

It was a pleasure to have the opportunity to give a one-off discussion of a topic not covered in the course syllabus, and an introduction to some of the physics of strongly-interacting many body electron systems. This is a write up of the notes I prepared for myself.

HISTORY AND PHENOMENOLOGY

Superconductivity was discovered in 1911 in Leiden by Kamerlingh Onnes. He had recently developed techniques to liquify helium and so obtain temperatures much lower than had previously been possible. He used these new cold conditions for a seemingly mundane experiment; the measurement of resistivity in conductors. The results, first for mercury (Hg), were striking. At a critical temperature of $\sim 4.2\text{K}$ the resistivity dropped to negligible values; the material was conducting without loss – a *superconductor*.

One can ask if the resistivity is really zero, or just some small value. The most accurate measurements come from the decay of persistent currents in superconducting rings. A current is set up in a superconducting sample in the shape of a circular ring and then left for a long period of time (several years; the longer the better). Any resistance in the material will cause the current to decay, $J(t) = J(0)e^{-t/\tau}$, with some decay constant, $\tau = RC$, related to the resistance. Measuring the (non-)decay of the current produces an upper bound for the resistivity of $\sim 10^{-26}\ \Omega\text{m}$. If this seems impressive, it should be compared with a standard value of $\sim 10^{-8}\ \Omega\text{m}$ for copper; a change of 18 orders of magnitude is certainly striking.

However, it is important not to get too swept up by the perfect conducting property of superconductors, for, indeed, they are *not* ‘perfect conductors’. This is on account of their equally striking magnetic properties, first uncovered rather later in 1933 by Walther Meissner and Robert Ochsenfeld. Today this phenomenon is perhaps the most recognisable facet of superconductivity, or at least the one people are most likely to have seen demonstrated, for it is the basis behind simple magnetic levitation experiments. Indeed, we use just such a demonstration as part of our Physics Department open days. The basic phenomenon is one of *flux expulsion*; the magnetic field is expelled from the interior of a superconductor. As a result, a more accurate characterisation of superconductors is that they are *perfect diamagnets*¹.

Of course, this is not completely true. More correctly, we should say that superconductors expel magnetic flux up to some critical field strength, $H_c(T)$, above which the

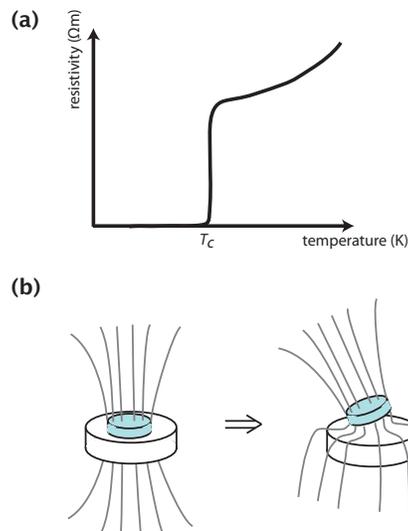


Figure 1: (a) Measurements of the resistivity show a sudden drop to negligible values at a critical temperature T_c . The material then conducts without resistance. This was first discovered in mercury where $T_c \approx 4.2\text{K}$. (b) Magnetic flux is expelled from the interior of a superconductor – the Meissner-Ochsenfeld effect. This is the basis behind magnetic levitation experiments.

¹If $B = 0$ then, since $B = \mu_0(H + M)$, it must be that $M = -H$, so that $\chi = -1$ – a perfect diamagnet.

