9 Transport Properties of Solids

9.1 Introduction

So far, we have almost exclusively discussed in solids in thermodynamic equilibrium. In this chapter, we will now discuss transport effects, i.e., how solids react to an external perturbation, .e.g, to an external electric field $\mathbf{E}$, i.e., to the gradient of an electric potential $\mathbf{E} = -\nabla U$, or to a temperature gradient ∇T. In all this cases, a **flux** ($\mathbf{J}_e$ and $\mathbf{J}_h$, see below) develops as reaction to the perturbation and tries to re-establish thermodynamic equilibrium. The effectiveness of this mechanism is characterized by the respective transport coefficients. These are material, temperature, and pressure dependent constants that describe the linear relationship between the respective fluxes and perturbations, e.g., the electrical conductivity σ in *Ohm's law*

$$\mathbf{J}_e = -\sigma \nabla U \tag{9.1}$$

and the thermal conductivity κ in *Fourier's law*

$$\mathbf{J}_h = -\kappa \nabla T \ . \tag{9.2}$$

Please note that both σ and κ are tensorial quantities, e.g., a gradient along the x-axis can in principle lead to fluxes along the y- or z-axis. In most cases, however, these non-diagonal terms of σ and κ are orders of magnitude smaller than the diagonal terms, so that we will restrict our discussion to the diagonal terms in this chapter. Furthermore, it is important to realize that Eq. (9.1) and Eq. (9.2) are truncated first-order Taylor expansions of the full relationships for $\mathbf{J}_e(U)$ and $\mathbf{J}_h(T)$. For the purposes of this chapter, using such a *linear response* approximation is more than justified, given that the typical voltages $\Delta U < 1,000$ V and temperature differences $\Delta T < 1,000$ K applied in real-world applications to macroscopic solids (volume $V > 1\mu\text{m}^3$) correspond to minute electric fields[1] and temperature gradients at the microscopic level $V < 10$ nm^3.

In this regime, we can thus consider the solid in the so called "Onsager picture" as consisting of microscopic, individual sections: Each of this section is assumed to so large that thermodynamic equilibrium rules hold and allow to define thermodynamic quantities such as the temperature for each individual section. However, the individual sections are not in thermodynamic equilibrium with respect to each other. At first sight, this seems to be an assumption that apparently simplifies the discussion. As we will see in this chapter, this is not the case for practical considerations: The fundamental reason is that we

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[1]As already mentioned in the previous chapter, this approximation would not longer hold for the interactions of solids with lasers. Today's laser can generate huge electrical fields at a microscopic level that in turn lead to non-linear responses.

are now discussing macroscopic effects driven by microscopic interactions, which requires spanning several orders of magnitude in time and length scales. Developing theories that accurately describe the microscopic level but still allow insights on the macroscopic level within affordable computational effort is still topic of scientific research.

9.2 The Definition of Transport Coefficients

In the following, we will discuss electronic transport. For phonons, see Chap. 7, very similar relations are applicable with two important differences: Electrons carry charge and are Fermions, while phonons carry no charge and are Bosons.

If the fluxes consist of particles that carry both energy and charge, as it is the case for electrons with charge e described by a chemical potential μ (i.e. the *local* Fermi energy in the respective "Onsager section"), the respective fluxes $\mathbf{J}_e$ and $\mathbf{J}_h$ are coupled. An electron that is contributing to a heat flux driven by a thermal gradient still carries a charge and thus also leads to a electrical flux (and vice versa). Formally this is described by the so called Onsager coefficients $\mathbf{L}^{ij}$:

$$\mathbf{J}_e = \mathbf{L}^{11}\left(-\nabla U - \frac{\nabla \mu}{e}\right) + \mathbf{L}^{12}\left(-\nabla T\right) \tag{9.3}$$

$$\mathbf{J}_h = \mathbf{L}^{21}\left(-\nabla U - \frac{\nabla \mu}{e}\right) + \mathbf{L}^{22}\left(-\nabla T\right) . \tag{9.4}$$

As we will show with microscopic considerations later, $\mathbf{L}^{21} = T\mathbf{L}^{12}$. With that, a comparison of the Onsager relations above with Eq. (9.1) and (9.2) shows that the electrical conductivity corresponds to $\sigma = \mathbf{L}^{11}$ and that the thermal conductivity corresponds to

$$\kappa = \mathbf{L}^{22} - \frac{\mathbf{L}^{21}\mathbf{L}^{12}}{\mathbf{L}^{11}} = \mathbf{L}^{22} - T\frac{(\mathbf{L}^{12})^2}{\mathbf{L}^{11}} . \tag{9.5}$$

The formal asymmetry in the definition of σ and κ stems in fact from their experimental definition. While σ is defined for measurements in thermodynamic equilibrium, in which both cathode and anode are kept at the same temperature via interactions with the environment (so heat is added and taken from the system), κ is typically measured in an open circuit, in which an electronic flux and the respective charges cannot leave the system. This leads to a pile-up of charge on the cold side, which in turn leads to an electric flux in the opposite direction that needs to be accounted for by the non-diagonal $\mathbf{L}^{ij}$ terms. This leads to the definition given in Eq. (9.5).

In turn, the considerations discussed above highlight an interesting and peculiar effect, the *thermoelectric* effect. For a non-zero temperature gradient in a closed circuit, Eq. (9.3) and (9.4) imply that a residual voltage is induced by a temperature gradient

$$\left(-\nabla U - \frac{\nabla \mu}{e}\right) = \frac{L^{12}}{\mathbf{L}^{11}}\nabla T = \mathbf{S}\nabla T , \tag{9.6}$$

as described by the Seebeck coefficient S. This thermoelectric effect is currently very much in the focus of many scientific and industrial studies, since it in principle allows to recover a useful voltage from otherwise wasted heat, e.g., from industrial plants operating at high temperatures, from exhaustion fumes from vehicles, and even from electronics such

as CPUs. However, the conversion efficiency of the currently exhisting thermoelectric materials is still too low for a large-scale, economically attractive deployment. To enable such applications, thermoelectric materials with higher efficiency are needed, which is typically characterized by the figure-of-merit zT defined as:

$$zT = \frac{\sigma S^2 T}{\kappa_{\text{el}} + \kappa_{\text{ph}}} \ , \tag{9.7}$$

whereby currently known thermoelectric materials exhibit values of zT of ~ 2 at most. Improving zT is far from trivial: Metals typically exhibit high values of σ but also high values of κ_{el}, which essentially leads to $zT \approx 0$. Vice versa, $\kappa = \kappa_{\text{ph}}$ becomes small in insulators due to the absence of charge carriers, but then σ and thus zT vanish again. Accordingly, (highly doped) semiconductors are the most attractive material class for these kind of applications. Eventually, let us note that the Seebeck effect also works "the other way round": The so called Peltier effect describes how an electric current through a closed circuit induces a heat current

$$\mathbf{J}_h = T\frac{\mathbf{L}^{12}}{\mathbf{L}^{11}}\mathbf{J_e} = T\ \mathbf{S} \cdot \mathbf{J_e} \tag{9.8}$$

that allows cooling. For instance, this technique is used to date in so called solid state fridges, e.g., in airplanes.

To understand these effects and to estimate and compute this quantities, it is necessary to introduce concepts stemming from the still very active and quite complex research field of non-equilibrium quantum-mechanical thermodynamics and statistical mechanics. At first, let's just discuss the qualitative results of such a derivation. The microscopic, local flux densities $\mathbf{j}(\mathbf{r}, t)$ and $\mathbf{j}_H(\mathbf{r}, t)$ have to fulfill the respective continuity equations

$$e\frac{\partial n(\mathbf{r}, t)}{\partial t} + \nabla \cdot \mathbf{j}(\mathbf{r}, t) = 0 \Rightarrow \mathbf{J}(t) = \frac{1}{V}\int_V \mathbf{j}(\mathbf{r}, t)d\mathbf{r} \tag{9.9}$$

$$\frac{\partial \varepsilon(\mathbf{r}, t)}{\partial t} + \nabla \cdot \mathbf{j}_H(\mathbf{r}, t) = 0 \Rightarrow \mathbf{J}_H(t) = \frac{1}{V}\int_V \mathbf{j}_H(\mathbf{r}, t)d\mathbf{r} \ , \tag{9.10}$$

in which $e\,n(\mathbf{r}, t)$ is the charge density, $\varepsilon(\mathbf{r}, t)$ the energy density, and V the volume of an Onsager system. This allows to define the quantum-mechanical flux operators

$$\hat{\mathbf{j}} = \frac{e}{m}\hat{\mathbf{p}} \tag{9.11}$$

$$\hat{\mathbf{j_H}} = \frac{1}{2m}[H, \hat{\mathbf{p}}] - h_e\hat{\mathbf{p}} \ . \tag{9.12}$$

In the last equation, h_e denotes the enthalpy per electron. A full quantum-mechanical treatment of these equations involves quite elaborate derivations. For this exact reason, we will consider these effects in a semi-classical approximation first.

9.3 Semiclassical Theory of Transport

To introduce non-equilibrium in our system, we first define a wave packet

$$\Psi_n(\mathbf{r}, \mathbf{k}, t) = \sum_{\mathbf{k}} g(\mathbf{k})\Phi_n(\mathbf{k}, \mathbf{r}) \exp\left(-\frac{i}{\hbar}\varepsilon_n(\mathbf{k})\right) \ \text{with} \ g(\mathbf{k}') \approx 0 \ \text{for} \ |\mathbf{k} - \mathbf{k}'| > \Delta k \tag{9.13}$$
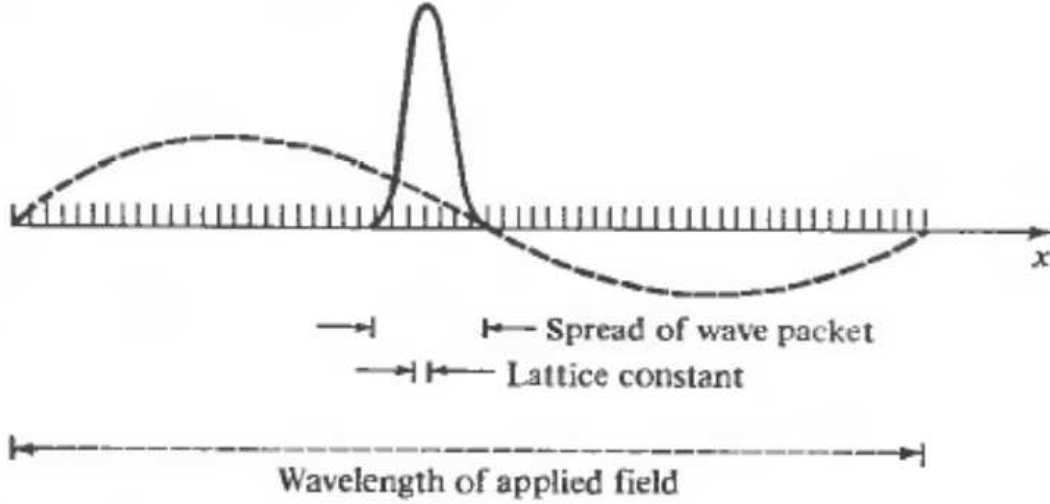
Figure 9.1: Sketch of an electron wavepacket, as described by Eq. (9.13): The wavepacket shall be spread out over multiple unit cells, i.e., it shall be larger that typical lattice constants. Also, the wavepacket shall be smaller than the wavelength of the applied field.

