

Thermodynamic and response properties of superconductors (other than EM)

Recap: For any temperature $< T_c$, superconductor characterized by ‘energy gap’ $\Delta_{\mathbf{k}}(T)$ which under normal conditions $\rightarrow \Delta(T)$ [independent of \mathbf{k}] for $|\epsilon_{\mathbf{k}}| \leq k_B T_c$. Quantity $\Delta(T)$ satisfies gap equation, $\rightarrow 0$ at T_c and $\rightarrow \text{const}$ ($= \Delta(0) \sim 1.75 k_B T_c$) for $T \rightarrow 0$. Many body density matrix is product of density matrices over ‘occupation space’ of $\mathbf{k} \uparrow, -\mathbf{k} \downarrow$ and is diagonal with respect to 4 states:

$$\begin{aligned} |\text{GP}\rangle &= u_{\mathbf{k}}|00\rangle + v_{\mathbf{k}}|11\rangle \\ |\text{EP}\rangle &= v_{\mathbf{k}}^*|00\rangle - u_{\mathbf{k}}|11\rangle & E &= 2E_{\mathbf{k}}(T) \\ |\text{BP}\rangle &= |10\rangle, |01\rangle & E &= E_{\mathbf{k}}(T) \end{aligned}$$

with $u_{\mathbf{k}}v_{\mathbf{k}} = \Delta_{\mathbf{k}}/2E_{\mathbf{k}}$: here $E_{\mathbf{k}} \equiv (\epsilon_{\mathbf{k}}^2 + |\Delta_{\mathbf{k}}|^2)^{1/2}$.

Most important expectation value characterizing the S phase is the ‘pair wave function’ $F(\mathbf{r}) \equiv \langle \psi_{\downarrow}(\mathbf{r})\psi_{\uparrow}(0) \rangle \equiv \sum_{\mathbf{k}} F_{\mathbf{k}} \exp i\mathbf{k}\mathbf{r}$, $F_{\mathbf{k}} \equiv \langle a_{-\mathbf{k}\downarrow}a_{\mathbf{k}\uparrow} \rangle$.

We saw in Lecture 6 that

$$F_{\mathbf{k}} = u_{\mathbf{k}}v_{\mathbf{k}} \tanh \beta E_{\mathbf{k}}/2 = (\Delta_{\mathbf{k}}/2E_{\mathbf{k}}) \tanh \beta E_{\mathbf{k}}/2 \quad (1)$$

and so

$$F(\mathbf{r}) = \sum_{\mathbf{k}} \frac{\Delta_{\mathbf{k}}}{2E_{\mathbf{k}}} \tanh(\beta E_{\mathbf{k}}/2) \exp i\mathbf{k}\mathbf{r} \quad (2)$$

In the case of s -wave pairing, $\Delta_{\mathbf{k}}$ is not a function of $\hat{\mathbf{k}}$ and we can write

$$\sum_{\mathbf{k}} \exp i\mathbf{k}\mathbf{r} = N(0) \int d\epsilon_{\mathbf{k}} \int \frac{d\Omega_{\mathbf{k}}}{4\pi} \exp i\mathbf{k}\mathbf{r} = N(0) \int d\epsilon_{\mathbf{k}} \frac{\sin kr}{kr} \quad (3)$$

so

$$F(\mathbf{r}) \equiv F(r) = N(0) \int d\epsilon_{\mathbf{k}} \frac{\sin kr}{kr} \frac{\Delta_{\mathbf{k}}}{2E_{\mathbf{k}}} \tanh(\beta E_{\mathbf{k}}/2) \quad (4)$$

For the moment, no restrictions on $\int d\epsilon_{\mathbf{k}}$ (though lower limit cannot be $< \mu!$). We will assume in what follows

$$T_c \ll \epsilon_F \quad (5)$$

and hence $k_F \xi^t \gg 1$ where $\xi^t \sim \hbar v_F / \Delta(0)$ (see below), as found experimentally.

3 Regimes:

- (1) For $r \lesssim k_F^{-1}$, integral dominated by $k \gtrsim k_F$, i.e. $|\epsilon| \gtrsim \epsilon_F \gg T_c$ (or Δ). In this regime, behavior of ‘exact’ $F_{\mathbf{k}}$ similar * to that of 2 particle wave function $\psi_{\mathbf{k}}$, and $E_{\mathbf{k}} \rightarrow |\epsilon_{\mathbf{k}}|$, $\tanh \beta E_{\mathbf{k}}/2 \rightarrow 1$. Hence, apart from overall constant, wave function in this regime is that of 2 particles at Fermi energy colliding in free space.