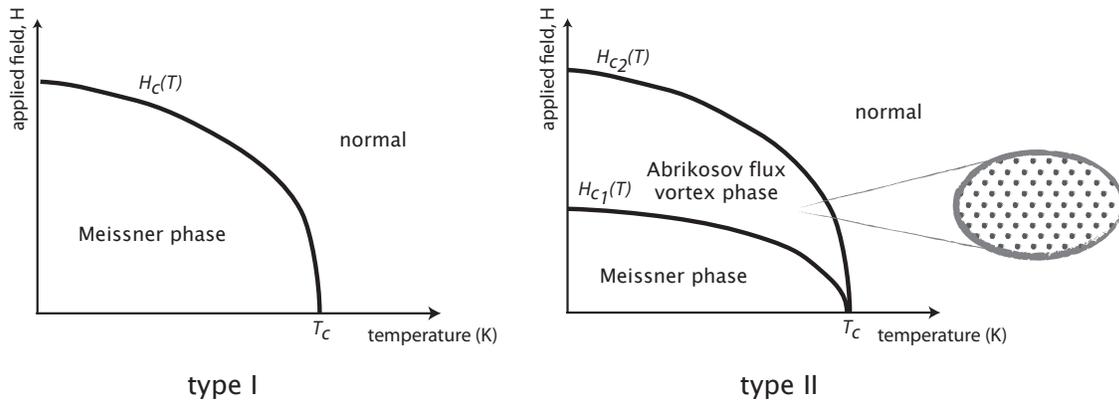


Figure 2: Schematic phase diagram for superconductors as a function of temperature and applied field. Superconductors can be separated into two classes – type I and type II – according to their phase behaviour. In type II materials an intermediate phase in which the magnetic field partially penetrates and the material remains superconducting exists. This is the Abrikosov phase, characterised by flux penetration in quantised vortices that arrange themselves into a triangular lattice (sketched).

superconductivity is destroyed. This destruction of superconductivity at large enough applied fields is a *phase transition*, and in this case the transition is *discontinuous* or *first order*. It is first order except exactly in zero applied field at the critical transition temperature, T_c ². Here the transition is *continuous*, and in fact is one of the very few examples of a continuous transition that is well described by mean field theory.

Again, we must acknowledge that this is not completely true. What we have described is the situation for *type I* superconductors, such as mercury. *Type II* materials, such as all of the high temperature superconductors, behave differently. They undergo two transitions as the field strength is increased from zero. Initially the material is in the Meissner phase and the flux is expelled completely. Then at a *lower critical field* $H_{c_1}(T)$ there is a continuous transition to a state of partial flux penetration that is still superconducting. Only at much larger field strengths – the *upper critical field* $H_{c_2}(T)$ – is the superconductivity destroyed in a second continuous transition. The intermediate state is the celebrated *Abrikosov flux vortex phase* in which the magnetic field penetrates the sample in individual (quantised) flux lines, that arrange themselves into the structure of a triangular lattice.

THEORY OF SUPERCONDUCTIVITY

As the foregoing whistlestop survey of basic phenomenology highlights, there are a lot of fascinating things to be understood about superconductivity. Unfortunately it is not possible to cover much and, even more unfortunately, it will not be possible for us to get to an understanding of *any* of these germane experimental features. What we will do is provide an introduction to the theoretical framework that has successfully done so. As seems appropriate for a course on Electrons in Solids, I am going to focus exclusively on the description of electron states in superconductors. This is especially apt because the electron states in a superconductor are different from the electron states you have encountered so

²Equal to $\sim 4.2\text{K}$ in mercury.

far. They are not free electrons, nor nearly free electrons, they are something different; they are a true *many body* phenomenon corresponding to a *strongly correlated* electron state.

The basic facts about the superconducting state are the following. The state is one in which there is *macroscopic quantum coherence* and the electrons are all described by the *same* wavefunction. This wavefunction may be heuristically characterised as a state in which pairs of electrons form bound states, known as *Cooper pairs*, which subsequently Bose condense into the superconducting state. This is a useful conceptual picture, but it is heuristic because of course the two suggested parts do not happen consecutively; the transition is a single coherent process and should be treated as such. The mechanism by which electrons bind together into pairs is interaction with lattice vibrations, or phonons. Thus Cooper pairs (and the superconducting state more generally) are eigenstates of a Hamiltonian representing free electrons interacting with phonons (and each other). This gives some heuristic insight into why the superconducting state has zero resistance. The resistance of the normal state comes from scattering of free electron states by any perturbing interaction. At low temperatures the main such perturbation comes from phonons (and other low energy excitations – ‘Goldstone modes’). The superconducting state eliminates this scattering mechanism by forming an eigenstate of the perturbing Hamiltonian.

THE COOPER PROBLEM

We build up an understanding of the electron states in superconductors by a step-wise process that parallels the historical development, starting with what has become known as the Cooper problem. This is something of a ‘toy’ model, although it is enormously insightful. The basic idea is easy enough to grasp. Consider two free electrons at the Fermi surface. They have energy $2E_F$. Can we cook up a *pair wavefunction* for these two electrons such that their energy will be *less* than this? If so, they will surely drop down into this lower energy state.

