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Chapter 5

Superconductivity

5.1 Basic Phenomenology of Superconductors

The superconducting state is a phase of matter, as is ferromagnetism, metallicity, *etc.* The phenomenon was discovered in the Spring of 1911 by the Dutch physicist H. Kamerlingh Onnes, who observed an abrupt vanishing of the resistivity of solid mercury at $T = 4.15\,\mathrm{K}$[1]. Under ambient pressure, there are 33 elemental superconductors[2], all of which have a metallic phase at higher temperatures, and hundreds of compounds and alloys which exhibit the phenomenon. A timeline of superconductors and their critical temperatures is provided in Fig. 5.2. The related phenomenon of superfluidity was first discovered in liquid helium below $T = 2.17\,\mathrm{K}$, at atmospheric pressure, independently in 1937 by P. Kapitza (Moscow) and by J. F. Allen and A. D. Misener (Cambridge). At some level, a superconductor may be considered as a charged superfluid. Here we recite the basic phenomenology of superconductors:

- *Vanishing electrical resistance* : The DC electrical resistance at zero magnetic field vanishes in the superconducting state. This is established in some materials to better than one part in 10^{15} of the normal state resistance. Above the critical temperature T_c, the DC resistivity at $H = 0$ is finite. The AC resistivity remains zero up to a critical frequency, $\omega_c = 2\Delta/\hbar$, where Δ is the gap in the electronic excitation spectrum. The frequency threshold is 2Δ because the superconducting condensate is made up of electron *pairs*, so breaking a pair results in two *quasiparticles*, each with energy Δ or greater. For *weak coupling* superconductors, which are described by the famous BCS theory (1957), there is a relation between the gap energy and the superconducting transition temperature, $2\Delta_0 = 3.5\,k_B T_c$, which we derive when we study the BCS model. The gap $\Delta(T)$ is temperature-dependent and vanishes at T_c.

- *Flux expulsion* : In 1933 it was descovered by Meissner and Ochsenfeld that magnetic fields in superconducting tin and lead to not penetrate into the bulk of a superconductor, but rather are confined to a surface layer of thickness λ, called the *London penetration depth*. Typically λ in on the scale of tens to hundreds of nanometers.

[1]Coincidentally, this just below the temperature at which helium liquefies under atmospheric pressure.
[2]An additional 23 elements are superconducting under high pressure.

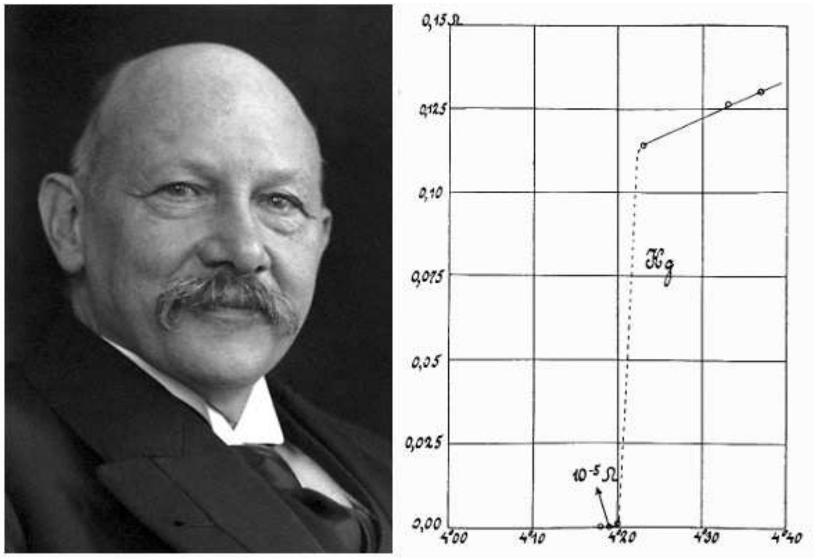

Figure 5.1: Left: H. Kamerlingh Onnes. Right: Onnes' resistivity *vs.* temperature data demonstrating the first observed superconductor, Hg ($T_c = 4.2\,\mathrm{K}$).

It is important to appreciate the difference between a superconductor and a perfect metal. If we set $\sigma = \infty$ then from $\boldsymbol{j} = \sigma \boldsymbol{E}$ we must have $\boldsymbol{E} = 0$, hence Faraday's law $\boldsymbol{\nabla} \times \boldsymbol{E} = -c^{-1}\partial_t \boldsymbol{B}$ yields $\partial_t \boldsymbol{B} = 0$, which says that $\boldsymbol{B}$ remains *constant* in a perfect metal. Yet Meissner and Ochsenfeld found that below T_c the flux was *expelled* from the bulk of the superconductor. If, however, the superconducting sample is not simply connected, *i.e.* if it has holes, such as in the case of a superconducting ring, then in the Meissner phase flux may be trapped in the holes. Such trapped flux is quantized in integer units of the superconducting fluxoid $\phi_L = hc/2e = 2.07 \times 10^{-7}\,\mathrm{G\,cm^2}$ (see Fig. 5.3).

- *Critical field(s)* : The Meissner state exists for $T < T_c$ only when the applied magnetic field H is smaller than the *critical field* $H_c(T)$, with

$$H_c(T) \simeq H_c(0)\left(1 - \frac{T^2}{T_c^2}\right) \quad . \tag{5.1}$$

In so-called type-I superconductors, the system goes normal[3] for $H > H_c(T)$. For most elemental type-I materials (*e.g.*, Hg, Pb, Nb, Sn) one has $H_c(0) \le 1\,\mathrm{kG}$. In type-II materials, there are two critical fields, $H_{c1}(T)$ and $H_{c2}(T)$. For $H < H_{c1}$, we have flux expulsion, and the system is in the Meissner phase. For $H > H_{c2}$, we have uniform flux penetration and the system is normal. For $H_{c1} < H < H_{c2}$, the system in a *mixed state* in which quantized vortices of flux ϕ_L penetrate the system (see Fig. 5.4). There is a depletion of what we shall describe as the superconducting order parameter $\Psi(\boldsymbol{r})$ in the vortex cores over a length scale ξ, which is the *coherence length* of the superconductor. The upper critical field is set by the condition that the vortex cores start to overlap: $H_{c2} = \phi_L/2\pi\xi^2$. The vortex cores can be pinned by disorder. Vortices also interact with each other out to a distance λ, and at low temperatures in the absence of disorder the vortices order into a

[3]Here and henceforth, "normal" is an abbreviation for "normal metal".

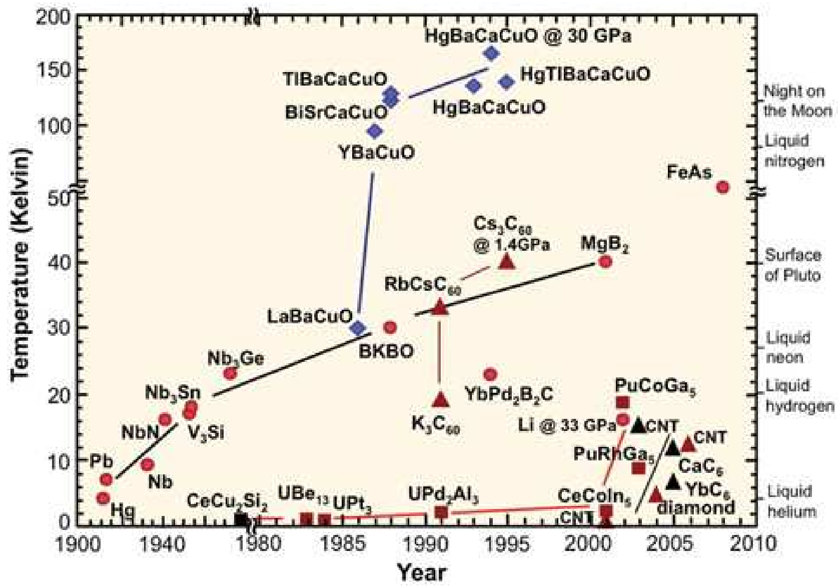

Figure 5.2: Timeline of superconductors and their transition temperatures (from Wikipedia).

(typically triangular) *Abrikosov vortex lattice* (see Fig. 5.5). Typically one has $H_{c2} = \sqrt{2}\kappa\, H_{c1}$, where $\kappa = \lambda/\xi$ is a ratio of the two fundamental length scales. Type-II materials exist when $H_{c2} > H_{c1}$, *i.e.* when $\kappa > \frac{1}{\sqrt{2}}$. Type-II behavior tends to occur in superconducting alloys, such as Nb-Sn.

- *Persistent currents* : We have already mentioned that a metallic ring in the presence of an external magnetic field may enclosed a quantized trapped flux $n\phi_{\rm L}$ when cooled below its superconducting transition temperature. If the field is now decreased to zero, the trapped flux remains, and is generated by a *persistent current* which flows around the ring. In thick rings, such currents have been demonstrated to exist undiminished for years, and may be stable for astronomically long times.

- *Specific heat jump* : The heat capacity of metals behaves as $c_V \equiv C_V/V = \frac{\pi^2}{3}\, k_{\rm B}^2 T g(\varepsilon_{\rm F})$, where $g(\varepsilon_{\rm F})$ is the density of states at the Fermi level. In a superconductor, once one subtracts the low temperature phonon contribution $c_V^{\rm phonon} = AT^3$, one is left for $T < T_{\rm c}$ with an electronic contribution behaving as $c_V^{\rm elec} \propto e^{-\Delta/k_{\rm B}T}$. There is also a jump in the specific heat at $T = T_{\rm c}$, the magnitude of which is generally about three times the normal specific heat just above $T_{\rm c}$. This jump is consistent with a second order transition with critical exponent $\alpha = 0$.

- *Tunneling and Josephson effect* : The energy gap in superconductors can be measured by electron tunneling between a superconductor and a normal metal, or between two superconductors separated by an insulating layer. In the case of a weak link between two superconductors, current can flow at zero bias voltage, a situation known as the *Josephson effect*.

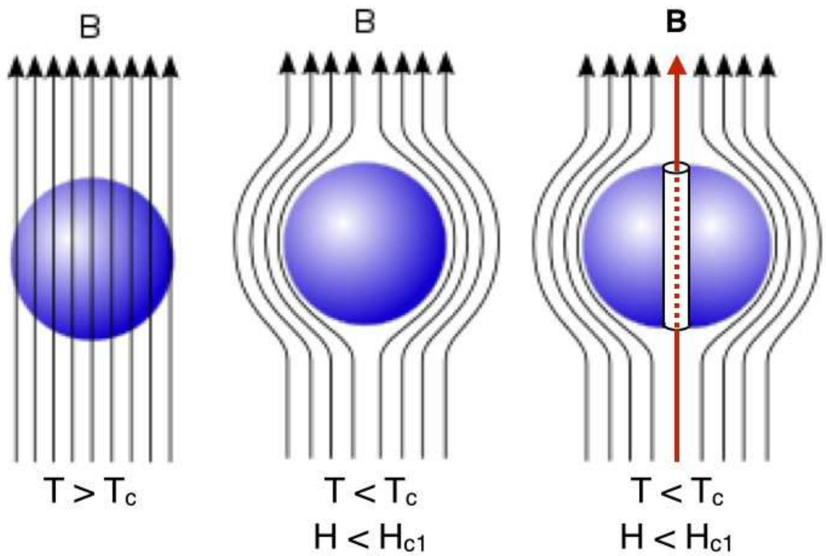

Figure 5.3: Flux expulsion from a superconductor in the Meissner state. In the right panel, quantized trapped flux penetrates a hole in the sample.

5.2 Thermodynamics of Superconductors

The differential free energy density of a magnetic material is given by

$$df = -s\,dT + \frac{1}{4\pi}\,\boldsymbol{H}\cdot d\boldsymbol{B} \quad , \tag{5.2}$$

which says that $f = f(T, \boldsymbol{B})$. Here s is the entropy density, and $\boldsymbol{B}$ the magnetic field. The quantity $\boldsymbol{H}$ is called the *magnetizing field* and is thermodynamically conjugate to $\boldsymbol{B}$:

$$s = -\left(\frac{\partial f}{\partial T}\right)_{\boldsymbol{B}} \quad , \quad \boldsymbol{H} = 4\pi \left(\frac{\partial f}{\partial \boldsymbol{B}}\right)_T \quad . \tag{5.3}$$

In the Ampère-Maxwell equation, $\nabla \times \boldsymbol{H} = 4\pi c^{-1}\boldsymbol{j}_{\rm ext} + c^{-1}\partial_t \boldsymbol{D}$, the sources of $\boldsymbol{H}$ appear on the RHS[4]. Usually $c^{-1}\partial_t\boldsymbol{D}$ is negligible, in which $\boldsymbol{H}$ is generated by external sources such as magnetic solenoids. The magnetic field $\boldsymbol{B}$ is given by $\boldsymbol{B} = \boldsymbol{H} + 4\pi\boldsymbol{M} \equiv \mu\boldsymbol{H}$, where $\boldsymbol{M}$ is the magnetization density. We therefore have no direct control over $\boldsymbol{B}$, and it is necessary to discuss the thermodynamics in terms of the Gibbs free energy density, $g(T, \boldsymbol{H})$:

$$\begin{aligned} g(T,\boldsymbol{H}) &= f(T,\boldsymbol{B}) - \frac{1}{4\pi}\boldsymbol{B}\cdot\boldsymbol{H} \\ dg &= -s\,dT - \frac{1}{4\pi}\,\boldsymbol{B}\cdot d\boldsymbol{H} \quad . \end{aligned} \tag{5.4}$$

Thus,

$$s = -\left(\frac{\partial g}{\partial T}\right)_{\boldsymbol{H}} \quad , \quad \boldsymbol{B} = -4\pi \left(\frac{\partial g}{\partial \boldsymbol{H}}\right)_T \quad . \tag{5.5}$$

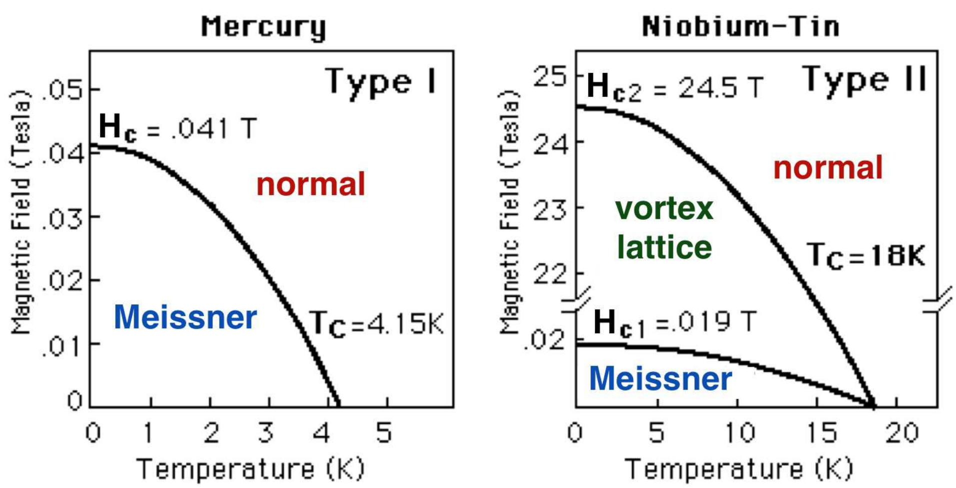

Figure 5.4: Phase diagrams for type I and type II superconductors in the (T, H) plane.

Assuming a bulk sample which is isotropic, we then have

$$g(T,H) = g(T,0) - \frac{1}{4\pi} \int\limits_0^H dH'\, B(H') \quad . \tag{5.6}$$

In a normal metal, $\mu \approx 1$ (cgs units), which means $B \approx H$, which yields

$$g_{\mathrm{n}}(T,H) = g_{\mathrm{n}}(T,0) - \frac{H^2}{8\pi} \quad . \tag{5.7}$$

In the Meissner phase of a superconductor, $B = 0$, so

$$g_{\mathrm{s}}(T,H) = g_{\mathrm{s}}(T,0) \quad . \tag{5.8}$$

For a type-I material, the free energies cross at $H = H_{\mathrm{c}}$, so

$$g_{\mathrm{s}}(T,0) = g_{\mathrm{n}}(T,0) - \frac{H_{\mathrm{c}}^2}{8\pi} \quad , \tag{5.9}$$

which says that there is a negative *condensation energy density* $-\frac{H_{\mathrm{c}}^2(T)}{8\pi}$ which stabilizes the superconducting phase. We call H_{c} the *thermodynamic critical field*. We may now write

$$g_{\mathrm{s}}(T,H) - g_{\mathrm{n}}(T,H) = \frac{1}{8\pi}\Big(H^2 - H_{\mathrm{c}}^2(T)\Big) \quad , \tag{5.10}$$

so the superconductor is the equilibrium state for $H < H_{\mathrm{c}}$. Taking the derivative with respect to temperature, the entropy difference is given by

$$s_{\mathrm{s}}(T,H) - s_{\mathrm{n}}(T,H) = \frac{1}{4\pi}\, H_{\mathrm{c}}(T)\, \frac{dH_{\mathrm{c}}(T)}{dT} < 0 \quad , \tag{5.11}$$

[4]Throughout these notes, RHS/LHS will be used to abbreviate "right/left hand side".

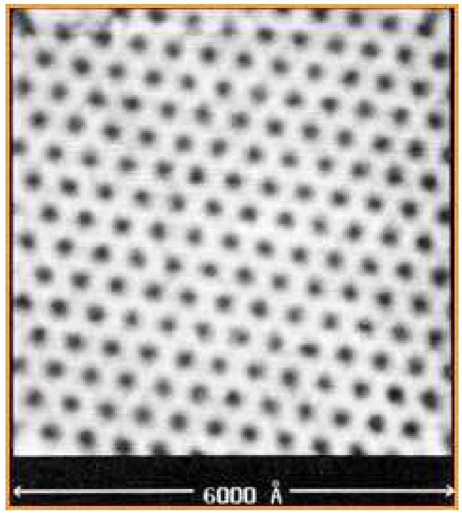

Figure 5.5: STM image of a vortex lattice in $NbSe_2$ at $H = 1\,\text{T}$ and $T = 1.8\,\text{K}$. From H. F. Hess *et al.*, *Phys. Rev. Lett.* **62**, 214 (1989).

since $H_c(T)$ is a decreasing function of temperature. Note that the entropy difference is independent of the external magnetizing field H. As we see from Fig. 5.4, the derivative $H_c'(T)$ changes discontinuously at $T = T_c$. The latent heat $\ell = T\,\Delta s$ vanishes because $H_c(T_c)$ itself vanishes, but the specific heat is discontinuous:

$$c_s(T_c, H=0) - c_n(T_c, H=0) = \frac{T_c}{4\pi}\left(\frac{dH_c(T)}{dT}\right)^2_{T_c} \quad , \tag{5.12}$$

and from the phenomenological relation of Eqn. 5.1, we have $H_c'(T_c) = -2H_c(0)/T_c$, hence

$$\Delta c \equiv c_s(T_c, H=0) - c_n(T_c, H=0) = \frac{H_c^2(0)}{\pi T_c} \quad . \tag{5.13}$$

We can appeal to Eqn. 5.11 to compute the difference $\Delta c(T, H)$ for general $T < T_c$:

$$\Delta c(T,H) = \frac{T}{8\pi}\frac{d^2}{dT^2}\,H_c^2(T) \quad . \tag{5.14}$$

With the approximation of Eqn. 5.1, we obtain

$$c_s(T,H) - c_n(T,H) \simeq \frac{T H_c^2(0)}{2\pi T_c^2}\left\{3\left(\frac{T}{T_c}\right)^2 - 1\right\} \quad . \tag{5.15}$$

In the limit $T \to 0$, we expect $c_s(T)$ to vanish exponentially as $e^{-\Delta/k_B T}$, hence we have $\Delta c(T \to 0) = -\gamma T$, where γ is the coefficient of the linear T term in the metallic specific heat. Thus, we expect $\gamma \simeq H_c^2(0)/2\pi T_c^2$. Note also that this also predicts the ratio $\Delta c(T_c, 0)/c_n(T_c, 0) = 2$. In fact, within BCS theory, this ratio is approximately 1.43. BCS also yields the low temperature form

$$H_c(T) = H_c(0)\left\{1 - \alpha\left(\frac{T}{T_c}\right)^2 + \mathcal{O}\big(e^{-\Delta/k_B T}\big)\right\} \tag{5.16}$$

with $\alpha \simeq 1.07$. Thus, $H_c^{\text{BCS}}(0) = \big(2\pi\gamma T_c^2/\alpha\big)^{1/2}$.