*To get this right we need to use the true potential $V_{kk'}$, not the BCS approximation to it.

- (2) For $r \gg k_F^{-1}$ but $r \ll \hbar v_F/\Delta$ ($\sim \xi$, see below), energies entering integral are mostly $\gg \Delta$, and so again can put $E_{\mathbf{k}} \rightarrow |\epsilon_{\mathbf{k}}|$, $\tanh \beta E_{\mathbf{k}}/2 \rightarrow 1$. If also $\Delta_k \sim \text{const}$ in this regime (true provided ‘range’ of $V_{\mathbf{k}\mathbf{k}'}$ $\sim \epsilon_F$), then in this regime

$$\begin{aligned} F(r) &\approx \Delta(T)N(0) \int d\epsilon_k \frac{\sin kr}{2kr|\epsilon_k|} \approx \frac{\Delta(T)N(0)}{2k_F r} \sin k_F r \int d\epsilon \frac{\cos(\epsilon r/\hbar v_F)}{|\epsilon|} \\ &\approx \frac{1}{2} \Delta(T)N(0) \frac{\sin k_F r}{k_F r} \times \ln \text{factor} \end{aligned} \quad (6)$$

where the ln factor is crudely $\sim \ln r/\xi$, ($\xi \sim \hbar v_F/\Delta$). This expression is, apart from a multiplying constant and the ln, essentially the wave function of the free particles in an s -state at the Fermi energy:

$$\psi(r) \sim \sum_{|\mathbf{k}|=k_F} e^{i\mathbf{k}\mathbf{r}} \sim \frac{\sin k_F r}{k_F r} \quad (7)$$

- (3) The most interesting regime is $r \gtrsim \hbar v_F/\Delta$. Here the relevant energies are all $\lesssim k_B T_c$ and we can write (again approximating $k \sim k_F$ in denominator, etc.)

$$\begin{aligned} F(r) &= \frac{1}{2} \Delta(T)N(0) \frac{\sin k_F r}{k_F r} \int_0^\infty d\epsilon \frac{\cos(\epsilon r/\hbar v_F) \tanh \beta \sqrt{\epsilon^2 + \Delta^2(T)}/2}{\sqrt{\epsilon^2 + \Delta^2(T)}} \\ &\equiv \Delta(T)N(0) \frac{\sin k_F r}{k_F r} \times J(r, \Delta, \beta) \end{aligned} \quad (8)$$

Since $\Delta/\Delta(0) = f(T/T_c)$, J can in fact be a function only of the variables (r/ξ') and T/T_c (for ξ' , see below).

Consider two limits:

- (1) In the limit $T \rightarrow 0$ define $\xi' \equiv \hbar v_F/\Delta(0)$, then

$$J(r) = \int_0^\infty dx \frac{\cos x}{\sqrt{x^2 + (r/\xi')^2}} \quad (9)$$

This expression is in fact the Bessel function $K_0(r/\xi')$: for small values of the argument, it diverges as $\ln(\xi'/r)$ [cf. above] while for large values we have

$$J(r) \sim \exp -\sqrt{2} r/\xi' \quad (10)$$

Thus the quantity $\xi' \equiv \hbar v_F/\Delta(0)$ characterizes (to an order of magnitude) the ‘radius’ of a Cooper pair. (In the literature, it is conventional to use the quantity $\xi_0 \equiv \hbar v_F/\pi\Delta(0) = \pi^{-1}\xi'$ known as the Pippard coherence length).

- (2) In the limit $T \rightarrow T_c$ the gap $\Delta(T)$ tends to zero, and the expression for $J(r)$ becomes

$$J(r) = \int_0^\infty \frac{d\epsilon}{\epsilon} \cos(r\epsilon/\hbar v_F) \tanh \beta_c \epsilon/2 \quad (11)$$

or introducing $\xi'' \equiv \hbar v_F / k_B T_c$ ($\sim \xi'$)

$$J(r) = \int_0^\infty \frac{dx}{x} \cos x \tanh \frac{x}{2r/\xi''} \equiv f(r/\xi'') \quad (12)$$

Again it is clear that J diverges as $\ln(r/\xi'')$ for $r \rightarrow 0$, and somewhat less obvious (but true) that it tends to zero exponentially for $r \gg \xi''$. Thus as $T \rightarrow T_c$, pair radius is $\sim \xi''$: note that this is of the same order as ξ' (or ξ_0) and doesn't diverge in this limit.