using the one-particles states $\Phi_n(\mathbf{k}, \mathbf{r})$ and their eigenvalues $\varepsilon_n(\mathbf{k})$. The condition $|\mathbf{k}-\mathbf{k}'| > \delta k$ implies that the wave packet is localized in $\mathbf{k}$ space and can thus be meaningfully approximated by an average $\mathbf{k}$ value. In turn, this implies that this wave packet is delocalized in real space, see Fig. 9.1. Accordingly, such a description is consistent with the Onsager picture defined in the introduction. Given that this wave packet is so wide spread, we can describes its dynamics in an electric field by classical equations of motion:

$$\dot{\mathbf{r}} = \mathbf{v}_n(\mathbf{k}) = \frac{1}{\hbar}\frac{\partial \varepsilon_n(\mathbf{k})}{\partial \mathbf{k}} \quad \text{and} \quad \hbar\dot{\mathbf{k}} = -e\mathbf{E}(\mathbf{r}, t) . \tag{9.14}$$

While the first equation just makes use of the fact that a wave-packet travels with a well-defined group velocity, a fully correct, formal derivation of the second equations is tricky. Still, one can qualitatively derive them by considering that energy conservation needs to hold during this motion:

$$\varepsilon_n(\mathbf{k}) - eU = \text{constant} \tag{9.15}$$

Then, its time derivative must vanish:

$$0 = \frac{\partial \varepsilon_n(\mathbf{k})}{\partial \mathbf{k}}\dot{\mathbf{k}} - e\nabla U \cdot \dot{\mathbf{r}} \tag{9.16}$$

$$= \mathbf{v}_n(\mathbf{k}) \cdot \left[\hbar\dot{\mathbf{k}} - e\nabla U\right] = \mathbf{v}_n(\mathbf{k}) \cdot \left[\hbar\dot{\mathbf{k}} + e\mathbf{E}\right] \tag{9.17}$$

Please note that in this case we have assumed that the band index n is a constant of the motion, i.e., that the considered electrical and thermal fields cannot induce electronic transition between different electronic bands. The flux associated to such a wave packets then becomes

$$\mathbf{J}_n(\mathbf{k}) = -e\mathbf{v}_n(\mathbf{k}) \quad \text{and} \quad \mathbf{J}_n^H(\mathbf{k}) = \varepsilon_n(\mathbf{k})\mathbf{v}_n(\mathbf{k}) \tag{9.18}$$

In this formalism, the individual electrons thus just travel with a velocity $\mathbf{v}_n(\mathbf{k})$ and thereby carry a charge $-e$ and an energy $\varepsilon_n(\mathbf{k})$ with them.

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Already this very simple considerations allow some very important insight in the physics of transport:

- Solving this equations of motion for a constant DC field $\mathbf{E}(\mathbf{r}, t) = \mathbf{E}$ yields

$$\mathbf{k}(t) = \mathbf{k}(0) - \frac{e\mathbf{E}t}{\hbar} \ . \tag{9.19}$$

  Given that our group velocity is periodic and obeys time reversal symmetry $\mathbf{v}_n(\mathbf{k}) = -\mathbf{v}_n(-\mathbf{k})$, this implies that the group velocity can change sign over time. In turn, this means that a DC field could induce an AC current if the electrons travel long enough to overcome zone boundaries. We will see later that this is generally not the case.

- For the exact same reasons $(\mathbf{v}_n(\mathbf{k}) = -\mathbf{v}_n(-\mathbf{k}), \varepsilon_n(\mathbf{k}) = \varepsilon_n(-\mathbf{k}))$, we can see that a fully filled band is inert, i.e., it does not carry any flux

$$\mathbf{J}_n = \int d\mathbf{k}\, \mathbf{J}_n(\mathbf{k}) = 0 \ , \tag{9.20}$$

  since the contributions from $\mathbf{k}$ and $-\mathbf{k}$ cancel each other out. That's why insulators are insulators and electronic transport only happens in semiconductors and metals with partially filled bands. This implies that the only relevant portion of the electronic band structure that contributes to transport is situated around the Fermi energy $\varepsilon_{\mathrm{F}} \pm k_{\mathrm{B}}T$.

- Electrons & Holes: Now, let's assume that band n contains only one electron at $\mathbf{k}'$ viz. $\varepsilon_n(\mathbf{k}')$, i.e.,

$$f(\varepsilon_n(\mathbf{k})) = \begin{cases} 1 & \text{for } \mathbf{k} = \mathbf{k}' \\ 0 & \text{else} \end{cases} . \tag{9.21}$$

In this case, the electric flux becomes:

$$\mathbf{J}_n = \int d\mathbf{k}\, f(\varepsilon_n(\mathbf{k}))\mathbf{J}_n(\mathbf{k}) = -e\mathbf{v}_n(\mathbf{k}') \ . \tag{9.22}$$

If the band would be fully filled except one electron at $\mathbf{k}'$ viz. $\varepsilon_n(\mathbf{k}')$, the respective occupation numbers become $f'(\varepsilon_n(\mathbf{k})) = 1 - f(\varepsilon_n(\mathbf{k}))$ and we get the flux

$$\mathbf{J}_n = \int d\mathbf{k}\, f'(\varepsilon_n(\mathbf{k}))\mathbf{J}_n(\mathbf{k}) = \int d\mathbf{k}\, \mathbf{J}_n(\mathbf{k}) - \int d\mathbf{k}\, f(\varepsilon_n(\mathbf{k}))\mathbf{J}_n(\mathbf{k}) = e\mathbf{v}_n(\mathbf{k}') \ . \tag{9.23}$$

The first integral vanishes due to Eq. (9.20); the second one describes the flux of **one** "electron with opposite charge", i.e., a **hole**. Although formally equivalent, it is often more convenient to discuss conduction in almost fully filled bands in terms of moving holes instead of electrons.

There is one additional important implication: Since in full thermodynamic equilibrium the Fermi distribution is symmetric $f(\varepsilon_n(-\mathbf{k})) = f(\varepsilon_n(\mathbf{k}))$, no flux can be present even in not fully filled bands. That is why we will have to look at non-equilibrium distributions in the next section to understand the transport.

- In semiconductors, in which only electrons/holes close to the valence band maximum/conduction band minimum contribute, one can often approximate the respective band structure with a second order Taylor expansion:

$$\varepsilon_n(\mathbf{k}) \approx \varepsilon_n(\mathbf{k}) + \frac{1}{2}\sum_{i,j}\frac{\partial^2\varepsilon_n(\mathbf{k})}{\partial\mathbf{k}_i\mathbf{k}_j}\mathbf{k}_i\mathbf{k}_j \ . \tag{9.24}$$

Formally, the dispersion thus corresponds to the one of a free electron with a slightly different, not necessarily isotropic mass, as described by the tensor:

$$[M]_{ij} = \left(\frac{1}{\hbar^2}\frac{\partial^2\varepsilon_n(\mathbf{k})}{\partial\mathbf{k}_i\partial\mathbf{k}_j}\right)^{-1} \ . \tag{9.25}$$

Accordingly, one can speak about fast (light) and slow (heavy) electrons/holes in a solid.

9.4 Boltzmann Transport Theory

With the formalisms introduced in the previous sections, we are now able to discuss how an arbitrary electron population $g(\mathbf{r}, \mathbf{k}, t)$, i.e., one that is not necessarily in thermodynamic equilibrium, evolves over time. Using Liouville's theorem (conservation of phase space) and the relations derived for $\mathbf{r}(t)$ and $\mathbf{k}(t)$ in the previous section, we thus get:

$$g(\mathbf{r}, \mathbf{k}, t)d\mathbf{r}d\mathbf{k} = g(\mathbf{r} - \mathbf{v}(\mathbf{k})dt, \mathbf{k} + \frac{e\mathbf{E}}{\hbar}, t - dt)d\mathbf{r}d\mathbf{k} \tag{9.26}$$

By linearizing these equation, we get the so called "drift" terms that in an Onsager picture have to be counterbalance by a scattering or collision mechanism:

$$\left(\frac{dg(\mathbf{r}, \mathbf{k}, t)}{dt}\right)_{\text{drift}} = \frac{\partial g}{\partial t} + \mathbf{v}\cdot\frac{\partial g}{\partial \mathbf{r}} - \frac{e\mathbf{E}}{\hbar}\frac{\partial g}{\partial \mathbf{k}} = \left(\frac{\partial g}{\partial t}\right)_{\text{coll}} \tag{9.27}$$

By defining a collision scattering probability from state $\mathbf{k}$ into $\mathbf{k}'$

$$\frac{W_{\mathbf{k}\mathbf{k}'}}{(2\pi)^3}dtd\mathbf{k}' \ , \tag{9.28}$$

we find that these collisions can either lead to less electrons at $\mathbf{k}$ (scattering from $\mathbf{k}$ into any state $\mathbf{k}'$):

$$\left(\frac{\partial g}{\partial t}\right)_{\text{coll,out}} = -g(\mathbf{k})\int\frac{d\mathbf{k}'}{(2\pi)^3}W_{\mathbf{k}\mathbf{k}'}[1 - g(\mathbf{k}')] \tag{9.29}$$

or to additional electrons at $\mathbf{k}$ (scattering from any state $\mathbf{k}'$ into state $\mathbf{k}$)[2]:

$$\left(\frac{\partial g}{\partial t}\right)_{\text{coll,in}} = [1 - g(\mathbf{k})]\int\frac{d\mathbf{k}'}{(2\pi)^3}W_{\mathbf{k}'\mathbf{k}}g(\mathbf{k}') \ . \tag{9.30}$$

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[2]Please note that the respective collision rates in Eq. (9.29) and (9.30) are proportional to the population g of electrons that are actually scattered and proportional to $1 - g$ of states in which these electrons can be scattered.