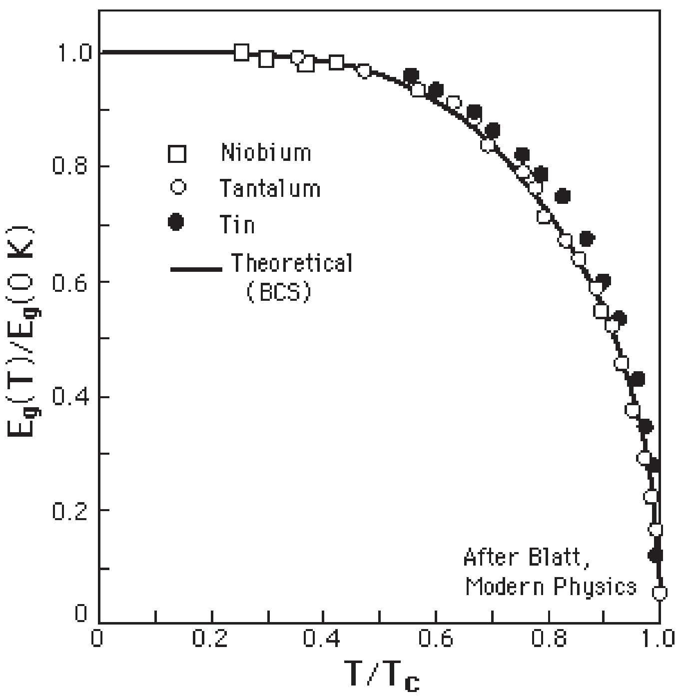

Figure 5.6: Dimensionless energy gap $\Delta(T)/\Delta_0$ in niobium, tantalum, and tin. The solid curve is the prediction from BCS theory, derived in chapter 3 below.

5.3 London Theory

Fritz and Heinz London in 1935 proposed a two fluid model for the macroscopic behavior of superconductors. The two fluids are: (i) the normal fluid, with electron number density $n_{\rm n}$, which has finite resistivity, and (ii) the superfluid, with electron number density $n_{\rm s}$, and which moves with zero resistance. The associated velocities are $v_{\rm n}$ and $v_{\rm s}$, respectively. Thus, the total number density and current density are

$$\begin{aligned} n &= n_{\rm n} + n_{\rm s} \\ \boldsymbol{j} &= \boldsymbol{j}_{\rm n} + \boldsymbol{j}_{\rm s} = -e\big(n_{\rm n}\boldsymbol{v}_{\rm n} + n_{\rm s}\boldsymbol{v}_{\rm s}\big) \quad . \end{aligned} \tag{5.17}$$

The normal fluid is dissipative, hence $\boldsymbol{j}_{\rm n} = \sigma_{\rm n}\boldsymbol{E}$, but the superfluid obeys $F = m\boldsymbol{a}$, *i.e.*

$$m\,\frac{d\boldsymbol{v}_{\rm s}}{dt} = -e\boldsymbol{E} \quad \Rightarrow \quad \frac{d\boldsymbol{j}_{\rm s}}{dt} = \frac{n_{\rm s}e^2}{m}\,\boldsymbol{E} \quad . \tag{5.18}$$

In the presence of an external magnetic field, the superflow satisfies

$$\begin{aligned} \frac{d\boldsymbol{v}_{\rm s}}{dt} &= -\frac{e}{m}\big(\boldsymbol{E} + c^{-1}\boldsymbol{v}_{\rm s}\times\boldsymbol{B}\big) \\ &= \frac{\partial\boldsymbol{v}_{\rm s}}{\partial t} + (\boldsymbol{v}_{\rm s}\cdot\boldsymbol{\nabla})\boldsymbol{v}_{\rm s} = \frac{\partial\boldsymbol{v}_{\rm s}}{\partial t} + \boldsymbol{\nabla}\big(\tfrac{1}{2}\boldsymbol{v}_{\rm s}^2\big) - \boldsymbol{v}_{\rm s}\times(\boldsymbol{\nabla}\times\boldsymbol{v}_{\rm s}) \quad . \end{aligned} \tag{5.19}$$

We then have

$$\frac{\partial \boldsymbol{v}_{\rm s}}{\partial t} + \frac{e}{m}\,\boldsymbol{E} + \boldsymbol{\nabla}\big(\tfrac{1}{2}\boldsymbol{v}_{\rm s}^2\big) = \boldsymbol{v}_{\rm s}\times\bigg(\boldsymbol{\nabla}\times\boldsymbol{v}_{\rm s} - \frac{e\boldsymbol{B}}{mc}\bigg) \quad . \tag{5.20}$$

Taking the curl, and invoking Faraday's law $\boldsymbol{\nabla}\times\boldsymbol{E} = -c^{-1}\partial_t\boldsymbol{B}$, we obtain

$$\frac{\partial}{\partial t}\bigg(\boldsymbol{\nabla}\times\boldsymbol{v}_{\rm s} - \frac{e\boldsymbol{B}}{mc}\bigg) = \boldsymbol{\nabla}\times\bigg\{\boldsymbol{v}_{\rm s}\times\bigg(\boldsymbol{\nabla}\times\boldsymbol{v}_{\rm s} - \frac{e\boldsymbol{B}}{mc}\bigg)\bigg\} \quad , \tag{5.21}$$

which may be written as

$$\frac{\partial\boldsymbol{Q}}{\partial t} = \boldsymbol{\nabla}\times(\boldsymbol{v}_{\rm s}\times\boldsymbol{Q}) \quad , \tag{5.22}$$

where

$$\boldsymbol{Q} \equiv \boldsymbol{\nabla}\times\boldsymbol{v}_{\rm s} - \frac{e\boldsymbol{B}}{mc} \quad . \tag{5.23}$$

Eqn. 5.22 says that if $\boldsymbol{Q}=0$, it remains zero for all time. Assumption: the equilibrium state has $\boldsymbol{Q}=0$. Thus,

$$\boldsymbol{\nabla}\times\boldsymbol{v}_{\rm s} = \frac{e\boldsymbol{B}}{mc} \quad\Rightarrow\quad \boldsymbol{\nabla}\times\boldsymbol{j}_{\rm s} = -\frac{n_{\rm s}e^2}{mc}\,\boldsymbol{B} \quad . \tag{5.24}$$

This equation implies the Meissner effect, for upon taking the curl of the last of Maxwell's equations (and assuming a steady state so $\dot{\boldsymbol{E}} = \dot{\boldsymbol{D}} = 0$),

$$-\nabla^2\boldsymbol{B} = \boldsymbol{\nabla}\times(\boldsymbol{\nabla}\times\boldsymbol{B}) = \frac{4\pi}{c}\,\boldsymbol{\nabla}\times\boldsymbol{j} = -\frac{4\pi n_{\rm s}e^2}{mc^2}\,\boldsymbol{B} \quad\Rightarrow\quad \nabla^2\boldsymbol{B} = \lambda_{\rm L}^{-2}\boldsymbol{B} \quad , \tag{5.25}$$

where $\lambda_{\rm L} = \sqrt{mc^2/4\pi n_{\rm s}e^2}$ is the *London penetration depth*. The magnetic field can only penetrate up to a distance on the order of $\lambda_{\rm L}$ inside the superconductor.

Note that

$$\boldsymbol{\nabla}\times\boldsymbol{j}_{\rm s} = -\frac{c}{4\pi\lambda_{\rm L}^2}\,\boldsymbol{B} \tag{5.26}$$

and the definition $\boldsymbol{B} = \boldsymbol{\nabla}\times\boldsymbol{A}$ licenses us to write

$$\boldsymbol{j}_{\rm s} = -\frac{c}{4\pi\lambda_{\rm L}^2}\,\boldsymbol{A} \quad , \tag{5.27}$$

provided an appropriate gauge choice for $\boldsymbol{A}$ is taken. Since $\boldsymbol{\nabla}\cdot\boldsymbol{j}_{\rm s} = 0$ in steady state, we conclude $\boldsymbol{\nabla}\cdot\boldsymbol{A} = 0$ is the proper gauge. This is called the Coulomb gauge. Note, however, that this still allows for the little gauge transformation $\boldsymbol{A}\to\boldsymbol{A}+\boldsymbol{\nabla}\chi$, provided $\nabla^2\chi = 0$. Consider now an isolated body which is simply connected, *i.e.* any closed loop drawn within the body is continuously contractable to a point. The normal component of the superfluid at the boundary, $\boldsymbol{J}_{{\rm s},\perp}$ must vanish, hence $\boldsymbol{A}_\perp = 0$ as well. Therefore $\nabla_{\!\perp}\chi$ must also vanish everywhere on the boundary, which says that χ is determined up to a global constant.

If the superconductor is multiply connected, though, the condition $\nabla_{\!\perp}\chi = 0$ allows for non-constant solutions for χ. The line integral of $\boldsymbol{A}$ around a closed loop surrounding a hole $\mathcal{D}$ in the superconductor is, by Stokes' theorem, the magnetic flux through the loop:

$$\oint\limits_{\partial\mathcal{D}} d\boldsymbol{l}\cdot\boldsymbol{A} = \int\limits_{\mathcal{D}} dS\;\hat{\boldsymbol{n}}\cdot\boldsymbol{B} = \Phi_{\mathcal{D}} \quad . \tag{5.28}$$

On the other hand, within the interior of the superconductor, since $\boldsymbol{B} = \boldsymbol{\nabla} \times \boldsymbol{A} = 0$, we can write $\boldsymbol{A} = \boldsymbol{\nabla}\chi$, which says that the trapped flux $\Phi_{\mathcal{D}}$ is given by $\Phi_{\mathcal{D}} = \Delta\chi$, then change in the gauge function as one proceeds counterclockwise around the loop. F. London argued that if the gauge transformation $\boldsymbol{A} \to \boldsymbol{A} + \boldsymbol{\nabla}\chi$ is associated with a quantum mechanical wavefunction associated with a charge e object, then the flux $\Phi_{\mathcal{D}}$ will be quantized in units of the Dirac quantum $\phi_0 = hc/e = 4.137 \times 10^{-7}\,\mathrm{G\,cm^2}$. The argument is simple. The transformation of the wavefunction $\Psi \to \Psi\, e^{-i\alpha}$ is cancelled by the replacement $\boldsymbol{A} \to \boldsymbol{A} + (\hbar c/e)\boldsymbol{\nabla}\alpha$. Thus, we have $\chi = \alpha\phi_0/2\pi$, and single-valuedness requires $\Delta\alpha = 2\pi n$ around a loop, hence $\Phi_{\mathcal{D}} = \Delta\chi = n\phi_0$.

The above argument is almost correct. The final piece was put in place by Lars Onsager in 1953. Onsager pointed out that if the particles described by the superconducting wavefunction Ψ were of charge $e^* = 2e$, then, *mutatis mutandis*, one would conclude the quantization condition is $\Phi_{\mathcal{D}} = n\phi_{\mathrm{L}}$, where $\phi_{\mathrm{L}} = hc/2e$ is the London flux quantum, which is half the size of the Dirac flux quantum. This suggestion was confirmed in subsequent experiments by Deaver and Fairbank, and by Doll and Näbauer, both in 1961.

De Gennes' derivation of London Theory

De Gennes writes the total free energy of the superconductor as

$$\begin{aligned} F &= \int\! d^3x\; f_{\mathrm{s}} + E_{\mathrm{kinetic}} + E_{\mathrm{field}} \\ E_{\mathrm{kinetic}} &= \int\! d^3x\; \tfrac{1}{2} m n_{\mathrm{s}} \boldsymbol{v}_{\mathrm{s}}^2(\boldsymbol{x}) = \int\! d^3x\; \frac{m}{2n_{\mathrm{s}}e^2}\, \boldsymbol{j}_{\mathrm{s}}^2(\boldsymbol{x}) \\ E_{\mathrm{field}} &= \int\! d^3x\; \frac{\boldsymbol{B}^2(\boldsymbol{x})}{8\pi} \quad . \end{aligned} \tag{5.29}$$

But under steady state conditions $\boldsymbol{\nabla} \times \boldsymbol{B} = 4\pi c^{-1} \boldsymbol{j}_{\mathrm{s}}$, so

$$F = \int\! d^3x \left\{ f_s + \frac{\boldsymbol{B}^2}{8\pi} + \lambda_{\mathrm{L}}^2\, \frac{(\boldsymbol{\nabla} \times \boldsymbol{B})^2}{8\pi} \right\} \quad . \tag{5.30}$$

Taking the functional variation and setting it to zero,

$$4\pi\, \frac{\delta F}{\delta \boldsymbol{B}} = \boldsymbol{B} + \lambda_{\mathrm{L}}^2\, \boldsymbol{\nabla} \times (\boldsymbol{\nabla} \times \boldsymbol{B}) = \boldsymbol{B} - \lambda_{\mathrm{L}}^2\, \nabla^2 \boldsymbol{B} = 0 \quad . \tag{5.31}$$

5.4 Ginzburg-Landau Theory

The basic idea behind Ginzburg-Landau theory is to write the free energy as a simple functional of the *order parameter(s)* of a thermodynamic system and their derivatives. In ^{4}He, the order parameter $\Psi(\boldsymbol{x}) = \langle \psi(\boldsymbol{x}) \rangle$ is the quantum and thermal average of the field operator $\psi(\boldsymbol{x})$ which destroys a helium atom at position $\boldsymbol{x}$. When Ψ is nonzero, we have Bose condensation with condensate density $n_0 = |\Psi|^2$. Above the lambda transition, one has $n_0(T > T_\lambda) = 0$.

In an s-wave superconductor, the order parameter field is given by

$$\Psi(\boldsymbol{x}) \propto \big\langle \psi_\uparrow(\boldsymbol{x})\,\psi_\downarrow(\boldsymbol{x})\big\rangle \quad , \tag{5.32}$$

where $\psi_\sigma(\boldsymbol{x})$ destroys a conduction band electron of spin σ at position $\boldsymbol{x}$. Owing to the anticommuting nature of the fermion operators, the fermion field $\psi_\sigma(\boldsymbol{x})$ itself cannot condense, and it is only the *pair field* $\Psi(\boldsymbol{x})$ (and other products involving an even number of fermion field operators) which can take a nonzero value.

5.4.1 Landau theory for superconductors

The superconducting order parameter $\Psi(\boldsymbol{x})$ is thus a complex scalar, as in a superfluid. As we shall see, the difference is that the superconductor is *charged*. In the absence of magnetic fields, the Landau free energy density is approximated as

$$f = a\,|\Psi|^2 + \tfrac{1}{2} b\,|\Psi|^4 \quad . \tag{5.33}$$

The coefficients a and b are real and temperature-dependent but otherwise constant in a spatially homogeneous system. The sign of a is negotiable, but $b > 0$ is necessary for thermodynamic stability. The free energy has an $\mathrm{O}(2)$ symmetry, *i.e.* it is invariant under the substitution $\Psi \to \Psi\, e^{i\alpha}$. For $a < 0$ the free energy is minimized by writing

$$\Psi = \sqrt{-\frac{a}{b}}\; e^{i\phi} \quad , \tag{5.34}$$

where ϕ, the phase of the superconductor, is a constant. The system spontaneously breaks the $\mathrm{O}(2)$ symmetry and chooses a direction in Ψ space in which to point.

In our formulation here, the free energy of the normal state, *i.e.* when $\Psi = 0$, is $f_\mathrm{n} = 0$ at all temperatures, and that of the superconducting state is $f_\mathrm{s} = -a^2/2b$. From thermodynamic considerations, therefore, we have

$$f_\mathrm{s}(T) - f_\mathrm{n}(T) = -\frac{H_\mathrm{c}^2(T)}{8\pi} \quad \Rightarrow \quad \frac{a^2(T)}{b(T)} = \frac{H_\mathrm{c}^2(T)}{4\pi} \quad . \tag{5.35}$$

Furthermore, from London theory we have that $\lambda_\mathrm{L}^2 = mc^2/4\pi n_\mathrm{s} e^2$, and if we normalize the order parameter according to

$$\big|\Psi\big|^2 = \frac{n_\mathrm{s}}{n} \quad , \tag{5.36}$$

where n_s is the number density of superconducting electrons and n the total number density of conduction band electrons, then

$$\frac{\lambda_\mathrm{L}^2(0)}{\lambda_\mathrm{L}^2(T)} = \big|\Psi(T)\big|^2 = -\frac{a(T)}{b(T)} \quad . \tag{5.37}$$

Here we have taken $n_\mathrm{s}(T=0) = n$, so $|\Psi(0)|^2 = 1$. Putting this all together, we find

$$a(T) = -\frac{H_\mathrm{c}^2(T)}{4\pi}\cdot\frac{\lambda_\mathrm{L}^2(T)}{\lambda_\mathrm{L}^2(0)} \qquad , \qquad b(T) = \frac{H_\mathrm{c}^2(T)}{4\pi}\cdot\frac{\lambda_\mathrm{L}^4(T)}{\lambda_\mathrm{L}^4(0)} \tag{5.38}$$

Close to the transition, $H_\mathrm{c}(T)$ vanishes in proportion to $\lambda_\mathrm{L}^{-2}(T)$, so $a(T_\mathrm{c}) = 0$ while $b(T_\mathrm{c}) > 0$ remains finite at T_c. Later on below, we shall relate the penetration depth λ_L to a stiffness parameter in the Ginzburg-Landau theory.