In intermediate range of T , J is somewhat complicated but still has range $\sim \xi'$.

Normalization: Consider the quantity:

$$N \equiv \int |F(\mathbf{r})|^2 d\mathbf{r} = \sum_{\mathbf{k}} \frac{\Delta_{\mathbf{k}}^2}{4E_{\mathbf{k}}^2} \tanh^2(\beta E_{\mathbf{k}}/2) \quad (13)$$

It is clear that the main contribution comes from $|\epsilon| < \Delta(T), k_B T_c$, where we can approximate $\Delta_{\mathbf{k}} \sim \Delta(T)$. Thus $N = |\Delta(T)|^2 N(0) \int_0^\infty (d\epsilon/4E^2) \tanh^2 \beta E/2$. For $T \rightarrow 0$, this is $\sim N(0)\Delta(0)$; for $T \rightarrow T_c$, it is $\sim N(0)|\Delta(T)|^2/T$. (Interpretation as 'number of Cooper pairs').

Thermodynamics

The most directly observable property is the specific heat $c_v(T)$. Recall that in the normal phase we have

$$c_n(T) = \gamma T + \beta T^3 \quad (14)$$

$$\gamma \equiv \frac{\pi^2}{3} \left(\frac{dn}{d\epsilon} \right) k_B^2 \sim n k_B / \epsilon_F, \quad \beta \sim n k_B \theta_D^{-3}$$

Since for $T \sim T_c$ we usually have $T_c/\epsilon_F \ll (T_c/\theta_D)^3$, phonon contribution is usually negligible (if not, it can be subtracted out since it is expected to change little in the superconducting phase). Note in type I superconductors, c_s can be measurable not only directly but from $H_c(T)$.

To calculate $c_s(T)$, can either (a) calculate temperature-dependent mean energy $E(T)$ and differentiate; (b) calculate entropy $S(T)$ and use $c_s = T dS/dT$. Do latter:

$$S(T) = \sum_{\mathbf{k}} S_{\mathbf{k}}(T) \quad (15)$$

For each 'pair space' $\mathbf{k} \uparrow, -\mathbf{k}, \downarrow$, we have

$$S_{\mathbf{k}}(T) = -k_B \sum_n p_n \ln p_n = -k_B (P_{\text{GP}} \ln P_{\text{GP}} + 2P_{\text{BP}} \ln P_{\text{BP}} + P_{\text{EP}} \ln P_{\text{EP}}) \quad (16)$$

Since $P_{\text{GP}} : P_{\text{BP}} : P_{\text{EP}} = 1 : e^{-\beta E_{\mathbf{k}}} : e^{-2\beta E_{\mathbf{k}}}$, this gives

$$S_{\mathbf{k}}(T) = 2k_{\text{B}} \left\{ \frac{\beta E_{\mathbf{k}}}{e^{\beta E_{\mathbf{k}}} + 1} + \ln(1 + e^{-\beta E_{\mathbf{k}}}) \right\} \quad (17)$$

where recall that $E_{\mathbf{k}} \equiv E_{\mathbf{k}}(T)$. When we differentiate with respect to temperature, the explicit $d/d\beta$ gives a contribution to c of $(1/2)k_{\text{B}}\beta^2 \text{sech}^2 \beta E_{\mathbf{k}}/2$, and the dependence of $E_{\mathbf{k}}$ on T gives a contribution $\beta E_{\mathbf{k}}^{-1} dE_{\mathbf{k}}/d\beta$ times this. Thus

$$c_s/k_{\text{B}} = \frac{1}{2} \beta^2 \sum_{\mathbf{k}} (E_{\mathbf{k}} + \beta dE_{\mathbf{k}}/d\beta) E_{\mathbf{k}} \text{sech}^2 \beta E_{\mathbf{k}}/2 \quad (18)$$

- (A) In limit $T \rightarrow 0$, can neglect the second term: result is thus the specific heat of a gas of independent Fermi particles of fixed energy $E_{\mathbf{k}}$. [note one \mathbf{k} contains both $\mathbf{k} \uparrow$ and $-\mathbf{k} \downarrow$], i.e.,

$$E(T) = \sum_{\mathbf{k}} \frac{2E_{\mathbf{k}}}{e^{\beta E_{\mathbf{k}}} + 1}, \quad c_s(T) = dE/dT \quad (19)$$

Explicitly,

$$c_s(T)_{T \rightarrow 0} = \text{const } \beta^{3/2} [\Delta(0)]^{5/2} (dn/d\epsilon) \exp -\beta \Delta(0) \quad (20)$$

hence can measure zero- T gap $\Delta(0)$.