With that, we get the full collision term

$$\left(\frac{\partial g}{\partial t}\right)_{\text{coll}} = \left(\frac{\partial g}{\partial t}\right)_{\text{coll,in}} + \left(\frac{\partial g}{\partial t}\right)_{\text{coll,out}} \tag{9.31}$$

$$= -\int \frac{d\mathbf{k}'}{(2\pi)^3} \left\{ W_{\mathbf{k}\mathbf{k}'} g(\mathbf{k})[1 - g(\mathbf{k}')] - W_{\mathbf{k}'\mathbf{k}}[1 - g(\mathbf{k})]g(\mathbf{k}') \right\} \tag{9.32}$$

$$\approx -\frac{[g(\mathbf{k}) - g^0(\mathbf{k})]}{\tau(\mathbf{k})} \tag{9.33}$$

In the last step, we have applied the so called *relaxation time approximation* (RTA) that allows to solve the Boltzmann transport equation analytically. This relaxation time approximation assumes (a) that the electron distribution is close to the equilibrium one, i.e., to the Fermi function (b) that scattering generates equilibrium, i.e., drives the population $g(\mathbf{k})$ towards $g^0(\mathbf{k})$, and (c) that all the involved scattering rates can be subsumed into single state-specific lifetime or relaxation time $\tau(\mathbf{k})$ that does not depend on $g(\mathbf{k})$. Formally this implies:

$$\left(\frac{\partial g}{\partial t}\right)_{\text{coll,out}} = -g(\mathbf{k}) \int \frac{d\mathbf{k}'}{(2\pi)^3} W_{\mathbf{k}\mathbf{k}'}[1 - g(\mathbf{k}')] \approx -\frac{g(\mathbf{k})}{\tau(\mathbf{k})} \tag{9.34}$$

$$\left(\frac{\partial g}{\partial t}\right)_{\text{coll,in}} = [1 - g(\mathbf{k})] \int \frac{d\mathbf{k}'}{(2\pi)^3} W_{\mathbf{k}'\mathbf{k}} g(\mathbf{k}') \approx \frac{g^0(\mathbf{k})}{\tau(\mathbf{k})} \tag{9.35}$$

Now, lets solve the Boltzmann transport equation under different boundary conditions:

- If no external forces/fields are present ($\mathbf{E} = 0$) and the electrons are uniformly distributed in space ($\nabla g = 0$), Eq. (9.27) becomes

$$\frac{\partial g}{\partial t} = -\frac{[g(\mathbf{k}) - g^0(\mathbf{k})]}{\tau(\mathbf{k})} \tag{9.36}$$

in the RTA. Its solution is

$$g(t) = \left(g(\mathbf{k}, t = 0) - g^0(\mathbf{k}) \right) \exp\left(-\frac{t}{\tau(\mathbf{k})} \right) + g^0(\mathbf{k}) , \tag{9.37}$$

which describes the relaxation of a non-equilibrium population $g(\mathbf{k}, t = 0)$ to the equilibrium one in an exponential decay characterized by the relaxation time τ.

- Under steady state ($\partial g/\partial t = 0$), closed circuit conditions ($\nabla g = 0$) with an external field $\mathbf{E}$, Eq. (9.27) becomes

$$-\frac{e\mathbf{E}}{\hbar} \frac{\partial g}{\partial \mathbf{k}} = -\frac{[g(\mathbf{k}) - g^0(\mathbf{k})]}{\tau(\mathbf{k})} \tag{9.38}$$

in the RTA. Its solution is

$$g(t) = g^0(t) + \tau \frac{e\mathbf{E}}{\hbar} \frac{\partial g}{\partial \mathbf{k}} \approx g^0(t) + \tau \frac{e\mathbf{E}}{\hbar} \frac{\partial g^0}{\partial \mathbf{k}} = g^0(t) + e \frac{\partial g^0}{\partial \epsilon(\mathbf{k})} \mathbf{v}(\mathbf{k})\tau\mathbf{E} \tag{9.39}$$

In the last step, we have simplified the expression by assuming $\partial g/\partial \mathbf{k} \approx \partial g^0/\partial \mathbf{k}$ and using the definition of the group velocity. With that, we can write the flux as

$$\mathbf{j} = -e \sum_n \int \frac{d\mathbf{k}}{4\pi^3} g_n(\mathbf{k}, t) \mathbf{v}_n(\mathbf{k}) = \underbrace{e^2 \sum_n \int \frac{d\mathbf{k}}{4\pi^3} \mathbf{v}_n^2(\mathbf{k}) \tau_n(\mathbf{k}) \frac{\partial g^0}{\partial \epsilon_n(k)}}_{\sigma} \mathbf{E} . \qquad (9.40)$$

A comparison with Ohm's law yields the definition of σ. Again, the fact that the derivative $\partial g^0/\partial \epsilon_n(k)$ enters the definition of σ above highlights that filled bands are inert and that only electrons/holes close to the Fermi-energy matter. Please note that the derivation can be generalized to the AC case

$$\sigma(\omega) = e^2 \sum_n \int \frac{d\mathbf{k}}{4\pi^3} \mathbf{v}_n^2(\mathbf{k}) \frac{\partial g^0}{\partial \epsilon_n(k)} \frac{1}{1/\tau_n(\mathbf{k}) - i\omega} \qquad (9.41)$$

by using

$$\mathbf{E} \to \mathrm{Re}[\mathbf{E} \exp(i\omega t)] . \qquad (9.42)$$

- Eventually, we can generalize this derivation to describe all Onsager coefficients by defining the respective heat $\mathbf{j}_q$ and entropy $\mathbf{j}_s$ fluxes from the respective thermodynamic relation:

$$dQ = T dS \Rightarrow \mathbf{j}_q = T \mathbf{j}_s . \qquad (9.43)$$

Similarly, the respective particle $\mathbf{j}_n$ and energy flux $\mathbf{j}_e$ can be defined using the respective thermodynamic relation and the chemical potential μ:

$$T dS = dU - \mu dN \Rightarrow T\mathbf{j}_s = \mathbf{j}_e - \mu \mathbf{j}_n . \qquad (9.44)$$

Accordingly, we get:

$$\mathbf{j}_e = \sum_n \int \frac{d\mathbf{k}}{4\pi^3} g_n(\mathbf{k}, t) \mathbf{v}_n(\mathbf{k}) \varepsilon_n(\mathbf{k}) \qquad (9.45)$$

$$\mathbf{j}_n = \sum_n \int \frac{d\mathbf{k}}{4\pi^3} g_n(\mathbf{k}, t) \mathbf{v}_n(\mathbf{k}) \qquad (9.46)$$

$$\Rightarrow \mathbf{j}_q = \sum_n \int \frac{d\mathbf{k}}{4\pi^3} g_n(\mathbf{k}, t) \mathbf{v}_n(\mathbf{k}) (\varepsilon_n(\mathbf{k}) - \mu) \qquad (9.47)$$

Solving the respective BTEs in the RTA yields:

$$g(t) \approx g^0(t) - \left(\frac{\partial g^0}{\partial \epsilon k}\right) \mathbf{v}(\mathbf{k}) \tau(\mathbf{k}) \left[-e\mathbf{E} - \nabla\mu + \frac{\varepsilon_n(\mathbf{k}) - \mu}{T} (-\nabla T) \right] . \qquad (9.48)$$

Again, a comparison with the Onsager relations introduced before

$$\mathbf{j} = L^{11}(\mathbf{E} + \nabla\mu) + L^{12}(-\nabla T) \qquad (9.49)$$
$$\mathbf{j}_q = L^{21}(\mathbf{E} + \nabla\mu) + L^{22}(-\nabla T) \qquad (9.50)$$

yields the following definition for the Onsager coefficients

$$\mathbb{L}^\alpha = e^2 \sum_n \int \frac{d\mathbf{k}}{4\pi^3} \mathbf{v}_n^2(\mathbf{k}) \tau_n(\mathbf{k}) \frac{\partial g^0}{\partial \epsilon_n(k)} (\varepsilon_n(\mathbf{k}) - \mu)^\alpha , \qquad (9.51)$$

where $L^{11} = \mathbb{L}^0$, $L^{21} = TL^{12} = -\frac{1}{e}\mathbb{L}^1$, and $L^{22} = \frac{1}{e^2 T}\mathbb{L}^2$.

From the derived equations, one can immediately derive some important material properties: For metals, which feature a large amount of free carriers, the electrical and thermal conductivity is typically. Using the Sommerfeld expansion around ε_{F} introduced in the exercises, one can immediately show that the thermal conductivity and the electrical conductivity are proportional to each other, as described by the Wiedemann-Franz law:

$$\kappa = \frac{\pi^2}{3}\left(\frac{k_{\mathrm{B}}}{e}\right)^2 T\sigma \; . \tag{9.52}$$

As shown in Fig. 9.2, the typical temperature dependence of the resistivity $\rho = 1/\sigma$ follows the following rule:

$$\rho(T) \approx \rho(0) + BT^5 \; . \tag{9.53}$$

At low temperatures, we have a finite (residual) resistivity $\rho(0)$ that is caused by scattering with (intrinsic) defects, grain boundaries, and surfaces. At elevated temperatures, the resistivity increases with T^5 due to the scattering of electrons with phonons that determine the lifetimes $\tau(\mathbf{k})$. As we will see in the next section, the resistivity can, however, drop to 0 (infinite conductivity) under certain circumstances.

9.5   Superconductivity

So far in this lecture we have considered materials as many-body "mix" of electrons and ions. The key approximations that we have made are

- the Born-Oppenheimer approximation that allowed us to separate electronic and ionic degrees of freedom and to concentrate on the solution of the electronic many-body Hamiltonian with the nuclei only entering parameterically.

- the independent-electron approximation, which greatly simplifies the theoretical description and facilitates our understanding of matter. For density-functional theory we have shown in Chapter 3 that the independent-electron approximation is always possible for the many-electron ground state.

- that the independent quasiparticle can be seen as a simple extension of the independent-electron approximation (e.g. photoemission, Fermi liquid theory for metals, etc.).

We have also considered cases in which these approximations break down. The treatment of electron-phonon (or electron-nuclei) coupling, for example, requires a more sophisticated approach, as we saw. Also most magnetic orderings are many-body phenomena. In Chapter 8 we studied, for example, how spin coupling is introduced through the many-body form of the wave function.

