Miscellaneous topics in BCS theory (relevant to SC2)

1. Limits on T_c in BCS-type theories

BCS theory:

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

so, prima facie, limiting value is $1.13\hbar\omega_c \gtrsim \text{RT}$ if $\omega_c \sim \omega_{\text{D}}$. (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 $\gg \omega_{\text{D}}$. This can be handled by renormalization technique of lecture 6: recall,

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

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 $V_{\mathbf{kk}'}$ is roughly constant at some value V_c, then we have

$$V_c \sum_{\mathbf{k}} \frac{1}{2\epsilon_{\mathbf{k}}} \simeq V_c N(0) \ln(\epsilon_{\text{F}}/\omega_{\text{D}}) \tag{3}$$

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

$$t = \frac{V_c}{1 + N(0)V_c \ln(\epsilon_{\text{F}}/\omega_{\text{D}})} \tag{4}$$

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

$$\mu^* = \mu/(1 + \mu \ln(\epsilon_{\text{F}}/\omega_{\text{D}})) \tag{5}$$

so for $\mu \to \infty$, $\mu^* \to (\ln \epsilon_{\text{F}}/\omega_{\text{D}})^{-1}$ (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

$$T_c = 1.13\hbar\omega_{\text{D}} \exp -1/(\lambda - \mu^*) \tag{6}$$

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

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

Eliashberg equations (at $T = 0$):

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

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

($\alpha^2(\Omega) \equiv$ mean-square coupling constant to phonons in frequency range $[\Omega, \Omega + d\Omega]$, $F(\Omega) =$ phonon DOS in this range) Note: 1st Eliashberg equation (7a) is, apart from $Z(\omega)$ correction, simply†

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

The second Eliashberg equation (7b), which is also valid in the normal phase ($\Delta(\omega') = 0$), expresses the renormalization of the single-electron energy by emission and absorption of virtual phonons; by comparing (7b) to the standard second-order perturbation theory expression, we see that $Z(\omega)$ is the ratio of the value of ϵ_k as renormalized by the electron-phonon interaction to the original value. Thus the $1/Z(\omega)$ in eqn. (7a) expresses the corresponding renormalization of the DOS. Note that in the limit of weak coupling ($\Delta \ll \omega_{\mathrm{D}}$) we can renormalize and introduce cutoff $\omega_c \ll \omega_{\mathrm{D}}$ 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 $Z(\omega) = 1(+0(\lambda))$, $\Delta(\omega) =$ const, and thus obtain a BCS theory, with the effective λ given by

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

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

$$\big(\partial I / \partial V\big)_{\mathrm{S}}(\omega) / \big(\partial I / \partial V\big)_{\mathrm{N}} = \mathrm{Re} \left\{ \frac{\omega}{\left(\omega^2 - \Delta^2(\omega)\right)^{1/2}} \right\}, \quad \hbar\omega \equiv eV \tag{10}$$

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

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

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

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

$$T_c^{\max} = \frac{\theta_{\mathrm{D}}}{1.45} \exp - \left(\frac{1.04}{1 - 0.63\mu^*} \right) \lesssim \frac{\theta_{\mathrm{D}}}{5} \tag{12}$$

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 $\lambda \propto 1/M{\omega_{\mathrm{D}}}^2$: thus, any attempt to increase λ is accompanied by a decrease in the prefactor ($\sim \theta_{\mathrm{D}}$). By extrapolating empirical values McMillan empirically predicted a $T_c \sim 40\mathrm{K}$ for V_3Si (actually $T_c \sim 24\mathrm{K}$).

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 $T_c \sim 0.15\,\lambda\langle\omega^2\rangle^{1/2}$]

[Excursion: how good is experimental evidence for Eliashberg equations as such? McMillan & Rowell: 'believed to be correct to lowest order in $\hbar\omega_{\mathrm{D}}/\epsilon_{\mathrm{F}} \sim 10^{-2} - 10^{-3}$, 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!]

[H_2S at ∼200 GPa: See Duan et al. Sci. Rep. **4**, 6968 (2014). Li et al., J. Chem. Phys. **140**, 174712(2014): Drozhdov et al., ArXiv: 1412.0460]

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 its expectation value U is given by

$$U = \langle K_m \rangle + \langle K_M \rangle + \langle V \rangle \tag{13}$$

The second input is the virial theorem, which states that

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

where Q is so called virial, namely

$$Q \equiv -\sum_{ij} \mathbf{r}_{ij} \boldsymbol{\nabla}_{\mathbf{r}_{ij}} V(\mathbf{r}_{ij}) \tag{15}$$

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

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

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

Finally, we have Feynman-Hellmann theorem

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

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

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:

$$\Delta\langle K_m \rangle + \Delta\langle K_M \rangle + \Delta\langle V \rangle = \Delta U \tag{18}$$

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

$$-M\frac{\partial\langle U \rangle}{\partial M} = \Delta\langle K_M \rangle \tag{20}$$

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

$$\Delta\langle K_m \rangle + \Delta\langle K_M \rangle + \Delta\langle V \rangle = \Delta U \tag{21}$$

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

$$\Delta\langle K_M \rangle = 2\alpha\Delta U \tag{23}$$

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

$$\boxed{\begin{aligned} \Delta\langle V \rangle &= 2\Delta U && (24)\\ \Delta\langle K_m \rangle &= -(1+2\alpha)\Delta U && (25)\\ \Delta\langle K_M \rangle &= 2\alpha\Delta U && (26)\end{aligned}}$$

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

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

$$\Delta\langle K_M \rangle = \Delta U \tag{28}$$

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!).

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

3. d-vector notation§

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

concise notation:

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

(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 $|\Psi\rangle$. If $\mathbf{d}$ 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:

$$F_{\alpha\beta} = \frac{\Delta_{\alpha\beta}}{2E_\mathbf{k}} \tag{30}$$

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

$$|\Delta(\mathbf{k})|^2 = \mathrm{Tr}\,\Delta(\mathbf{k})\Delta^\dagger(\mathbf{k}) \sim |\mathbf{d}(\mathbf{k})|^2 \tag{31}$$

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

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