We may now compute the specific heat discontinuity from $c = -T\,\frac{\partial^2 f}{\partial T^2}$. It is left as an exercise to the reader to show

$$\Delta c = c_{\rm s}(T_{\rm c}) - c_{\rm n}(T_{\rm c}) = \frac{T_{\rm c}\,\big[a'(T_{\rm c})\big]^2}{b(T_{\rm c})} \quad , \tag{5.39}$$

where $a'(T) = da/dT$. Of course, $c_n(T)$ isn't zero! Rather, here we are accounting only for the specific heat due to that part of the free energy associated with the condensate. The Ginzburg-Landau description completely ignores the metal, and doesn't describe the physics of the normal state Fermi surface, which gives rise to $c_{\rm n} = \gamma T$. The discontinuity Δc is a mean field result. It works extremely well for superconductors, where, as we shall see, the Ginzburg criterion is satisfied down to extremely small temperature variations relative to $T_{\rm c}$. In ^{4}He, one sees an cusp-like behavior with an apparent weak divergence at the lambda transition. Recall that in the language of critical phenomena, $c(T) \propto |T - T_{\rm c}|^{-\alpha}$. For the $\mathrm{O}(2)$ model in $d = 3$ dimensions, the exponent α is very close to zero, which is close to the mean field value $\alpha = 0$. The order parameter exponent is $\beta = \frac{1}{2}$ at the mean field level; the exact value is closer to $\frac{1}{3}$. One has, for $T < T_{\rm c}$,

$$\big|\Psi(T < T_{\rm c})\big| = \sqrt{-\frac{a(T)}{b(T)}} = \sqrt{\frac{a'(T_{\rm c})}{b(T_{\rm c})}}\,(T_{\rm c} - T)^{1/2} + \ldots \quad . \tag{5.40}$$

5.4.2 Ginzburg-Landau Theory

The Landau free energy is minimized by setting $|\Psi|^2 = -a/b$ for $a < 0$. The phase of Ψ is therefore free to vary, and indeed free to vary independently everywhere in space. Phase fluctuations should cost energy, so we posit an augmented free energy functional,

$$F\big[\Psi,\Psi^*\big] = \int\! d^d\!x\, \Big\{ a\,\big|\Psi(\boldsymbol{x})\big|^2 + \tfrac{1}{2}\,b\,\big|\Psi(\boldsymbol{x})\big|^4 + K\,\big|\boldsymbol{\nabla}\Psi(\boldsymbol{x})\big|^2 + \ldots \Big\} \quad . \tag{5.41}$$

Here K is a stiffness with respect to spatial variation of the order parameter $\Psi(\boldsymbol{x})$. From K and a, we can form a length scale, $\xi = \sqrt{K/|a|}$, known as the *coherence length*. This functional in fact is very useful in discussing properties of neutral superfluids, such as ^{4}He, but superconductors are *charged*, and we have instead

$$F\big[\Psi,\Psi^*,\boldsymbol{A}\big] = \int\! d^d\!x\, \Big\{ a\,\big|\Psi(\boldsymbol{x})\big|^2 + \tfrac{1}{2}\,b\,\big|\Psi(\boldsymbol{x})\big|^4 + K\,\Big|\big(\boldsymbol{\nabla} + \tfrac{ie^*}{\hbar c}\,\boldsymbol{A}\big)\Psi(\boldsymbol{x})\Big|^2 + \tfrac{1}{8\pi}\,(\boldsymbol{\nabla}\times\boldsymbol{A})^2 + \ldots \Big\} \quad . \tag{5.42}$$

Here $q = -e^* = -2e$ is the *charge* of the condensate. We assume $\boldsymbol{E} = 0$, so $\boldsymbol{A}$ is not time-dependent.

Under a local transformation $\Psi(\boldsymbol{x}) \to \Psi(\boldsymbol{x})\,e^{i\alpha(\boldsymbol{x})}$, we have

$$\big(\boldsymbol{\nabla} + \tfrac{ie^*}{\hbar c}\,\boldsymbol{A}\big)\big(\Psi\,e^{i\alpha}\big) = e^{i\alpha}\big(\boldsymbol{\nabla} + i\boldsymbol{\nabla}\alpha + \tfrac{ie^*}{\hbar c}\boldsymbol{A}\big)\,\Psi \quad , \tag{5.43}$$

which, upon making the gauge transformation $\boldsymbol{A} \to \boldsymbol{A} - \frac{\hbar c}{e^*}\,\boldsymbol{\nabla}\alpha$, reverts to its original form. Thus, the free energy is unchanged upon replacing $\Psi \to \Psi e^{i\alpha}$ and $\boldsymbol{A} \to \boldsymbol{A} - \frac{\hbar c}{e^*}\,\boldsymbol{\nabla}\alpha$. Since gauge transformations result in no physical consequences, we conclude that the *longitudinal* phase fluctuations of a charged order parameter do not really exist.

5.4.3 Equations of motion

Varying the free energy in Eqn. 5.42 with respect to Ψ^* and $\boldsymbol{A}$, respectively, yields

$$\begin{aligned} 0 &= \frac{\delta F}{\delta \Psi^*} = a\,\Psi + b\,|\Psi|^2\,\Psi - K\left(\boldsymbol{\nabla} + \tfrac{ie^*}{\hbar c}\,\boldsymbol{A}\right)^2\Psi \\ 0 &= \frac{\delta F}{\delta \boldsymbol{A}} = \frac{2Ke^*}{\hbar c}\left[\frac{1}{2i}\big(\Psi^*\boldsymbol{\nabla}\Psi - \Psi\boldsymbol{\nabla}\Psi^*\big) + \frac{e^*}{\hbar c}\,|\Psi|^2\boldsymbol{A}\right] + \frac{1}{4\pi}\,\boldsymbol{\nabla}\times\boldsymbol{B} \quad . \end{aligned} \tag{5.44}$$

The second of these equations is the Ampère-Maxwell law, $\boldsymbol{\nabla}\times\boldsymbol{B} = 4\pi c^{-1}\boldsymbol{j}$, with

$$\boldsymbol{j} = -\frac{2Ke^*}{\hbar^2}\left[\frac{\hbar}{2i}\big(\Psi^*\boldsymbol{\nabla}\Psi - \Psi\boldsymbol{\nabla}\Psi^*\big) + \frac{e^*}{c}\,|\Psi|^2\boldsymbol{A}\right] \quad . \tag{5.45}$$

If we set Ψ to be constant, we obtain $\boldsymbol{\nabla}\times(\boldsymbol{\nabla}\times\boldsymbol{B}) + \lambda_{\rm L}^{-2}\boldsymbol{B} = 0$, with

$$\lambda_{\rm L}^{-2} = 8\pi K\left(\frac{e^*}{\hbar c}\right)^2|\Psi|^2 \quad . \tag{5.46}$$

Thus we recover the relation $\lambda_{\rm L}^{-2} \propto |\Psi|^2$. Note that $|\Psi|^2 = |a|/b$ in the ordered phase, hence

$$\lambda_{\rm L}^{-1} = \left[\frac{8\pi a^2}{b}\cdot\frac{K}{|a|}\right]^{1/2}\frac{e^*}{\hbar c} = \frac{\sqrt{2}\,e^*}{\hbar c}H_{\rm c}\,\xi \quad , \tag{5.47}$$

which says

$$H_{\rm c} = \frac{\phi_{\rm L}}{\sqrt{8}\,\pi\,\xi\lambda_{\rm L}} \quad . \tag{5.48}$$

At a superconductor-vacuum interface, we should have

$$\hat{\boldsymbol{n}}\cdot\Big(\frac{\hbar}{i}\,\boldsymbol{\nabla} + \frac{e^*}{c}\boldsymbol{A}\Big)\Psi\big|_{\partial\Omega} = 0 \quad , \tag{5.49}$$

where Ω denotes the superconducting region and $\hat{\boldsymbol{n}}$ the surface normal. This guarantees $\hat{\boldsymbol{n}}\cdot\boldsymbol{j}\big|_{\partial\Omega} = 0$, since

$$\boldsymbol{j} = -\frac{2Ke^*}{\hbar^2}\,\mathsf{Re}\left(\frac{\hbar}{i}\,\Psi^*\boldsymbol{\nabla}\Psi + \frac{e^*}{c}\,|\Psi|^2\boldsymbol{A}\right) \quad . \tag{5.50}$$

Note that $\hat{\boldsymbol{n}}\cdot\boldsymbol{j} = 0$ also holds if

$$\hat{\boldsymbol{n}}\cdot\Big(\frac{\hbar}{i}\,\boldsymbol{\nabla} + \frac{e^*}{c}\,\boldsymbol{A}\Big)\Psi\big|_{\partial\Omega} = ir\Psi \quad , \tag{5.51}$$

with r a real constant. This boundary condition is appropriate at a junction with a normal metal.

5.4.4 Critical current

Consider the case where $\Psi = \Psi_0$. The free energy density is

$$f = a\,|\Psi_0|^2 + \tfrac{1}{2}\,b\,|\Psi_0|^4 + K\left(\frac{e^*}{\hbar c}\right)^2 \boldsymbol{A}^2\,|\Psi_0|^2 \quad . \tag{5.52}$$

If $a > 0$ then f is minimized for $\Psi_0 = 0$. What happens for $a < 0$, *i.e.* when $T < T_{\rm c}$. Minimizing with respect to $|\Psi_0|$, we find

$$|\Psi_0|^2 = \frac{|a| - K(e^*/\hbar c)^2 \boldsymbol{A}^2}{b} \quad . \tag{5.53}$$

The current density is then

$$\boldsymbol{j} = -2cK\left(\frac{e^*}{\hbar c}\right)^2 \left(\frac{|a| - K(e^*/\hbar c)^2 \boldsymbol{A}^2}{b}\right)\boldsymbol{A} \quad . \tag{5.54}$$

Taking the magnitude and extremizing with respect to $A = |\boldsymbol{A}|$, we obtain the *critical current density* $j_{\rm c}$:

$$A^2 = \frac{|a|}{3K(e^*/\hbar c)^2} \qquad \Rightarrow \qquad j_{\rm c} = \frac{4}{3\sqrt{3}}\,\frac{c\,K^{1/2}\,|a|^{3/2}}{b} \quad . \tag{5.55}$$

Physically, what is happening is this. When the kinetic energy density in the superflow exceeds the condensation energy density $H_{\rm c}^2/8\pi = a^2/2b$, the system goes normal. Note that $j_{\rm c}(T) \propto (T_{\rm c} - T)^{3/2}$.

Should we feel bad about using a gauge-covariant variable like $\boldsymbol{A}$ in the above analysis? Not really, because when we write $\boldsymbol{A}$, what we really mean is the gauge-*invariant* combination $\boldsymbol{A} + \frac{\hbar c}{e^*}\boldsymbol{\nabla}\varphi$, where $\varphi = \mathrm{arg}(\Psi)$ is the phase of the order parameter.

London limit

In the so-called *London limit*, we write $\Psi = \sqrt{n_0}\,e^{i\varphi}$, with n_0 constant. Then

$$\boldsymbol{j} = -\frac{2Ke^*n_0}{\hbar}\left(\boldsymbol{\nabla}\varphi + \frac{e^*}{\hbar c}\boldsymbol{A}\right) = -\frac{c}{4\pi\lambda_{\rm L}^2}\left(\frac{\phi_{\rm L}}{2\pi}\,\boldsymbol{\nabla}\varphi + \boldsymbol{A}\right) \quad . \tag{5.56}$$

Thus,

$$\begin{aligned}\boldsymbol{\nabla}\times\boldsymbol{j} &= \frac{c}{4\pi}\boldsymbol{\nabla}\times(\boldsymbol{\nabla}\times\boldsymbol{B}) \\ &= -\frac{c}{4\pi\lambda_{\rm L}^2}\,\boldsymbol{B} - \frac{c}{4\pi\lambda_{\rm L}^2}\,\frac{\phi_{\rm L}}{2\pi}\,\boldsymbol{\nabla}\times\boldsymbol{\nabla}\varphi \quad ,\end{aligned} \tag{5.57}$$

which says

$$\lambda_{\rm L}^2\,\nabla^2\boldsymbol{B} = \boldsymbol{B} + \frac{\phi_{\rm L}}{2\pi}\,\boldsymbol{\nabla}\times\boldsymbol{\nabla}\varphi \quad . \tag{5.58}$$

If we assume $\boldsymbol{B} = B\hat{\boldsymbol{z}}$ and the phase field φ has singular vortex lines of topological index $n_i \in \mathbb{Z}$ located at position $\boldsymbol{\rho}_i$ in the (x, y) plane, we have

$$\lambda_{\rm L}^2\,\nabla^2 B = B + \phi_{\rm L}\sum_i n_i\,\delta\big(\boldsymbol{\rho} - \boldsymbol{\rho}_i\big) \quad . \tag{5.59}$$

Taking the Fourier transform, we solve for $\hat{B}(\boldsymbol{q})$, where $\boldsymbol{k} = (\boldsymbol{q}, k_z)$:

$$\hat{B}(\boldsymbol{q}) = -\frac{\phi_{\rm L}}{1 + \boldsymbol{q}^2 \lambda_{\rm L}^2} \sum_i n_i \, e^{-i\boldsymbol{q}\cdot\boldsymbol{\rho}_i} \quad , \tag{5.60}$$

whence

$$B(\boldsymbol{\rho}) = -\frac{\phi_{\rm L}}{2\pi\lambda_{\rm L}^2} \sum_i n_i \, K_0\bigg(\frac{|\boldsymbol{\rho} - \boldsymbol{\rho}_i|}{\lambda_{\rm L}}\bigg) \quad , \tag{5.61}$$

where $K_0(z)$ is the MacDonald function, whose asymptotic behaviors are given by

$$K_0(z) \sim \begin{cases} -{\rm C} - \ln(z/2) & (z \to 0) \\ (\pi/2z)^{1/2} \exp(-z) & (z \to \infty) \end{cases} \quad , \tag{5.62}$$

where ${\rm C} = 0.57721566\ldots$ is the Euler-Mascheroni constant. The logarithmic divergence as $\rho \to 0$ is an artifact of the London limit. Physically, the divergence should be cut off when $|\boldsymbol{\rho} - \boldsymbol{\rho}_i| \sim \xi$. The current density for a single vortex at the origin is

$$\boldsymbol{j}(\boldsymbol{r}) = \frac{nc}{4\pi} \boldsymbol{\nabla} \times \boldsymbol{B} = -\frac{c}{4\pi\lambda_{\rm L}} \cdot \frac{\phi_{\rm L}}{2\pi\lambda_{\rm L}^2} \, K_1\big(\rho/\lambda_{\rm L}\big) \, \hat{\boldsymbol{\varphi}} \quad , \tag{5.63}$$

where $n \in \mathbb{Z}$ is the vorticity, and $K_1(z) = -K_0'(z)$ behaves as z^{-1} as $z \to 0$ and $\exp(-z)/\sqrt{2\pi z}$ as $z \to \infty$. Note the $i^{\rm th}$ vortex carries magnetic flux $n_i \, \phi_{\rm L}$.

5.4.5 Ginzburg criterion

Consider fluctuations in $\Psi(\boldsymbol{x})$ above $T_{\rm c}$. If $|\Psi| \ll 1$, we may neglect quartic terms and write

$$F = \int\! d^d\!x \, \Big(a \, |\Psi|^2 + K \, |\boldsymbol{\nabla}\Psi|^2 \Big) = \sum_{\boldsymbol{k}} \big(a + K\boldsymbol{k}^2\big) |\hat{\Psi}(\boldsymbol{k})|^2 \quad , \tag{5.64}$$

where we have expanded

$$\Psi(\boldsymbol{x}) = \frac{1}{\sqrt{V}} \sum_{\boldsymbol{k}} \hat{\Psi}(\boldsymbol{k}) \, e^{i\boldsymbol{k}\cdot\boldsymbol{x}} \quad . \tag{5.65}$$

The Helmholtz free energy $A(T)$ is given by

$$e^{-A/k_{\rm B}T} = \int\! D[\Psi, \Psi^*] \, e^{-F/T} = \prod_{\boldsymbol{k}} \bigg(\frac{\pi k_{\rm B} T}{a + K\boldsymbol{k}^2} \bigg) \quad , \tag{5.66}$$

which is to say

$$A(T) = k_{\rm B}T \sum_{\boldsymbol{k}} \ln\!\bigg(\frac{\pi k_{\rm B} T}{a + K\boldsymbol{k}^2} \bigg) \quad . \tag{5.67}$$

We write $a(T) = \alpha t$ with $t = (T - T_{\rm c})/T_{\rm c}$ the reduced temperature. We now compute the singular contribution to the specific heat $C_V = -TA''(T)$, which only requires we differentiate with respect to T

as it appears in $a(T)$. Dividing by $N_s k_B$, where $N_s = V/\mathsf{a}^d$ is the number of lattice sites, we obtain the dimensionless heat capacity per unit cell,

$$c = \frac{\alpha^2 \mathsf{a}^d}{K^2} \int^{\Lambda\xi} \frac{d^d\!k}{(2\pi)^d} \, \frac{1}{(\xi^{-2} + \boldsymbol{k}^2)^2} \quad , \tag{5.68}$$

where $\Lambda \sim \mathsf{a}^{-1}$ is an ultraviolet cutoff on the order of the inverse lattice spacing, and $\xi = (K/a)^{1/2} \propto |t|^{-1/2}$. We define $R_* \equiv (K/\alpha)^{1/2}$, in which case $\xi = R_* \, |t|^{-1/2}$, and

$$c = R_*^{-4} \, \mathsf{a}^d \, \xi^{4-d} \int^{\Lambda\xi} \frac{d^d\bar{q}}{(2\pi)^d} \, \frac{1}{(1 + \bar{q}^2)^2} \; , \tag{5.69}$$

where $\bar{\boldsymbol{q}} \equiv \boldsymbol{q}\xi$. Thus,

$$c(t) \sim \begin{cases} \text{const.} & \text{if } d > 4 \\ -\ln t & \text{if } d = 4 \\ t^{\frac{d}{2}-2} & \text{if } d < 4 \; . \end{cases} \tag{5.70}$$

For $d > 4$, mean field theory is qualitatively accurate, with finite corrections. In dimensions $d \leq 4$, the mean field result is overwhelmed by fluctuation contributions as $t \to 0^+$ (*i.e.* as $T \to T_c^+$). We see that the Ginzburg-Landau mean field theory is sensible provided the fluctuation contributions are small, *i.e.* provided

$$R_*^{-4} \, \mathsf{a}^d \, \xi^{4-d} \ll 1 \; , \tag{5.71}$$

which entails $t \gg t_G$, where

$$t_G = \left(\frac{\mathsf{a}}{R_*} \right)^{\frac{2d}{4-d}} \tag{5.72}$$

is the *Ginzburg reduced temperature*. The criterion for the sufficiency of mean field theory, namely $t \gg t_G$, is known as the *Ginzburg criterion*. The region $|t| < t_G$ is known as the *critical region*.

In a lattice ferromagnet, as we have seen, $R_* \sim \mathsf{a}$ is on the scale of the lattice spacing itself, hence $t_G \sim 1$ and the critical regime is very large. Mean field theory then fails quickly as $T \to T_c$. In a (conventional) three-dimensional superconductor, R_* is on the order of the Cooper pair size, and $R_*/\mathsf{a} \sim 10^2 - 10^3$, hence $t_G = (a/R_*)^6 \sim 10^{-18} - 10^{-12}$ is negligibly narrow. The mean field theory of the superconducting transition – BCS theory – is then valid essentially all the way to $T = T_c$.