In 1911 H. Kamerlingh Onnes discovered superconductivity in Leiden. He observed that the electrical resistance of various metals such as mercury, lead and tin disappeared completely at low enough temperatures (see Fig. 9.2). Instead of dropping off as T^5 to a finite resistivity that is given by impurity scattering in normal metals, the resistivity of superconductors drops of sharply to zero at a critical temperature T_c. The record for the longest unstained current in a material is now 2 1/2 years. However, according to the theories for ordinary metals developed in this lecture, perfect conductivity should not exist at $T > 0$. Moreover, superconductivity is not an isolated phenomenon. Figure 9.3 shows the
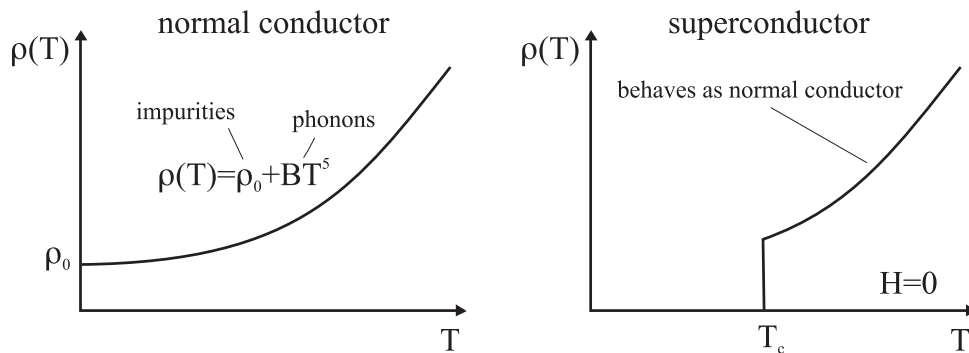
Figure 9.2: The resistivity of a normal (left) and a superconductor (right) as a function of temperature.
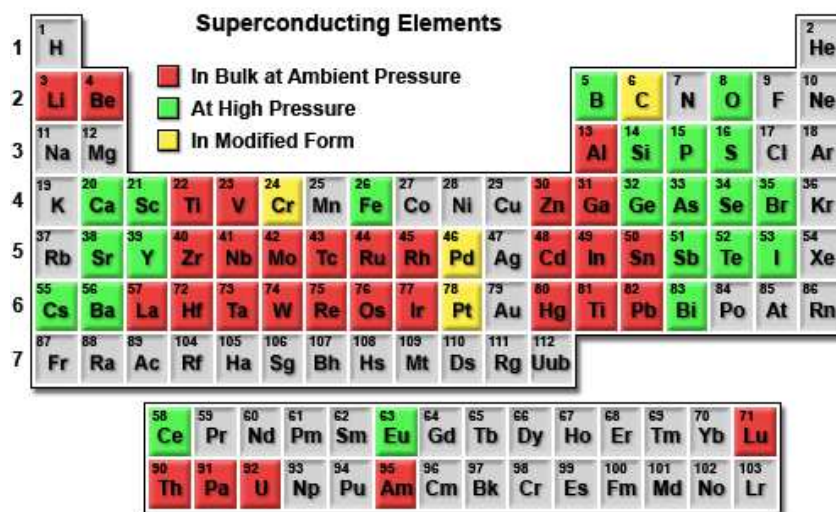

Figure 9.3: Superconducting elements in the periodic table. From *Center for Integrated Research & Learning.*

elements in the periodic table that exhibit superconductivity, which is surprisingly large. Much larger, in fact, than the number of ferromagnetic elements in Fig. 8.1. However, compared to the ferromagnetic transition temperatures discussed in the previous Chapter typical critical temperatures for elemental superconductors are very low (see Tab. 9.1).

The phenomenon of superconductivity eluded a proper understanding and theoretical description for many decades, which did not emerge until the 1950s and 1960s. Then in 1986 the picture that had been developed for "classical" superconductor was turned on its head by the discovery of high temperature superconductivity by Bednorz and Müller. This led to a sudden jump in achievable critical temperatures as Fig. 9.4 illustrates. The record

element	Hg (α)	Sn	Pb	Nb
T_c/K	4.15	3.72	7.19	9.26

Table 9.1: Critical temperatures in Kelvin for selected elemental superconductor.
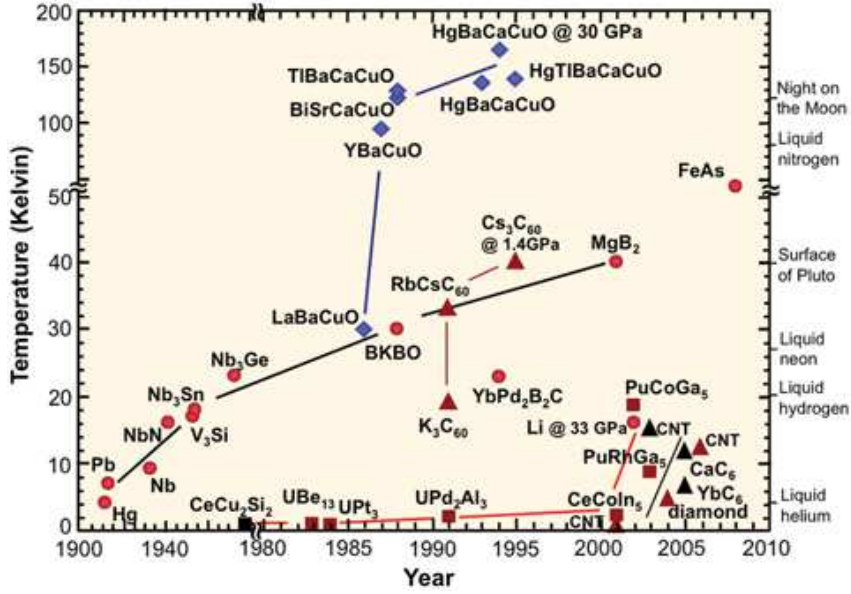
Figure 9.4: Timeline of superconducting materials and their critical temperature. Red symbols mark conventional superconductors and blue high temperature superconductors. From *Wikipedia*.

now lies upwards of 150 Kelvin, but although this is significantly higher than what has so far been achieved with "conventional" superconductors (red symbols in Fig. 9.4), the dream of room temperature superconductivity still remains elusive. What also remains elusive is the mechanism that leads to high temperature superconductivity. In this Chapter we will therefore focus on "classical" or "conventional" superconductivity and recap the most important historic steps that led to the formulation of the BCS (Bardeen, Cooper, and Schrieffer) theory of superconductivity. Suggested reading for this Chapter are the books by A. S. Alexandrov *Theory of Superconductivity – From Weak to Strong Coupling*, M. Tinkham *Introduction to Superconductivity* and D. L. Goodstein *States of Matter*.

9.6   Meissner effect

Perfect conductivity is certainly the first hallmark of superconductivity. The next hallmark was discovered in 1933 by Meissner and Ochsenfeld. They observed that in the superconducting state the material behaves like a perfect *diamagnet*. Not only can an external field not enter the superconductor, which could still be explained by perfect conductivity, but also a field that was originally present in the normal state is expelled in the superconducting state (see Fig. 9.5). Expressed in the language of the previous Chapter this implies

$$\mathbf{B} = \mu_0 \mu \mathbf{H} = \mu_0 (1 + \chi) \mathbf{H} = 0 \tag{9.54}$$

and therefore $\chi = -1$, which is not only diamagnetic, but also very large. The expulsion of a magnetic field cannot be explained by perfect conductivity, which would tend to trap flux. The existence of such a reversible *Meissner effect* implies that superconductivity will be destroyed by a critical magnetic field H_c. The phase diagram of such a superconductor (denoted type I, as we will see in the following) is shown in Fig. 9.6.
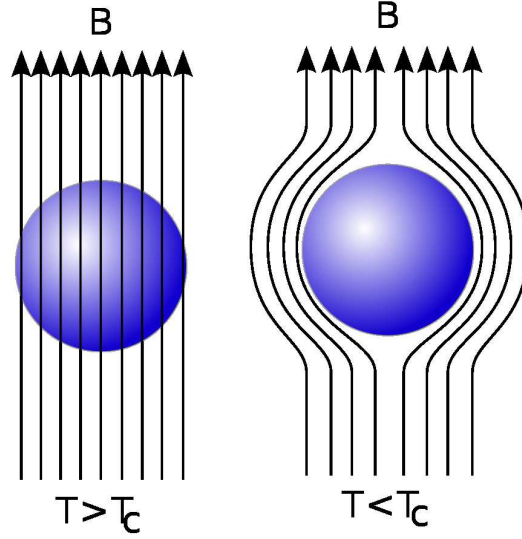
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Figure 9.5: Diagram of the Meissner effect. Magnetic field lines, represented as arrows, are excluded from a superconductor when it is below its critical temperature.

To understand this odd behavior we first consider a perfect conductor. However, we assume that only a certain portion n_s of all electrons conduct perfectly. All others conduct dissipatively. In an electric field $\mathbf{E}$ the electrons will be accelerated

$$m\frac{d\mathbf{v}_s}{dt} = -e\mathbf{E} \tag{9.55}$$

and the current density is given by $\mathbf{j} = -e\mathbf{v}_s n_s$. Inserting this into eq. 9.55 gives

$$\frac{d\mathbf{j}}{dt} = \frac{n_s e^2}{m}\mathbf{E} \quad . \tag{9.56}$$

Substituting this into Faraday's law of induction

$$\nabla \times \mathbf{E} = -\frac{1}{c}\frac{\partial B}{\partial t} \tag{9.57}$$

we obtain

$$\frac{\partial}{\partial t}\left(\nabla \times \mathbf{j} + \frac{n_s e^2}{mc}\mathbf{B}\right) = 0 \quad . \tag{9.58}$$

Together with Maxwell's equation

$$\nabla \times \mathbf{B} = \frac{4\pi}{c}\mathbf{j} \tag{9.59}$$

this determines the fields and currents that can exist in the superconductor. Eq. 9.58 tells us that any change in the magnetic field B will be screened immediately. This is consistent with Meissner's and Ochsenfeld's observation. However, there are static currents and magnetic fields that satisfy the two equations. This is inconsistent with the observation
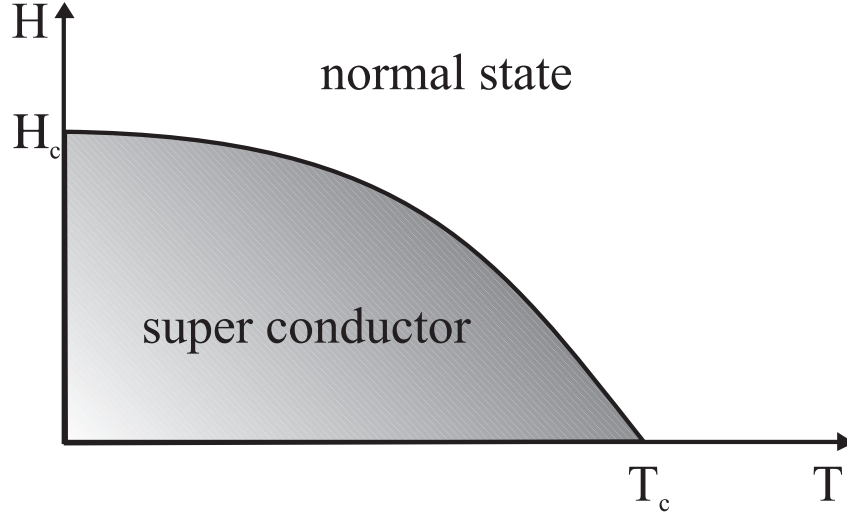
Figure 9.6: The phase diagram of a type I superconductor as a function temperature and the magnetic field H.

that fields are expelled from the superconducting region. Therefore perfect conductivity alone does not explain the Meissner effect.

