Physics 127c: Statistical Mechanics

Superconductivity: Thermodynamics

We could continue to evaluate the finite temperature thermodynamics by enumerating the states by hand. However it is more convenient to switch to the notation used in Homework 2. There you showed that the Hamiltonian for the excited states can be reduced to

$$H_{eff} = \text{const} + \sum_{\vec{k}} E_k(\alpha^+_{\mathbf{k}}\alpha_{\mathbf{k}} + \beta^+_{-\mathbf{k}}\beta_{-\mathbf{k}}) \tag{1}$$

with $\alpha_{\mathbf{k}}$, $\beta_{\mathbf{k}}$ independent Fermion operators related to the original operators by the canonical transformation

$$\begin{aligned} \alpha_{\vec{k}} &= u_k a_{\mathbf{k}\uparrow} - v_k a^+_{-\mathbf{k}\downarrow}, \\ \beta_{-\vec{k}} &= u_k a_{-\mathbf{k}\downarrow} + v_k a^+_{\mathbf{k}\uparrow}, \end{aligned} \tag{2}$$

and the inverse

$$a_{\vec{k}\uparrow} = u_k\alpha_{\mathbf{k}} + v_k\beta^+_{-\mathbf{k}}, \tag{3}$$

$$a_{-\vec{k}\downarrow} = u_k\beta_{-\mathbf{k}} - v_k\alpha^+_{\mathbf{k}}, \tag{4}$$

with

$$u_k = \sqrt{\frac{1}{2}(1+\frac{\varepsilon_k}{E_k})} \tag{5}$$

$$v_k = \sqrt{\frac{1}{2}(1-\frac{\varepsilon_k}{E_k})} \tag{6}$$

and $E_k = \sqrt{\varepsilon_k^2 + \Delta_k^2}$. The gap equation is

$$\Delta_k = -\frac{1}{V}\sum_{\mathbf{k}'} \tilde{u}(\mathbf{k},\mathbf{k}') \left\langle a_{-\mathbf{k}'\downarrow} a_{\mathbf{k}'\uparrow} \right\rangle. \tag{7}$$

The averages of combinations of the $a_{\mathbf{k}}$ operators can be found from the result for the statistically independent Fermion occupation numbers

$$\left\langle \alpha^+_{\mathbf{k}}\alpha_{\mathbf{k}'} \right\rangle = \left\langle \beta^+_{\mathbf{k}}\beta_{\mathbf{k}'} \right\rangle = f(E_k)\delta_{\mathbf{k}\mathbf{k}'}, \tag{8}$$

whereas

$$0 = \left\langle \alpha^+_{\mathbf{k}}\beta_{\mathbf{k}'} \right\rangle = \left\langle \alpha^+_{\mathbf{k}}\beta^+_{\mathbf{k}'} \right\rangle = \ldots \text{etc}, \tag{9}$$

with $f(E_k)$ the Fermi function

$$f(E_k) = \frac{1}{e^{E_k/k_B T}+1}. \tag{10}$$

For example

$$\left\langle a_{-\mathbf{k}\downarrow}a_{\mathbf{k}\uparrow} \right\rangle = \left\langle \left(u_k\beta_{-\mathbf{k}} - v_k\alpha^+_{\mathbf{k}}\right)\left(u_k\alpha_{\mathbf{k}} + v_k\beta^+_{-\mathbf{k}}\right) \right\rangle \tag{11}$$

$$= u_k v_k \left\langle -\alpha^+_{\mathbf{k}}\alpha_{\mathbf{k}} + \beta_{-\mathbf{k}}\beta^+_{-\mathbf{k}} \right\rangle, \tag{12}$$

since these are the only nonzero averages. Thus

$$\left\langle a_{-\mathbf{k}\downarrow}a_{\mathbf{k}\uparrow} \right\rangle = u_k v_k \left(-\frac{2}{e^{\beta E_k}+1} + 1\right) \tag{13}$$

$$= \frac{\Delta_k^2}{2E_k}\tanh\left(\frac{1}{2}\beta E_k\right). \tag{14}$$

Other averages can be calculated similarly.