- (B) In limit $T \rightarrow T_c$, put $E_{\mathbf{k}} \rightarrow |\epsilon_{\mathbf{k}}|$ except in $dE_{\mathbf{k}}/d\beta$, then first term simply gives N-state specific heat. The difference between the S- and N-state specific heat at T_c is therefore given by

$$\Delta c_{sn} = \frac{1}{2} k_{\text{B}} \beta_c^3 \sum_{\mathbf{k}} E_{\mathbf{k}} (dE_{\mathbf{k}}/d\beta) \text{sech}^2 \beta |\epsilon_{\mathbf{k}}|/2 \quad (21)$$

$$= \frac{1}{4} k_{\text{B}} \beta_c^3 \frac{d}{d\beta} \Delta^2(T)_{T \rightarrow T_c} (dn/d\epsilon) \int_0^{\infty} \text{sech}^2 \beta_c |\epsilon|/2 \leftarrow 2\beta_c^{-1} \quad (22)$$

$$= \frac{1}{2} \left(\frac{dn}{d\epsilon} \right) \left[-\frac{d}{dT} \Delta^2(T) \right]_{T \rightarrow T_c} \quad (23)$$

Now for $T \rightarrow T_c$ BCS gap equation gives $\Delta^2(T) = (3.06 k_{\text{B}} T_c)^2 (1 - T/T_c)$ so

$$\Delta c_{sn} = (1/2)(3.06 k_{\text{B}})^2 T_c (dn/d\epsilon) \quad (24)$$

or

$$\begin{aligned} \Delta c_{sn}/c_n(T_c) &= (1/2)3.06^2/(\pi^2/3) = 1.43 \\ \Delta c_{sn}/c_n(T_c) &= 1.43 \end{aligned} \quad (25)$$

Note, refers to electronic contribution only

in reasonable agreement with experiment on most superconductors other than Pb and Hg, where the experimental value is larger (see Table in Kuper p. 36: ratio is 1.15–1.6 for most elemental superconductors, 2.07 for Nb, 2.1 for Hg, and 2.65 for Pb).

Response to external fields

Spin susceptibility χ : in real life, if apply magnetic field, couple to both spin + orbital motion. Can sometimes separate out ‘spin’ effect by using very thin/dirty samples. Usual measurement is from Knight shift. Assume for the moment simple BCS model, and in particular neglect any Landau Fermi liquid-type effects. Then apply weak field:

Magnetic field cannot shift energy of states $|00\rangle$ or $|11\rangle$ since these both have total spin 0. But shifts energy of $|10\rangle$ and $|01\rangle$:

$$E_{\mathbf{k}}(1,0) = E_{\mathbf{k}} - \mu_B H, \quad E_{\mathbf{k}}(0,1) = E_{\mathbf{k}} + \mu_B H$$

$$P_{\mathbf{k}}(1,0) \cong \frac{\exp -\beta(E_{\mathbf{k}} - \mu_B H)}{(1 + \exp -\beta E_{\mathbf{k}})^2} \quad \text{etc.} \quad (26)$$

(neglect 2nd-order changes in normalization),

$$M = \mu_B \sum_{\mathbf{k}} (P_{\mathbf{k}}(1,0) - P_{\mathbf{k}}(0,1)) \cong \mu_B \sum_{\mathbf{k}} \frac{\exp -\beta(E_{\mathbf{k}} - \mu_B H) - \exp -\beta(E_{\mathbf{k}} + \mu_B H)}{(1 + \exp -\beta E_{\mathbf{k}})^2}$$

$$\cong 2\mu_B^2 H \sum_{\mathbf{k}} \frac{\beta \exp -\beta E_{\mathbf{k}}}{(1 + \exp -\beta E_{\mathbf{k}})^2} = \mu_B^2 H \left(\frac{dn}{d\epsilon} \right) \int_0^\infty d\epsilon (\beta/2) \operatorname{sech}^2(\beta E/2) \quad (27)$$

Since $\chi_n = \mu_B^2 (dn/d\epsilon)$, this gives

$$\chi(T)/\chi_n = \int_0^\infty d\epsilon (\beta/2) \operatorname{sech}^2(\beta E/2) \equiv Y(T/T_c) \quad \leftarrow \quad \text{Yosida function} \quad (28)$$

The Yosida function is characteristic of the response to fields which cannot affect the Cooper pairs: it is in a sense a measure of the ‘density (fraction) of normal component’. For $T \rightarrow 0$ Y tends to zero exponentially: for $T \rightarrow T_c$, it is equal (in the simple BCS model) to $1 - 2(1 - T/T_c)$ (The number 2 is exact!).