To solve this conundrum F. and H. London proposed to restrict the solutions for superconductors to fields and currents that satisfy

$$\nabla \times \mathbf{j} + \frac{n_s e^2}{mc} \mathbf{B} = 0 \quad . \tag{9.60}$$

This equation is known as London equation and inserting it into Maxwell's equation yields

$$\nabla \times (\nabla \times \mathbf{B}) + \frac{4\pi n_s e^2}{mc^2} \mathbf{B} = 0 \quad . \tag{9.61}$$

Using the relation $\nabla \times (\nabla \times \mathbf{B}) = \nabla(\nabla \mathbf{B}) - \nabla^2 \mathbf{B}$ and applying Gauss' law $\nabla \mathbf{B} = 0$ we obtain

$$\nabla^2 \mathbf{B} = \frac{4\pi n_s e^2}{mc^2} \mathbf{B} \quad . \tag{9.62}$$

For the solution of this differential equation we consider a half infinite superconductor $(x > 0)$. The magnetic field then decays exponentially

$$\mathbf{B}(x) = \mathbf{B}(0) e^{-\frac{x}{\lambda_L}} \quad , \tag{9.63}$$

where the London penetration depth is given by

$$\lambda_L = \sqrt{\frac{mc^2}{4\pi n_s e^2}} = 41.9 \left(\frac{r_s}{a_0}\right)^{\frac{3}{2}} \left(\frac{n}{n_s}\right)^{\frac{1}{2}} \text{Å} \quad . \tag{9.64}$$

The magnetic field at the boarder between a normal material and a superconductor is shown schematically in Fig. 9.7. Inside the superconductor the field is expelled from the superconductor by eddy currents at its surface. The field subsequently decays exponentially fast. The decay length is given by the London penetration depth, which for

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B(x)

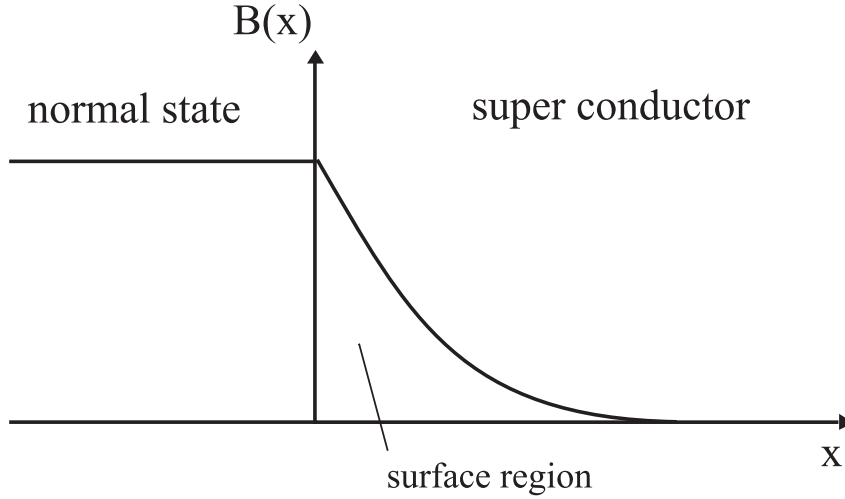normal state   super conductor

surface region

X

Figure 9.7: The magnetic field inside a type I superconductor drops off exponentially fast from its surface.

typical superconductors is of the order of 10^2 to 10^3 Å. Although London's explanation phenomenologically explains the Meissner effect it begs the question if we can create a microscopic theory (i.e. version of London's equation) that goes beyond standard electro-dynamics. And how can we create a phase transition in the electronic structure that leads to the absence of all scattering.

9.7   London theory

F. London first noticed that a degenerate Bose-Einstein gas provides a good basis for a phenomenological model of superconductivity. F. and H. London then proposed a quantum mechanical analog of London's electrodynamical derivation shown in the previous section. They showed that the Meissner effect could be interpreted very simply by a peculiar coupling in momentum space, as if there was something like a condensed phase of the Bose gas. The idea to replace Fermi statistics by Bose statistics in the theory of metals led them to an equation for the current, which turned out to be microscopically exact. The quantum mechanical current density is given by

$$\mathbf{j}(\mathbf{r}) = \frac{ie}{2m} \left(\psi^* \nabla \psi - \psi \nabla \psi^* \right) - \frac{e^2}{m} \mathbf{A} \psi^* \psi \tag{9.65}$$

where $\mathbf{A} \equiv \mathbf{A}(\mathbf{r})$ is a vector potential such that $\nabla \times \mathbf{A} = \mathbf{B}$. One should sum this expression over all electron states below the Fermi level of the normal metal. If the particles governed by the wave functions ψ in this expression were electrons we would only observe weak Landau diamagnetism (see previous Chapter). So let us instead assume bosons with charge e^* and mass m^*. They satisfy their Schrödinger equation

$$-\frac{1}{2m^*} \left(\nabla + ie^* \mathbf{A} \right) \phi(\mathbf{r}) = E \phi(\mathbf{r}) \quad . \tag{9.66}$$

Choosing the Maxwell gauge for the vector field ($\nabla \mathbf{A} = 0$) we obtain

$$\left(-\frac{1}{2m^*} \nabla^2 - \frac{ie^*}{m^*} \mathbf{A} \nabla + \frac{e^*}{2m^*} \mathbf{A}^2 \right) \phi(\mathbf{r}) = E \phi(\mathbf{r}) \quad . \tag{9.67}$$

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Now we assume $\mathbf{A}$ to be small so that we can apply perturbation theory

$$\phi(\mathbf{r}) = \phi_0(\mathbf{r}) + \phi_l(\mathbf{r}) \quad , \tag{9.68}$$

where $\phi_0(\mathbf{r})$ is the ground state wave function in the absence of the field and $\phi_l(\mathbf{r})$ the perturbation introduced by $\mathbf{A}$. We know from the theory of Bose condensates that at low temperatures the condensate wave function is a constant

$$\phi_0(\mathbf{r}) = \frac{1}{\sqrt{V}}, \quad \mathbf{k} = 0, E_0 = 0, \tag{9.69}$$

where V is the volume of the condensate. Next we insert eq. 9.68 into eq. 9.67 and expand to first order in $\mathbf{A}$ and ϕ_l

$$-\frac{1}{2m^*}\nabla^2\phi_0(\mathbf{r}) - \frac{1}{2m^*}\nabla^2\phi_l(\mathbf{r}) - \frac{ie^*}{m^*}\mathbf{A}\nabla\phi_0(\mathbf{r}) = E_0\phi_l(\mathbf{r}) + E_1\phi_0(\mathbf{r}) \quad . \tag{9.70}$$

The first and third term on the left hand side of this equation and the first term on the right hand side are zero. Since we are first order in $\mathbf{A}$, E_1 has to be proportional to $\mathbf{A}$ and because E_1 is a scalar our only choice is for it to be proportional to $\nabla\mathbf{A}$. This means it vanishes in the Maxwell gauge and $\phi_l(\mathbf{r}) = 0$ to first order in $\mathbf{A}$. Inserting $\phi(\mathbf{r}) = \phi_0(\mathbf{r})$ into the equation for the current density (eq. 9.65) the term in brackets evaluates to zero and we are left with

$$\mathbf{j}(\mathbf{r}) = -\frac{e^{*2}}{2m^*}\frac{N_s}{V}\mathbf{A} = -\frac{e^{*2}n_s}{2m^*}\mathbf{A} \quad . \tag{9.71}$$

With $\nabla \times \mathbf{A} = \mathbf{B}$ and Maxwell's equation $\nabla \times \mathbf{B} = \frac{4\pi}{c}\mathbf{j}$ we finally arrive at

$$\mathbf{B} + \lambda_L\nabla \times \nabla\mathbf{B} = 0, \tag{9.72}$$

which is identical to the London equation derived from electrodynamics in the previous section (cf eq. 9.61). We now have a quantum mechanical derivation of the London equation and the London penetration depth and we have identified the carriers in the superconducting state to be bosons. However, this begs the question where these bosons come from?

9.8 Flux quantization

If the superconducting state is a condensate of Bosons, as proposed by London, then its wave function is of the form

$$\phi(\mathbf{r}) = \sqrt{n_s}e^{-\varphi(\mathbf{r})} \quad . \tag{9.73}$$

n_s is the superconducting density, that we introduced in section 9.6 and which we assume to be constant throughout the superconducting region. $\varphi(\mathbf{r})$ is the phase factor of the wave function, which is yet undetermined. To pin down the phase let us consider a hole in our superconductor (cf Fig. 9.8) or alternatively a superconducting ring. The magnetic flux through this hole is

$$\Phi_B = \int_{surf} d\mathbf{s}\,\mathbf{B} = \int_{surf} d\mathbf{s}\,\nabla \times \mathbf{A}(\mathbf{r}) = \oint_C d\mathbf{l}\,\mathbf{A}(\mathbf{r}) , \tag{9.74}$$
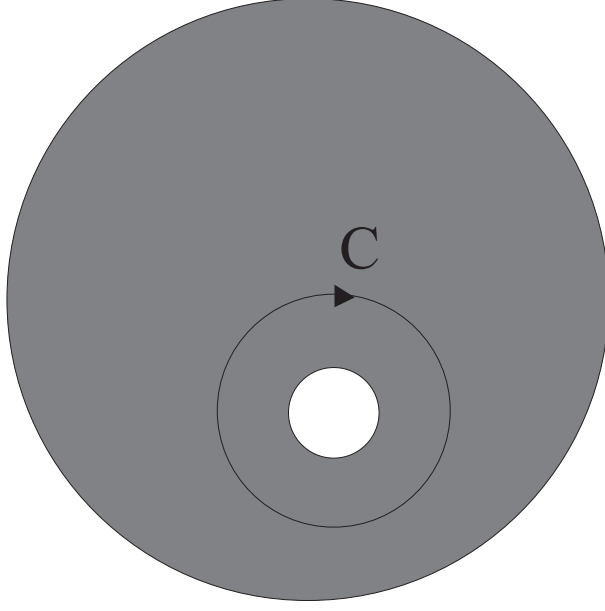
Figure 9.8: Flux trapped in a hole in a superconductor is quantized.

where we have used Stoke's theorem to convert the surface integral into the line integral over the contour C. But according to London's theory the magnetic field inside the superconductor falls off exponential so that we can find a contour on which $\mathbf{B}$ and $\mathbf{j}$ are zero. Using the equation for the current density (eq. 9.65) this yields

$$0 = \mathbf{j}(\mathbf{r}) = \frac{ie^*}{2m^*}\left(\psi^*\nabla\psi - \psi\nabla\psi^*\right) - \frac{e^{*2}}{m^*}\mathbf{A}\psi^*\psi\,. \tag{9.75}$$

Inserting our wave function (eq. 9.73) for the condensate gives the following equation for the phase

$$\frac{ie^*}{2m^*}\left(i\nabla\varphi\phi^*\phi + i\nabla\varphi\phi\phi^*\right) - \frac{e^{*2}}{m^*}\mathbf{A}\phi^*\phi = 0 \tag{9.76}$$

or

$$-\frac{e^*}{m^*}\phi^*\phi\left(\nabla\varphi + e^*\mathbf{A}\right) = 0\,. \tag{9.77}$$

This implies that there is a relation between the phase and the vector potential

$$\mathbf{A}(\mathbf{r}) = -\frac{\nabla\varphi(\mathbf{r})}{e^*}. \tag{9.78}$$

Inserting this result into our expression for the magnetic flux (eq. 9.74) we finally obtain

$$\Phi_B = -\oint_C d\mathbf{l}\,\frac{\nabla\varphi}{e^*} = \frac{\delta\varphi}{e^*}. \tag{9.79}$$

Here $\delta\varphi$ is the change of the phase in the round trip along the contour, which is only given up to modulo 2π: $\delta\varphi = 2\pi p$ with $p=0, 1, 2,\ldots$ This means the magnetic flux is quantized

$$\Phi_B = \frac{2\pi\hbar c}{e^*}p. \tag{9.80}$$

Experimentally this was confirmed by Deaver and Fairbank in 1961 who found $e^* = 2e$!