Gap Equation

The gap equation at nonzero temperature is then

$$\Delta_k = -\frac{1}{V}\sum_{\mathbf{k}'} \tilde{u}(\mathbf{k},\mathbf{k}') \left\langle a_{-\mathbf{k}'\downarrow} a_{\mathbf{k}'\uparrow} \right\rangle, \tag{15}$$

$$= -\frac{1}{V}\sum_{\mathbf{k}'} \tilde{u}(\mathbf{k},\mathbf{k}') \frac{\Delta_{k'}}{2E_{k'}} \tanh\left(\frac{1}{2}\beta E_{k'}\right). \tag{16}$$

For the separable potential

$$\tilde{u}(\vec{k}-\vec{k}') \rightarrow \begin{cases} -g & \text{for} \quad |k-k_F|, |k'-k_F| < k_c \\ 0 & \text{otherwise} \end{cases}, \tag{17}$$

the gap equation reduces to the equation for the temperature dependent energy gap $\Delta(T)$

$$1 = N(0)g \int_{-\hbar\omega_c}^{\hbar\omega_c} \frac{1}{2E} \tanh\left(\frac{1}{2}\beta E\right) d\xi, \tag{18}$$

with $E = \sqrt{\xi^2 + \Delta^2(T)}$.

The transition temperature T_c is when $\Delta \rightarrow 0$, i.e.

$$1 = N(0)g \int_{-\hbar\omega_c}^{\hbar\omega_c} \frac{1}{2\xi} \tanh\left(\frac{1}{2}\beta_c \xi\right) d\xi. \tag{19}$$

Without the tanh the integral would depend logarithmically on $\hbar\omega_c$ and would diverge logarithmically from the $\xi \rightarrow 0$ region. The tanh cuts off the divergence at $\xi \sim k_B T_c$ so that the integral is about $\ln(\hbar\omega_c / k_B T_c)$. In the weak coupling limit $k_B T_c \ll \hbar\omega_c$ the integral can be evaluated precisely to give

$$k_B T_c \simeq 1.14\hbar\omega_c e^{-1/N(0)g}. \tag{20}$$

The zero temperature gap and the transition temperature are related by

$$\frac{2\Delta_0}{k_B T_c} \simeq 3.52, \tag{21}$$

a universal result in the weak coupling limit independent of the parameters and the cutoff frequency $\hbar\omega_c$.

In fact, although Eq. (18) for $\Delta(T)$ appears to depend on the cutoff, if we subtract Eq. (19) we get

$$\int_{-\infty}^{\infty} \left[\frac{1}{\sqrt{\xi^2 + \Delta^2(T)}} \tanh\left(\frac{1}{2}\beta\sqrt{\xi^2 + \Delta^2(T)}\right) - \frac{1}{\xi} \tanh\left(\frac{1}{2}\beta_c \xi\right) \right] d\xi = 0, \tag{22}$$

where since the integrand now goes to zero for $\xi \geq \Delta, k_B T_c$ the limits can be replaced by $\pm\infty$. This is a universal equation for $\Delta / k_B T_c$ as a function of T/T_c. Although we have derived this for the special separable potential, the result actually just depends on the weak coupling assumption $k_B T_c \ll \hbar\omega_c$. Thus Eq. (22) gives a quantitative prediction for many experimental superconductors.

Energetics

It is straightforward, although somewhat tedious, to calculate the free energy $E - \mu N - TS$. The kinetic energy can be written as

$$\langle E_{\text{kin}} - \mu N \rangle = \sum_{\mathbf{k}} \xi_k \left[\left\langle a^+_{\mathbf{k}\uparrow} a_{\mathbf{k}\uparrow} \right\rangle + \left\langle a^+_{-\mathbf{k}\downarrow} a_{-\mathbf{k}\downarrow} \right\rangle \right] \tag{23}$$

$$= \sum_{\mathbf{k}} \xi_k \left[1 - \frac{\xi_k}{E_k} \tanh\left(\frac{1}{2} \beta E_k \right) \right]. \tag{24}$$

The pairing energy is

$$\left\langle E_{\text{pot}} \right\rangle = \frac{1}{V} \sum_{\mathbf{k},\mathbf{k}'} \tilde{u}(\mathbf{k}, \mathbf{k}') \left\langle a^+_{\mathbf{k}'\uparrow} a^+_{-\mathbf{k}'\downarrow} \right\rangle \left\langle a_{-\mathbf{k}\downarrow} a_{\mathbf{k}\uparrow} \right\rangle \tag{25}$$

$$= -\sum_{\mathbf{k}} \frac{\Delta_k^2}{2E_k} \tanh\left(\frac{1}{2} \beta E_k \right). \tag{26}$$

Using the gap equation to simplify the double sum.

