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Lecture 9 – Dirty Superconductors

Experimental fact:

Quite strong nonmagnetic disorder (e.g. alloying) does little harm to superconductivity, while even tiny amounts (~ a few ppm) of magnetic impurities suppress it completely.

Why?

A. Nonmagnetic Disorder

$$\hat{H} = \hat{H}_0 + \hat{V}$$

single-electron

inter-electron interaction

potential due to atomic cores

$$\hat{H}_0 = \sum_i \left(\frac{\hat{p}_i^2}{2m} + \hat{U}(\boldsymbol{r}_i) \right)$$

spin-independent

Assume: $k_f l \gg 1$ (but possibly $l \lesssim \xi_0$)

Eigenstates of $\hat{H}_0$ are of form

$$\psi_n(\boldsymbol{r}, \sigma) = \phi_n(\boldsymbol{r})|\sigma\rangle \equiv |n, \sigma\rangle \, , |\sigma\rangle \equiv (|\uparrow\rangle, |\downarrow\rangle) \text{ with energy } \epsilon_n$$

where $\phi_n(r)$ is very complicated.

However, note that average density of states

$$\frac{dn}{d\epsilon} \equiv 2 \textstyle\sum_n \delta(\epsilon - \epsilon_n)$$

is much the same (for $k_f l \gg 1$) as in original (crystalline) case.

Crucial point: since $\hat{H}_0$ is invariant under time-reversal

$$(|\uparrow\rangle \rightleftarrows |\downarrow\rangle \, , \phi_n(\boldsymbol{r}) \rightleftarrows \phi_n^*(\boldsymbol{r}) \equiv |\bar{n}\rangle),$$

then if state $|n, \uparrow\rangle$ is an eigenstate of $\hat{H}_0$ with energy ϵ_n,
then $|\bar{n}, \downarrow\rangle$ is also eigenstate of $\hat{H}_0$ with energy ϵ_n .

Note: $\phi_{\bar{n}}(\boldsymbol{r})$ may or may not be identical to $\phi_n(\boldsymbol{r})$, *i.e.* $\varphi_n(\boldsymbol{r})$ may or may not be real, (doesn't matter!)

Recall that in free space, BCS ground state was

$$\Psi = \prod_k \Phi_k$$

$\Phi_k \equiv$ state vector in "occupation space" of $|k, \uparrow\rangle, |-k, \downarrow\rangle$

So, replace $|k \uparrow\rangle, |-k \downarrow\rangle$ by $|n \uparrow\rangle, |\bar{n} \downarrow\rangle$ and generalize BCS ansatz:

$$\Psi = \prod_n \Phi_n$$

$\Phi_k \equiv$ state vector in "occupation space" of $|n, \uparrow\rangle, |\bar{n}, \downarrow\rangle$

Assume as in free-space case that at T=0 $|0{,}1\rangle, |1{,}0\rangle$ are irrelevant, then
$\Phi_n = u_n|0{,}0\rangle + v_n|1{,}1\rangle$ $\qquad |u_n|^2 + |v_n|^2 = 1$

i.e. pair in time-reversed states

KE is identical to free-space case with $\boldsymbol{k} \rightarrow n$:

$$\langle T\rangle = 2\sum_n \epsilon_n |v_n|^2$$

For the PE, as in the free-space case, we need to calculate the matrix element

$\langle\psi_f|\hat{V}|\psi_{in}\rangle$ with $\psi_{in} \equiv (n\uparrow, \bar{n}\downarrow \text{ occupied;} \;\; n'\uparrow, \bar{n}'\downarrow \text{ empty})$

$\psi_f \equiv (n\uparrow, \bar{n}\downarrow \text{ empty;} \;\; n'\uparrow, \bar{n}'\downarrow \text{ occupied})$

For a δ-function interaction $V(r_i - r_j) = V_0\delta(r_i - r_j)$, this is equal to

$$V_0 u_n v^*_{n'} u_{n'} v_n \int \phi^*_{n'}(r)\phi^*_{\bar{n}'}(r)\phi_n(r)\phi_{\bar{n}}(r)\mathrm{d}r$$