9.9 Ogg's pairs

Recapping at this point, we have learned that the superconducting state is made up of bosons with twice the electron charge. This led Richard Ogg Jr to propose in 1946 that electrons might pair in real space. Like for the hydrogen molecule discussed in section 8.4.4.1 the two electrons could pair chemically and form a boson with spin $S=0$ or 1. Ogg suggested that an ensemble of such two-electron entities could, in principle, form a superconducting Bose-Einstein condensate. The idea was motivated by his demonstration that electron pairs were a stable constituent of fairly dilute solutions of alkali metals in liquid ammonia. The theory was further developed by Schafroth, Butler and Blatt, but did not produce a quantitative description of superconductivity (e.g. the T_c of $\sim 10^4$ K is much too high). The theory could also not provide a microscopic force to explain the pairing of normally repulsive electrons. It was therefore concluded that electron pairing in real-space does not work and the theory was forgotten.

9.10 Microscopic theory - BCS theory

9.10.1 Cooper pairs

The basic idea behind the weak attraction between two electrons was presented by Cooper in 1956. He showed that the Fermi sea of electrons is unstable against the formation of at least one bound pair, regardless of how weak the interaction is, son long as it is attractive. This result is a consequence of Fermi statistics and of the existence of the Fermi-sea background, since it is well known that binding does not ordinarily occur in the two-body problem in three dimensions until the strength of the potential exceeds a finite threshold value.

To see how the binding comes about, we consider the model of two quasiparticles with momentum $\mathbf{k}$ and $-\mathbf{k}$ in a Fermi liquid (e.g. free-electron metal). The spatial part of the two-particle wave function of this pair is then

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\mathbf{k}} g_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}_1} e^{-i\mathbf{k}\mathbf{r}_2} . \tag{9.81}$$

For the spin part we assume singlet pairing $|\chi_{\text{spin}} >_{\text{S}} = 2^{-1/2} (| \uparrow\downarrow> - | \downarrow\uparrow>)$ (see also section 8.4.4.1), which gives us $\mathbf{S}=0$, i.e. a boson. The triplet with $\mathbf{S}=1$ would also be possible, but is of higher energy for conventional superconductors (see e.g. unconventional superconductivity). $|\chi_{\text{spin}} >_{\text{S}}$ is antisymmetric with respect to particle exchange and $\psi_0(\mathbf{r}_1, \mathbf{r}_2)$ therefore has to be symmetric:

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\mathbf{k}>\mathbf{k}_F} g_{\mathbf{k}} \cos \mathbf{k}(\mathbf{r}_1 - \mathbf{r}_2) . \tag{9.82}$$

If we insert this wave function into our two-particle Schrödinger equation

$$\left[\sum_{i=1,2} \frac{\mathbf{p_i}^2}{2m} + V(\mathbf{r}_1, \mathbf{r}_2) \right] \psi_0 = E\psi_0 \tag{9.83}$$

we obtain

$$(E - 2\epsilon_{\mathbf{k}})g_{\mathbf{k}} = \sum_{\mathbf{k}'>\mathbf{k}_F} V_{\mathbf{k}\mathbf{k}'} g_{\mathbf{k}'} . \tag{9.84}$$

$V_{\mathbf{kk'}}$ is the characteristic strength of the scattering potential and is given by the Fourier transform of the potential V

$$V_{\mathbf{kk'}} = \frac{1}{\Omega} \int d\mathbf{r} V(\mathbf{r}) e^{-(\mathbf{k}-\mathbf{k'})\mathbf{r}} \tag{9.85}$$

with $\mathbf{r} = \mathbf{r_1} - \mathbf{r_2}$ and Ω the normalized volume. The energies $\epsilon_{\mathbf{k}}$ in eq. 9.84 are the unperturbed plane-wave energies and are larger than ϵ_F, because the sum runs over $\mathbf{k} > \mathbf{k}_F$. If a set of $g_{\mathbf{k}}$ exists such that $E < 2\epsilon_F$ then we would have a bound state of two electrons.

But how can this be? Recall that the Fourier transform of the bare Coulomb potential (i.e. free electrons) is

$$V_{\mathbf{kk'}} = V_{\mathbf{q}=\mathbf{k}-\mathbf{k'}} = \frac{4\pi^2}{\mathbf{q}^2} > 0 \ . \tag{9.86}$$

This is always larger than zero and therefore not attractive, as expected. However, quasiparticles are not free electrons and are screened by the electron sea. Let us consider Thomas-Fermi screening introduced in Chapter 3. The dielectric function becomes

$$\varepsilon(\mathbf{k}) = \frac{\mathbf{k}^2 + \mathbf{k}_0^2}{\mathbf{k}^2} \neq 1 \ . \tag{9.87}$$

The bare Coulomb potential is screened by ε

$$V(\mathbf{r_1} - \mathbf{r_2}) = \frac{\varepsilon^{-1}(\mathbf{r_1} - \mathbf{r_2})}{|\mathbf{r_1} - \mathbf{r_2}|} \ . \tag{9.88}$$

Its Fourier transform

$$V_{\mathbf{q}} = \frac{4\pi^2}{\mathbf{q}^2 + \mathbf{k}_0^2} \tag{9.89}$$

is still positive, but now reduced compared to the bare Coulomb interaction. Building on the idea of screening we should also consider the ion cores. They are positively charged and also move to screen the negative charge of our electron pair. However, their "reaction speed" is much smaller than those of the electrons and of the order of typical phonon frequencies. A rough estimate (see e.g. Ashcroft Chapter 26) to further screen the Thomas-Fermi expression could look like

$$V_{\mathbf{q}} = \frac{4\pi^2}{\mathbf{q}^2 + \mathbf{k}_0^2} \left(1 + \frac{\omega^2}{\omega^2 - \omega_{\mathbf{q}}^2}\right) \ , \tag{9.90}$$

where $\omega_{\mathbf{q}}$ is a phonon frequency of wave vector $\mathbf{q}$ and $\omega = \frac{1}{\hbar}(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}}')$. If now $\omega < \omega_{\mathbf{q}}$ this (oversimplified) potential would be negative and therefore attractive. In other words, phonons could provide our attractive interaction that is schematically depicted in Fig. 9.9. At normal temperatures, the positive ions in a superconducting material vibrate away on the spot and constantly collide with the electron bath around them. It is these collisions that cause the electrical resistance that wastes energy and produces heat in any normal circuit. But the cooler the material gets, the less energy the ions have, so the less they vibrate. When the material reaches its critical temperature, the ions' vibrations are incredibly weak and no longer the dominant form of motion in the lattice. The tiny
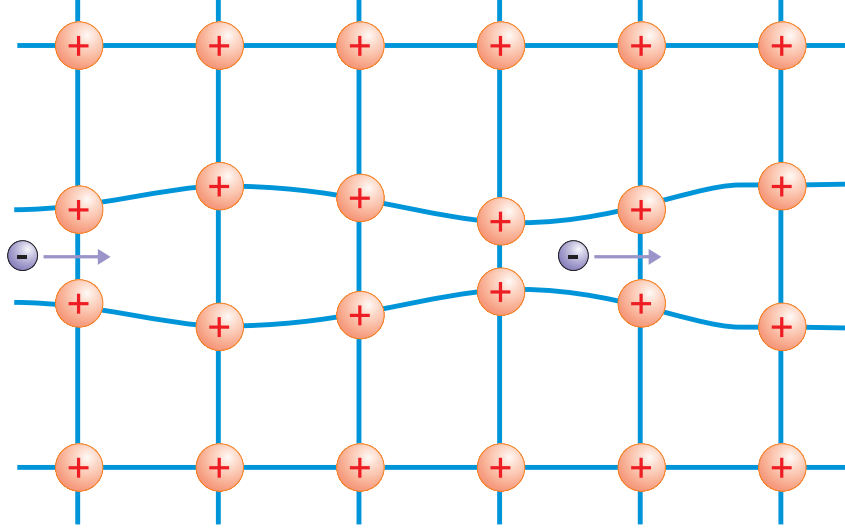
Figure 9.9: Cooper pair formation schematically: at extremely low temperatures, an electron can draw the positive ions in a superconductor towards it. This movement of the ions creates a more positive region that attracts another electron to the area.

attractive force of passing electrons that's always been there is suddenly enough to drag the positive ions out of position towards them. And that dragging affects the behaviour of the solid as a whole. When positive ions are drawn towards a passing electron, they create an area that is more positive than their surroundings, so another nearby electron is drawn towards them. However, those electrons are on the move, so by the time the second one has arrived the first one has moved on and created a path of higher positivity that the second electron keeps on following. The electrons are hitched in a game of catch-up that lasts as long as the temperature stays low.

To proceed Cooper then further simplified the potential

$$V_{\mathbf{kk'}} = \begin{cases} -V & \text{for } |\epsilon_{\mathbf{k}} - \epsilon_F|, |\epsilon_{\mathbf{k'}} - \epsilon_F| < \hbar\omega_c \\ 0 & \text{otherwise} \end{cases} \tag{9.91}$$

where ω_c is the Debye frequency. Now V pulls out of the sum on the right-hand side of eq. 9.84 and we can rearrange for $g_{\mathbf{k}}$:

$$g_{\mathbf{k}} = V \frac{\sum_{\mathbf{k'}} g_{\mathbf{k'}}}{E - 2\epsilon_{\mathbf{k}}} . \tag{9.92}$$

Applying $\sum_{\mathbf{k}}$ on both sides and canceling $\sum_{\mathbf{k}} g_{\mathbf{k}}$ we obtain

$$\frac{1}{V} = \sum_{\mathbf{k} > \mathbf{k}_F} (2\epsilon_{\mathbf{k}} - E)^{-1} . \tag{9.93}$$

Replacing the sum by an integral yields

$$\frac{1}{V} = \int_{\epsilon_F}^{\epsilon_F + \hbar\omega_c} d\epsilon N(\epsilon) \frac{1}{2\epsilon - E} \approx \frac{1}{2} N(\epsilon_F) \ln \frac{2\epsilon_F - E + 2\hbar\omega_c}{2\epsilon_F - E} \tag{9.94}$$

where we have made the assumption $N(\epsilon) \approx N(\epsilon_F)$. Solving this expression for E we obtain

$$E(e^{-\frac{2}{NV}} - 1) = 2\epsilon_F(e^{-\frac{2}{NV}} - 1) + 2\hbar\omega_c e^{-\frac{2}{NV}} . \tag{9.95}$$

Now we make the "weak coupling" approximation $N(\epsilon_F)V \ll 1$ such that $1 - e^{-\frac{2}{NV}} \approx 1$ to arrive at the final expression

$$E \approx 2\epsilon_F - 2\hbar\omega_c e^{-\frac{2}{NV}} < 2\epsilon_F . \tag{9.96}$$

We see that we indeed find a bound state, in which the binding outweighs the gain in kinetic energy for states above ϵ_F, regardless of how small V is. It is important to note that the binding energy is not analytic at $V = 0$, i.e. it cannot be expanded in powers of V. This means that perturbation theory is not applicable, which slowed down the development of the theory significantly. With view to the Ogg pairs discussed in section 9.9 we note that the Cooper pair is bound in reciprocal space:

$$\psi_0 = \sum_{\mathbf{k} > \mathbf{k}_F} g_{\mathbf{k}} \cos \mathbf{k}(\mathbf{r}_1 - \mathbf{r}_2) \tag{9.97}$$

$$\sim \sum_{\mathbf{k} > \mathbf{k}_F} \frac{V}{2(\epsilon_k - \epsilon_F) + 2\epsilon_F - E} \cos \mathbf{k}(\mathbf{r}_1 - \mathbf{r}_2) \tag{9.98}$$

The denominator assumes its maximum value for electrons at the Fermi level and falls off from there. Thus the electron states within a range $2\epsilon_F - E$ above ϵ_F are those most strongly involved in forming the bound states.

