

Miscellaneous topics in BCS theory (relevant to SC2)

1. Limits on T_c in BCS-type theories

BCS theory:

$$T_c = 1.13\hbar\omega_c \exp -1/g \quad g \equiv N(0)|V_{\text{eff}}| > 0 \quad (1)$$

so, prima facie, limiting value is $1.13\hbar\omega_c \gtrsim RT$ if $\omega_c \sim \omega_D$. (but formulae not quantitatively valid then!)

Two problems with BCS theory:

- (i) no account of repulsive Coulomb interaction
- (ii) if indeed T_c , hence Δ , is comparable to ω_D then frequency dependence of interaction ('retardation') may be important.

(i) *Inclusion of Coulomb interaction:*

A prima facie problem is that the Coulomb interaction scatters into states with energies $\gg \Delta$ and even $\gg \omega_D$. This can be handled by renormalization technique of lecture 6: recall,

$$\hat{t} = \hat{V}/(1 + \hat{P}_1\hat{Q}\hat{V}), \quad \hat{P}_1\hat{Q} \approx \sum_{|\epsilon| > \epsilon_c} (2\epsilon_{\mathbf{k}})^{-1} \quad (2)$$

where the sum goes over states beyond a cutoff ϵ_c which it is convenient to take as (\sim) ω_D . If the matrix element $V_{\mathbf{k}\mathbf{k}'}$ is roughly constant at some value V_c , then we have

$$V_c \sum_{\mathbf{k}} \frac{1}{2\epsilon_{\mathbf{k}}} \simeq V_c N(0) \ln(\epsilon_F/\omega_D) \quad (3)$$

and hence the effective interaction to within the shell is constant and given by

$$t = \frac{V_c}{1 + N(0)V_c \ln \epsilon_F/\omega_D} \quad (4)$$

In the general case the effect is to adjust the 'effective' ϵ_c . In the literature it is conventional to write $N(0)V_c \equiv \mu$, $N(0)t \equiv \mu^*$, then we have

$$\mu^* = \mu/(1 + \mu \ln \epsilon_F/\omega_D) \quad (5)$$

so for $\mu \rightarrow \infty$, $\mu^* \rightarrow (\ln \epsilon_F/\omega_D)^{-1}$ (typically $\sim (\ln 10^2)^{-1} \sim 0.15 - 0.2$). So, if phonon coupling constant $N(0)|V_{\text{ph}}|$ is λ (see below), then the total effective value of g is $\lambda - \mu^*$, and so we obtain

$$T_c = 1.13\hbar\omega_D \exp -1/(\lambda - \mu^*) \quad (6)$$

(ii)* *Inclusion of phonon 'retardation':*

*For a detailed account of Eliashberg theory, see article by Scalapino in Parks.

Eliashberg equations (at $T = 0$):

$$\Delta(\omega) = \frac{1}{Z(\omega)} \int_0^\infty d\omega' \operatorname{Re} \left\{ \frac{\Delta(\omega')}{(\omega'^2 - \Delta^2(\omega'))^{1/2}} \right\} \left[\int_0^\infty d\Omega \alpha^2(\Omega) F(\Omega) \times \frac{2(\omega' + \Omega)}{(\omega' + \Omega)^2 - \omega^2} - \mu^* \right] \quad (7a)$$

$$(1 - Z(\omega)) \omega = \int_0^\infty d\omega' \operatorname{Re} \left\{ \frac{\omega'}{(\omega'^2 - \Delta^2(\omega'))^{1/2}} \right\} \left[\int_0^\infty d\Omega \alpha^2(\Omega) F(\Omega) \times \frac{2(\omega + \Omega)}{(\omega' + \Omega)^2 - \omega^2} \right] \quad (7b)$$

($d^2(\Omega) \equiv$ mean-square coupling constant to phonons in frequency range $[\Omega, \Omega + d\Omega]$, $F(\Omega) =$ phonon DOS in this range) Note: 1st Eliashberg equation is, apart from $Z(\omega)$ correction, simply[†]

$$\Delta_{\mathbf{k}} = \sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} \frac{\Delta_{\mathbf{k}'}}{2E_{\mathbf{k}'}} \quad V_{\mathbf{k}\mathbf{k}'} \equiv |g_{\mathbf{k}\mathbf{k}'}|^2 \frac{E_{\mathbf{k}'} + \omega_{\text{ph}}(\mathbf{k} - \mathbf{k}')}{(E_{\mathbf{k}'} + \omega_{\text{ph}}(\mathbf{k} - \mathbf{k}'))^2 - E_{\mathbf{k}}^2} \quad (8)$$

Note that in the limit of weak coupling ($\Delta \ll \omega_D$) we can renormalize and introduce cutoff $\omega_c \ll \omega_D$ on ω' : Then the term $(\omega' + \Omega)/((\omega' + \Omega)^2 - \omega^2)$ can be just approximated as Ω^{-1} , and we find it is consistent to put $Z(\omega) = 1$, $\Delta(\omega) = \text{const}$, and thus obtain a BCS theory, with the effective λ given by

$$\lambda = 2 \int_0^\infty d\Omega \frac{\alpha^2(\Omega) F(\Omega)}{\Omega} \quad (9)$$