But since $\phi^*_{\bar{n}}(r) = \phi_n(r)$ (etc.), this can be rewritten (regrouping the u's and v's)

$$V_0 u_n v_n u_{n'} v^*_{n'} \int |\phi_{n'}(r)|^2 \cdot |\phi_n(r)|^2 \mathrm{d}r$$

For normalization in unit volume the integral, thought not exactly equal to 1, is very close to it, so

$$\langle V\rangle \cong V_0 \sum_{n,n'} (u_n v_n)(u_{n'} v^*_{n'}) \equiv V_0 \sum_n F_n F^*_{n'}$$

$\equiv u_n v_n$

The subsequent algebra goes through exactly as in the free-space case, and we end up with the gap equation

$$\Delta_n = -V_0 \sum_{n'} \frac{\Delta_{n'}}{2E_{n'}} \qquad E_n \equiv (\epsilon_n^2 + |\Delta_n|^2)^{\frac{1}{2}}$$

Assuming $\Delta_n = \Delta = \text{const}$ and turning the Σ_n into $\int \mathrm{d}\epsilon$:

$$1 = -V_0 \int_{-\epsilon_c}^{\epsilon_c} \frac{\rho(\epsilon)\mathrm{d}\epsilon}{2(\epsilon^2 + |\Delta|^2)^{1/2}}$$

Since $\rho(\epsilon)$ is (almost) the same as for the original free-space case, this is (almost) the original BCS gap equation and has the same solution

$$\Delta = 2\epsilon_c e^{-1/N(0)V} \qquad \left(N(0) \equiv \frac{1}{2}\left(\frac{\mathrm{d}n}{\mathrm{d}\epsilon}\right)_{\epsilon=\epsilon_f}\right)$$

Thus,

thermodynamics almost unaffected by alloying

(in zero magnetic field, for $k_F l \gg 1$)

(we have simply "shuffled the original plane-wave states around")

Similar results at non-zero T, e.g. $\frac{\chi(T)}{\chi_n} = Y(T)$ (Yoshida function)

(since $n \uparrow, \bar{n} \downarrow$ still eigenstates of spin)

However, calculation of normal density does not go through

(∵single-particle energy eigenstates n, σ are not eigenstates of momentum)

OK, so which properties are affected by alloying?

(a) Pair radius

Recall: in pure metal, with pairs at rest, “pair wave function” F is independent of COM variable R, and as function of relative coordinates r is given (at $T = 0$) by

$$F(r) = \sum_k F_k \exp(ik \cdot r) \qquad F_k \equiv \Delta/2E_k \qquad E_k \equiv (\epsilon_k^2 + |\Delta|^2)^{1/2}$$

The “range” of F in ϵ is $\sim\Delta$, hence in k it is $\Delta/\hbar v_F$, so by indeterminancy principle $\Delta \mathrm{k} \cdot \Delta r \sim 1$ we have,

$$\Delta r \sim \hbar v_F/\pi\Delta \equiv \xi_0 (\equiv \text{“pair radius”})$$

(Technically, $F(r) \sim \exp -r/\xi', \quad \xi' \sim \xi_0$)

In the dirty system, pair wave function F is given by

$$F(\boldsymbol{r}, \boldsymbol{r}') = \sum_n u_n v_n \varphi_n(\boldsymbol{r})\, \varphi_{\bar{n}}(\boldsymbol{r}')$$

$$\equiv \sum_n u_n v_n \varphi_n(\boldsymbol{R} + \boldsymbol{r}/2)\, \varphi_{\bar{n}}(\boldsymbol{R} - \boldsymbol{r}'/2)$$

so is technically a function also of COM variable R. So let's define

$$\overline{F(r)} \equiv \overline{F(R + r/2, R - r'/2)} \quad \text{where average is over } R$$