9.11   Bardeen-Cooper-Schrieffer (BCS) Theory

Having seen that the Fermi sea is unstable against formation of a bound Cooper pair when the net interaction is attractive, we then expect pairs to condense until an equilibrium point is reached. This will occur when the state of the system is so greatly changed from the Fermi sea due to the large number of pairs that the binding energy for an additional pair has gone to zero. The wave function for such a state appears to be quite complex and it was the ingenuity of Bardeen, Cooper and Schrieffer to develop it. The basic idea is to create the total many-electron wave function from the pair wave functions ϕ we discussed in the previous section

$$\Psi = \phi(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2)\phi(\mathbf{r}_3\sigma_3, \mathbf{r}_4\sigma_4)\dots\phi(\mathbf{r}_{N-1}\sigma_{N-1}, \mathbf{r}_N\sigma_N) \tag{9.99}$$

and then to antisymmeterize ($\Psi_{\mathrm{BCS}} = \hat{A}\Psi$). The coefficients of Ψ_{BCS} could then be found by minimizing the total energy of the many-body Hamiltonian. BCS introduced a simplified *pairing* Hamiltonian

$$H = \sum_{\mathbf{k},\sigma} \xi_{\mathbf{k}} c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}\sigma} + \sum_{\mathbf{k}\mathbf{k}'} c_{\mathbf{k}\uparrow}^{\dagger} c_{-\mathbf{k}\downarrow}^{\dagger} V_{\mathbf{k}\mathbf{k}'} c_{-\mathbf{k}'\downarrow} c_{\mathbf{k}'\uparrow} , \tag{9.100}$$

with $\xi = \epsilon_{\mathbf{k}} - \epsilon_F$ and the usual electron creation and annihilation operators $c_{\mathbf{k}\sigma}^{\dagger}$ and $c_{\mathbf{k}\sigma}$. $V_{\mathbf{k}\mathbf{k}'}$ again is our attractive interaction as in Eq. (9.91), but it is restricted to $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$ pairs. The problem is solvable in principle but this may be not too illustrative. Instead, we will consider a mean-field approximation.

We start with the observation that the characteristic BCS pairing Hamiltonian will lead to a ground state which is some phase-coherent superposition of many-body states with pairs of Bloch states $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$ occupied or unoccupied. Because of the coherence, operators such as $c_{-\mathbf{k}'\downarrow}c_{\mathbf{k}'\uparrow}$ can have nonzero expectation values $b_{\mathbf{k}} = \langle c_{-\mathbf{k}'\downarrow}c_{\mathbf{k}'\uparrow}\rangle_{\text{avg}}$ in such a state, rather than averaging to zero as in a normal metal, where the phases are random. Moreover, because of the large number of particles involved, the fluctuations about these expectation values should be small. This suggests that it will be useful to express such a product of operators formally as

$$c_{-\mathbf{k}'\downarrow}c_{\mathbf{k}'\uparrow} = b_{\mathbf{k}} + (c_{-\mathbf{k}'\downarrow}c_{\mathbf{k}'\uparrow} - b_{\mathbf{k}}) \, , \tag{9.101}$$

and subsequently neglect quantities which are quadratic in the (presumably small) fluctuation term in parentheses. By making the following mean-field approximation for the potential term

$$\sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} c_{-\mathbf{k}'\downarrow}c_{\mathbf{k}'\uparrow} \approx -V\Theta(\hbar\omega_c - |\xi_{\mathbf{k}}|) \sum_{\mathbf{k}'} \Theta(\hbar\omega_c - |\xi_{\mathbf{k}'}|)\langle c_{-\mathbf{k}'\downarrow}c_{\mathbf{k}'\uparrow}\rangle_{\text{avg}} \tag{9.102}$$

$$=: \Delta_{\mathbf{k}} = \begin{cases} \Delta & \text{for } |\epsilon_{\mathbf{k}} - \epsilon_F|, |\epsilon_{\mathbf{k}'} - \epsilon_F| < \hbar\omega_c \\ 0 & \text{otherwise} \end{cases} , \tag{9.103}$$

inserting all into the BCS Hamiltonian Eq. (9.100), and expanding to first order, we write

$$H_{\text{MF}} = \sum_{\mathbf{k},\sigma} \xi_{\mathbf{k}} c^\dagger_{\mathbf{k}\sigma}c_{\mathbf{k}\sigma} + \sum_{\mathbf{k}\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} \left(c^\dagger_{\mathbf{k}\uparrow}c^\dagger_{-\mathbf{k}\downarrow}b_{\mathbf{k}'} + b^\dagger_{\mathbf{k}}c_{-\mathbf{k}'\downarrow}c_{\mathbf{k}'\uparrow} - b^\dagger_{\mathbf{k}}b_{\mathbf{k}'} \right) \tag{9.104}$$

$$= \sum_{\mathbf{k},\sigma} \xi_{\mathbf{k}} c^\dagger_{\mathbf{k}\sigma}c_{\mathbf{k}\sigma} - \sum_{\mathbf{k}} \left(\Delta_{\mathbf{k}} c^\dagger_{\mathbf{k}\uparrow}c^\dagger_{-\mathbf{k}\downarrow} + \Delta^*_{\mathbf{k}}c_{-\mathbf{k}'\downarrow}c_{\mathbf{k}'\uparrow} - \Delta_{\mathbf{k}}b^\dagger_{\mathbf{k}} \right) \, . \tag{9.105}$$

This is an effective single particle Hamiltonian (two c-operators instead of four), which we can solve. To diagonalize this mean-field Hamiltonian, we define a suitable linear transformation onto a new set of Fermi operators

$$c_{\mathbf{k}\uparrow} = u_{\mathbf{k}}\alpha_{\mathbf{k}} + v_{\mathbf{k}}\beta^\dagger_{\mathbf{k}} \tag{9.106}$$

$$c_{-\mathbf{k}\downarrow} = u_{\mathbf{k}}\beta_{\mathbf{k}} - v_{\mathbf{k}}\alpha^\dagger_{\mathbf{k}} \, , \tag{9.107}$$

where $\alpha_{\mathbf{k}}$ and $\beta_{\mathbf{k}}$ are two types of new non-interacting Fermions (i.e. quasiparticles). The expansion coefficients are

$$u^2_{\mathbf{k}} = \frac{1}{2}\left(1 + \frac{\xi_{\mathbf{k}}}{\tilde{\epsilon}_{\mathbf{k}}}\right) \tag{9.108}$$

$$v^2_{\mathbf{k}} = \frac{1}{2}\left(1 - \frac{\xi_{\mathbf{k}}}{\tilde{\epsilon}_{\mathbf{k}}}\right) \tag{9.109}$$

$$u_{\mathbf{k}}v_{\mathbf{k}} = -\frac{\Delta_{\mathbf{k}}}{2\tilde{\epsilon}_{\mathbf{k}}} \tag{9.110}$$

and

$$\tilde{\epsilon}_{\mathbf{k}} = \sqrt{\xi^2_{\mathbf{k}} + |\Delta_{\mathbf{k}}|^2} \, . \tag{9.111}$$

With this so-called Bogoliubov transformation, the mean-field Hamiltonian becomes diagonal

$$H_{\text{MF}} = E_0 + \sum_{\mathbf{k}} \tilde{\epsilon}_{\mathbf{k}}(\alpha^\dagger_{\mathbf{k}}\alpha_{\mathbf{k}} + \beta^\dagger_{\mathbf{k}}\beta_{\mathbf{k}}) \, , \tag{9.112}$$

with

$$E_0 = 2 \sum_{\mathbf{k}} \left(\xi_k v_{\mathbf{k}} + \Delta_{\mathbf{k}} u_{\mathbf{k}} v_{\mathbf{k}} \right) + \frac{|\Delta|^2}{V}. \tag{9.113}$$

The order parameter Δ is given as before by

$$\Delta = -V \sum_{\mathbf{k}'} \Theta(\hbar\omega_c - |\xi_{\mathbf{k}'}|) \langle c_{-\mathbf{k}'\downarrow} c_{\mathbf{k}'\uparrow} \rangle_{\text{avg}}. \tag{9.114}$$

If we now replace $\langle c_{-\mathbf{k}'\downarrow} c_{\mathbf{k}'\uparrow} \rangle_{\text{avg}}$ by $\alpha_{\mathbf{k}}$ and $\beta_{\mathbf{k}}$ as given in Eq. (9.106) and (9.107), we obtain the following relation

$$\Delta = V \sum_{\mathbf{k}'} \frac{\Delta}{\tilde{\epsilon}_{\mathbf{k}}} (1 - 2f_{\mathbf{k}'}). \tag{9.115}$$

$f_{\mathbf{k}}$ is the quasiparticle distribution function $f_{\mathbf{k}} = < \alpha_{\mathbf{k}}^\dagger \alpha_{\mathbf{k}} > = < \beta_{\mathbf{k}}^\dagger \beta_{\mathbf{k}} >$. Unlike in the case of bare electrons, the total average number of quasi-particles is not fixed. Therefore, their chemical potential is zero in thermal equilibrium. Since they do not interact, their distribution is described by the usual Fermi-Dirac function, so that

$$f_{\mathbf{k}} = \frac{1}{e^{\frac{\tilde{\epsilon}_{\mathbf{k}}}{k_B T}} + 1}. \tag{9.116}$$

We see that at $T = 0$, $f_{\mathbf{k}} = 0$, so there are no quasiparticles in the ground state. This implies that E_0 is the ground state energy of the BCS superconductor at $T=0$.