Again, what it is that we have to do is easy enough to state; we have to write down the Schrödinger equation for the two electrons and solve it. As I’m sure you have grasped by now, this is hard. So we need a smart guess to get us going in the right direction. This comes in the form of an ansatz for the pair wavefunction

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \underbrace{\frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right)}_{\text{spin part}} \times \underbrace{\phi(\mathbf{r}_1 - \mathbf{r}_2)}_{\text{orbital part}}, \quad (1)$$

where the ‘spin part’ indicates that we should consider a spin singlet state, and the ‘orbital part’ depends only on the relative position of the two electrons by translational symmetry. For it we assume a Fourier decomposition in terms of free electron states

$$\phi(\mathbf{r}_1 - \mathbf{r}_2) = \sum_{\substack{\mathbf{k} \\ |\mathbf{k}| > k_F}} g_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{r}_1 - \mathbf{r}_2)}. \quad (2)$$

Note that the sum is restricted to be only over wavevectors that lie outside the Fermi surface, $|\mathbf{k}| > k_F$. This incorporates, albeit in a rather crude way, the interaction of these two electrons with all the others in the material, a crucial component of strongly interacting many body systems.

Applying the Schrödinger equation, and ignoring the spin part as it plays no essential role here, we have

$$\left[-\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) + U(\mathbf{r}_1 - \mathbf{r}_2) \right] \sum_{|\mathbf{k}| > k_F} g_{\mathbf{k}} e^{i\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2)} = (2E_F + E) \sum_{|\mathbf{k}| > k_F} g_{\mathbf{k}} e^{i\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2)}, \quad (3)$$

where we have chosen to write the energy as $2E_F + E$ so that we can focus on the *difference* E between the energy of this paired state and that of two ordinary free electrons. For the kinetic energy we will of course get $2 \times \frac{\hbar^2 k^2}{2m}$, for each mode \mathbf{k} . We choose to write this as $2(E_F + \epsilon_{\mathbf{k}})$ to again focus on the energy difference with the free electron state. Thus we find the Schrödinger equation becomes

$$\sum_{\substack{\mathbf{k} \\ |\mathbf{k}| > k_F}} (2\epsilon_{\mathbf{k}} - E) g_{\mathbf{k}} e^{i\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2)} + \sum_{|\mathbf{k}| > k_F} g_{\mathbf{k}} U(\mathbf{r}_1 - \mathbf{r}_2) e^{i\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2)} = 0. \quad (4)$$

As free electron states are orthogonal, we can isolate the modes in the usual way, by multiplying by $e^{-i\mathbf{q} \cdot (\mathbf{r}_1 - \mathbf{r}_2)}$ and integrating over all values of $\mathbf{r}_1 - \mathbf{r}_2$ (with V the volume of the material)

$$\frac{1}{V} \int d^3(r_1 - r_2) \sum_{\substack{\mathbf{k} \\ |\mathbf{k}| > k_F}} (2\epsilon_{\mathbf{k}} - E) g_{\mathbf{k}} e^{i(\mathbf{k} - \mathbf{q}) \cdot (\mathbf{r}_1 - \mathbf{r}_2)} = (2\epsilon_{\mathbf{q}} - E) g_{\mathbf{q}}, \quad (5)$$

$$\frac{1}{V} \int d^3(r_1 - r_2) \sum_{\substack{\mathbf{k} \\ |\mathbf{k}| > k_F}} g_{\mathbf{k}} U(\mathbf{r}_1 - \mathbf{r}_2) e^{i(\mathbf{k} - \mathbf{q}) \cdot (\mathbf{r}_1 - \mathbf{r}_2)} = \sum_{|\mathbf{k}| > k_F} g_{\mathbf{k}} U_{\mathbf{q} - \mathbf{k}}, \quad (6)$$

where we have identified

$$U_{\mathbf{q} - \mathbf{k}} = \frac{1}{V} \int d^3(r_1 - r_2) e^{-i(\mathbf{q} - \mathbf{k}) \cdot (\mathbf{r}_1 - \mathbf{r}_2)} U(\mathbf{r}_1 - \mathbf{r}_2), \quad (7)$$

as the Fourier coefficient of the interaction potential. The Schrödinger equation then becomes equivalent to the relation

$$g_{\mathbf{q}} = \frac{-1}{2\epsilon_{\mathbf{q}} - E} \sum_{\substack{\mathbf{k} \\ |\mathbf{k}| > k_F}} g_{\mathbf{k}} U_{\mathbf{q} - \mathbf{k}}. \quad (8)$$

between the Fourier coefficient of the pair wavefunction, $g_{\mathbf{k}}$, and the binding energy E .