Another way to think about it is as follows. In dimensions $d > 2$, for $|\boldsymbol{r}|$ fixed and $\xi \to \infty$, one has[5]

$$\big\langle \Psi^*(\boldsymbol{r}) \Psi(0) \big\rangle \simeq \frac{C_d}{k_B T \, R_*^2} \, \frac{e^{-r/\xi}}{r^{d-2}} \quad , \tag{5.73}$$

where C_d is a dimensionless constant. If we compute the ratio of fluctuations to the mean value over a

[5]Exactly at $T = T_c$, the correlations behave as $\big\langle \Psi^*(\boldsymbol{r}) \, \Psi(0) \big\rangle \propto r^{-(d-2+\eta)}$, where η is a critical exponent.

patch of linear dimension ξ, we have

$$\begin{aligned}\frac{\text{fluctuations}}{\text{mean}} &= \frac{\int^{\xi} d^d\!r \, \langle \Psi^*(\boldsymbol{r}) \, \Psi(0) \rangle}{\int^{\xi} d^d\!r \, \langle |\Psi(\boldsymbol{r})|^2 \rangle} \\ &\propto \frac{1}{R_*^2 \, \xi^d \, |\Psi|^2} \int^{\xi} d^d\!r \, \frac{e^{-r/\xi}}{r^{d-2}} \propto \frac{1}{R_*^2 \, \xi^{d-2} \, |\Psi|^2} \quad .\end{aligned} \tag{5.74}$$

Close to the critical point we have $\xi \propto R_* \, |t|^{-\nu}$ and $|\Psi| \propto |t|^{\beta}$, with $\nu = \frac{1}{2}$ and $\beta = \frac{1}{2}$ within mean field theory. Setting the ratio of fluctuations to mean to be small, we recover the Ginzburg criterion.

5.4.6 Domain wall solution

Consider first the simple case of the neutral superfluid. The additional parameter K provides us with a new length scale, $\xi = \sqrt{K/|a|}$, which is called the coherence length. Varying the free energy with respect to $\Psi^*(\boldsymbol{x})$, one obtains

$$\frac{\delta F}{\delta \Psi^*(\boldsymbol{x})} = a \, \Psi(\boldsymbol{x}) + b \, \big|\Psi(\boldsymbol{x})\big|^2 \Psi(\boldsymbol{x}) - K \nabla^2 \Psi(\boldsymbol{x}) \quad . \tag{5.75}$$

Rescaling, we write $\Psi \equiv \big(|a|/b\big)^{1/2} \psi$, and setting the above functional variation to zero, we obtain

$$-\xi^2 \nabla^2 \psi + \, \text{sgn}\,(T - T_{\rm c}) \, \psi + |\psi|^2 \psi = 0 \quad . \tag{5.76}$$

Consider the case of a domain wall when $T < T_{\rm c}$. We assume all spatial variation occurs in the x-direction, and we set $\psi(x = 0) = 0$ and $\psi(x = \infty) = 1$. Furthermore, we take $\psi(x) = f(x) \, e^{i\alpha}$ where α is a constant[6]. We then have $-\xi^2 f''(x) - f + f^3 = 0$, which may be recast as

$$\xi^2 \frac{d^2 f}{dx^2} = \frac{\partial}{\partial f} \left[\tfrac{1}{4} \big(1 - f^2\big)^2 \right] \quad . \tag{5.77}$$

This looks just like $F = ma$ if we regard f as the coordinate, x as time, and $-V(f) = \frac{1}{4}\big(1 - f^2\big)^2$. Thus, the potential describes an *inverted* double well with symmetric minima at $f = \pm 1$. The solution to the equations of motion is then that the 'particle' rolls starts at 'time' $x = -\infty$ at 'position' $f = +1$ and 'rolls' down, eventually passing the position $f = 0$ exactly at time $x = 0$. Multiplying the above equation by $f'(x)$ and integrating once, we have

$$\xi^2 \left(\frac{df}{dx} \right)^2 = \tfrac{1}{2} \big(1 - f^2\big)^2 + C \quad , \tag{5.78}$$

where C is a constant, which is fixed by setting $f(x \to \infty) = +1$, which says $f'(\infty) = 0$, hence $C = 0$. Integrating once more,

$$f(x) = \tanh\!\left(\frac{x - x_0}{\sqrt{2}\, \xi} \right) \quad , \tag{5.79}$$

[6] Remember that for a superconductor, phase fluctuations of the order parameter are nonphysical since they are eliiminable by a gauge transformation.

where x_0 is the second constant of integration. This, too, may be set to zero upon invoking the boundary condition $f(0) = 0$. Thus, the width of the domain wall is $\xi(T)$. This solution is valid provided that the local magnetic field averaged over scales small compared to ξ, *i.e.* $\boldsymbol{b} = \langle \boldsymbol{\nabla} \times \boldsymbol{A} \rangle$, is negligible.

The energy per unit area of the domain wall is given by $\tilde{\sigma}$, where

$$\begin{aligned}\tilde{\sigma} &= \int_0^\infty \! dx \left\{ K \left| \frac{d\Psi}{dx} \right|^2 + a\,|\Psi|^2 + \tfrac{1}{2}\, b\,|\Psi|^4 \right\} \\ &= \frac{a^2}{b} \int_0^\infty \! dx \left\{ \xi^2 \left(\frac{df}{dx} \right)^2 - f^2 + \tfrac{1}{2}\, f^4 \right\} \quad .\end{aligned} \tag{5.80}$$

Now we ask: is domain wall formation energetically favorable in the superconductor? To answer, we compute the difference in surface energy between the domain wall state and the uniform superconducting state. We call the resulting difference σ, the true domainwall energy relative to the superconducting state:

$$\begin{aligned}\sigma &= \tilde{\sigma} - \int_0^\infty \! dx \left(-\frac{H_c^2}{8\pi} \right) \\ &= \frac{a^2}{b} \int_0^\infty \! dx \left\{ \xi^2 \left(\frac{df}{dx} \right)^2 + \tfrac{1}{2}\left(1 - f^2\right)^2 \right\} \equiv \frac{H_c^2}{8\pi}\, \delta \quad ,\end{aligned} \tag{5.81}$$

where we have used $H_c^2 = 4\pi a^2/b$. Invoking the previous result $f' = (1 - f^2)/\sqrt{2}\,\xi$, the parameter δ is given by

$$\delta = 2 \int_0^\infty \! dx \left(1 - f^2\right)^2 = 2 \int_0^1 \! df \, \frac{\left(1 - f^2\right)^2}{f'} = \frac{4\sqrt{2}}{3}\, \xi(T) \quad . \tag{5.82}$$

Had we permitted a field to penetrate over a distance $\lambda_L(T)$ in the domain wall state, we'd have obtained

$$\delta(T) = \frac{4\sqrt{2}}{3}\, \xi(T) - \lambda_L(T) \quad . \tag{5.83}$$

Detailed calculations show

$$\delta = \begin{cases} \frac{4\sqrt{2}}{3}\, \xi \approx 1.89\, \xi & \text{if } \xi \gg \lambda_L \\ 0 & \text{if } \xi = \sqrt{2}\, \lambda_L \\ -\frac{8(\sqrt{2}-1)}{3}\, \lambda_L \approx -1.10\, \lambda_L & \text{if } \lambda_L \gg \xi \quad . \end{cases} \tag{5.84}$$

Accordingly, we define the Ginzburg-Landau parameter $\kappa \equiv \lambda_L/\xi$, which is temperature-dependent near $T = T_c$, as we'll soon show.

So the story is as follows. In type-I materials, the positive ($\delta > 0$) N-S surface energy keeps the sample spatially homogeneous for all $H < H_c$. In type-II materials, the negative surface energy causes the system to break into domains, which are vortex structures, as soon as H exceeds the lower critical field H_{c1}. This is known as the *mixed state*.

5.5 Binding and Dimensionality

Consider a spherically symmetric potential $U(\boldsymbol{r}) = -U_0\,\Theta(a-r)$. Are there bound states, *i.e.* states in the eigenspectrum of negative energy? What role does dimension play? It is easy to see that if $U_0 > 0$ is large enough, there are always bound states. A trial state completely localized within the well has kinetic energy $T_0 \simeq \hbar^2/ma^2$, while the potential energy is $-U_0$, so if $U_0 > \hbar^2/ma^2$, we have a variational state with energy $E = T_0 - U_0 < 0$, which is of course an upper bound on the true ground state energy.

What happens, though, if $U_0 < T_0$? We again appeal to a variational argument. Consider a Gaussian or exponentially localized wavefunction with characteristic size $\xi \equiv \lambda a$, with $\lambda > 1$. The variational energy is then

$$E \simeq \frac{\hbar^2}{m\xi^2} - U_0\left(\frac{a}{\xi}\right)^d = T_0\,\lambda^{-2} - U_0\,\lambda^{-d} \quad . \tag{5.85}$$

Extremizing with respect to λ, we obtain $-2T_0\,\lambda^{-3} + d\,U_0\,\lambda^{-(d+1)}$ and $\lambda = \big(d\,U_0/2T_0\big)^{1/(d-2)}$. Inserting this into our expression for the energy, we find

$$E = \left(\frac{2}{d}\right)^{2/(d-2)}\left(1 - \frac{2}{d}\right) T_0^{d/(d-2)}\, U_0^{-2/(d-2)} \quad . \tag{5.86}$$

We see that for $d = 1$ we have $\lambda = 2T_0/U_0$ and $E = -U_0^2/4T_0 < 0$. In $d = 2$ dimensions, we have $E = (T_0 - U_0)/\lambda^2$, which says $E \geq 0$ unless $U_0 > T_0$. For weak attractive $U(\boldsymbol{r})$, the minimum energy solution is $E \to 0^+$, with $\lambda \to \infty$. It turns out that $d = 2$ is a marginal dimension, and we shall show that we always get localized states with a ballistic dispersion and an attractive potential well. For $d > 2$ we have $E > 0$ which suggests that we cannot have bound states unless $U_0 > T_0$, in which case $\lambda \leq 1$ and we must appeal to the analysis in the previous paragraph.

We can firm up this analysis a bit by considering the Schrödinger equation,

$$-\frac{\hbar^2}{2m}\,\nabla^2\psi(\boldsymbol{x}) + V(\boldsymbol{x})\,\psi(\boldsymbol{x}) = E\,\psi(\boldsymbol{x}) \quad . \tag{5.87}$$

Fourier transforming, we have

$$\varepsilon(\boldsymbol{k})\,\hat\psi(\boldsymbol{k}) + \int\!\frac{d^d\!k'}{(2\pi)^d}\,\hat V(\boldsymbol{k}-\boldsymbol{k}')\,\hat\psi(\boldsymbol{k}') = E\,\hat\psi(\boldsymbol{k}) \quad , \tag{5.88}$$

where $\varepsilon(\boldsymbol{k}) = \hbar^2\boldsymbol{k}^2/2m$. We may now write $\hat V(\boldsymbol{k}-\boldsymbol{k}') = \sum_n \lambda_n\,\alpha_n(\boldsymbol{k})\,\alpha_n^*(\boldsymbol{k}')$, which is a decomposition of the Hermitian matrix $\hat V_{\boldsymbol{k},\boldsymbol{k}'} \equiv \hat V(\boldsymbol{k}-\boldsymbol{k}')$ into its (real) eigenvalues λ_n and eigenvectors $\alpha_n(\boldsymbol{k})$. Let's approximate $V_{\boldsymbol{k},\boldsymbol{k}'}$ by its leading eigenvalue, which we call λ, and the corresponding eigenvector $\alpha(\boldsymbol{k})$. That is, we write $\hat V_{\boldsymbol{k},\boldsymbol{k}'} \simeq \lambda\,\alpha(\boldsymbol{k})\,\alpha^*(\boldsymbol{k}')$. We then have

$$\hat\psi(\boldsymbol{k}) = \frac{\lambda\,\alpha(\boldsymbol{k})}{E-\varepsilon(\boldsymbol{k})}\int\!\frac{d^d\!k'}{(2\pi)^d}\,\alpha^*(\boldsymbol{k}')\,\hat\psi(\boldsymbol{k}') \quad . \tag{5.89}$$

Multiply the above equation by $\alpha^*(\boldsymbol{k})$ and integrate over $\boldsymbol{k}$, resulting in

$$\frac{1}{\lambda} = \int\!\frac{d^d\!k}{(2\pi)^d}\,\frac{\big|\alpha(\boldsymbol{k})\big|^2}{E-\varepsilon(\boldsymbol{k})} = \frac{1}{\lambda} = \int\limits_0^\infty\! d\varepsilon\,\frac{g(\varepsilon)}{E-\varepsilon}\,\big|\alpha(\varepsilon)\big|^2 \quad , \tag{5.90}$$

where $g(\varepsilon)$ is the density of states $g(\varepsilon) = \mathsf{Tr}\ \delta\big(\varepsilon - \varepsilon(\boldsymbol{k})\big)$. Here, we assume that $\alpha(\boldsymbol{k}) = \alpha(k)$ is isotropic. It is generally the case that if $V_{\boldsymbol{k},\boldsymbol{k}'}$ is isotropic, *i.e.* if it is invariant under a simultaneous $\mathsf{O}(3)$ rotation $\boldsymbol{k} \to R\boldsymbol{k}$ and $\boldsymbol{k}' \to R\boldsymbol{k}'$, then so will be its lowest eigenvector. Furthermore, since $\varepsilon = \hbar^2 k^2/2m$ is a function of the scalar $k = |\boldsymbol{k}|$, this means $\alpha(k)$ can be considered a function of ε. We then have

$$\frac{1}{|\lambda|} = \int\limits_0^\infty \! d\varepsilon\, \frac{g(\varepsilon)}{|E| + \varepsilon}\, \big|\alpha(\varepsilon)\big|^2 \quad , \tag{5.91}$$

where we have we assumed an attractive potential ($\lambda < 0$), and, as we are looking for a bound state, $E < 0$.

If $\alpha(0)$ and $g(0)$ are finite, then in the limit $|E| \to 0$ we have

$$\frac{1}{|\lambda|} = g(0)\, |\alpha(0)|^2\ \ln\big(1/|E|\big) + \text{finite} \ . \tag{5.92}$$

This equation may be solved for arbitrarily small $|\lambda|$ because the RHS of Eqn. 5.91 diverges as $|E| \to 0$. If, on the other hand, $g(\varepsilon) \sim \varepsilon^p$ where $p > 0$, then the RHS is finite even when $E = 0$. In this case, bound states can only exist for $|\lambda| > \lambda_{\rm c}$, where

$$\lambda_{\rm c} = 1 \bigg/ \int\limits_0^\infty \! d\varepsilon\, \frac{g(\varepsilon)}{\varepsilon}\, \big|\alpha(\varepsilon)\big|^2 \quad . \tag{5.93}$$

Typically the integral has a finite upper limit, given by the bandwidth B. For the ballistic dispersion, one has $g(\varepsilon) \propto \varepsilon^{(d-2)/2}$, so $d = 2$ is the marginal dimension. In dimensions $d \le 2$, bound states form for arbitrarily weak attractive potentials.

5.6 Cooper's Problem

In 1956, Leon Cooper considered the problem of two electrons interacting in the presence of a quiescent Fermi sea. The background electrons comprising the Fermi sea enter the problem only through their *Pauli blocking*. Since spin and total momentum are conserved, Cooper first considered a zero momentum singlet,

$$|\,\Psi\,\rangle = \sum_{\boldsymbol{k}} A_{\boldsymbol{k}}\, \big(c^\dagger_{\boldsymbol{k}\uparrow} c^\dagger_{-\boldsymbol{k}\downarrow} - c^\dagger_{\boldsymbol{k}\downarrow} c^\dagger_{-\boldsymbol{k}\uparrow}\big)|\,\mathrm{F}\,\rangle \quad , \tag{5.94}$$

where $|\,\mathrm{F}\,\rangle$ is the filled Fermi sea, $|\,\mathrm{F}\,\rangle = \prod_{|\boldsymbol{p}|<k_{\rm F}} c^\dagger_{\boldsymbol{p}\uparrow} c^\dagger_{\boldsymbol{p}\downarrow}\,|\,0\,\rangle$. Only states with $k > k_{\rm F}$ contribute to the RHS of Eqn. 5.94, due to Pauli blocking. The real space wavefunction is

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \sum_{\boldsymbol{k}} A_{\boldsymbol{k}}\, e^{i\boldsymbol{k}\cdot(\boldsymbol{r}_1 - \boldsymbol{r}_2)}\, \big(|\!\uparrow_1\downarrow_2\rangle - |\!\downarrow_1\uparrow_2\rangle\big) \quad , \tag{5.95}$$

with $A_{\boldsymbol{k}} = A_{-\boldsymbol{k}}$ to enforce symmetry of the orbital part. It should be emphasized that this is a two-particle wavefunction, and not an $(N+2)$-particle wavefunction, with N the number of electrons in the

Fermi sea. Again, the Fermi sea in this analysis has no dynamics of its own. Its presence is reflected only in the restriction $k > k_{\rm F}$ for the states which participate in the Cooper pair.

The many-body Hamiltonian is written

$$\hat{H} = \sum_{\boldsymbol{k}\sigma} \varepsilon_{\boldsymbol{k}}\, c^\dagger_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} + \tfrac{1}{2} \sum_{\boldsymbol{k}_1\sigma_1} \sum_{\boldsymbol{k}_2\sigma_2} \sum_{\boldsymbol{k}_3\sigma_3} \sum_{\boldsymbol{k}_4\sigma_4} \langle\, \boldsymbol{k}_1\sigma_1, \boldsymbol{k}_2\sigma_2 \,|\, v \,|\, \boldsymbol{k}_3\sigma_3, \boldsymbol{k}_4\sigma_4 \,\rangle\, c^\dagger_{\boldsymbol{k}_1\sigma_1} c^\dagger_{\boldsymbol{k}_2\sigma_2} c_{\boldsymbol{k}_4\sigma_4} c_{\boldsymbol{k}_3\sigma_3} \ . \tag{5.96}$$

We treat $|\,\Psi\,\rangle$ as a variational state, which means we set

$$\frac{\delta}{\delta A^*_{\boldsymbol{k}}}\, \frac{\langle\, \Psi \,|\, \hat{H} \,|\, \Psi \,\rangle}{\langle\, \Psi \,|\, \Psi \,\rangle} = 0 \quad , \tag{5.97}$$

resulting in

$$(E - E_0)\, A_{\boldsymbol{k}} = 2\varepsilon_{\boldsymbol{k}}\, A_{\boldsymbol{k}} + \sum_{\boldsymbol{k}'} V_{\boldsymbol{k},\boldsymbol{k}'}\, A_{\boldsymbol{k}'} \quad , \tag{5.98}$$

where

$$V_{\boldsymbol{k},\boldsymbol{k}'} = \langle\, \boldsymbol{k}\!\uparrow, -\boldsymbol{k}\!\downarrow \,|\, v \,|\, \boldsymbol{k}'\!\uparrow, -\boldsymbol{k}'\!\downarrow \,\rangle = \frac{1}{V}\int\! d^3\!r\; v(\boldsymbol{r})\, e^{i(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{r}} \quad . \tag{5.99}$$

Here $E_0 = \langle\, {\rm F} \,|\, \hat{H} \,|\, {\rm F} \,\rangle$ is the energy of the Fermi sea.