McMillan and Rowell: differential conductance measures $\Delta(\omega)$ via

$$(\partial I / \partial V)_S / (\partial I / \partial V)_N = \operatorname{Re} \left\{ \frac{\omega}{(\omega^2 - \Delta^2(\omega))^{1/2}} \right\}, \quad \hbar\omega \equiv eV \quad (10)$$

then can reconstruct $\alpha^2(\Omega)F(\Omega)$, compare with e.g. neutron scattering data. Fits in general very good.

McMillan:

Compute T_c from (finite- T variant of) Eliashberg equations: in practice must use definite form of $\alpha^2(\Omega)F(\Omega)$, so take the one for Nb. Result well fitted by

$$T_c = \frac{\theta_D}{1.45} \exp - \left\{ \frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.63\lambda)} \right\}, \quad \lambda \equiv 2 \int_0^\infty d\Omega \frac{\alpha^2(\Omega)F(\Omega)}{\Omega} \quad (11)$$

One sees that even in the limit $\lambda \rightarrow \infty$ (which is probably unrealistic, because the lattice is likely to be unstable in this limit) the maximum value attainable is

$$T_c^{\text{max}} = \frac{\theta_D}{1.45} \exp - \left(\frac{1.04}{1 - 0.63\mu^*} \right) \lesssim \frac{\theta_D}{5} \quad (12)$$

[†]since $\int \frac{dE}{\epsilon} = \int \frac{d\epsilon}{E}$.

However, McMillan suggested that even this is rather optimistic, since there seems empirically to be a cancellation such that for a given class of materials $\lambda \propto 1/M\omega_D^2$: thus, any attempt to increase λ is accompanied by a decrease in the prefactor ($\sim \theta_D$). By extrapolating empirical values McMillan empirically predicted a $T_c \sim 40\text{K}$ for V_3Si (actually $T_c \sim 24\text{K}$).

Nb. Empirically,[†] values of λ appear to be in the range 0.25–1.12 (for Pb) and those for μ^* in the range 0.1–0.2. [Allen & Dynes, Phys. Rev. B **12**, 95 (1975) suggest $T_c \sim 0.15 \lambda (\omega^2)^{1/2}$]

[Excursion: how good is experimental evidence for Eliashberg equations as such? McMillan & Rowell: ‘believed to be correct to lowest order in $\hbar\omega_D/\epsilon_F \sim 10^{-2} - 10^{-3}$, and *we are able to show experimentally that errors not larger a few %*’: but T_c/ω_D is only of order of few % even for Pb!]

2. Where is the energy saved?

G.V. Chester, Phys. Rev. B **103**, 1693 (1956)

Consider an arbitrary metal (in zero magnetic field) at $T = 0$. The total energy is the sum of electron KE K_m , nuclear KE K_M and the total Coulomb energy V , which is the sum of e–e, e–n and n–n terms. Thus

$$U = \langle K_m \rangle + \langle K_M \rangle + \langle V \rangle \quad (13)$$

The second input is the virial theorem, which states that

$$\langle K_m \rangle + \langle K_M \rangle + \frac{1}{2} \langle Q \rangle = \frac{3}{2} p \Omega \quad (\Omega = \text{volume}) \quad (14)$$

where Q is so called virial, namely

$$Q \equiv - \sum_{ij} \mathbf{r}_{ij} \nabla_{\mathbf{r}_{ij}} V(\mathbf{r}_{ij}) \quad (15)$$

which sums over all particles (e and n). Because $V(\mathbf{r}_{ij}) = \pm Ze^2/|\mathbf{r}_{ij}|$, we have the simple equality $Q = V$. Thus, the second relation is

$$\langle K_m \rangle + \langle K_M \rangle + \frac{1}{2} \langle V \rangle = \frac{3}{2} p \Omega \quad (\Omega = \text{volume}) \quad (16)$$

Finally, we have Feynman-Hellmann theorem

$$-M \left(\frac{\partial U}{\partial M} \right) = \langle K_M \rangle \quad (17)$$

(we have a similar theorem for K_m , but it is not much use since the electron mass is not variable).

[†]i.e. by taking λ from independent data and fitting T_c to McMillan formula.

