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 $\to \Delta(T)$ [independent of $\mathbf{k}$] for $|\epsilon_{\mathbf{k}}| \leq k_{\mathrm{B}}T_c$. Quantity $\Delta(T)$ satisfies gap equation, $\to 0$ at T_c and $\to$ const ($= \Delta(0) \sim 1.75 k_{\mathrm{B}}T_c$) for $T \to 0$. 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:

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

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

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

and so

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

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

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

so

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

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

$$T_c \ll \epsilon_{\mathrm{F}} \tag{5}$$

and hence $k_{\mathrm{F}}\xi' \gg 1$ where $\xi' \sim \hbar v_{\mathrm{F}}/\Delta(0)$ (see below), as found experimentally.

3 Regimes:

(1) For $r \lesssim k_{\mathrm{F}}{}^{-1}$, integral dominated by $k \gtrsim k_{\mathrm{F}}$, i.e. $|\epsilon| \gtrsim \epsilon_{\mathrm{F}} \gg T_c$ (or Δ). In this regime, behavior of 'exact' $F_{\mathbf{k}}$ similar to that of 2 particle wave function $\psi_{\mathbf{k}}$, and $E_{\mathbf{k}} \to |\epsilon_{\mathbf{k}}|$, $\tanh \beta E_{\mathbf{k}}/2 \to 1$. Hence, apart from overall constant, wave function in this regime is that of 2 particles at Fermi energy interacting in free space (i.e. in the absence of the Fermi sea) via the effective potential $V_{kk'}$ derived in lecture 4.*

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

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

$$F(r) \approx \Delta(T)N(0) \int d\epsilon_k \frac{\sin kr}{2kr|\epsilon_k|} \approx \frac{\Delta(T)N(0)}{2k_{\rm F}r} \sin k_{\rm F}r \int d\epsilon \frac{\cos(\epsilon r/\hbar v_{\rm F})}{|\epsilon|}$$
$$\approx \frac{1}{2}\Delta(T)N(0)\frac{\sin k_{\rm F}r}{k_{\rm F}r} \times \ln \text{factor} \tag{6}$$

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

$$\psi(r) \sim \sum_{|\mathbf{k}|=k_{\rm F}} e^{i\mathbf{kr}} \sim \frac{\sin k_{\rm F}r}{k_{\rm F}r} \tag{7}$$

(3) The most interesting regime is $r \gtrsim \hbar v_{\rm F}/\Delta$. Here the relevant energies are all $\lesssim k_{\rm B}T_c$ and we can write (again approximating $k \sim k_{\rm F}$ in denominator, etc.)

$$F(r) = \frac{1}{2}\Delta(T)N(0)\frac{\sin k_{\rm F}r}{k_{\rm F}r}\int_0^\infty d\epsilon \frac{\cos(\epsilon r/\hbar v_{\rm F}) \tanh \beta\sqrt{\epsilon^2+\Delta^2(T)}/2}{\sqrt{\epsilon^2+\Delta^2(T)}}$$
$$\equiv \Delta(T)N(0)\frac{\sin k_{\rm F}r}{k_{\rm F}r} \times J(r,\Delta,\beta) \tag{8}$$

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 $T \to 0$ define $\xi' \equiv \hbar v_{\rm F}/\Delta(0)$, then

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

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

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

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

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

$$J(r) = \int_0^\infty \frac{d\epsilon}{\epsilon} \cos(r\epsilon/\hbar v_{\rm F}) \tanh \beta_c\epsilon/2 \tag{11}$$

or introducing $\xi'' \equiv \hbar v_\mathrm{F}/k_\mathrm{B}T_c$ ($\sim \xi'$)

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

Again it is clear that J diverges as $\ln(r/\xi'')$ for $r \to 0$, and somewhat less obvious (but true) that it tends to zero exponentially for $r \gg \xi''$. Thus as $T \to T_c$, 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:

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

It is clear that the main contribution comes from $|\epsilon| < \Delta(T), k_\mathrm{B}T_c$, where we can approximate $\Delta_k \sim \Delta(T)$. Thus $N = |\Delta(T)|^2 N(0) \int_0^\infty (d\epsilon/4E^2) \tanh^2 \beta E/2$. For $T \to 0$, this is $\sim N(0)\Delta(0)$; for $T \to T_c$, 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

$$c_n(T) = \gamma T + \beta T^3 \tag{14}$$

$$\gamma \equiv \frac{\pi^2}{3}\left(\frac{dn}{d\epsilon}\right) {k_\mathrm{B}}^2 \sim nk_\mathrm{B}/\epsilon_\mathrm{F}, \quad \beta \sim nk_\mathrm{B}\theta_\mathrm{D}^{-3}$$

Since for $T \sim T_c$ we usually have $T_c/\epsilon_\mathrm{F} \ll (T_c/\theta_\mathrm{D})^3$, 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:

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

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

$$S_\mathbf{k}(T) = -k_\mathrm{B} \sum_n p_n \ln p_n = -k_\mathrm{B}(P_\mathrm{GP} \ln P_\mathrm{GP} + 2P_\mathrm{BP} \ln P_\mathrm{BP} + P_\mathrm{EP} \ln P_\mathrm{EP}) \tag{16}$$

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

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

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

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

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

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

Explicitly,

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

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

(B) In limit $T \to T_c$, put $E_{\bf k} \to |\epsilon_{\bf k}|$ except in $dE_{\bf k}/d\beta$, 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

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

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

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

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

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

or

$$\Delta c_{sn}/c_n(T_c) = (1/2)3.06^2/(\pi^2/3) = 1.43$$

$$\Delta c_{sn}/c_n(T_c) = 1.43 \tag{25}$$

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 $|01\rangle$:

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

(neglect 2nd-order changes in normalization),

$$M = \mu_{\mathrm{B}} \sum_{\mathbf{k}} (P_{\mathbf{k}}(1,0) - P_{\mathbf{k}}(0,1)) \cong \mu_{\mathrm{B}} \sum_{\mathbf{k}} \frac{\exp -\beta(E_{\mathbf{k}} - \mu_{\mathrm{B}}H) - \exp -\beta(E_{\mathbf{k}} + \mu_{\mathrm{B}}H)}{(1+\exp -\beta E_{\mathbf{k}})^2}$$
$$\cong 2\mu_{\mathrm{B}}^2 H \sum_{\mathbf{k}} \frac{\beta \exp -\beta E_{\mathbf{k}}}{(1+\exp -\beta E_{\mathbf{k}})^2} = \mu_{\mathrm{B}}^2 H \left(\frac{dn}{d\epsilon}\right) \int_0^\infty d\epsilon\, (\beta/2)\,\mathrm{sech}^2(\beta E/2) \tag{27}$$

Since $\chi_n = \mu_{\mathrm{B}}^2 (dn/d\epsilon)$, this gives

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

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 $T \to 0$ Y tends to zero exponentially: for $T \to T_c$, 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 $E_{\mathbf{k}}(1,0) \to E_{\mathbf{k}} - \hbar\,\mathbf{vk}$, $E_{\mathbf{k}}(0,1) \to E_{\mathbf{k}} + \hbar\,\mathbf{vk}$. 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

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

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 $(1/3)v^2 k_{\mathrm{F}}{}^2$. Hence

$$\mathbf{P} = (1/3)(dn/d\epsilon)\,\hbar^2 k_{\mathrm{F}}{}^2\, Y(T/T_c)\,\mathbf{v} \tag{30}$$

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

$$\rho_n/\rho = Y(T/T_c) \tag{31}$$

[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

$$\chi(T) = \frac{\chi_0(T)}{1 + f_0^a \mu_{\rm B}^{-2} \chi_0(T)} \tag{32}$$

Since $\chi_0(T) = \mu_{\rm B}^2 (dn/d\epsilon) Y(T)$, this gives at once

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

or

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

In superfluid ^{3}He, 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:

$$\rho_n = \frac{\rho_{n0}}{1 + (1/3) F_1^s p_{\rm f}^{-2} (dn/d\epsilon)^{-1} \rho_{0n}} = \frac{n m^* Y(T)}{1 + (1/3) F_1^s Y(T)} \tag{35}$$

or

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

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 ^{3}He) it is possible to measure F_1^s exactly in the superconducting state, independently of m^* (but beware strong coupling effects!). In the limit $T \to T_c$, ρ_n/ρ tends to 1 as we expect.

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