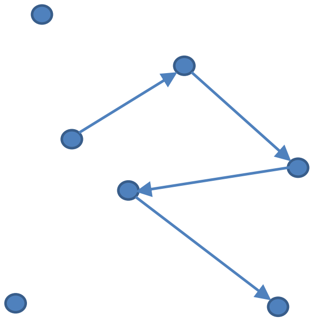
What is dependence of $\overline{F(r)}$ on relative coordinate r? Rewrite

$$\overline{F(r)} = \sum_n (\Delta/2E_n)\overline{\varphi_n(\boldsymbol{R}+\boldsymbol{r}/2)\varphi_n^*(\boldsymbol{R}-\boldsymbol{r}'/2)}$$

$\uparrow$

since $\varphi_{\bar{n}} \equiv \varphi_n^*$

Intuitive (semiclassical) argument:



$\overline{F(\boldsymbol{r})}$ will drop below its $\boldsymbol{r} = 0$ value as soon as difference in phase of the product $\varphi_n(\boldsymbol{R}+\boldsymbol{r}/2)\ \varphi_n^*(\boldsymbol{R}-\mathbf{r}'/2)$ for different n becomes $\sim 2\pi$. Semiclassically, a wave packet with spread in energy $\Delta\epsilon$ will be dephased (indeterminacy!) in a time $\Delta t \sim \hbar/\Delta\epsilon$. In our case $\Delta\epsilon \sim \Delta$, so dephasing time is

$$\Delta\mathrm{t} \sim \hbar/\Delta$$

How far does the packet travel in Δt? In pure metal, $r \sim v_F t$ so

$$\Delta r \sim \hbar v_F/\Delta$$

leading to $r_p \sim \hbar v_F/\Delta$ as above. But in a dirty metal ($l \ll \xi_0$) motion is diffusive, and we have

$$r^2 \sim D\Delta t \qquad D \sim \frac{1}{3} v_F l$$

so putting $\Delta\mathrm{t} \sim \hbar/\Delta$

$$r_p \sim (\hbar v_F l/\Delta)^{1/2}$$ or since $\xi_0 \sim \hbar v_F/\Delta$

$$r_p \sim (\xi_0 l)^{1/2}$$ (dirty limit)

i.e. pair radius decreases by factor $(l/\xi_0)^{1/2}$ (which can be $\ll 1$).

(Also in limit $T \rightarrow T_c$, i.e. $\rho_s^{(dirty)}(T) \sim (l/\xi_0)^{1/2} \rho_s^{(clean)}(T)$).

(b) Superfluid density

The superfluid density ρ_s can be defined in two apparently different ways:

(1) as the coefficient of the dependence of the GL free energy on "bending" of the GL order parameter, for $A = 0$,

$$\Delta F = \frac{1}{2}\rho_s v_s^2 \qquad \text{with } v_s \equiv \frac{\hbar}{2m}(\nabla\varphi) \qquad \Psi \sim |\Psi| exp i\varphi$$

for $\mathrm{A} = 0$

(2) as the (diamagnetic) response of the current to a weak transverse EM vector potential,

$$J = -\rho_s\left(\frac{e}{m}\right)^2 A$$

(In pure case at $T = 0$, $\rho_s =$ nm so recover London equation)

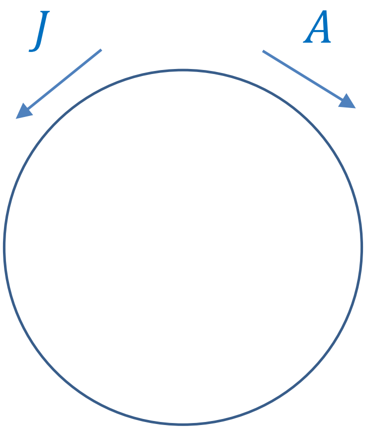
To see that the two definitions are equivalent, consider a thin superconducting ring in a weak circumferential (i.e. transverse) vector potential A: then must generalize definition of v_s to

$$v_s = \frac{\hbar}{2m}\left(\nabla\varphi - \frac{2eA}{\hbar}\right)$$

If A is weak, SVBC enforces $\varphi = const.$ so

$$v_s = -\frac{e}{m}A$$

$$\Longrightarrow \qquad \Delta F = \frac{1}{2}\rho_s\left(\frac{e}{m}\right)^2 A^2$$



but quite generally, $J = -\partial(\Delta F)/\partial A$

$$\mathrm{J} = -\rho_s\left(\frac{e}{m}\right)^2 A$$

in accordance with second definition.