Now let us subtract these results for the superconducting ground state from those for the normal one,[‡] and denote $X_s - X_n \equiv \Delta X$ (so that in particular $\Delta U < 0$). We get:

$$\Delta\langle K_m \rangle + \Delta\langle K_M \rangle + \Delta\langle V \rangle = \Delta U \quad (18)$$

$$\Delta\langle K_m \rangle + \Delta\langle K_M \rangle + \frac{1}{2}\Delta\langle V \rangle = \frac{3}{2}\Delta(p\Omega) \quad (19)$$

$$-M \frac{\partial\langle U \rangle}{\partial M} = \Delta\langle K_M \rangle \quad (20)$$

It is convenient to work at constant pressure: then the term $\frac{3}{2}p\Delta\Omega$ is known, experimentally, to be extremely small compared to ΔU , so we may legitimately neglect it. Also, we use the experimental fact that the shape of the curve $U(T)$ is to a high degree of approximation independent of M , and thus $\Delta U \propto T_c^2 \propto M^{-2\alpha}$, where α is the isotopic exponent. Thus eqn.'s (18-20) reduce to

$$\Delta\langle K_m \rangle + \Delta\langle K_M \rangle + \Delta\langle V \rangle = \Delta U \quad (21)$$

$$\Delta\langle K_m \rangle + \Delta\langle K_M \rangle + \frac{1}{2}\Delta\langle V \rangle = 0 \quad (22)$$

$$\Delta\langle K_M \rangle = 2\alpha\Delta U \quad (23)$$

[note that eqn. (23) is independent of the assumption of negligible $\Delta\Omega$]. Thus,

$$\Delta\langle V \rangle = 2\Delta U \quad (24)$$

$$\Delta\langle K_m \rangle = -(1 + 2\alpha)\Delta U \quad (25)$$

$$\Delta\langle K_M \rangle = 2\alpha\Delta U \quad (26)$$

For most of the simple BCS superconductors, the experimental value of α is approximately 1/2. Thus, we find

$$\Delta\langle V \rangle = -2\Delta\langle K_m \rangle = 2\Delta\langle U \rangle \quad (\text{note } \Delta U < 0!) \quad (27)$$

$$\Delta\langle K_M \rangle = \Delta U \quad (28)$$

Thus, we get the surprising result that the decrease in Coulomb energy by formation of the superconducting state is exactly balanced, in the limit $\alpha = 1/2$, by the increase in electron kinetic energy, and the condensation energy can be attributed entirely to a saving in *nuclear kinetic energy*! Note that this conclusion is completely independent of any microscopic theory, in particular of BCS theory which postdates Chester's work (by a month or so!).

3. *d*-vector notation[§]

Definition: $\langle \psi_\alpha(\mathbf{r})\psi_\beta(\mathbf{r}') \rangle \equiv F_{\alpha\beta}(\mathbf{r} - \mathbf{r}')$ or $\langle a_{\mathbf{k}\alpha}a_{-\mathbf{k}\beta} \rangle \equiv F_{\alpha\beta}(\mathbf{k})$

[‡]With the magnetic field energy which in practice is necessary to stabilize the normal state subtracted

[§]This notation is useful for the description of Fermi superfluids with spin triplet pairing, such as superfluid ³He. See e.g. AJL QL §6.2

concise notation:

$$\mathbf{d} = (i\sigma_y \boldsymbol{\sigma})_{\alpha\beta} F_{\beta\alpha} \quad (29)$$

(if in doubt, play with Zeeman states of $S = 1$ molecule!)

Consider a given value of \mathbf{k} and let the relevant spin-space ‘wave function’ be $|\Psi\rangle$. Iff \mathbf{d} real, $\mathbf{S} \cdot \mathbf{d} |\Psi\rangle = 0$, i.e. $S = 1$, $S_z = 0$ along \mathbf{d} also, along any axis $\perp \mathbf{d}$, $|\uparrow\uparrow\rangle + e^{i\phi} |\downarrow\downarrow\rangle$.

If for any single value of \mathbf{k} $\mathbf{d} \equiv \mathbf{d}(\mathbf{k})$ is real (though its direction may depend on the direction of \mathbf{k}) then the many-body state in question called ‘unitary’. For unitary states, easier to choose axes separately for each \mathbf{k} , (e.g. along \mathbf{d}) simply described by *scalar* $F(\mathbf{k})$, and scalar gap $\Delta(\mathbf{k})$, with $F_{\mathbf{k}} = \Delta(\mathbf{k})/2E_{\mathbf{k}}$, $E_{\mathbf{k}} = (\epsilon_{\mathbf{k}} + |\Delta(\mathbf{k})|^2)^{1/2}$. In a single reference frame F and Δ are matrices in spin space:

$$F_{\alpha\beta} = \frac{\Delta_{\alpha\beta}}{2E_{\mathbf{k}}} \quad (30)$$

and $|\Delta|^2$ is given by

$$|\Delta(\mathbf{k})|^2 = \text{Tr} \Delta(\mathbf{k}) \Delta^\dagger(\mathbf{k}) \sim |\mathbf{d}(\mathbf{k})|^2 \quad (31)$$

Examples of unitary states (in superfluid ^3He): ABM ($\mathbf{d} = \text{const}$), BW ($\mathbf{d}(\hat{\mathbf{n}}) \propto \hat{\mathbf{n}}$).