We write $\varepsilon_{\boldsymbol{k}} = \varepsilon_{\rm F} + \xi_{\boldsymbol{k}}$, and we define $E \equiv E_0 + 2\varepsilon_{\rm F} + W$. Then

$$W\, A_{\boldsymbol{k}} = 2\xi_{\boldsymbol{k}}\, A_{\boldsymbol{k}} + \sum_{\boldsymbol{k}'} V_{\boldsymbol{k},\boldsymbol{k}'}\, A_{\boldsymbol{k}'} \quad . \tag{5.100}$$

If $V_{\boldsymbol{k},\boldsymbol{k}'}$ is rotationally invariant, meaning it is left unchanged by $\boldsymbol{k} \to R\boldsymbol{k}$ and $\boldsymbol{k}' \to R\boldsymbol{k}'$ where $R \in {\sf O}(3)$, then we may write

$$V_{\boldsymbol{k},\boldsymbol{k}'} = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} V_\ell(k,k')\, Y^\ell_m(\hat{\boldsymbol{k}})\, Y^\ell_{-m}(\hat{\boldsymbol{k}}') \quad . \tag{5.101}$$

We assume that $V_l(k,k')$ is *separable*, meaning we can write

$$V_\ell(k,k') = \frac{1}{V}\, \lambda_\ell\, \alpha_\ell(k)\, \alpha^*_\ell(k') \quad . \tag{5.102}$$

This simplifies matters and affords us an exact solution, for now we take $A_{\boldsymbol{k}} = A_k\, Y^\ell_m(\hat{\boldsymbol{k}})$ to obtain a solution in the ℓ angular momentum channel:

$$W_\ell\, A_k = 2\xi_k\, A_k + \lambda_\ell\, \alpha_\ell(k) \cdot \frac{1}{V} \sum_{k'} \alpha^*_\ell(k')\, A_{k'} \quad , \tag{5.103}$$

which may be recast as

$$A_k = \frac{\lambda_\ell\, \alpha_\ell(k)}{W_\ell - 2\xi_k} \cdot \frac{1}{V} \sum_{k'} \alpha^*_\ell(k')\, A_{k'} \quad . \tag{5.104}$$

Now multiply by α^*_k and sum over k to obtain

$$\frac{1}{\lambda_\ell} = \frac{1}{V} \sum_k \frac{\big|\alpha_\ell(k)\big|^2}{W_\ell - 2\xi_k} \equiv \Phi(W_\ell) \quad . \tag{5.105}$$

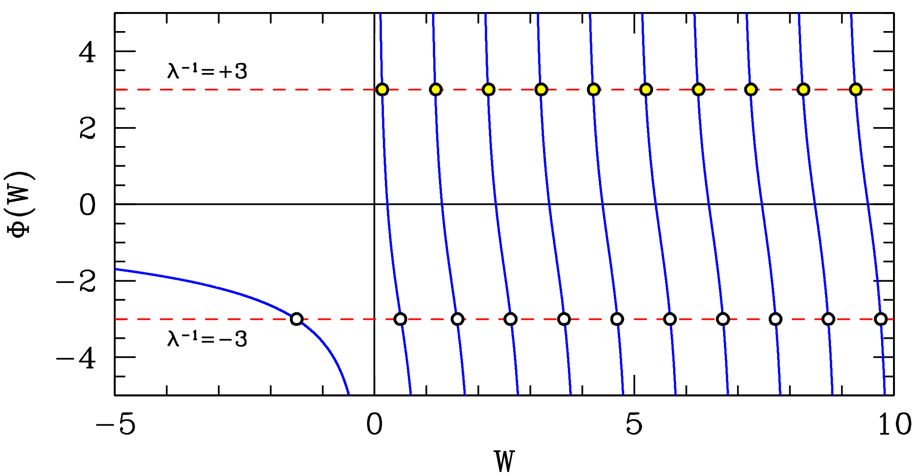

Figure 5.7: Graphical solution to the Cooper problem. A bound state exists for arbitrarily weak $\lambda < 0$.

We solve this for W_ℓ.

We may find a graphical solution. Recall that the sum is restricted to $k > k_{\rm F}$, and that $\xi_k \geq 0$. The denominator on the RHS of Eqn. 5.105 changes sign as a function of W_ℓ every time $\frac{1}{2}W_\ell$ passes through one of the ξ_k values[7]. A sketch of the graphical solution is provided in Fig. 5.7. One sees that if $\lambda_\ell < 0$, *i.e.* if the potential is attractive, then a bound state exists. This is true for arbitrarily weak $|\lambda_\ell|$, a situation not usually encountered in three-dimensional problems, where there is usually a critical strength of the attractive potential in order to form a bound state[8]. This is a density of states effect – by restricting our attention to electrons near the Fermi level, where the DOS is roughly constant at $g(\varepsilon_{\rm F}) = m^* k_{\rm F}/\pi^2\hbar^2$, rather than near $\boldsymbol{k} = 0$, where $g(\varepsilon)$ vanishes as $\sqrt{\varepsilon}$, the pairing problem is effectively rendered two-dimensional. We can make further progress by assuming a particular form for $\alpha_\ell(k)$:

$$\alpha_\ell(k) = \begin{cases} 1 & \text{if } 0 < \xi_k < B_\ell \\ 0 & \text{otherwise} \end{cases} , \tag{5.106}$$

where B_ℓ is an effective bandwidth for the ℓ channel. Then

$$1 = \tfrac{1}{2}\,|\lambda_\ell| \int\limits_0^{B_\ell} \! d\xi \, \frac{g(\varepsilon_{\rm F} + \xi)}{\big|W_\ell\big| + 2\xi} \quad . \tag{5.107}$$

The factor of $\frac{1}{2}$ is because it is the DOS per spin here, and not the total DOS. We assume $g(\varepsilon)$ does not vary significantly in the vicinity of $\varepsilon = \varepsilon_{\rm F}$, and pull $g(\varepsilon_{\rm F})$ out from the integrand. Integrating and solving for $\big|W_\ell\big|$,

$$\big|W_\ell\big| = \frac{2B_\ell}{\exp\!\Big(\frac{4}{|\lambda_\ell|\, g(\varepsilon_{\rm F})}\Big) - 1} \quad . \tag{5.108}$$

[7]We imagine quantizing in a finite volume, so the allowed k values are discrete.

[8]For example, the ^{2}He molecule is unbound, despite the attractive $-1/r^6$ van der Waals attractive tail in the interatomic potential.

In the *weak coupling* limit, where $|\lambda_\ell|\, g(\varepsilon_{\rm F}) \ll 1$, we have

$$\big|W_\ell\big| \simeq 2B_\ell\, \exp\!\bigg(-\frac{4}{|\lambda_\ell|\, g(\varepsilon_{\rm F})}\bigg) \quad . \tag{5.109}$$

As we shall see when we study BCS theory, the factor in the exponent is twice too large. The coefficient $2B_\ell$ will be shown to be the Debye energy of the phonons; we will see that it is only over a narrow range of energies about the Fermi surface that the effective electron-electron interaction is attractive. For strong coupling,

$$|W_\ell| = \tfrac{1}{2}\,|\lambda_\ell|\, g(\varepsilon_{\rm F}) \quad . \tag{5.110}$$

Finite momentum Cooper pair

We can construct a finite momentum Cooper pair as follows:

$$|\,\Psi_{\boldsymbol{q}}\,\rangle = \sum_{\boldsymbol{k}} A_{\boldsymbol{k}}\,\big(c^\dagger_{\boldsymbol{k}+\frac{1}{2}\boldsymbol{q}\uparrow} c^\dagger_{-\boldsymbol{k}+\frac{1}{2}\boldsymbol{q}\downarrow} - c^\dagger_{\boldsymbol{k}+\frac{1}{2}\boldsymbol{q}\downarrow} c^\dagger_{-\boldsymbol{k}+\frac{1}{2}\boldsymbol{q}\uparrow}\big)\,|\,{\rm F}\,\rangle \quad . \tag{5.111}$$

This wavefunction is a momentum eigenstate, with total momentum $\boldsymbol{P} = \hbar\boldsymbol{q}$. The eigenvalue equation is then

$$W A_{\boldsymbol{k}} = \big(\xi_{\boldsymbol{k}+\frac{1}{2}\boldsymbol{q}} + \xi_{-\boldsymbol{k}+\frac{1}{2}\boldsymbol{q}}\big) A_{\boldsymbol{k}} + \sum_{\boldsymbol{k}'} V_{\boldsymbol{k},\boldsymbol{k}'}\, A_{\boldsymbol{k}'} \quad . \tag{5.112}$$

Assuming $\xi_{\boldsymbol{k}} = \xi_{-\boldsymbol{k}}$,

$$\xi_{\boldsymbol{k}+\frac{1}{2}\boldsymbol{q}} + \xi_{-\boldsymbol{k}+\frac{1}{2}\boldsymbol{q}} = 2\,\xi_{\boldsymbol{k}} + \tfrac{1}{4}\, q^\alpha q^\beta\, \frac{\partial^2 \xi_{\boldsymbol{k}}}{\partial k^\alpha\, \partial k^\beta} + \ldots \quad . \tag{5.113}$$

The binding energy is thus reduced by an amount proportional to q^2; the $\boldsymbol{q} = 0$ Cooper pair has the greatest binding energy[9].

Mean square radius of the Cooper pair

We have

$$\begin{aligned}\big\langle \boldsymbol{r}^2 \big\rangle &= \frac{\int\! d^3\!r\, \big|\Psi(\boldsymbol{r})\big|^2\, \boldsymbol{r}^2}{\int\! d^3\!r\, \big|\Psi(\boldsymbol{r})\big|^2} = \frac{\int\! d^3\!k\, \big|\boldsymbol{\nabla}_{\!\boldsymbol{k}} A_{\boldsymbol{k}}\big|^2}{\int\! d^3\!k\, \big|A_{\boldsymbol{k}}\big|^2} \\ &\simeq \frac{g(\varepsilon_{\rm F})\, \xi'(k_{\rm F})^2 \int_0^\infty\! d\xi\, \big|\frac{\partial A}{\partial \xi}\big|^2}{g(\varepsilon_{\rm F}) \int_0^\infty\! d\xi\, |A|^2}\end{aligned} \tag{5.114}$$

[9]We assume the matrix $\partial_\alpha \partial_\beta\, \xi_{\boldsymbol{k}}$ is positive definite.

with $A(\xi) = -C/\big(|W| + 2\xi\big)$ and thus $A'(\xi) = 2C/\big(|W| + 2\xi\big)^2$, where C is a constant independent of ξ. Ignoring the upper cutoff on ξ at B_ℓ, we have

$$\big\langle \boldsymbol{r}^2 \big\rangle = 4\,\xi'(k_{\rm F})^2 \cdot \frac{\int\limits_{|W|}^{\infty} du\, u^{-4}}{\int\limits_{|W|}^{\infty} du\, u^{-2}} = \tfrac{4}{3}\,(\hbar v_{\rm F})^2\,|W|^{-2} \quad , \tag{5.115}$$

where we have used $\xi'(k_{\rm F}) = \hbar v_{\rm F}$. Thus, $R_{\rm RMS} = 2\hbar v_{\rm F}\big/\sqrt{3}\,|W|$. In the weak coupling limit, where $|W|$ is exponentially small in $1/|\lambda|$, the Cooper pair radius is huge. Indeed it is so large that many other Cooper pairs have their centers of mass within the radius of any given pair. This feature is what makes the BCS mean field theory of superconductivity so successful. Recall in our discussion of the Ginzburg criterion in §1.4.5, we found that mean field theory was qualitatively correct down to the Ginzburg reduced temperature $t_{\rm G} = (\mathsf{a}/R_*)^{2d/(4-d)}$, *i.e.* $t_{\rm G} = (\mathsf{a}/R_*)^6$ for $d = 3$. In this expression, R_* should be the mean Cooper pair size, and a a microscopic length (*i.e.* lattice constant). Typically $R_*/\mathsf{a} \sim 10^2 - 10^3$, so $t_{\rm G}$ is very tiny indeed.

5.7 Reduced BCS Hamiltonian

The operator which creates a Cooper pair with total momentum $\boldsymbol{q}$ is $b^\dagger_{\boldsymbol{k},\boldsymbol{q}} + b^\dagger_{-\boldsymbol{k},\boldsymbol{q}}$, where

$$b^\dagger_{\boldsymbol{k},\boldsymbol{q}} = c^\dagger_{\boldsymbol{k}+\frac{1}{2}\boldsymbol{q}\uparrow}\, c^\dagger_{-\boldsymbol{k}+\frac{1}{2}\boldsymbol{q}\downarrow} \tag{5.116}$$

is a composite operator which creates the state $|\,\boldsymbol{k}+\frac{1}{2}\boldsymbol{q}\uparrow,\, -\boldsymbol{k}+\frac{1}{2}\boldsymbol{q}\downarrow\rangle$. We learned from the solution to the Cooper problem that the $\boldsymbol{q}=0$ pairs have the greatest binding energy. This motivates consideration of the so-called *reduced BCS Hamiltonian*,

$$\hat{H}_{\rm red} = \sum_{\boldsymbol{k},\sigma} \varepsilon_{\boldsymbol{k}}\, c^\dagger_{\boldsymbol{k}\sigma}\, c_{\boldsymbol{k}\sigma} + \sum_{\boldsymbol{k},\boldsymbol{k}'} V_{\boldsymbol{k},\boldsymbol{k}'}\, b^\dagger_{\boldsymbol{k},0}\, b_{\boldsymbol{k}',0} \quad . \tag{5.117}$$

The most general form for a momentum-conserving interaction is

$$\hat{V} = \frac{1}{2V} \sum_{\boldsymbol{k},\boldsymbol{p},\boldsymbol{q}} \sum_{\sigma,\sigma'} \hat{u}_{\sigma\sigma'}(\boldsymbol{k},\boldsymbol{p},\boldsymbol{q})\, c^\dagger_{\boldsymbol{k}+\boldsymbol{q}\,\sigma}\, c^\dagger_{\boldsymbol{p}-\boldsymbol{q}\,\sigma'}\, c_{\boldsymbol{p}\,\sigma'}\, c_{\boldsymbol{k}\,\sigma} \quad . \tag{5.118}$$

Taking $\boldsymbol{p} = -\boldsymbol{k}$, $\sigma' = -\sigma$, and defining $\boldsymbol{k}' \equiv \boldsymbol{k} + \boldsymbol{q}$, we have

$$\hat{V} \to \frac{1}{2V} \sum_{\boldsymbol{k},\boldsymbol{k}',\sigma} \hat{v}(\boldsymbol{k},\boldsymbol{k}')\, c^\dagger_{\boldsymbol{k}'\sigma}\, c^\dagger_{-\boldsymbol{k}'\,-\sigma}\, c_{-\boldsymbol{k}\,-\sigma}\, c_{\boldsymbol{k}\sigma} \quad , \tag{5.119}$$

where $\hat{v}(\boldsymbol{k},\boldsymbol{k}') = \hat{u}_{\uparrow\downarrow}(\boldsymbol{k},-\boldsymbol{k},\boldsymbol{k}'-\boldsymbol{k})$, which is equivalent to $\hat{H}_{\rm red}$.

If $V_{\boldsymbol{k},\boldsymbol{k}'}$ is attractive, then the ground state will have no pair $(\boldsymbol{k}\uparrow,\, -\boldsymbol{k}\downarrow)$ occupied by a single electron; the pair states are either empty or doubly occupied. In that case, the reduced BCS Hamiltonian may be

Figure 5.8: John Bardeen, Leon Cooper, and J. Robert Schrieffer.

written as[10]

$$H^0_{\rm red} = \sum_{\boldsymbol{k}} 2\varepsilon_{\boldsymbol{k}}\, b^\dagger_{\boldsymbol{k},0}\, b_{\boldsymbol{k},0} + \sum_{\boldsymbol{k},\boldsymbol{k}'} V_{\boldsymbol{k},\boldsymbol{k}'}\, b^\dagger_{\boldsymbol{k},0}\, b_{\boldsymbol{k}',0} \quad . \tag{5.120}$$

This has the innocent appearance of a noninteracting bosonic Hamiltonian – an exchange of Cooper pairs restores the many-body wavefunction without a sign change because the Cooper pair is a composite object consisting of an even number of fermions[11]. However, this is not quite correct, because the operators $b_{\boldsymbol{k},0}$ and $b_{\boldsymbol{k}',0}$ do not satisfy canonical bosonic commutation relations. Rather,

$$\begin{aligned} \big[b_{\boldsymbol{k},0}\,,\,b_{\boldsymbol{k}',0}\big] = \big[b^\dagger_{\boldsymbol{k},0}\,,\,b^\dagger_{\boldsymbol{k}',0}\big] &= 0 \\ \big[b_{\boldsymbol{k},0}\,,\,b^\dagger_{\boldsymbol{k}',0}\big] &= \big(1 - c^\dagger_{\boldsymbol{k}\uparrow}c_{\boldsymbol{k}\uparrow} - c^\dagger_{-\boldsymbol{k}\downarrow}c_{-\boldsymbol{k}\downarrow}\big)\,\delta_{\boldsymbol{k}\boldsymbol{k}'} \quad . \end{aligned} \tag{5.121}$$

Because of this, $\hat{H}^0_{\rm red}$ cannot naïvely be diagonalized. The extra terms inside the round brackets on the RHS arise due to the Pauli blocking effects. Indeed, one has $(b^\dagger_{\boldsymbol{k},0})^2 = 0$, so $b^\dagger_{\boldsymbol{k},0}$ is no ordinary boson operator.

Suppose, though, we try a mean field Hartree-Fock approach. We write

$$b_{\boldsymbol{k},0} = \langle b_{\boldsymbol{k},0}\rangle + \overbrace{\big(b_{\boldsymbol{k},0} - \langle b_{\boldsymbol{k},0}\rangle\big)}^{\delta b_{\boldsymbol{k},0}} \quad , \tag{5.122}$$

and we neglect terms in $\hat{H}_{\rm red}$ proportional to $\delta b^\dagger_{\boldsymbol{k},0}\,\delta b_{\boldsymbol{k}',0}$. We have

$$\hat{H}_{\rm red} = \sum_{\boldsymbol{k},\sigma} \varepsilon_{\boldsymbol{k}}\, c^\dagger_{\boldsymbol{k}\sigma}\, c_{\boldsymbol{k}\sigma} + \sum_{\boldsymbol{k},\boldsymbol{k}'} V_{\boldsymbol{k},\boldsymbol{k}'} \Big(\overbrace{-\langle b^\dagger_{\boldsymbol{k},0}\rangle\,\langle b_{\boldsymbol{k}',0}\rangle}^{\text{energy shift}} + \overbrace{\langle b_{\boldsymbol{k}',0}\rangle\, b^\dagger_{\boldsymbol{k},0} + \langle b^\dagger_{\boldsymbol{k},0}\rangle\, b_{\boldsymbol{k}',0}}^{\text{keep this}} + \overbrace{\delta b^\dagger_{\boldsymbol{k},0}\,\delta b_{\boldsymbol{k}',0}}^{\text{drop this!}} \Big) \quad . \tag{5.123}$$

[10]Spin rotation invariance and a singlet Cooper pair requires that $V_{\boldsymbol{k},\boldsymbol{k}'} = V_{\boldsymbol{k},-\boldsymbol{k}'} = V_{-\boldsymbol{k},\boldsymbol{k}'}$.

[11]Recall that the atom ^{4}He, which consists of six fermions (two protons, two neutrons, and two electrons), is a boson, while ^{3}He, which has only one neutron and thus five fermions, is itself a fermion.