To estimate effects of disorder on ρ_s (at $T = 0$), proceed as follows: Although we have up to now assumed that when A is a function of r the current $J(r)$ is related to $A(r)$ by the London relation

$$J(r) = -\rho_s \left(\frac{e}{m}\right)^2 A(r)$$

this is actually not quite right. In fact, the more correct formula is

$$J(r) = \int \mathrm{K}(r, r')A(r')\mathrm{d}r'$$

For the pure case the "range" of $\mathrm{K}(r, r\,') = \mathrm{K}(r - r\,')$is ~ the pair radius ξ_0. In fact the exact formula in BCS theory is close to Pippard's original guess,

$$\mathrm{K}(r - r') \sim -\frac{3ne^2}{4\pi m\xi_0}\frac{1}{|r - r'|^2} exp - |r - r'|/\xi_0$$

If $A(r)$ is slowly varying over distances $\sim\xi_0$, this gives back the London relation

$$J(r) \cong A(r) \int \mathrm{K}(r - r')\mathrm{d}r' = -\frac{ne^2}{m} A(r)$$

Now, if $l \lesssim \xi_0$, expect intuitively that induced current falls off as $e^{-|r-r'|/l}$, i.e.

$$\mathrm{K}(r - r') \sim (prefactor\ x) exp - |r - r'|(\frac{1}{\xi_0} + \frac{1}{l})$$

(Pippard)

Hence, integral is reduced by factor

$$\frac{1/\xi_0}{1/\xi_0 + 1/l} \equiv \frac{1}{1+\xi_0/l} \qquad \sim l/\xi_0, \quad \text{for} \quad l \ll \xi_0.$$

Hence in dirty limit,

$$\rho_s^{dirty} \sim (l/\xi_0)\rho_s^{clean} \ll \rho_s^{clean}$$

(also in limit $T \rightarrow T_c$).

Effects of disorder in language of GL theory (T→T$_C$):

$$\mathcal{F}\{\Psi(r):T\} = (\alpha_0(T-T_c)|\Psi|^2 + \frac{1}{2}\beta_0|\Psi|^4 + \gamma_0|\nabla\Psi|^2)$$

In dirty limit ($l \ll \xi_0$ but still $k_F l \gg 1$)

$$\left.\begin{aligned}\alpha_0^{\mathrm{dirty}} &\cong \alpha_0^{\mathrm{clean}}\\ \beta_0^{\mathrm{dirty}} &\cong \beta_0^{\mathrm{clean}}\end{aligned}\right\}\quad \text{so, } \Psi_{\mathrm{dirty}}(T) \cong \Psi_{\mathrm{clean}}(T)$$

but,

$$\gamma_0^{\mathrm{dirty}} \sim \left(\frac{\lambda}{\xi_0}\right)\gamma_0^{\mathrm{clean}} \ll \gamma_0^{\mathrm{clean}}$$

Recall:

$$\xi(T) \sim (\gamma_0/\alpha_0(T-T_c))^{1/2}$$
$$\lambda(T) \sim (\gamma_0|\Psi(T)|^2)^{-1/2}$$

Thus,

$$\xi_{\mathrm{dirty}}(T) \sim (l/\xi_0)^{1/2}\xi_{\mathrm{clean}}(T)$$
$$\lambda_{\mathrm{dirty}}(T) \sim (\xi_0/l)^{1/2}\lambda_{\mathrm{clean}}(T)$$

⇒ $\kappa_{\mathrm{dirty}} \equiv (\lambda/\xi)_{\mathrm{dirty}} \sim (\xi_0/l)\kappa_{\mathrm{clean}} \gg \kappa_{\mathrm{clean}}$

