined by

$$\frac{3}{\bar{c}^3} = \sum_a \int \frac{d\hat{\mathbf{k}}}{4\pi} \frac{1}{c_a^3(\hat{\mathbf{k}})}\tag{1.292}$$

and  $\omega_D$  is a cutoff known as the *Debye frequency*. The cutoff is necessary because the phonon branch does not extend forever, but only to the boundaries of the Brillouin zone. Thus,  $\omega_D$  should roughly be equal to the energy of a zone boundary phonon. Alternatively, we can define  $\omega_D$  by the normalization condition

$$\int_0^\infty d\omega \tilde{g}(\omega) = 3 \quad \Longrightarrow \quad \omega_D = (6\pi^2/\mathcal{V}_0)^{1/3} \bar{c}.\tag{1.293}$$

This allows us to write  $\tilde{g}(\omega) = (9\omega^2/\omega_D^3) \Theta(\omega_D - \omega)$ .

The specific heat due to the acoustic phonons is then

$$\begin{aligned}C_V(T) &= \frac{9Nk_B}{\omega_D^3} \int_0^{\omega_D} d\omega \omega^2 \left( \frac{\hbar\omega}{2k_B T} \right)^2 \operatorname{csch}^2 \left( \frac{\hbar\omega}{2k_B T} \right) \\ &= 9Nk_B \left( \frac{2T}{\Theta_D} \right)^3 \phi(\Theta_D/2T),\end{aligned}\tag{1.294}$$

where  $\Theta_D = \hbar\omega_D/k_B$  is the *Debye temperature* and

$$\phi(x) = \int_0^x dt t^4 \operatorname{csch}^2 t = \begin{cases} \frac{1}{3}x^3 & x \rightarrow 0 \\ \frac{\pi^4}{30} & x \rightarrow \infty. \end{cases}\tag{1.295}$$

Therefore,

$$C_V(T) = \begin{cases} \frac{12\pi^4}{5} Nk_B \left( \frac{T}{\Theta_D} \right)^3 & T \ll \Theta_D \\ 3Nk_B & T \gg \Theta_D. \end{cases}\tag{1.296}$$



Element	Ag	Al	Au	C	Cd	Cr	Cu	Fe	Mn
$\Theta_D$ (K)	227	433	162	2250	210	606	347	477	409
$T_{\text{melt}}$ (K)	962	660	1064	3500	321	1857	1083	1535	1245
Element	Ni	Pb	Pt	Si	Sn	Ta	Ti	W	Zn
$\Theta_D$ (K)	477	105	237	645	199	246	420	383	329
$T_{\text{melt}}$ (K)	1453	327	1772	1410	232	2996	1660	3410	420

Table 1.4: Debye temperatures (at  $T = 0$ ) and melting points for some common elements (carbon is assumed to be diamond and not graphite). (*Source: the internet!*)

Thus, the heat capacity due to acoustic phonons obeys the Dulong-Petit rule in that  $C_V(T \rightarrow \infty) = 3Nk_B$ , corresponding to the three acoustic degrees of freedom per unit cell. The remaining contribution of  $3(r - 1)Nk_B$  to the high temperature heat capacity comes from the optical modes not considered in the Debye model. The low temperature  $T^3$  behavior of the heat capacity of crystalline solids is a generic feature, and its detailed description is a triumph of the Debye model.

### 1.10.6 Phenomenological theory of melting

#### Atomic fluctuations in a crystal

For the one-dimensional chain, eqn. 1.259 gives

$$\tilde{u}_k = i \left( \frac{\hbar}{2m\omega_k} \right)^{1/2} (a_k - a_{-k}^\dagger). \quad (1.297)$$

Therefore the RMS fluctuations at each site are given by

$$\begin{aligned} \langle u_n^2 \rangle &= \frac{1}{N} \sum_k \langle \tilde{u}_k \tilde{u}_{-k} \rangle \\ &= \frac{1}{N} \sum_k \frac{\hbar}{m\omega_k} \left( n(k) + \frac{1}{2} \right), \end{aligned} \quad (1.298)$$

where  $n(k, T) = [\exp(\hbar\omega_k/k_B T) - 1]^{-1}$  is the Bose occupancy function.