Dropping the last term, which is quadratic in fluctuations, we obtain

$$\hat{H}^{\rm MF}_{\rm red} = \sum_{\boldsymbol{k},\sigma} \varepsilon_{\boldsymbol{k}}\, c^\dagger_{\boldsymbol{k}\sigma}\, c_{\boldsymbol{k}\sigma} + \sum_{\boldsymbol{k}} \big(\Delta_{\boldsymbol{k}}\, c^\dagger_{\boldsymbol{k}\uparrow}\, c^\dagger_{-\boldsymbol{k}\downarrow} + \Delta^*_{\boldsymbol{k}}\, c_{-\boldsymbol{k}\downarrow}\, c_{\boldsymbol{k}\uparrow}\big) - \sum_{\boldsymbol{k},\boldsymbol{k}'} V_{\boldsymbol{k},\boldsymbol{k}'}\, \langle b^\dagger_{\boldsymbol{k},0}\rangle\, \langle b_{\boldsymbol{k}',0}\rangle \quad , \tag{5.124}$$

where

$$\Delta_{\boldsymbol{k}} = \sum_{\boldsymbol{k}'} V_{\boldsymbol{k},\boldsymbol{k}'}\, \langle c_{-\boldsymbol{k}'\downarrow}\, c_{\boldsymbol{k}'\uparrow}\rangle \qquad , \qquad \Delta^*_{\boldsymbol{k}} = \sum_{\boldsymbol{k}'} V^*_{\boldsymbol{k},\boldsymbol{k}'}\, \langle c^\dagger_{\boldsymbol{k}'\uparrow}\, c^\dagger_{-\boldsymbol{k}'\downarrow}\rangle \quad . \tag{5.125}$$

The first thing to notice about $\hat{H}^{\rm MF}_{\rm red}$ is that it does not preserve particle number, *i.e.* it does not commute with $\hat{N} = \sum_{\boldsymbol{k},\sigma} c^\dagger_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma}$. Accordingly, we are practically forced to work in the grand canonical ensemble, and we define the grand canonical Hamiltonian $\hat{K} \equiv \hat{H} - \mu\hat{N}$.

5.8 Solution of the mean field Hamiltonian

We now subtract $\mu\hat{N}$ from Eqn. 5.124, and define $\hat{K}_{\rm BCS} \equiv \hat{H}^{\rm MF}_{\rm red} - \mu\hat{N}$. Thus,

$$\hat{K}_{\rm BCS} = \sum_{\boldsymbol{k}} \begin{pmatrix} c^\dagger_{\boldsymbol{k}\uparrow} & c_{-\boldsymbol{k}\downarrow}\end{pmatrix} \overbrace{\begin{pmatrix} \xi_{\boldsymbol{k}} & \Delta_{\boldsymbol{k}} \\ \Delta^*_{\boldsymbol{k}} & -\xi_{\boldsymbol{k}}\end{pmatrix}}^{K_{\boldsymbol{k}}} \begin{pmatrix} c_{\boldsymbol{k}\uparrow} \\ c^\dagger_{-\boldsymbol{k}\downarrow}\end{pmatrix} + K_0 \quad , \tag{5.126}$$

with $\xi_{\boldsymbol{k}} = \varepsilon_{\boldsymbol{k}} - \mu$, and where

$$K_0 = \sum_{\boldsymbol{k}} \xi_{\boldsymbol{k}} - \sum_{\boldsymbol{k},\boldsymbol{k}'} V_{\boldsymbol{k},\boldsymbol{k}'}\, \langle c^\dagger_{\boldsymbol{k}\uparrow} c^\dagger_{-\boldsymbol{k}\downarrow}\rangle\, \langle c_{-\boldsymbol{k}'\downarrow}\, c_{\boldsymbol{k}'\uparrow}\rangle \tag{5.127}$$

is a constant. This problem may be brought to diagonal form via a unitary transformation,

$$\begin{pmatrix} c_{\boldsymbol{k}\uparrow} \\ c^\dagger_{-\boldsymbol{k}\downarrow}\end{pmatrix} = \overbrace{\begin{pmatrix} \cos\vartheta_{\boldsymbol{k}} & -\sin\vartheta_{\boldsymbol{k}}\, e^{i\phi_{\boldsymbol{k}}} \\ \sin\vartheta_{\boldsymbol{k}}\, e^{-i\phi_{\boldsymbol{k}}} & \cos\vartheta_{\boldsymbol{k}}\end{pmatrix}}^{U_{\boldsymbol{k}}} \begin{pmatrix} \gamma_{\boldsymbol{k}\uparrow} \\ \gamma^\dagger_{-\boldsymbol{k}\downarrow}\end{pmatrix} \quad . \tag{5.128}$$

In order for the $\gamma_{\boldsymbol{k}\sigma}$ operators to satisfy fermionic anticommutation relations, the matrix $U_{\boldsymbol{k}}$ must be unitary[12]. We then have

$$\begin{aligned} c_{\boldsymbol{k}\sigma} &= \cos\vartheta_{\boldsymbol{k}}\, \gamma_{\boldsymbol{k}\sigma} - \sigma \sin\vartheta_{\boldsymbol{k}}\, e^{i\phi_{\boldsymbol{k}}}\, \gamma^\dagger_{-\boldsymbol{k}\,-\sigma} \\ \gamma_{\boldsymbol{k}\sigma} &= \cos\vartheta_{\boldsymbol{k}}\, c_{\boldsymbol{k}\sigma} + \sigma \sin\vartheta_{\boldsymbol{k}}\, e^{i\phi_{\boldsymbol{k}}}\, c^\dagger_{-\boldsymbol{k}\,-\sigma} \quad . \end{aligned} \tag{5.129}$$

EXERCISE: Verify that $\big\{\gamma_{\boldsymbol{k}\sigma}\, , \, \gamma^\dagger_{\boldsymbol{k}'\sigma'}\big\} = \delta_{\boldsymbol{k}\boldsymbol{k}'}\, \delta_{\sigma\sigma'}$.

[12]The most general 2×2 unitary matrix is of the above form, but with each row multiplied by an independent phase. These phases may be absorbed into the definitions of the fermion operators themselves. After absorbing these harmless phases, we have written the most general unitary transformation.

We now must compute the transformed Hamiltonian. Dropping the $\boldsymbol{k}$ subscript for notational convenience, we have

$$\widetilde{K} = U^\dagger\, K\, U = \begin{pmatrix} \cos\vartheta & \sin\vartheta\, e^{i\phi} \\ -\sin\vartheta\, e^{-i\phi} & \cos\vartheta \end{pmatrix} \begin{pmatrix} \xi & \Delta \\ \Delta^* & -\xi \end{pmatrix} \begin{pmatrix} \cos\vartheta & -\sin\vartheta\, e^{i\phi} \\ \sin\vartheta\, e^{-i\phi} & \cos\vartheta \end{pmatrix} \tag{5.130}$$

$$= \begin{pmatrix} (\cos^2\!\vartheta - \sin^2\!\vartheta)\,\xi + \sin\vartheta\cos\vartheta\,(\Delta\, e^{-i\phi} + \Delta^* e^{i\phi}) & \Delta\cos^2\!\vartheta - \Delta^* e^{2i\phi}\sin^2\!\vartheta - 2\xi\sin\vartheta\cos\vartheta\, e^{i\phi} \\ \Delta^*\cos^2\!\vartheta - \Delta e^{-2i\phi}\sin^2\!\vartheta - 2\xi\sin\vartheta\cos\vartheta\, e^{-i\phi} & (\sin^2\!\vartheta - \cos^2\!\vartheta)\,\xi - \sin\vartheta\cos\vartheta\,(\Delta\, e^{-i\phi} + \Delta^* e^{i\phi}) \end{pmatrix} .$$

We now use our freedom to choose ϑ and ϕ to render $\widetilde{K}$ diagonal. That is, we demand $\phi = \mathsf{arg}(\Delta)$ and

$$2\xi\sin\vartheta\cos\vartheta = \Delta\,(\cos^2\!\vartheta - \sin^2\!\vartheta) \quad . \tag{5.131}$$

This says $\tan(2\vartheta) = \Delta/\xi$, which means

$$\cos(2\vartheta) = \frac{\xi}{E} \quad , \quad \sin(2\vartheta) = \frac{\Delta}{E} \quad , \quad E = \sqrt{\xi^2 + \Delta^2} \quad . \tag{5.132}$$

The upper left element of $\widetilde{K}$ then becomes

$$(\cos^2\!\vartheta - \sin^2\!\vartheta)\,\xi + \sin\vartheta\cos\vartheta\,(\Delta\, e^{-i\phi} + \Delta^* e^{i\phi}) = \frac{\xi^2}{E} + \frac{\Delta^2}{E} = E \quad , \tag{5.133}$$

and thus $\widetilde{K} = \begin{pmatrix} E & 0 \\ 0 & -E \end{pmatrix}$. This unitary transformation, which mixes particle and hole states, is called a *Bogoliubov transformation*, because it was first discovered by Valatin.

Restoring the $\boldsymbol{k}$ subscript, we have $\phi_{\boldsymbol{k}} = \mathsf{arg}(\Delta_{\boldsymbol{k}})$, and $\tan(2\vartheta_{\boldsymbol{k}}) = |\Delta_{\boldsymbol{k}}|/\xi_{\boldsymbol{k}}$, which means

$$\cos(2\vartheta_{\boldsymbol{k}}) = \frac{\xi_{\boldsymbol{k}}}{E_{\boldsymbol{k}}} \quad , \quad \sin(2\vartheta_{\boldsymbol{k}}) = \frac{|\Delta_{\boldsymbol{k}}|}{E_{\boldsymbol{k}}} \quad , \quad E_{\boldsymbol{k}} = \sqrt{\xi_{\boldsymbol{k}}^2 + |\Delta_{\boldsymbol{k}}|^2} \quad . \tag{5.134}$$

Assuming that $\Delta_{\boldsymbol{k}}$ is not strongly momentum-dependent, we see that the dispersion $E_{\boldsymbol{k}}$ of the excitations has a nonzero minimum at $\xi_{\boldsymbol{k}} = 0$, *i.e.* at $k = k_{\rm F}$. This minimum value of $E_{\boldsymbol{k}}$ is called the *superconducting energy gap*.

We may further write

$$\cos\vartheta_{\boldsymbol{k}} = \sqrt{\frac{E_{\boldsymbol{k}} + \xi_{\boldsymbol{k}}}{2E_{\boldsymbol{k}}}} \quad , \quad \sin\vartheta_{\boldsymbol{k}} = \sqrt{\frac{E_{\boldsymbol{k}} - \xi_{\boldsymbol{k}}}{2E_{\boldsymbol{k}}}} \quad . \tag{5.135}$$

The grand canonical BCS Hamiltonian then becomes

$$\hat{K}_{\rm BCS} = \sum_{\boldsymbol{k},\sigma} E_{\boldsymbol{k}}\, \gamma^\dagger_{\boldsymbol{k}\sigma}\, \gamma_{\boldsymbol{k}\sigma} + \sum_{\boldsymbol{k}} (\xi_{\boldsymbol{k}} - E_{\boldsymbol{k}}) - \sum_{\boldsymbol{k},\boldsymbol{k}'} V_{\boldsymbol{k},\boldsymbol{k}'}\, \langle c^\dagger_{\boldsymbol{k}\uparrow} c^\dagger_{-\boldsymbol{k}\downarrow}\rangle\, \langle c_{-\boldsymbol{k}'\downarrow}\, c_{\boldsymbol{k}'\uparrow}\rangle \quad . \tag{5.136}$$

Finally, what of the ground state wavefunction itself? We must have $\gamma_{\boldsymbol{k}\sigma}|\,{\rm G}\,\rangle = 0$. This leads to

$$|\,{\rm G}\,\rangle = \prod_{\boldsymbol{k}} \big(\cos\vartheta_{\boldsymbol{k}} - \sin\vartheta_{\boldsymbol{k}}\, e^{i\phi_{\boldsymbol{k}}}\, c^\dagger_{\boldsymbol{k}\uparrow}\, c^\dagger_{-\boldsymbol{k}\downarrow}\big)\,|\,0\,\rangle \quad . \tag{5.137}$$

Note that $\langle\,{\rm G}\,|\,{\rm G}\,\rangle = 1$. J. R. Schrieffer conceived of this wavefunction during a subway ride in New York City sometime during the winter of 1957. At the time he was a graduate student at the University of Illinois.

Sanity check

It is good to make contact with something familiar, such as the case $\Delta_{\boldsymbol{k}}=0$. Note that $\xi_{\boldsymbol{k}}<0$ for $k<k_{\rm F}$ and $\xi_{\boldsymbol{k}}>0$ for $k>k_{\rm F}$. We now have

$$\cos\vartheta_{\boldsymbol{k}}=\Theta(k-k_{\rm F}) \qquad , \qquad \sin\vartheta_{\boldsymbol{k}}=\Theta(k_{\rm F}-k) \quad . \tag{5.138}$$

Note that the wavefunction $|\,\text{G}\,\rangle$ in Eqn. 5.137 correctly describes a filled Fermi sphere out to $k=k_{\rm F}$. Furthermore, the constant on the RHS of Eqn. 5.136 is $2\sum_{k<k_{\rm F}}\xi_{\boldsymbol{k}'}$, which is the Landau free energy of the filled Fermi sphere. What of the excitations? We are free to take $\phi_{\boldsymbol{k}}=0$. Then

$$\begin{aligned} k<k_{\rm F}\ &:\ \gamma^\dagger_{\boldsymbol{k}\sigma}=\sigma\,c_{-\boldsymbol{k}\,-\sigma}\\ k>k_{\rm F}\ &:\ \gamma^\dagger_{\boldsymbol{k}\sigma}=c^\dagger_{\boldsymbol{k}\sigma} \quad . \end{aligned} \tag{5.139}$$

Thus, the elementary excitations are holes below $k_{\rm F}$ and electrons above $k_{\rm F}$. All we have done, then, is to effect a (unitary) particle-hole transformation on those states lying within the Fermi sea.

5.9 Self-consistency

We now demand that the following two conditions hold:

$$\begin{aligned} N&=\sum_{\boldsymbol{k}\sigma}\langle c^\dagger_{\boldsymbol{k}\sigma}\,c_{\boldsymbol{k}\sigma}\rangle\\ \Delta_{\boldsymbol{k}}&=\sum_{\boldsymbol{k}'}V_{\boldsymbol{k},\boldsymbol{k}'}\,\langle c_{-\boldsymbol{k}'\downarrow}\,c_{\boldsymbol{k}'\uparrow}\rangle \quad , \end{aligned} \tag{5.140}$$

the second of which is from Eqn. 5.125. Thus, we need

$$\begin{aligned} \langle c^\dagger_{\boldsymbol{k}\sigma}\,c_{\boldsymbol{k}\sigma}\rangle&=\big\langle(\cos\vartheta_{\boldsymbol{k}}\,\gamma^\dagger_{\boldsymbol{k}\sigma}-\sigma\sin\vartheta_{\boldsymbol{k}}\,e^{-i\phi_{\boldsymbol{k}}}\,\gamma_{-\boldsymbol{k}\,-\sigma})(\cos\vartheta_{\boldsymbol{k}}\,\gamma_{\boldsymbol{k}\sigma}-\sigma\sin\vartheta_{\boldsymbol{k}}\,e^{i\phi_{\boldsymbol{k}}}\,\gamma^\dagger_{-\boldsymbol{k}\,-\sigma})\big\rangle\\ &=\cos^2\!\vartheta_{\boldsymbol{k}}\,f_{\boldsymbol{k}}+\sin^2\!\vartheta_{\boldsymbol{k}}\,(1-f_{\boldsymbol{k}})=\frac{1}{2}-\frac{\xi_{\boldsymbol{k}}}{2E_{\boldsymbol{k}}}\tanh\!\big(\tfrac{1}{2}\beta E_{\boldsymbol{k}}\big) \quad , \end{aligned} \tag{5.141}$$

where

$$f_{\boldsymbol{k}}=\langle\gamma^\dagger_{\boldsymbol{k}\sigma}\,\gamma_{\boldsymbol{k}\sigma}\rangle=\frac{1}{e^{\beta E_{\boldsymbol{k}}}+1}=\tfrac{1}{2}-\tfrac{1}{2}\tanh\!\big(\tfrac{1}{2}\beta E_{\boldsymbol{k}}\big) \tag{5.142}$$

is the Fermi function, with $\beta=1/k_{\rm B}T$. We also have

$$\begin{aligned} \langle c_{-\boldsymbol{k}\,-\sigma}\,c_{\boldsymbol{k}\sigma}\rangle&=\big\langle(\cos\vartheta_{\boldsymbol{k}}\,\gamma_{-\boldsymbol{k}\,-\sigma}+\sigma\sin\vartheta_{\boldsymbol{k}}\,e^{i\phi_{\boldsymbol{k}}}\,\gamma^\dagger_{\boldsymbol{k}\sigma})(\cos\vartheta_{\boldsymbol{k}}\,\gamma_{\boldsymbol{k}\sigma}-\sigma\sin\vartheta_{\boldsymbol{k}}\,e^{i\phi_{\boldsymbol{k}}}\,\gamma^\dagger_{-\boldsymbol{k}\,-\sigma})\big\rangle\\ &=\sigma\sin\vartheta_{\boldsymbol{k}}\cos\vartheta_{\boldsymbol{k}}\,e^{i\phi_{\boldsymbol{k}}}\,\big(2f_{\boldsymbol{k}}-1\big)=-\frac{\sigma\Delta_{\boldsymbol{k}}}{2E_{\boldsymbol{k}}}\,\tanh\!\big(\tfrac{1}{2}\beta E_{\boldsymbol{k}}\big) \quad . \end{aligned} \tag{5.143}$$

Let's evaluate at $T=0$:

$$\begin{aligned} N&=\sum_{\boldsymbol{k}}\bigg(1-\frac{\xi_{\boldsymbol{k}}}{E_{\boldsymbol{k}}}\bigg)\\ \Delta_{\boldsymbol{k}}&=-\sum_{\boldsymbol{k}'}V_{\boldsymbol{k},\boldsymbol{k}'}\,\frac{\Delta_{\boldsymbol{k}'}}{2E_{\boldsymbol{k}'}} \quad . \end{aligned} \tag{5.144}$$

The second of these is known as the BCS gap equation. Note that $\Delta_{\boldsymbol{k}} = 0$ is always a solution of the gap equation.

To proceed further, we need a model for $V_{\boldsymbol{k},\boldsymbol{k}'}$. We shall assume

$$V_{\boldsymbol{k},\boldsymbol{k}'} = \begin{cases} -v/V & \text{if } |\xi_{\boldsymbol{k}}| < \hbar\omega_{\mathrm{D}} \text{ and } |\xi_{\boldsymbol{k}'}| < \hbar\omega_{\mathrm{D}} \\ 0 & \text{otherwise} \end{cases} \quad . \tag{5.145}$$

Here $v > 0$, so the interaction is attractive, but only when $\xi_{\boldsymbol{k}}$ and $\xi_{\boldsymbol{k}'}$ are within an energy $\hbar\omega_{\mathrm{D}}$ of zero. For phonon-mediated superconductivity, ω_{D} is the Debye frequency, which is the phonon bandwidth.