The entropy is $-k_B \sum_n p_n \ln p_n$ for the two sets of noninteracting Fermions $\alpha_{\mathbf{k}}$ and $\beta_{\mathbf{k}}$: for each there is the one fermion state with probability $f(E_k)$ and the no Fermion state with probability $1 - f(E_k)$:

$$S = -2k_B \sum_{\mathbf{k}} f(E_k) \ln f(E_k) + (1 - f(E_k)) \ln (1 - f(E_k)). \tag{27}$$

At zero temperature the entropy term disappears and then

$$\langle E - \mu N \rangle = \sum_{\mathbf{k}} \xi_k \left(1 - \frac{\xi_k}{E_k} \right) - \frac{\Delta_k^2}{2E_k}. \tag{28}$$

We are more interested in the difference in the energy from what it would be in the normal state, which is given by the same expression with $\Delta_k \to 0$, $E_k \to |\xi_k|$. Thus

$$\langle E - \mu N \rangle_s - \langle E - \mu N \rangle_n = \sum_{\mathbf{k}} \left[|\xi_k| - \frac{\xi_k^2}{E_k} - \frac{\Delta_k^2}{2E_k} \right] \tag{29}$$

$$= V N(0) \int_{-\hbar\omega_c}^{\hbar\omega_c} \left[|\xi| - \frac{\xi^2}{\sqrt{\xi^2 + \Delta_0^2}} - \frac{\Delta_0^2}{2\sqrt{\xi^2 + \Delta_0^2}} \right] d\xi \tag{30}$$

$$= -\frac{1}{2} N(0) V \Delta_0^2. \tag{31}$$

Since $N(0) \sim N\varepsilon_F/V$ the lowering of the energy is of order $N\Delta_0^2/\varepsilon_F$. This is smaller than the value $N\Delta$ we might have expected; this is because only a fraction of order Δ/ε_F of the Fermi sea is affected by the pairing.

Order Parameter and Supercurrents

We would like some macroscopic order parameter that captures the new features of the BCS state, in particular the nonzero values of $\left\langle a_{\mathbf{k}\uparrow} a_{-\mathbf{k}\downarrow} \right\rangle$ in the band of states around the Fermi surface.

For the equilibrium state a convenient definition is

$$\Psi = \sum_{\text{band}} \left\langle a_{-\mathbf{k}\downarrow} a_{\mathbf{k}\uparrow} \right\rangle \tag{32}$$

$$= \sum_{\text{band}} \frac{\Delta_k}{2E_k} \tanh(\frac{1}{2}\beta E_k) \tag{33}$$

$$= N(0)\Delta \int_{-\hbar\omega_c}^{\hbar\omega_c} \frac{1}{2E} \tanh(\frac{1}{2}\beta E) d\xi \tag{34}$$

(where I have retained the phase factors and Δ is now complex with $E = \sqrt{\xi^2 + |\Delta|^2}$). Since the integral is a number that does not vary much with T or Δ, and the normalization of the order parameter is arbitrary, often the complex gap parameter Δ is used as the order parameter.

Just as in a superfluid, a spatial gradient of the phase of the order parameter corresponds to a state with mass flow, and, because the particles are charged, electric current. These currents are in an equilibrium state, and so are supercurrents. The flowing state corresponds to pair condensation in a state with center of mass momentum $\hbar\mathbf{q}$, i.e. the pair state is

$$\Phi(\mathbf{r}_1.\mathbf{r}_2) = e^{i\mathbf{q}(\mathbf{r}_1+\mathbf{r}_2)/2} \phi(\mathbf{r}_1 - \mathbf{r}_2)(\uparrow\downarrow - \downarrow\uparrow) \tag{35}$$

$$= \sum_{\mathbf{k}} e^{i(\mathbf{k}+\mathbf{q}/2)\cdot\mathbf{r}_1} e^{i(-\mathbf{k}+\mathbf{q}/2)\cdot\mathbf{r}_2} \chi(k)(\uparrow\downarrow - \downarrow\uparrow) \tag{36}$$

so that now the states $\mathbf{k}+\mathbf{q}/2, \uparrow$ and $-\mathbf{k}+\mathbf{q}/2, \downarrow$ are occupied or empty together in the BCS wave function. The order parameter would be defined generally as

$$\Psi(\mathbf{r}) = \sum_{\mathbf{q}} \sum_{\text{band}} \left\langle a_{-\mathbf{k}+\mathbf{q}/2,\downarrow} a_{\mathbf{k}+\mathbf{q}/2,\uparrow} \right\rangle e^{i\mathbf{q}\cdot\mathbf{r}}, \tag{37}$$

and in the special case of uniform flow $\Psi = |\Psi| e^{i\phi(r)}$ with $\phi = \mathbf{q}\cdot\mathbf{r}$. In a translationally invariant system and at zero temperature, the paired state is just a shift in momentum space by $\hbar\mathbf{q}/2$ of the ground state, and so the total momentum is $N\hbar\mathbf{q}/2$. Thus we can write for the electric current density in terms of the phase of the order parameter

$$\mathbf{j} = -n_s \frac{e\hbar}{2m} \nabla\phi, \tag{38}$$

with $n_s \to n = N/V$ for a translationally invariant system at $T = 0$.