Let us now generalize this expression to the case of a  $d$ -dimensional solid. The appropriate expression for the RMS position fluctuations of the  $i^{\text{th}}$  basis atom in each unit cell is

$$\langle \mathbf{u}_i^2(\mathbf{R}) \rangle = \frac{1}{N} \sum_{\mathbf{k}} \sum_{a=1}^{dr} \frac{\hbar}{M_{ia}(\mathbf{k}) \omega_a(\mathbf{k})} \left( n_a(\mathbf{k}) + \frac{1}{2} \right). \quad (1.299)$$

Here we sum over all wavevectors  $\mathbf{k}$  in the first Brillouin zone, and over all normal modes  $a$ . There are  $dr$  normal modes per unit cell *i.e.*  $d$  branches of the phonon dispersion  $\omega_a(\mathbf{k})$ .

(For the one-dimensional chain with  $d = 1$  and  $r = 1$  there was only one such branch to consider). Note also the quantity  $M_{ia}(\mathbf{k})$ , which has units of mass and is defined in terms of the polarization vectors  $\mathbf{e}_{i\alpha}^{(a)}(\mathbf{k})$  as

$$\frac{1}{M_{ia}(\mathbf{k})} = \sum_{\mu=1}^d |\mathbf{e}_{i\mu}^{(a)}(\mathbf{k})|^2 . \quad (1.300)$$

The dimensions of the polarization vector are  $[\text{mass}]^{-1/2}$ , since the generalized orthonormality condition on the normal modes is

$$\sum_{i,\mu} M_i \mathbf{e}_{i\mu}^{(a)*}(\mathbf{k}) \mathbf{e}_{i\mu}^{(b)}(\mathbf{k}) = \delta^{ab} , \quad (1.301)$$

where  $M_i$  is the mass of the atom of species  $i$  within the unit cell ( $i \in \{1, \dots, r\}$ ). For our purposes we can replace  $M_{ia}(\mathbf{k})$  by an appropriately averaged quantity which we call  $M_i$ ; this ‘effective mass’ is then independent of the mode index  $a$  as well as the wavevector  $\mathbf{k}$ . We may then write

$$\langle \mathbf{u}_i^2 \rangle \approx \int_0^\infty d\omega g(\omega) \frac{\hbar}{M_i \omega} \cdot \left\{ \frac{1}{e^{\hbar\omega/k_B T} - 1} + \frac{1}{2} \right\} , \quad (1.302)$$

where we have dropped the site label  $\mathbf{R}$  since translational invariance guarantees that the fluctuations are the same from one unit cell to the next. Note that the fluctuations  $\langle \mathbf{u}_i^2 \rangle$  can be divided into a temperature-dependent part  $\langle \mathbf{u}_i^2 \rangle_{\text{th}}$  and a temperature-independent quantum contribution  $\langle \mathbf{u}_i^2 \rangle_{\text{qu}}$ , where

$$\langle \mathbf{u}_i^2 \rangle_{\text{th}} = \frac{\hbar}{M_i} \int_0^\infty d\omega \frac{g(\omega)}{\omega} \cdot \frac{1}{e^{\hbar\omega/k_B T} - 1} \quad (1.303)$$

$$\langle \mathbf{u}_i^2 \rangle_{\text{qu}} = \frac{\hbar}{2M_i} \int_0^\infty d\omega \frac{g(\omega)}{\omega} . \quad (1.304)$$

Let’s evaluate these contributions within the Debye model, where we replace  $g(\omega)$  by

$$\bar{g}(\omega) = \frac{d^2 \omega^{d-1}}{\omega_D^d} \Theta(\omega_D - \omega) . \quad (1.305)$$

We then find

$$\langle \mathbf{u}_i^2 \rangle_{\text{th}} = \frac{d^2 \hbar}{M_i \omega_D} \left( \frac{k_B T}{\hbar \omega_D} \right)^{d-1} F_d(\hbar \omega_D / k_B T) \quad (1.306)$$

$$\langle \mathbf{u}_i^2 \rangle_{\text{qu}} = \frac{d^2}{d-1} \cdot \frac{\hbar}{2M_i \omega_D} , \quad (1.307)$$

where

$$F_d(x) = \int_0^x ds \frac{s^{d-2}}{e^s - 1} = \begin{cases} \frac{x^{d-2}}{d-2} & x \rightarrow 0 \\ \zeta(d-1) & x \rightarrow \infty \end{cases}. \quad (1.308)$$