5.9.1 Solution at zero temperature

We first solve the second of Eqns. 5.144, by assuming

$$\Delta_{\boldsymbol{k}} = \begin{cases} \Delta\, e^{i\phi} & \text{if } |\xi_{\boldsymbol{k}}| < \hbar\omega_{\mathrm{D}} \\ 0 & \text{otherwise} \end{cases} \quad , \tag{5.146}$$

with Δ real. We then have[13]

$$\begin{aligned} \Delta &= +v \int \frac{d^3k}{(2\pi)^3}\, \frac{\Delta}{2E_{\boldsymbol{k}}}\, \Theta\big(\hbar\omega_{\mathrm{D}} - |\xi_{\boldsymbol{k}}|\big) \\ &= \tfrac{1}{2} v\, g(\varepsilon_{\mathrm{F}}) \int\limits_0^{\hbar\omega_{\mathrm{D}}} \! d\xi\, \frac{\Delta}{\sqrt{\xi^2 + \Delta^2}} \quad . \end{aligned} \tag{5.147}$$

Cancelling out the common factors of Δ on each side, we obtain

$$1 = \tfrac{1}{2} v\, g(\varepsilon_{\mathrm{F}}) \int\limits_0^{\hbar\omega_{\mathrm{D}}/\Delta} \! ds\, (1+s^2)^{-1/2} = \tfrac{1}{2} v\, g(\varepsilon_{\mathrm{F}})\, \sinh^{-1}\!\big(\hbar\omega_{\mathrm{D}}/\Delta\big) \quad . \tag{5.148}$$

Thus, writing $\Delta_0 \equiv \Delta(0)$ for the zero temperature gap,

$$\Delta_0 = \frac{\hbar\omega_{\mathrm{D}}}{\sinh\!\big(2/g(\varepsilon_{\mathrm{F}})\, v\big)} \simeq 2\hbar\omega_{\mathrm{D}} \exp\!\left(-\frac{2}{g(\varepsilon_{\mathrm{F}})\, v}\right) \quad , \tag{5.149}$$

where $g(\varepsilon_{\mathrm{F}})$ is the total electronic DOS (for both spin species) at the Fermi level. Notice that, as promised, the argument of the exponent is one half as large as what we found in our solution of the Cooper problem, in Eqn. 5.109.

[13] We assume the density of states $g(\varepsilon)$ is slowly varying in the vicinity of the chemical potential and approximate it at $g(\varepsilon_{\mathrm{F}})$. In fact, we should more properly call it $g(\mu)$, but as a practical matter $\mu \simeq \varepsilon_{\mathrm{F}}$ at temperatures low enough to be in the superconducting phase. Note that $g(\varepsilon_{\mathrm{F}})$ is the total DOS for both spin species. In the literature, one often encounters the expression $N(0)$, which is the DOS per spin at the Fermi level, *i.e.* $N(0) = \frac{1}{2}\, g(\varepsilon_{\mathrm{F}})$.

5.9.2 Condensation energy

We now evaluate the zero temperature expectation of $\hat{K}_{\text{BCS}}$ from Eqn. 5.136. To get the correct answer, it is essential that we retain the term corresponding to the constant energy shift in the mean field Hamiltonian, *i.e.* the last term on the RHS of Eqn. 5.136. Invoking the gap equation $\Delta_{\boldsymbol{k}} = \sum_{\boldsymbol{k}'} V_{\boldsymbol{k},\boldsymbol{k}'} \langle c_{-\boldsymbol{k}'\downarrow}\, c_{\boldsymbol{k}'\uparrow}\rangle$, we have

$$\langle\, \text{G} \,|\, \hat{K}_{\text{BCS}} \,|\, \text{G} \,\rangle = \sum_{\boldsymbol{k}} \left(\xi_{\boldsymbol{k}} - E_{\boldsymbol{k}} + \frac{|\Delta_{\boldsymbol{k}}|^2}{2E_{\boldsymbol{k}}} \right) \quad . \tag{5.150}$$

From this we subtract the ground state energy of the metallic phase, *i.e.* when $\Delta_{\boldsymbol{k}} = 0$, which is $2\sum_{\boldsymbol{k}} \xi_{\boldsymbol{k}}\, \Theta(k_{\text{F}} - k)$. The difference is the condensation energy. Adopting the model interaction potential in Eqn. 5.145, we have

$$\begin{aligned} E_{\text{s}} - E_{\text{n}} &= \sum_{\boldsymbol{k}} \left(\xi_{\boldsymbol{k}} - E_{\boldsymbol{k}} + \frac{|\Delta_{\boldsymbol{k}}|^2}{2E_{\boldsymbol{k}}} - 2\xi_{\boldsymbol{k}}\, \Theta(k_{\text{F}} - k) \right) \\ &= 2\sum_{\boldsymbol{k}} \left(\xi_{\boldsymbol{k}} - E_{\boldsymbol{k}}\right) \Theta(\xi_{\boldsymbol{k}})\, \Theta(\hbar\omega_{\text{D}} - \xi_{\boldsymbol{k}}) + \sum_{\boldsymbol{k}} \frac{\Delta_0^2}{2E_{\boldsymbol{k}}}\, \Theta\big(\hbar\omega_{\text{D}} - |\xi_{\boldsymbol{k}}|\big) \quad , \end{aligned} \tag{5.151}$$

where we have linearized about $k = k_{\text{F}}$. We then have

$$\begin{aligned} E_{\text{s}} - E_{\text{n}} &= V g(\varepsilon_{\text{F}})\, \Delta_0^2 \int\limits_0^{\hbar\omega_{\text{D}}/\Delta_0} \! ds \left(s - \sqrt{s^2+1} + \frac{1}{2\sqrt{s^2+1}} \right) \\ &= \tfrac{1}{2}\, V g(\varepsilon_{\text{F}})\, \Delta_0^2 \Big(x^2 - x\sqrt{1+x^2} \Big) \approx -\tfrac{1}{4}\, V g(\varepsilon_{\text{F}})\, \Delta_0^2 \quad , \end{aligned} \tag{5.152}$$

where $x \equiv \hbar\omega_{\text{D}}/\Delta_0$. The condensation energy density is therefore $-\frac{1}{4}\, g(\varepsilon_{\text{F}})\, \Delta_0^2$, which may be equated with $-H_{\text{c}}^2/8\pi$, where H_{c} is the thermodynamic critical field. Thus, we find

$$H_{\text{c}}(0) = \sqrt{2\pi g(\varepsilon_{\text{F}})}\, \Delta_0 \quad , \tag{5.153}$$

which relates the thermodynamic critical field to the superconducting gap, at $T = 0$.

5.10 Coherence factors and quasiparticle energies

When $\Delta_{\boldsymbol{k}} = 0$, we have $E_{\boldsymbol{k}} = |\xi_{\boldsymbol{k}}|$. When $\hbar\omega_{\text{D}} \ll \varepsilon_{\text{F}}$, there is a very narrow window surrounding $k = k_{\text{F}}$ where $E_{\boldsymbol{k}}$ departs from $|\xi_{\boldsymbol{k}}|$, as shown in the bottom panel of Fig. 5.9. Note the *energy gap* in the quasiparticle dispersion, where the minimum excitation energy is given by[14]

$$\min_{\boldsymbol{k}} E_{\boldsymbol{k}} = E_{k_{\text{F}}} = \Delta_0 \quad . \tag{5.154}$$

In the top panel of Fig. 5.9 we plot the coherence factors $\sin^2\!\vartheta_{\boldsymbol{k}}$ and $\cos^2\!\vartheta_{\boldsymbol{k}}$. Note that $\sin^2\!\vartheta_{\boldsymbol{k}}$ approaches unity for $k < k_{\text{F}}$ and $\cos^2\!\vartheta_{\boldsymbol{k}}$ approaches unity for $k > k_{\text{F}}$, aside for the narrow window of width $\delta k \simeq \Delta_0/\hbar v_{\text{F}}$. Recall that

$$\gamma^\dagger_{\boldsymbol{k}\sigma} = \cos\vartheta_{\boldsymbol{k}}\, c^\dagger_{\boldsymbol{k}\sigma} + \sigma \sin\vartheta_{\boldsymbol{k}}\, e^{-i\phi_{\boldsymbol{k}}}\, c_{-\boldsymbol{k}\,-\sigma} \quad . \tag{5.155}$$

[14] Here we assume, without loss of generality, that Δ is real.

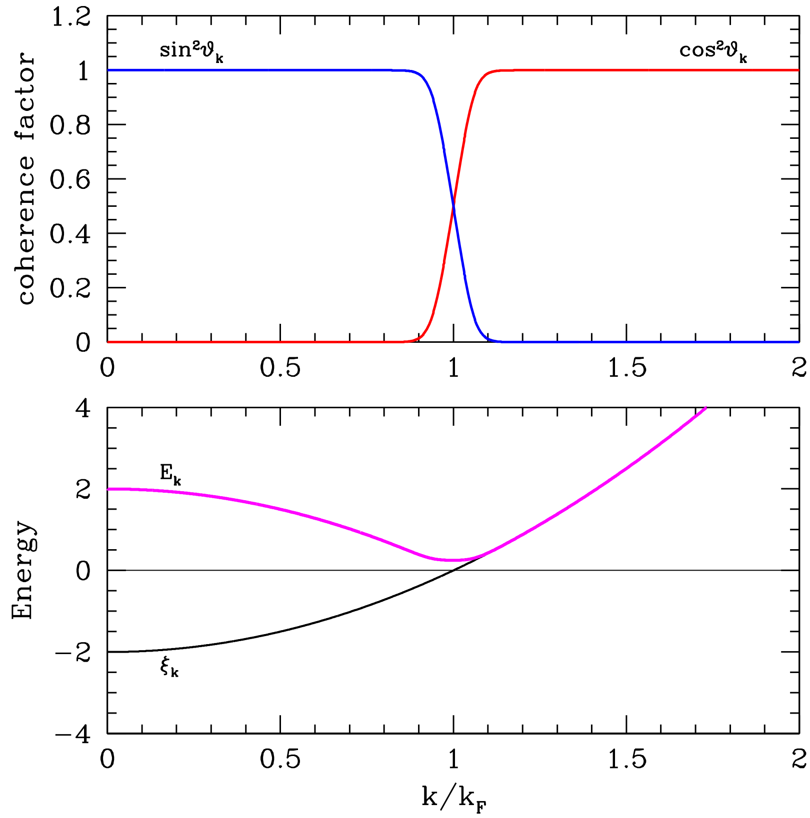

Figure 5.9: Top panel: BCS coherence factors $\sin^2\!\vartheta_{\boldsymbol{k}}$ (blue) and $\cos^2\!\vartheta_{\boldsymbol{k}}$ (red). Bottom panel: the functions $\xi_{\boldsymbol{k}}$ (black) and $E_{\boldsymbol{k}}$ (magenta). The minimum value of the magenta curve is the superconducting gap Δ_0.

Thus we see that the quasiparticle creation operator $\gamma^\dagger_{\boldsymbol{k}\sigma}$ creates an electron in the state $|\,\boldsymbol{k}\,\sigma\,\rangle$ when $\cos^2\!\vartheta_{\boldsymbol{k}} \simeq 1$, and a hole in the state $|\,-\boldsymbol{k}\,\,-\sigma\,\rangle$ when $\sin^2\!\vartheta_{\boldsymbol{k}} \simeq 1$. In the aforementioned narrow window $|k - k_{\rm F}| \lesssim \Delta_0/\hbar v_{\rm F}$, the quasiparticle creates a linear combination of electron and hole states. Typically $\Delta_0 \sim 10^{-4}\,\varepsilon_{\rm F}$, since metallic Fermi energies are on the order of tens of thousands of Kelvins, while Δ_0 is on the order of Kelvins or tens of Kelvins. Thus, $\delta k \lesssim 10^{-3} k_{\rm F}$. The difference between the superconducting state and the metallic state all takes place within an onion skin at the Fermi surface!

Note that for the model interaction $V_{\boldsymbol{k},\boldsymbol{k}'}$ of Eqn. 5.145, the solution $\Delta_{\boldsymbol{k}}$ in Eqn. 5.146 is actually *discontinuous* when $\xi_{\boldsymbol{k}} = \pm\hbar\omega_{\rm D}$, *i.e.* when $k = k^*_\pm \equiv k_{\rm F} \pm \omega_{\rm D}/v_{\rm F}$. Therefore, the energy dispersion $E_{\boldsymbol{k}}$ is also discontinuous along these surfaces. However, the magnitude of the discontinuity is

$$\delta E = \sqrt{(\hbar\omega_{\rm D})^2 + \Delta_0^2} - \hbar\omega_{\rm D} \approx \frac{\Delta_0^2}{2\hbar\omega_{\rm D}} \quad . \tag{5.156}$$

Therefore $\delta E/E_{k^*_\pm} \approx \Delta_0^2/2(\hbar\omega_{\rm D})^2 \propto \exp\big(-4/g(\varepsilon_{\rm F})\,v\big)$, which is very tiny in weak coupling, where $g(\varepsilon_{\rm F})\,v \ll 1$. Note that the ground state is largely unaffected for electronic states in the vicinity of this (unphysical) energy discontinuity. The coherence factors are distinguished from those of a Fermi liquid only in regions where $\langle c^\dagger_{\boldsymbol{k}\uparrow} c^\dagger_{-\boldsymbol{k}\downarrow}\rangle$ is appreciable, which requires $\xi_{\boldsymbol{k}}$ to be on the order of $\Delta_{\boldsymbol{k}}$. This only happens when $|k - k_{\rm F}| \lesssim \Delta_0/\hbar v_{\rm F}$, as discussed in the previous paragraph. In a more physical model, the interaction $V_{\boldsymbol{k},\boldsymbol{k}'}$ and the solution $\Delta_{\boldsymbol{k}}$ would not be discontinuous functions of $\boldsymbol{k}$.

5.11 Number and Phase

The BCS ground state wavefunction $|\,\mathrm{G}\,\rangle$ was given in Eqn. 5.137. Consider the state

$$|\,\mathrm{G}(\alpha)\,\rangle = \prod_{\boldsymbol{k}} \big(\cos\vartheta_{\boldsymbol{k}} - e^{i\alpha}\, e^{i\phi_{\boldsymbol{k}}} \sin\vartheta_{\boldsymbol{k}}\, c^\dagger_{\boldsymbol{k}\uparrow}\, c^\dagger_{-\boldsymbol{k}\downarrow}\big)\,|\,0\,\rangle \quad . \tag{5.157}$$

This is the ground state when the gap function $\Delta_{\boldsymbol{k}}$ is multiplied by the uniform phase factor $e^{i\alpha}$. We shall here abbreviate $|\,\alpha\,\rangle \equiv |\,\mathrm{G}(\alpha)\,\rangle$.

Now consider the action of the number operator on $|\,\alpha\,\rangle$:

$$\begin{aligned}
\hat{N}\,|\,\alpha\,\rangle &= \sum_{\boldsymbol{k}} \big(c^\dagger_{\boldsymbol{k}\uparrow} c_{\boldsymbol{k}\uparrow} + c^\dagger_{-\boldsymbol{k}\downarrow} c_{-\boldsymbol{k}\downarrow}\big)|\,\alpha\,\rangle \\
&= -2\sum_{\boldsymbol{k}} e^{i\alpha}\, e^{i\phi_{\boldsymbol{k}}}\, \sin\vartheta_{\boldsymbol{k}}\, c^\dagger_{\boldsymbol{k}\uparrow}\, c^\dagger_{-\boldsymbol{k}\downarrow} \prod_{\boldsymbol{k}'\neq\boldsymbol{k}} \big(\cos\vartheta_{\boldsymbol{k}'} - e^{i\alpha}\, e^{i\phi_{\boldsymbol{k}'}} \sin\vartheta_{\boldsymbol{k}'}\, c^\dagger_{\boldsymbol{k}'\uparrow}\, c^\dagger_{-\boldsymbol{k}'\downarrow}\big)\,|\,0\,\rangle \\
&= \frac{2}{i}\,\frac{\partial}{\partial\alpha}\,|\,\alpha\,\rangle \quad .
\end{aligned} \tag{5.158}$$

If we define the number of Cooper pairs as $\hat{M} \equiv \frac{1}{2}\hat{N}$, then we may identify $\hat{M} = \frac{1}{i}\frac{\partial}{\partial\alpha}$. Furthermore, we may project $|\,\mathrm{G}\,\rangle$ onto a state of definite particle number by defining

$$|\,M\,\rangle = \int\limits_{-\pi}^{\pi} \frac{d\alpha}{2\pi}\, e^{-iM\alpha}\,|\,\alpha\,\rangle \quad . \tag{5.159}$$

The state $|\,M\,\rangle$ has $N = 2M$ particles, *i.e.* M Cooper pairs. One can easily compute the number fluctuations in the state $|\,\mathrm{G}(\alpha)\,\rangle$:

$$\frac{\langle\,\alpha\,|\,\hat{N}^2\,|\,\alpha\,\rangle - \langle\,\alpha\,|\,\hat{N}\,|\,\alpha\,\rangle^2}{\langle\,\alpha\,|\,\hat{N}\,|\,\alpha\,\rangle} = \frac{2\int\! d^3\!k\, \sin^2\!\vartheta_{\boldsymbol{k}}\, \cos^2\!\vartheta_{\boldsymbol{k}}}{\int\! d^3\!k\, \sin^2\!\vartheta_{\boldsymbol{k}}} \quad . \tag{5.160}$$

Thus, $(\Delta N)_{\mathrm{RMS}} \propto \sqrt{\langle N\rangle}$. Note that $(\Delta N)_{\mathrm{RMS}}$ vanishes in the Fermi liquid state, where $\sin\vartheta_{\boldsymbol{k}}\cos\vartheta_{\boldsymbol{k}} = 0$.

5.12 Finite temperature

The gap equation at finite temperature takes the form

$$\Delta_{\boldsymbol{k}} = -\sum_{\boldsymbol{k}'} V_{\boldsymbol{k},\boldsymbol{k}'}\, \frac{\Delta_{\boldsymbol{k}'}}{2E_{\boldsymbol{k}'}}\, \tanh\!\left(\frac{E_{\boldsymbol{k}'}}{2k_{\mathrm{B}}T}\right) \quad . \tag{5.161}$$

It is easy to see that we have no solutions other than the trivial one $\Delta_{\boldsymbol{k}} = 0$ in the $T \to \infty$ limit, for the gap equation then becomes $\sum_{\boldsymbol{k}'} V_{\boldsymbol{k},\boldsymbol{k}'}\,\Delta_{\boldsymbol{k}'} = -4k_{\rm B}T\,\Delta_{\boldsymbol{k}}$, and if the eigenspectrum of $V_{\boldsymbol{k},\boldsymbol{k}'}$ is bounded, there is no solution for $k_{\rm B}T$ greater than the largest eigenvalue of $-V_{\boldsymbol{k},\boldsymbol{k}'}$.