To proceed further we need to know something about the potential, and we adopt the simplest approximation; the potential is attractive for some range of energies and zero otherwise

$$U_{\mathbf{q} - \mathbf{k}} = \begin{cases} -U & \epsilon_{\mathbf{q}}, \epsilon_{\mathbf{k}} < \hbar\omega_D, \\ 0 & \text{otherwise.} \end{cases} \quad (9)$$

This mimics the actual mechanism for electron-electron interactions, namely that they arise from interactions between the electrons and lattice vibrations; phonons are available to couple to only up to energies of $\sim \hbar\omega_D$ where ω_D is the Debye frequency. However, it is worth stressing also that this form of the potential is fairly generic so that almost any mechanism for generating an attractive interaction of this type will lead to the same general phenomena.

Taking this approximation, and summing over all values of \mathbf{q} we find

$$\sum_{\substack{\mathbf{q} \\ |\mathbf{q}| > k_F}} g_{\mathbf{q}} = \sum_{\substack{\mathbf{q} \\ |\mathbf{q}| > k_F}} \frac{U}{2\epsilon_{\mathbf{q}} - E} \sum_{\substack{\mathbf{k} \\ |\mathbf{k}| > k_F}} g_{\mathbf{k}}, \quad (10)$$

$$\text{or} \quad 1 = \sum_{\substack{\mathbf{q} \\ |\mathbf{q}| > k_F}} \frac{U}{2\epsilon_{\mathbf{q}} - E}. \quad (11)$$

This final expression determines the binding energy E in terms of the strength of the potential U . We approximate the sum by an integral and find

$$1 = \int_0^{\hbar\omega_D} g(\epsilon) d\epsilon \frac{U}{2\epsilon - E}, \quad (12)$$

$$\approx \frac{g(E_F)U}{2} \ln(2\epsilon - E) \Big|_0^{\hbar\omega_D} \quad (13)$$

$$= \frac{g(E_F)U}{2} \ln\left(1 - \frac{2\hbar\omega_D}{E}\right), \quad (14)$$

where $g(\epsilon)$ is the density of states (in energy ϵ), which we approximate by its value at the Fermi surface. Finally, rearranging for the energy we obtain

$$E = -2\hbar\omega_D \frac{1}{e^{2/g(E_F)U} - 1} \approx -2\hbar\omega_D e^{-2/g(E_F)U}, \quad (15)$$

since the interaction potential may be assumed small. Two aspects of the final answer are especially noteworthy. First, E is negative so that the energy of the electrons in this pair wavefunction is *less* than that of two free electrons. Thus generic attractive interactions in the presence of a background filled Fermi sea lead to the formation of paired electron states – Cooper pairs. And second, the binding energy, E , is *non-perturbative* in the strength of the attractive potential, U . This reflects the fact that superconductivity is a fundamentally new electronic state and not simply a standard perturbation around the free-electron, or nearly free-electron, state.

THE BCS WAVEFUNCTION

I did not have time to discuss any of this last section in the lecture – my apologies for poor timekeeping! – but I have included it here for those that are interested.

We learn from the Cooper problem that if electrons at the Fermi surface experience an attractive interaction (coming from exchange of phonons) then they can lower their energy by forming bound pairs. Naturally, if this can happen for two (arbitrarily chosen) electrons, then it can happen for all of them. This suggests that a correct description of superconductivity will involve constructing a wavefunction in which all (or at least a macroscopic fraction) of the electrons form Cooper pairs. This is known as the *BCS wavefunction*, after John Bardeen, Leon Cooper and Robert Schrieffer.

To motivate it, let us look back at the Cooper pair wavefunction

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right) \times \sum_{\substack{\mathbf{k} \\ |\mathbf{k}| > k_F}} g_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}_1} e^{-i\mathbf{k}\cdot\mathbf{r}_2}, \quad (16)$$

and describe its essential features. The two electrons are correlated in the following two ways: (i) one electron has spin up and the other has spin down, so that they form a singlet, and (ii) one electron has wavevector \mathbf{k} and the other has wavevector $-\mathbf{k}$; in the Cooper problem this was motivated by translational symmetry but we might equally motivate it by observing that the total momentum is zero. There is a concise way of writing this that is universally adopted in the description of BCS theory

$$c_{\mathbf{k}\uparrow}^\dagger c_{-\mathbf{k}\downarrow}^\dagger |0\rangle,$$

known as *second quantised notation*³. You should read this as follows: $|0\rangle$ denotes the ground state, in this case the filled Fermi sea, and $c_{\mathbf{k}\sigma}^\dagger$ means ‘create an electron with wavevector \mathbf{k} in spin state σ ’; it is called a *fermion creation operator*. Notation can be bewildering and it is important not to let it be, so let us state in plain terms what all this means: there are two electrons (in the presence of a filled Fermi sea), one of them has wavevector \mathbf{k} and spin up (\uparrow) and the other has wavevector $-\mathbf{k}$ and spin down (\downarrow). That is all there is to it⁴.