We can now extract from these expressions several important conclusions:

- 1) The  $T = 0$  contribution to the the fluctuations,  $\langle \mathbf{u}_i^2 \rangle_{\text{qu}}$ , diverges in  $d = 1$  dimensions. *Therefore there are no one-dimensional quantum solids.*
- 2) The thermal contribution to the fluctuations,  $\langle \mathbf{u}_i^2 \rangle_{\text{th}}$ , diverges for any  $T > 0$  whenever  $d \leq 2$ . This is because the integrand of  $F_d(x)$  goes as  $s^{d-3}$  as  $s \rightarrow 0$ . *Therefore, there are no two-dimensional classical solids.*
- 3) Both the above conclusions are valid in the thermodynamic limit. Finite size imposes a cutoff on the frequency integrals, because there is a smallest wavevector  $k_{\text{min}} \sim 2\pi/L$ , where  $L$  is the (finite) linear dimension of the system. This leads to a low frequency cutoff  $\omega_{\text{min}} = 2\pi\bar{c}/L$ , where  $\bar{c}$  is the appropriately averaged acoustic phonon velocity from eqn. 1.292, which mitigates any divergences.

### Lindemann melting criterion

An old phenomenological theory of melting due to Lindemann says that a crystalline solid melts when the RMS fluctuations in the atomic positions exceeds a certain fraction  $\eta$  of the lattice constant  $a$ . We therefore define the ratios

$$x_{i,\text{th}}^2 \equiv \frac{\langle \mathbf{u}_i^2 \rangle_{\text{th}}}{a^2} = d^2 \cdot \left( \frac{\hbar^2}{M_i a^2 k_B} \right) \cdot \frac{T^{d-1}}{\Theta_D^d} \cdot F(\Theta_D/T) \quad (1.309)$$

$$x_{i,\text{qu}}^2 \equiv \frac{\langle \mathbf{u}_i^2 \rangle_{\text{qu}}}{a^2} = \frac{d^2}{2(d-1)} \cdot \left( \frac{\hbar^2}{M_i a^2 k_B} \right) \cdot \frac{1}{\Theta_D}, \quad (1.310)$$

with  $x_i = \sqrt{x_{i,\text{th}}^2 + x_{i,\text{qu}}^2} = \sqrt{\langle \mathbf{u}_i^2 \rangle} / a$ .

Let's now work through an example of a three-dimensional solid. We'll assume a single element basis ( $r = 1$ ). We have that

$$\frac{9\hbar^2/4k_B}{1 \text{ amu } \text{\AA}^2} = 109 \text{ K}. \quad (1.311)$$

According to table 1.4, the melting temperature always exceeds the Debye temperature, and often by a great amount. We therefore assume  $T \gg \Theta_D$ , which puts us in the small  $x$  limit of  $F_d(x)$ . We then find

$$x_{\text{qu}}^2 = \frac{\Theta^*}{\Theta_D}, \quad x_{\text{th}}^2 = \frac{\Theta^*}{\Theta_D} \cdot \frac{4T}{\Theta_D}, \quad x = \sqrt{\left(1 + \frac{4T}{\Theta_D}\right) \frac{\Theta^*}{\Theta_D}}. \quad (1.312)$$

where

$$\Theta^* = \frac{109 \text{ K}}{M[\text{amu}] \cdot (a[\text{\AA}])^2} . \quad (1.313)$$

The total position fluctuation is of course the sum  $x^2 = x_{i,\text{th}}^2 + x_{i,\text{qu}}^2$ . Consider for example the case of copper, with  $M = 56 \text{ amu}$  and  $a = 2.87 \text{ \AA}$ . The Debye temperature is  $\Theta_D = 347 \text{ K}$ . From this we find  $x_{\text{qu}} = 0.026$ , which says that at  $T = 0$  the RMS fluctuations of the atomic positions are not quite three percent of the lattice spacing (*i.e.* the distance between neighboring copper atoms). At room temperature,  $T = 293 \text{ K}$ , one finds  $x_{\text{th}} = 0.048$ , which is about twice as large as the quantum contribution. How big are the atomic position fluctuations at the melting point? According to our table,  $T_{\text{melt}} = 1083 \text{ K}$  for copper, and from our formulae we obtain  $x_{\text{melt}} = 0.096$ . The *Lindemann criterion* says that solids melt when  $x(T) \approx 0.1$ .