To find the critical temperature where the gap collapses, again we assume the forms in Eqns. 5.145 and 5.146, in which case we have

$$1 = \tfrac{1}{2}\,g(\varepsilon_{\rm F})\,v \int\limits_0^{\hbar\omega_{\rm D}} \frac{d\xi}{\sqrt{\xi^2+\Delta^2}}\;\tanh\!\left(\frac{\sqrt{\xi^2+\Delta^2}}{2k_{\rm B}T}\right) \quad . \tag{5.162}$$

It is clear that $\Delta(T)$ is a decreasing function of temperature, which vanishes at $T = T_{\rm c}$, where $T_{\rm c}$ is determined by the equation

$$\int\limits_0^{\Lambda/2} ds\; s^{-1}\tanh(s) = \frac{2}{g(\varepsilon_{\rm F})\,v} \quad , \tag{5.163}$$

where $\Lambda = \hbar\omega_{\rm D}/k_{\rm B}T_{\rm c}$. One finds, for large Λ ,

$$\begin{aligned} I(\Lambda) = \int\limits_0^{\Lambda/2} ds\; s^{-1}\tanh(s) &= \ln\big(\tfrac{1}{2}\Lambda\big)\tanh\big(\tfrac{1}{2}\Lambda\big) - \int\limits_0^{\Lambda/2} ds\;\frac{\ln s}{\cosh^2 s} \\ &= \ln\Lambda + \ln\big(2\,e^{\rm C}/\pi\big) + \mathcal{O}\big(e^{-\Lambda/2}\big) \quad , \end{aligned} \tag{5.164}$$

where $\mathrm{C} = 0.57721566\ldots$ is the Euler-Mascheroni constant. One has $2\,e^{\rm C}/\pi = 1.134$, so

$$k_{\rm B}T_{\rm c} = 1.134\,\hbar\omega_{\rm D}\,e^{-2/g(\varepsilon_{\rm F})\,v} \quad . \tag{5.165}$$

Comparing with Eqn. 5.149, we obtain the famous result

$$2\Delta(0) = 2\pi e^{-\rm C}\,k_{\rm B}T_{\rm c} \simeq 3.52\,k_{\rm B}T_{\rm c} \quad . \tag{5.166}$$

As we shall derive presently, just below the critical temperature, one has

$$\Delta(T) = 1.734\,\Delta(0)\left(1-\frac{T}{T_{\rm c}}\right)^{1/2} \simeq 3.06\,k_{\rm B}T_{\rm c}\left(1-\frac{T}{T_{\rm c}}\right)^{1/2} \quad . \tag{5.167}$$

5.12.1 Isotope effect

The prefactor in Eqn. 5.165 is proportional to the Debye energy $\hbar\omega_{\rm D}$. Thus,

$$\ln T_{\rm c} = \ln\omega_{\rm D} - \frac{2}{g(\varepsilon_{\rm F})\,v} + \text{const.} \quad . \tag{5.168}$$

If we imagine varying only the mass of the ions, via isotopic substitution, then $g(\varepsilon_{\rm F})$ and v do not change, and we have

$$\delta\ln T_{\rm c} = \delta\ln\omega_{\rm D} = -\tfrac{1}{2}\,\delta\ln M \quad , \tag{5.169}$$

where M is the ion mass. Thus, isotopically increasing the ion mass leads to a concomitant reduction in $T_{\rm c}$ according to BCS theory. This is fairly well confirmed in experiments on low $T_{\rm c}$ materials.

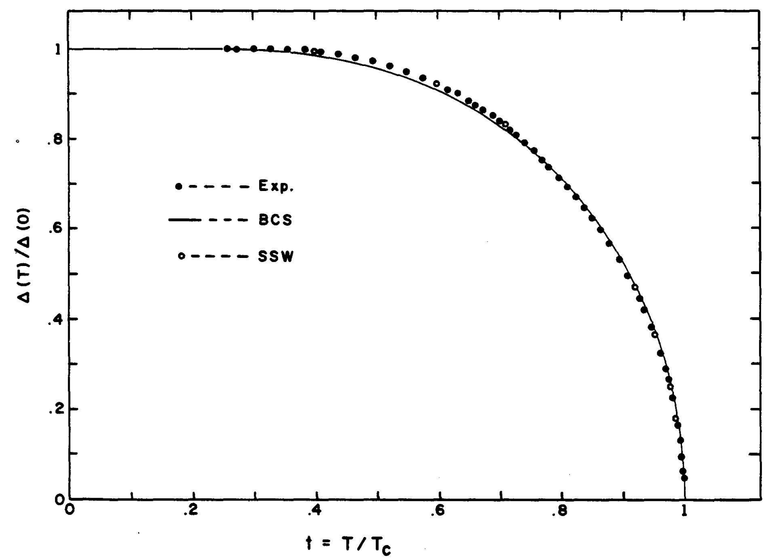

Figure 5.10: Temperature dependence of the energy gap in Pb as determined by tunneling *versus* prediction of BCS theory. From R. F. Gasparovic, B. N. Taylor, and R. E. Eck, *Sol. State Comm.* **4**, 59 (1966). Deviations from the BCS theory are accounted for by numerical calculations at strong coupling by Swihart, Scalapino, and Wada (1965).

5.12.2 Landau free energy of a superconductor

Quantum statistical mechanics of noninteracting fermions applied to $\hat{K}_{\rm BCS}$ in Eqn. 5.136 yields the Landau free energy

$$\Omega_{\rm s} = -2k_{\rm B}T\sum_{\boldsymbol{k}} \ln\big(1+e^{-E_{\boldsymbol{k}}/k_{\rm B}T}\big) + \sum_{\boldsymbol{k}} \Bigg\{ \xi_{\boldsymbol{k}} - E_{\boldsymbol{k}} + \frac{|\Delta_{\boldsymbol{k}}|^2}{2E_{\boldsymbol{k}}} \tanh\bigg(\frac{E_{\boldsymbol{k}}}{2k_{\rm B}T}\bigg)\Bigg\} \quad . \tag{5.170}$$

The corresponding result for the normal state ($\Delta_{\boldsymbol{k}} = 0$) is

$$\Omega_{\rm n} = -2k_{\rm B}T\sum_{\boldsymbol{k}} \ln\big(1+e^{-|\xi_{\boldsymbol{k}}|/k_{\rm B}T}\big) + \sum_{\boldsymbol{k}} \Big(\xi_{\boldsymbol{k}} - |\xi_{\boldsymbol{k}}|\Big) \quad . \tag{5.171}$$

Thus, the difference is

$$\Omega_{\rm s} - \Omega_{\rm n} = -2k_{\rm B}T\sum_{\boldsymbol{k}} \ln\Bigg(\frac{1+e^{-E_{\boldsymbol{k}}/k_{\rm B}T}}{1+e^{-|\xi_{\boldsymbol{k}}|/k_{\rm B}T}}\Bigg) + \sum_{\boldsymbol{k}} \Bigg\{ |\xi_{\boldsymbol{k}}| - E_{\boldsymbol{k}} + \frac{|\Delta_{\boldsymbol{k}}|^2}{2E_{\boldsymbol{k}}} \tanh\bigg(\frac{E_{\boldsymbol{k}}}{2k_{\rm B}T}\bigg)\Bigg\} \quad . \tag{5.172}$$

We now invoke the model interaction in Eqn. 5.145. Recall that the solution to the gap equation is of the form $\Delta_{\boldsymbol{k}}(T) = \Delta(T)\,\Theta\big(\hbar\omega_{\rm D} - |\xi_{\boldsymbol{k}}|\big)$. We then have

$$\begin{aligned}\frac{\Omega_{\rm s}-\Omega_{\rm n}}{V} &= \frac{\Delta^2}{v} - \tfrac{1}{2}\,g(\varepsilon_{\rm F})\,\Delta^2\left\{\frac{\hbar\omega_{\rm D}}{\Delta}\sqrt{1+\left(\frac{\hbar\omega_{\rm D}}{\Delta}\right)^2} - \left(\frac{\hbar\omega_{\rm D}}{\Delta}\right)^2 + \sinh^{-1}\!\left(\frac{\hbar\omega_{\rm D}}{\Delta}\right)\right\} \\ &\qquad - 2\,g(\varepsilon_{\rm F})\,k_{\rm B}T\,\Delta\int_0^\infty\! ds\;\ln\Big(1+e^{-\sqrt{1+s^2}\,\Delta/k_{\rm B}T}\Big) + \tfrac{1}{6}\,\pi^2\,g(\varepsilon_{\rm F})\,(k_{\rm B}T)^2 \quad .\end{aligned} \tag{5.173}$$

We will now expand this result in the vicinity of $T=0$ and $T=T_{\rm c}$. In the weak coupling limit, throughout this entire region we have $\Delta \ll \hbar\omega_{\rm D}$, so we proceed to expand in the small ratio, writing

$$\begin{aligned}\frac{\Omega_{\rm s}-\Omega_{\rm n}}{V} &= -\tfrac{1}{4}\,g(\varepsilon_{\rm F})\,\Delta^2\left\{1+2\ln\!\left(\frac{\Delta_0}{\Delta}\right) - \left(\frac{\Delta}{2\hbar\omega_{\rm D}}\right)^2 + \mathcal{O}\big(\Delta^4\big)\right\} \\ &\qquad - 2\,g(\varepsilon_{\rm F})\,k_{\rm B}T\Delta\int_0^\infty\! ds\;\ln\Big(1+e^{-\sqrt{1+s^2}\,\Delta/k_{\rm B}T}\Big) + \tfrac{1}{6}\,\pi^2\,g(\varepsilon_{\rm F})\,(k_{\rm B}T)^2 \quad .\end{aligned} \tag{5.174}$$

where $\Delta_0 = \Delta(0) = \pi e^{-{\rm C}}\,k_{\rm B}T_{\rm c}$.

$\underline{T \to 0^+}$

In the limit $T\to 0$, we find

$$\begin{aligned}\frac{\Omega_{\rm s}-\Omega_{\rm n}}{V} &= -\tfrac{1}{4}\,g(\varepsilon_{\rm F})\,\Delta^2\left\{1+2\ln\!\left(\frac{\Delta_0}{\Delta}\right) + \mathcal{O}\big(\Delta^2\big)\right\} \\ &\qquad - g(\varepsilon_{\rm F})\sqrt{2\pi(k_{\rm B}T)^3\Delta}\;e^{-\Delta/k_{\rm B}T} + \tfrac{1}{6}\,\pi^2\,g(\varepsilon_{\rm F})\,(k_{\rm B}T)^2 \quad .\end{aligned} \tag{5.175}$$

Differentiating the above expression with respect to Δ, we obtain a self-consistent equation for the gap $\Delta(T)$ at low temperatures:

$$\ln\!\left(\frac{\Delta}{\Delta_0}\right) = -\sqrt{\frac{2\pi k_{\rm B}T}{\Delta}}\;e^{-\Delta/k_{\rm B}T}\left(1-\frac{k_{\rm B}T}{2\Delta}+\ldots\right) \tag{5.176}$$

Thus,

$$\Delta(T) = \Delta_0 - \sqrt{2\pi\Delta_0 k_{\rm B}T}\;e^{-\Delta_0/k_{\rm B}T} + \ldots \quad . \tag{5.177}$$

Substituting this expression into Eqn. 5.175, we find

$$\frac{\Omega_{\rm s}-\Omega_{\rm n}}{V} = -\tfrac{1}{4}\,g(\varepsilon_{\rm F})\,\Delta_0^2 - g(\varepsilon_{\rm F})\sqrt{2\pi\Delta_0\,(k_{\rm B}T)^3}\;e^{-\Delta_0/k_{\rm B}T} + \tfrac{1}{6}\,\pi^2\,g(\varepsilon_{\rm F})\,(k_{\rm B}T)^2 \quad . \tag{5.178}$$

Equating this with the condensation energy density, $-H_{\rm c}^2(T)/8\pi$, and invoking our previous result, $\Delta_0 = \pi e^{-{\rm C}}\,k_{\rm B}T_{\rm c}$, we find

$$H_{\rm c}(T) = H_{\rm c}(0)\left\{1-\overbrace{\tfrac{1}{3}\,e^{2{\rm C}}}^{\approx 1.057}\left(\frac{T}{T_{\rm c}}\right)^2+\ldots\right\} \quad , \tag{5.179}$$

where $H_{\rm c}(0) = \sqrt{2\pi\,g(\varepsilon_{\rm F})}\;\Delta_0$.

<u>$T \to T_c^-$</u>

In this limit, one finds

$$\frac{\Omega_s - \Omega_n}{V} = \tfrac{1}{2}\, g(\varepsilon_F)\, \ln\!\left(\frac{T}{T_c}\right)\Delta^2 + \frac{7\,\zeta(3)}{32\pi^2}\,\frac{g(\varepsilon_F)}{(k_B T)^2}\,\Delta^4 + \mathcal{O}\big(\Delta^6\big) \quad . \tag{5.180}$$

This is of the standard Landau form,

$$\frac{\Omega_s - \Omega_n}{V} = \tilde{a}(T)\,\Delta^2 + \tfrac{1}{2}\,\tilde{b}(T)\,\Delta^4 \quad , \tag{5.181}$$

with coefficients

$$\tilde{a}(T) = \tfrac{1}{2}\, g(\varepsilon_F)\left(\frac{T}{T_c} - 1\right) \qquad , \qquad \tilde{b} = \frac{7\,\zeta(3)}{16\pi^2}\,\frac{g(\varepsilon_F)}{(k_B T_c)^2} \quad , \tag{5.182}$$

working here to lowest nontrivial order in $T - T_c$. The head capacity jump, according to Eqn. 1.44, is

$$c_s(T_c^-) - c_n(T_c^+) = \frac{T_c\big[\tilde{a}'(T_c)\big]^2}{\tilde{b}(T_c)} = \frac{4\pi^2}{7\,\zeta(3)}\, g(\varepsilon_F)\, k_B^2 T_c \quad . \tag{5.183}$$

The normal state heat capacity at $T = T_c$ is $c_n = \frac{1}{3}\pi^2 g(\varepsilon_F)\, k_B^2 T_c$, hence

$$\frac{c_s(T_c^-) - c_n(T_c^+)}{c_n(T_c^+)} = \frac{12}{7\,\zeta(3)} = 1.43 \quad . \tag{5.184}$$

This universal ratio is closely reproduced in many experiments; see, for example, Fig. 5.11.

The order parameter is given by

$$\Delta^2(T) = -\frac{\tilde{a}(T)}{\tilde{b}(T)} = \frac{8\pi^2 (k_B T_c)^2}{7\,\zeta(3)}\left(1 - \frac{T}{T_c}\right) = \frac{8\,e^{2\mathrm{C}}}{7\,\zeta(3)}\left(1 - \frac{T}{T_c}\right)\Delta^2(0) \quad , \tag{5.185}$$

where we have used $\Delta(0) = \pi\, e^{-\mathrm{C}}\, k_B T_c$. Thus,

$$\frac{\Delta(T)}{\Delta(0)} = \overbrace{\left(\frac{8\,e^{2\mathrm{C}}}{7\,\zeta(3)}\right)^{1/2}}^{\approx\, 1.734}\left(1 - \frac{T}{T_c}\right)^{1/2} \quad . \tag{5.186}$$

The thermodynamic critical field just below T_c is obtained by equating the energies $-\tilde{a}^2/2\tilde{b}$ and $-H_c^2/8\pi$. Therefore

$$\frac{H_c(T)}{H_c(0)} = \left(\frac{8\,e^{2\mathrm{C}}}{7\,\zeta(3)}\right)^{1/2}\left(1 - \frac{T}{T_c}\right) \simeq 1.734\left(1 - \frac{T}{T_c}\right) \quad . \tag{5.187}$$

5.13 Paramagnetic Susceptibility

Suppose we add a weak magnetic field, the effect of which is described by the perturbation Hamiltonian

$$\hat{H}_1 = -\mu_B H \sum_{\boldsymbol{k},\sigma} \sigma\, c^\dagger_{\boldsymbol{k}\sigma}\, c_{\boldsymbol{k}\sigma} = -\mu_B H \sum_{\boldsymbol{k},\sigma} \sigma\, \gamma^\dagger_{\boldsymbol{k}\sigma}\, \gamma_{\boldsymbol{k}\sigma} \quad . \tag{5.188}$$

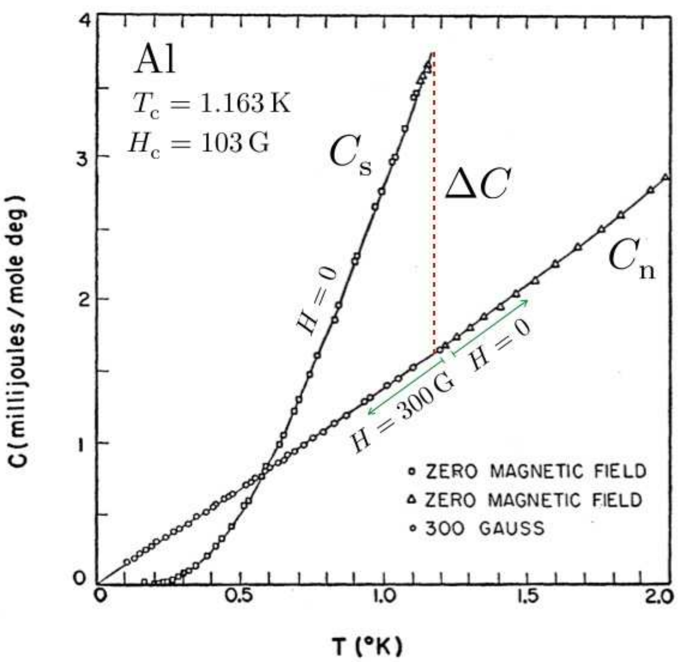

Figure 5.11: Heat capacity in aluminum at low temperatures, from N. K. Phillips, *Phys. Rev. 114*, **3** (1959). The zero field superconducting transition occurs at $T_c = 1.163\,\text{K}$. Comparison with normal state C below T_c is made possible by imposing a magnetic field $H > H_c$. This destroys the superconducting state, but has little effect on the metal. A jump ΔC is observed at T_c, quantitatively in agreement BCS theory.

The shift in the Landau free energy due to the field is then $\Delta\Omega_s(T,V,\mu,H) = \Omega_s(T,V,\mu,H) - \Omega_s(T,V,\mu,0)$. We have

$$\begin{aligned}\Delta\Omega_s(T,V,\mu,H) &= -k_B T \sum_{\boldsymbol{k},\sigma} \ln\left(\frac{1+e^{-\beta(E_{\boldsymbol{k}}+\sigma\mu_B H)}}{1+e^{-\beta E_{\boldsymbol{k}}}}\right) \\ &= -\beta\,(\mu_B H)^2 \sum_{\boldsymbol{k}} \frac{e^{\beta E_{\boldsymbol{k}}}}{\left(e^{\beta E_{\boldsymbol{k}}}+1\right)^2} + \mathcal{O}(H^4) \quad .\end{aligned} \tag{5.189}$$

The magnetic susceptibility is then

$$\chi_s = -\frac{1}{V}\frac{\partial^2 \Delta\Omega_s}{\partial H^2} = g(\varepsilon_F)\,\mu_B^2\,\mathcal{Y}(T) \quad , \tag{5.190}$$

where

$$\mathcal{Y}(T) = 2\int_0^\infty d\xi \left(-\frac{\partial f}{\partial E}\right) = \tfrac{1}{2}\beta \int_0^\infty d\xi\,\text{sech}^2\Big(\tfrac{1}{2}\beta\sqrt{\xi^2+\Delta^2}\Big) \tag{5.191}$$

is the *Yoshida function*. Note that $\mathcal{Y}(T_c) = \int_0^\infty du\,\text{sech}^2 u = 1$, and $\mathcal{Y}(T\to 0) \simeq (2\pi\beta\Delta)^{1/2}\exp(-\beta\Delta)$, which is exponentially suppressed. Since $\chi_n = g(\varepsilon_F)\,\mu_B^2$ is the normal state Pauli susceptibility, we have that the ratio of superconducting to normal state susceptibilities is $\chi_s(T)/\chi_n(T) = \mathcal{Y}(T)$. This vanishes exponentially as $T \to 0$ because it takes a finite energy Δ to create a Bogoliubov quasiparticle out of the spin singlet BCS ground state.

In metals, the nuclear spins experience a shift in their resonance energy in the presence of an external magnetic field, due to their coupling to conduction electrons via the hyperfine interaction. This is called the *Knight shift*, after Walter Knight, who first discovered this phenomenon at Berkeley in 1949. The magnetic field polarizes the metallic conduction electrons, which in turn impose an extra effective field, through the hyperfine coupling, on the nuclei. In superconductors, the electrons remain unpolarized in a weak magnetic field owing to the superconducting gap. Thus there is no Knight shift.

As we have seen from the Ginzburg-Landau theory, when the field is sufficiently strong, superconductivity is destroyed (type I), or there is a mixed phase at intermediate fields where magnetic flux penetrates the superconductor in the form of vortex lines. Our analysis here is valid only for weak fields.