⇒ alloying makes system much more type-II.

in particular,

$$H_{c1}^{\mathrm{dirty}} \sim \lambda_{\mathrm{dirty}}^{-2} \ll H_{c1}^{\mathrm{clean}}$$
$$H_{c2}^{\mathrm{dirty}} \sim \xi_{\mathrm{dirty}}^{-2} \gg H_{c2}^{\mathrm{clean}}$$

B. Magnetic disorder

Now we have

$$\hat{H} = \underbrace{\hat{H}_0}_{\text{single-electron}} + \underbrace{\hat{V}}_{\text{Inter-electron interaction}}$$

but now

$$\hat{H}_0 = \sum_i (\hat{p}_i/2m) + U(r_i : \sigma_i)$$

so now TRI (Time Reversal Invariance) is broken, and state $|\bar{n}, -\sigma\rangle$ (when $\varphi_{\bar{n}}(\boldsymbol{r}) \equiv \varphi_n^*(\boldsymbol{r})$) is no longer degenerate with $|n, \sigma\rangle$, indeed is in general not even an energy eigenstate.

Two obvious proposals for GS:

(a) Pair in exact eigenfunctions of single-particle Hamiltonian, i.e. if exact eigenstates of $\hat{H}_0$ for $\sigma = \downarrow$ are denoted φ_m, pair off n with some m ($\neq n$).

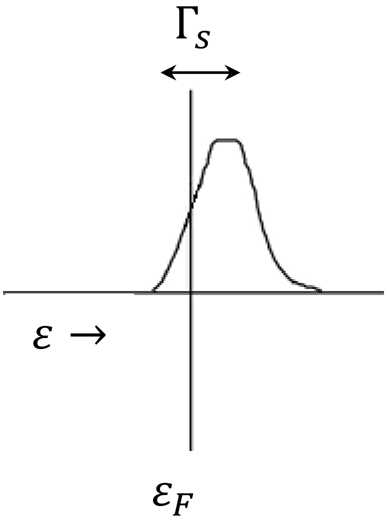
Then KE is much the same as in pure (BCS) case. However,

$$\langle V \rangle \sim V_0 \sum_{mm'} \int dr \varphi_n^*(r) \varphi_m^*(r) \varphi_{m'}(r) \varphi_{n'}(r)$$

and since we no longer have $\varphi_{\bar{n}}(r) = \varphi_n^*(r)$, (etc.) the integral is oscillating and hence very small. This scheme is usually very energetically disadvantageous.

(b) Continue to pair in time-reversed states, even though these are no longer eigenstates of $\widehat{H}_0$. How much extra energy does this cost? Suppose “lifetime for different scattering of ↑ and ↓” is $\tau_s \equiv \hbar\Gamma_s^{-1}$ then by indeterminacy principle extra energy necessary to keep state of ↓ the time-reverse of that of ↑ is

$\sim \Gamma_s \Rightarrow$ extra energy required $\sim \Gamma_s \times$ no. of perturbed states $\sim \Gamma_s(\Gamma_s dn/d\varepsilon) \equiv \Gamma_s^2 dn/d\varepsilon$.



On the other hand, this scheme keeps the whole of the pure-state condensation energy, which is

$E_{\text{cond}}^{(\text{pure})} \sim -\Delta_0^2(\frac{dn}{d\varepsilon})$ ($\Delta_0 \equiv$ gap of pure system)

Hence we expect that this scheme will give an energy lower than the $N-$state provided $|E_{\text{cond}}^{(\text{pure})}| > \Gamma^{2}{}_{s}\ dn/d\varepsilon$, i.e. condition for magnetic impurities to suppress superconductivity completely is

$$\Gamma_s \gtrsim \Delta_0$$

which is equivalent to $l_s \lesssim \xi_0$. (i.e. mean free path against spin-dependent scattering $\lesssim$ (pure metal) pair radius). Actually, exact calculation (Abrikosov-Gor'kov) shows that at $T = 0$ condition is in fact simply $\Gamma_s > \Delta_0$) .