We were very lucky to hit the magic number  $x_{\text{melt}} = 0.1$  with copper. Let's try another example. Lead has  $M = 208 \text{ amu}$  and  $a = 4.95 \text{ \AA}$ . The Debye temperature is  $\Theta_D = 105 \text{ K}$  ('soft phonons'), and the melting point is  $T_{\text{melt}} = 327 \text{ K}$ . From these data we obtain  $x(T = 0) = 0.014$ ,  $x(293 \text{ K}) = 0.050$  and  $x(T = 327 \text{ K}) = 0.053$ . Same ballpark.

We can turn the analysis around and predict a melting temperature based on the Lindemann criterion  $x(T_{\text{melt}}) = \eta$ , where  $\eta \approx 0.1$ . We obtain

$$T_L = \left( \frac{\eta^2 \Theta_D}{\Theta^*} - 1 \right) \cdot \frac{\Theta_D}{4} . \quad (1.314)$$

We call  $T_L$  the *Lindemann temperature*. Most treatments of the Lindemann criterion ignore the quantum correction, which gives the  $-1$  contribution inside the above parentheses. But if we are more careful and include it, we see that it may be possible to have  $T_L < 0$ . This occurs for any crystal where  $\Theta_D < \Theta^*/\eta^2$ .

Consider for example the case of  $^4\text{He}$ , which at atmospheric pressure condenses into a liquid at  $T_c = 4.2 \text{ K}$  and remains in the liquid state down to absolute zero. At  $p = 1 \text{ atm}$ , it never solidifies! Why? The number density of liquid  $^4\text{He}$  at  $p = 1 \text{ atm}$  and  $T = 0 \text{ K}$  is  $2.2 \times 10^{22} \text{ cm}^{-3}$ . Let's say the Helium atoms want to form a crystalline lattice. We don't know *a priori* what the lattice structure will be, so let's for the sake of simplicity assume a simple cubic lattice. From the number density we obtain a lattice spacing of  $a = 3.57 \text{ \AA}$ . OK now what do we take for the Debye temperature? Theoretically this should depend on the microscopic force constants which enter the small oscillations problem (*i.e.* the spring constants between pairs of helium atoms in equilibrium). We'll use the expression we derived for the Debye frequency,  $\omega_D = (6\pi^2/\mathcal{V}_0)^{1/3}\bar{c}$ , where  $\mathcal{V}_0$  is the unit cell volume. We'll take  $\bar{c} = 238 \text{ m/s}$ , which is the speed of sound in liquid helium at  $T = 0$ . This gives  $\Theta_D = 19.8 \text{ K}$ . We find  $\Theta^* = 2.13 \text{ K}$ , and if we take  $\eta = 0.1$  this gives  $\Theta^*/\eta^2 = 213 \text{ K}$ , which significantly exceeds  $\Theta_D$ . Thus, the solid should melt because the RMS fluctuations in the atomic positions at absolute zero are huge:  $x_{\text{qu}} = (\Theta^*/\Theta_D)^{1/2} = 0.33$ . By applying pressure, one can get  $^4\text{He}$  to crystallize above  $p_c = 25 \text{ atm}$  (at absolute zero). Under pressure, the unit cell volume  $\mathcal{V}_0$  decreases and the phonon velocity  $\bar{c}$  increases, so the Debye temperature itself increases.

It is important to recognize that the Lindemann criterion does not provide us with a theory of melting *per se*. Rather it provides us with a heuristic which allows us to predict roughly when a solid should melt.