Normal density ρ_n : momentum of $|00\rangle_{\mathbf{k}}$ and $|11\rangle_{\mathbf{k}}$ is 0, of $|10\rangle_{\mathbf{k}}$ is $\hbar \mathbf{k}$ etc. Let us imagine a probe which does not affect the pairs, but shifts the energies of the BP states by $E_{\mathbf{k}}(1,0) \rightarrow E_{\mathbf{k}} - \hbar \mathbf{v} \cdot \mathbf{k}$, $E_{\mathbf{k}}(0,1) \rightarrow E_{\mathbf{k}} + \hbar \mathbf{v} \cdot \mathbf{k}$. Such a probe is a uniform (in space) transverse vector potential \mathbf{A} (actually $\mathbf{v} = \mathbf{A}/m$), if we assume for the moment it does not act on the pairs. We are then interested in the mass current (momentum density) given by

$$\mathbf{P} = \sum_{\mathbf{k}} \hbar \mathbf{k} (P_{\mathbf{k}}(1,0) - P_{\mathbf{k}}(0,1)) \quad (29)$$

It is clear that the analysis goes through as for χ with $\hbar \mathbf{v} \cdot \mathbf{k}$ replacing μ_B : the average of $(\mathbf{v} \cdot \mathbf{k})^2$ over the Fermi surface gives $(1/3)v^2 k_F^2$. Hence

$$\mathbf{P} = (1/3)(dn/d\epsilon) \hbar^2 k_F^2 Y(T/T_c) \mathbf{v} \quad (30)$$

In the normal phase \mathbf{P} is just $(1/3)(dn/d\epsilon) \hbar^2 k_F^2 \mathbf{v}$, so define ρ_n/ρ as \mathbf{P}/\mathbf{P}_n :

$$\rho_n/\rho = Y(T/T_c) \quad (31)$$

[Note: in general it is difficult to realize this thought-experiment!]

Fermi-liquid effects

These are the most easily modeled by the molecular-field technique, which gives the general result (e.g.) that if χ_0 is the ‘free-superfluid-gas’ expression then

$$\chi(T) = \frac{\chi_0(T)}{1 + f_0^a \mu_B^{-2} \chi_0(T)} \quad (32)$$

Since $\chi_0(T) = \mu_B^2 (dn/d\epsilon) Y(T)$, this gives at once

$$\chi(T) = \frac{(dn/d\epsilon) \mu_B^2 Y(T)}{1 + F_0^a Y(T)}, \quad F_0^a \equiv (dn/d\epsilon) f_0^a \quad (33)$$

or

$$\chi(T)/\chi_0 = \frac{(1 + F_0^a) Y(T)}{1 + F_0^a Y(T)} \quad (34)$$

In superfluid ^3He , where F_0^a is large, the corresponding effect is quite dramatic.[†]

Normal density

Again the molecular-field technique can be applied. Quote result only for translational-invariant system:

$$\rho_n = \frac{\rho_{n0}}{1 + (1/3) F_1^s p_f^{-2} (dn/d\epsilon)^{-1} \rho_{n0}} = \frac{nm^* Y(T)}{1 + (1/3) F_1^s Y(T)} \quad (35)$$

or

$$\rho_n/\rho = \frac{(1 + (1/3) F_1^s) Y(T)}{1 + (1/3) F_1^s Y(T)} \quad (36)$$

Note that there is now no cancellation between m^*/m and $1 + (1/3) F_1^s$ as in the normal phase. Thus, in a translation-invariant system (such as ^3He) it is possible to measure F_1^s exactly in the superconducting state, independently of m^* . (but beware strong coupling effects!). In the limit $T \rightarrow T_c$, ρ_n/ρ tends to 1 as we expect.

[†] ^3He is not singlet-paired, so the result must be generalized.