To evaluate E_0 we need to know Δ. The trivial solution to Eq. (9.114) is $\Delta = 0$. It corresponds to the normal state and gives

$$E_0 = 2 \sum_{\mathbf{k}} \xi_{\mathbf{k}} v_{\mathbf{k}}^2 = 2 \sum_{\mathbf{k}} \frac{1}{2} \left(1 - \frac{\xi_{\mathbf{k}}}{\tilde{\epsilon}_{\mathbf{k}}} \right). \tag{9.117}$$

For $\Delta = 0$, we have $\tilde{\epsilon}_{\mathbf{k}} = |\xi_{\mathbf{k}}|$ and therefore

$$E_0 = 2 \sum_{\xi_{\mathbf{k}} < 0} \xi_{\mathbf{k}}, \tag{9.118}$$

as expected (the term for $|\mathbf{k}| > k_F$ gives zero since $\tilde{\epsilon}_{\mathbf{k}} = \xi_{\mathbf{k}}$). The non-trivial solution is obtained by canceling the Δ from Eq. (9.115):

$$1 = V \sum_{\mathbf{k}'} \frac{1}{\tilde{\epsilon}_{\mathbf{k}}}. \tag{9.119}$$

Since $\tilde{\epsilon}_{\mathbf{k}}$ still depends on Δ, we solve for it by replacing the momentum summation $\sum_{\mathbf{k}}$ by an energy integration $\int d\epsilon N(\epsilon)$ with the density of states $N(\epsilon)$. We again approximate the density of states by its value at the Fermi level , $N(\epsilon) = N(\epsilon_F)$. This yields

$$\frac{1}{N(\epsilon_F)V} = \int_0^{\hbar\omega_c} \frac{d\xi}{\sqrt{\Delta^2 + \xi^2}} = \sinh^{-1} \left(\frac{\hbar\omega_c}{\Delta} \right). \tag{9.120}$$

Solving for Δ in the weak coupling limit $N(\epsilon_F)V \ll 1$ finally gives

$$\Delta = \frac{\hbar\omega_c}{\sinh\left(\frac{1}{N(\epsilon_F)V} \right)} \approx 2\hbar\omega_c e^{-\frac{1}{N(\epsilon_F)V}}. \tag{9.121}$$
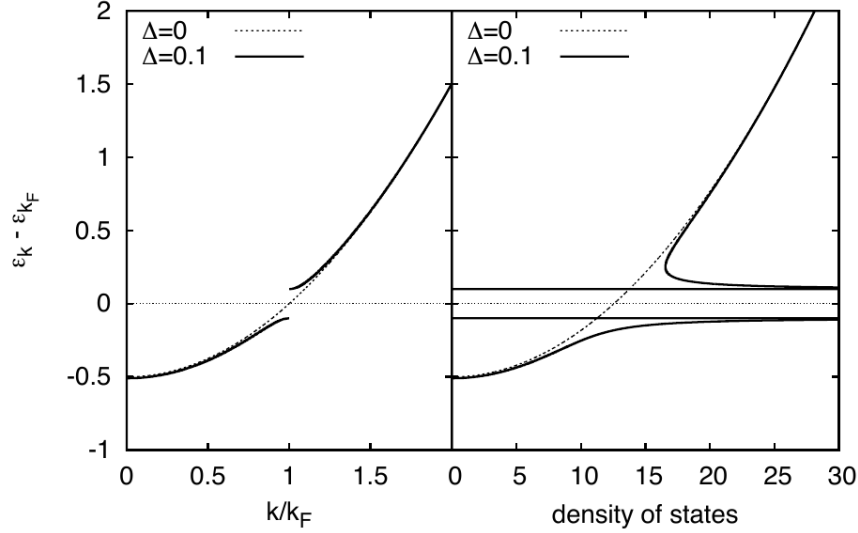
Figure 9.10: The dispersion of electron-like excitations in the SC state is gapped and differs from that of free electrons ($\Delta = 0$). Taken from *Mean-Field Theory: Hartree-Fock and BCS*, Erik Koch, `http://www.cond-mat.de/events/correl16/manuscripts/koch.pdf`

Inserting everything into the equation for the ground state energy (Eq. (9.113)), we obtain for the condensation energy

$$E_c = E_0(\Delta \neq 0) - E_0(\Delta = 0) \tag{9.122}$$

$$\approx 2 \sum_{\xi_{\mathbf{k}} < 0} \xi_{\mathbf{k}} - \frac{1}{2} N(\epsilon_F) \Delta^2 - 2 \sum_{\xi_{\mathbf{k}} < 0} \xi_{\mathbf{k}} \tag{9.123}$$

$$= -\frac{1}{2} N(\epsilon_F) \Delta^2 < 0 . \tag{9.124}$$

We see that the condensation energy is indeed smaller than zero at $T = 0$ and therefore favors Cooper pair formation. $\Delta = \Delta(T)$ is called the order parameter that determines when superconductivity sets in. The order parameter also affects the dispersion of the quasiparticles. Recall eq. 9.111 ($\tilde{\epsilon}_{\mathbf{k}} = \sqrt{\xi_{\mathbf{k}}^2 + |\Delta_{\mathbf{k}}|^2}$). Away from the Fermi surface, the quasiparticles α and β are electrons with up and down spin. In the vicinity of the Fermi surface they are a mixture of both and their energy dispersion is remarkably different from that of the non-interacting electrons and holes (see Fig. 9.10). Most importantly the dispersion now exhibits an energy gap. The existence of an energy gap in the superconducting state was confirmed by the optical experiments of Glover and Tinkham in 1956/1957 and is seen as the first, decisive early verification of the BCS theory.
The second strong evidence for the existence of an energy gap is given by the temperature dependence of the heat capacity (shown in Fig. 9.11). Corak and co-workers had determined in 1954 and 1956 that the electronic specific heat in the superconducting state was dominated by an exponential dependence ($e^{-\frac{\Delta}{k_B T}}$), whereas in the normal state it followed the expected linear dependence with temperature expected for the conduction electrons of an ordinary metal.
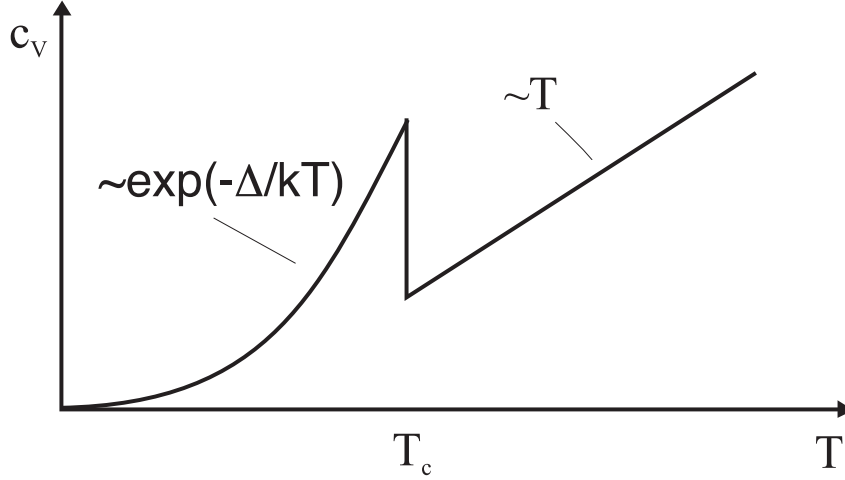
Figure 9.11: The heat capacity in the superconducting state exhibits an Einstein-like exponential behavior with temperature and assumes the linear behavior of a metal in the normal state.

Interestingly, it is the existence of this energy gap that is responsible for the vanishing electrical resistance of a superconductor, as a thought experiment by Landau shows: We consider a fluid of velocity $\boldsymbol{v}$ that flows in a rough pipe. Friction occurs when, via the interaction with the wall, an elementary excitation of momentum $\boldsymbol{p}$ and energy $\epsilon(\boldsymbol{p})$ is created. Landau showed that in order for this process to be possible, energy conservation requires

$$-\boldsymbol{p} \cdot \boldsymbol{v} = \epsilon(\boldsymbol{p}) \ .$$

Since $\boldsymbol{p} \cdot \boldsymbol{v} \geq -|\boldsymbol{p}||\boldsymbol{v}|$, the condition can only be met if $|\boldsymbol{p}||\boldsymbol{v}| \geq \epsilon(\boldsymbol{p})$. This is always the case for "normal" dispersions with $\epsilon(\boldsymbol{p}) \propto \boldsymbol{p}^2$, but for gapped dispersions with $\epsilon(\boldsymbol{p}) \xrightarrow{\to 0}$ const., and also for linear dispersions with $\epsilon(\boldsymbol{p}) \propto p$, the condition cannot be fulfilled if $\boldsymbol{v}$ becomes smaller than a certain critical velocity v^*. For currents slower than v^*, the flow is thus dissipationless. While Landau intended to explain the origin of *superfluidity* with this consideration, it can as well be applied to the case of superconductivity, where one can think of of the Cooper pairs as behaving like a condensed fluid that flows through the metal without friction due to the gap in the quasiparticle excitation spectrum. Since the Cooper pairs carry a charge of $-2e$ each, the resistivity of the metal drops to zero.

9.12   Outlook

It is a remarkable success of many-body theory that the BCS model with its essentially very simple approximations and considerations was able to explain the peculiar phenomenon of superconductivity. Still, there are superconductors that cannot be described in the language of BCS and that we want to mention briefly.
So far, we considered Cooper pairing that was mediated by weak electron-phonon coupling where it is sufficient to capture the essential physics by using a simple mean field to include the interaction. In fact, this works well on a qualitative level for many materials, but quantitatively only for few elemental superconductors. We only mention that there

exists a generalization of the ideas leading to the BCS theory that is able to describe a large class of superconductors quantitatively correct, also in the strong coupling regime of the electron-phonon interaction. This theory was developed by Eliashberg in the early sixties.[3]

While Eliashberg theory is a considerable improvement over BCS, there are still superconductors that cannot be described in this way. These are called *unconvential* in the literature, where the unconventional means that electron-phonon coupling alone seems not to be sufficient to provide the pairing mechanism. The most important example are the Cu-O-based high-temperature superconductors with critical temperatures up to $\sim 100\,\mathrm{K}$. The record at ambient pressure is currently held by the layered cuprate $HgBa_2Ca_2Cu_3O_8$ with a T_c of $135\,\mathrm{K}$. High-temperature superconductors are already of huge technological importance, as they, e.g., provide the magnetic fields necessary in Magnetic resonance imaging devices used in medicine.

There is experimental evidence that the gap function $\Delta_{\boldsymbol{k}}$ of these materials is explicitly $\boldsymbol{k}$ dependent with a symmetry that differs from those explained by BCS/Eliashberg theory (d-wave symmetry). The actual pairing mechanism leading to d-wave-pairing is still under debate. It could well be that the electron-phonon coupling is complemented by antiferromagnetic spin fluctuations that are able to explain pairing with d-wave symmetry, but a concise picture has not emerged yet and a lot of open questions remain.

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[3]Cf. this lecture script for an introduction to Eliashberg theory:
`http://www.cond-mat.de/events/correl13/manuscripts/ummarino.pdf`