### 1.10.7 Goldstone bosons

The vanishing of the acoustic phonon dispersion at  $\mathbf{k} = 0$  is a consequence of *Goldstone's theorem* which says that associated with every *broken generator* of a *continuous symmetry* there is an associated bosonic gapless excitation (*i.e.* one whose frequency  $\omega$  vanishes in the long wavelength limit). In the case of phonons, the 'broken generators' are the symmetries under spatial translation in the  $x$ ,  $y$ , and  $z$  directions. The crystal selects a particular location for its center-of-mass, which breaks this symmetry. There are, accordingly, three gapless acoustic phonons.

Magnetic materials support another branch of elementary excitations known as spin waves, or *magnons*. In *isotropic* magnets, there is a global symmetry associated with rotations in internal spin space, described by the group  $SU(2)$ . If the system spontaneously magnetizes, meaning there is long-ranged ferromagnetic order ( $\uparrow\uparrow\uparrow \dots$ ), or long-ranged antiferromagnetic order ( $\uparrow\downarrow\uparrow\downarrow \dots$ ), then global spin rotation symmetry is broken. Typically a particular direction is chosen for the magnetic moment (or staggered moment, in the case of an antiferromagnet). Symmetry under rotations about this axis is then preserved, but rotations which do not preserve the selected axis are 'broken'. In the most straightforward case, that of the antiferromagnet, there are two such rotations for  $SU(2)$ , and concomitantly two gapless magnon branches, with linearly vanishing dispersions  $\omega_a(\mathbf{k})$ . The situation is more subtle in the case of ferromagnets, because the total magnetization is conserved by the dynamics (unlike the total staggered magnetization in the case of antiferromagnets). Another wrinkle arises if there are long-ranged interactions present.

For our purposes, we can safely ignore the deep physical reasons underlying the gaplessness of Goldstone bosons and simply posit a gapless dispersion relation of the form  $\omega(\mathbf{k}) = A|\mathbf{k}|^\sigma$ . The density of states for this excitation branch is then

$$g(\omega) = \mathcal{C} \omega^{\frac{d}{\sigma}-1} \Theta(\omega_c - \omega) , \quad (1.315)$$

where  $\mathcal{C}$  is a constant and  $\omega_c$  is the cutoff, which is the bandwidth for this excitation branch.<sup>16</sup> Normalizing the density of states for this branch results in the identification  $\omega_c = (d/\sigma\mathcal{C})^{\sigma/d}$ .

The heat capacity is then found to be

$$\begin{aligned} C_V &= Nk_B \mathcal{C} \int_0^{\omega_c} d\omega \omega^{\frac{d}{\sigma}-1} \left( \frac{\hbar\omega}{k_B T} \right)^2 \operatorname{csch}^2 \left( \frac{\hbar\omega}{2k_B T} \right) \\ &= \frac{d}{\sigma} Nk_B \left( \frac{2T}{\Theta} \right)^{d/\sigma} \phi(\Theta/2T) , \end{aligned} \quad (1.316)$$

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<sup>16</sup>If  $\omega(\mathbf{k}) = Ak^\sigma$ , then  $\mathcal{C} = 2^{1-d} \pi^{-\frac{d}{2}} \sigma^{-1} A^{-\frac{d}{\sigma}} g/\Gamma(d/2)$ .

where  $\Theta = \hbar\omega_c/k_B$  and

$$\phi(x) = \int_0^x dt t^{\frac{d}{\sigma}+1} \operatorname{csch}^2 t = \begin{cases} \frac{\sigma}{d} x^{d/\sigma} & x \rightarrow 0 \\ 2^{-d/\sigma} \Gamma(2 + \frac{d}{\sigma}) \zeta(2 + \frac{d}{\sigma}) & x \rightarrow \infty, \end{cases} \quad (1.317)$$

which is a generalization of our earlier results. Once again, we recover Dulong-Petit for  $k_B T \gg \hbar\omega_c$ , with  $C_V(T \gg \hbar\omega_c/k_B) = Nk_B$ .

In an isotropic ferromagnet, *i.e.* a ferromagnetic material where there is full SU(2) symmetry in internal ‘spin’ space, the magnons have a  $k^2$  dispersion. Thus, a bulk three-dimensional isotropic ferromagnet will exhibit a heat capacity due to spin waves which behaves as  $T^{3/2}$  at low temperatures. For sufficiently low temperatures this will overwhelm the phonon contribution, which behaves as  $T^3$ .