Equation (38) is not yet quite right. Physical quantities such as the electric current must be *gauge invariant* but the quantum mechanical phase is not: a change of the gauge of the electromagnetic vector potential $\mathbf{A} \to \mathbf{A} + \nabla a(\mathbf{r})$ with a any function leads to a change in the phase of the wave function or annihilation operator of a particle of charge Q by $\psi \to \psi e^{iQa/\hbar c}$. Thus the current expression must take the gauge invariant form

$$\mathbf{j} = -n_s \frac{e\hbar}{2m} \left(\nabla\phi + \frac{2e}{\hbar c}\mathbf{A} \right) \tag{39}$$

where the factor of 2 multiplying e is because ϕ is the phase of a pair wave function. (I am using e as a positive quantity, so that the electron charge is $-e$.) It is important to note that his factor of 2 is exact, depending only on gauge invariance arguments. The factor outside the bracket only has significance as a whole. For a translationally invariant system Galilean invariance shows that including the factor of $2m$ from the pairing leads to the convenient result of $n_s \to n$ at zero temperature. However, the presence of a lattice for examle eliminates this argument, and then only the combination $n_s/2m$ is physically relevant so that the precise assignment of a "mass" is irrelevant.

Equation (39) is already enough to give us a key feature of the superconducting state: the *Meissner effect*. A superconductor is a perfect diamagnet and will expel any magnetic field from its interior. Equation (39) shows us that

$$\nabla \times \mathbf{j} = -\frac{n_s e^2}{mc}\mathbf{B}, \tag{40}$$

a result known as the *London equation*. Coupled with the Maxwell equations

$$\nabla \times \mathbf{B} = \frac{4\pi}{c}\mathbf{j} \tag{41}$$

$$\nabla \cdot \mathbf{B} = 0 \tag{42}$$

this gives

$$\nabla^2 \mathbf{B} = \lambda^{-2}\mathbf{B}, \tag{43}$$

with λ the *London penetration length*

$$\lambda^2 = \frac{mc^2}{4\pi n_s e^2} = \frac{\alpha^2}{4\pi}\frac{1}{n_s a_0}, \tag{44}$$

with α the fine structure constant and a_0 the Bohr radius. The solutions to Eq. (43) are exponentially decaying with the decay length λ, so in the bulk of a superconductor B, and therefore also the current $\mathbf{j}$, go to zero. Note that the Meissner effect is more than just perfect conductivity, which would imply that on turning on a magnetic field in the superconducting state, eddy currents would stop the field from invading the superconductor. The Meissner effect means that the field is actively expelled, e.g. on cooling through T_c in a magnetic field.

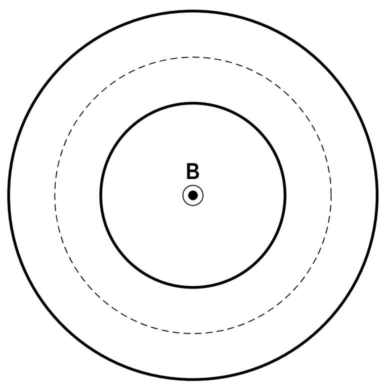

Figure 1: Flux quantization

Equation (39) also leads to the important phenomenon of flux quantization. Consider a loop of superconductor through which a magnetic field $\mathbf{B}$ passes. Except for within a few λ of the surfaces, $B, j \to 0$ in the superconductor, e.g. along the dashed contour in Fig. 1. Since the pair wave function must be single valued

$$\oint \nabla\phi \cdot \mathbf{dl} = \text{integer} \times 2\pi\,. \tag{45}$$

Then Eq. (39) with $j = 0$ gives

$$\int \mathbf{B} \cdot \mathbf{dS} = \oint \mathbf{A} \cdot \mathbf{dl} = \text{integer} \times \frac{hc}{2e} \tag{46}$$

so that the flux through a loop well within a superconductor is quantized in units of the flux quantum $hc/2e \simeq 2.07 \times 10^{-7}$gauss cm^2. This provides a scheme for very precise measurements of magnetic fields, currents, and other quantities.