We can now write down the BCS wavefunction. In a textbook treatment this would be preceded by more of an introduction, but here I will jump directly to the final version

$$|\text{BCS}\rangle = \prod_{\mathbf{k}} \left(u_{\mathbf{k}} + v_{\mathbf{k}} c_{\mathbf{k}\uparrow}^\dagger c_{-\mathbf{k}\downarrow}^\dagger \right) |0\rangle. \quad (17)$$

Again, do not be put off by the notation, what this means is quite simple and natural. For each possible wavevector \mathbf{k} either a pair of electrons occupies the Cooper pair state with that wavevector – $v_{\mathbf{k}} c_{\mathbf{k}\uparrow}^\dagger c_{-\mathbf{k}\downarrow}^\dagger$ part – or that Cooper pair is unoccupied – $u_{\mathbf{k}}$ part. Thus, the electrons fill Cooper pair states, and each possible Cooper pair state is either occupied, with probability amplitude $v_{\mathbf{k}}$, or not, with probability amplitude $u_{\mathbf{k}}$ ⁵. Several things are worthy of comment. First, note the radical structure of the BCS wavefunction. Although it seems natural when you get it, there is no sense in which it is a minor tweak, or variant, of a free electron state; we need a complete change to what we think electron states look like before superconductivity emerges in a natural way. It is a restructuring of the foundations, not a perturbative effect. Second, the occupancy of a given Cooper pair is probabilistic, so that the total number of occupied pairs is also probabilistic, *i.e.* the total number of electrons is not fixed. Thus the BCS state is a state in a grand canonical ensemble, rather than a canonical ensemble. Not all of the electrons have to be in Cooper pair states, but a macroscopic number of them are and that number is controlled by a chemical potential μ .

Finally, and without any explanation or discussion, we write the Hamiltonian for the BCS theory (in second quantised notation)

$$H - \mu N = \sum_{\mathbf{k}} (\epsilon_{\mathbf{k}} - \mu) \left[c_{\mathbf{k}\uparrow}^\dagger c_{\mathbf{k}\uparrow} + c_{-\mathbf{k}\downarrow}^\dagger c_{-\mathbf{k}\downarrow} \right] + \sum_{\mathbf{k}, \mathbf{q}} U_{\mathbf{k}, \mathbf{q}} c_{\mathbf{k}\uparrow}^\dagger c_{-\mathbf{k}\downarrow}^\dagger c_{-\mathbf{q}\downarrow} c_{\mathbf{q}\uparrow}. \quad (18)$$

The original BCS calculation was to evaluate the expectation value $\langle \text{BCS} | H - \mu N | \text{BCS} \rangle$ and determine $u_{\mathbf{k}}, v_{\mathbf{k}}$ by the variational method. A more modern approach is to construct a mean field theory and exact diagonalisation of the Hamiltonian.

³Indeed, this notation is used in virtually every aspect of condensed matter physics beyond introductory level.

⁴Not quite all, one more thing remains. Fermions are antisymmetric under exchange, so that if we swap the order of our operators we should pick up appropriate minus signs. This is captured by the *anticommutation relations* $\{c_{\mathbf{k}\sigma}, c_{\mathbf{k}'\sigma'}^\dagger\} = \delta_{\sigma\sigma'} \delta_{\mathbf{k}, \mathbf{k}'}$ and $\{c_{\mathbf{k}\sigma}^\dagger, c_{\mathbf{k}'\sigma'}^\dagger\} = 0$. The operator $c_{\mathbf{k}\sigma}$ is the Hermitian adjoint of $c_{\mathbf{k}\sigma}^\dagger$ and called a *fermion annihilation operator*.

⁵So we have $|u_{\mathbf{k}}|^2 + |v_{\mathbf{k}}|^2 = 1$.