

Magnetic impurity and other 'pair-breaking' effects

References: de Gennes Chapter 8; AJL QL section 5.9

One of the most striking experimental facts about (classical) superconductivity is that while it is rather insensitive to nonmagnetic impurities, even a rather small concentration of magnetic impurities (ie, those corresponding to a finite local moment) can lead to a drastic suppression of T_c or even the complete vanishing of superconductivity. The basic reason for this and related affects is that such impurities destroy the invariance of the (conduction-electron) Hamiltonian under time reversal. In the following, we suppose until further notice that the effect of magnetic impurities is to add to the conduction-electron Hamiltonian a term of the form

$$\Delta\mathcal{K} = \sum_m J_m \mathbf{S}_m \cdot \boldsymbol{\sigma}(\mathbf{r}_m) \quad (1)$$

where $\boldsymbol{\sigma}(\mathbf{r}) \equiv \sigma_{\alpha\beta} \psi_\alpha^\dagger(\mathbf{r}) \psi_\beta(\mathbf{r})$ is the conduction-electron spin density at the point \mathbf{r} . The spins \mathbf{S}_m are taken to be classical and random both in orientation and in position.

In lecture 9 we considered the case of nonmagnetic impurities, and showed that by pairing time-reversed eigenstates ($|n \uparrow\rangle, |\bar{n} \downarrow\rangle$) of the single-particle Hamiltonian, we would obtain almost as large an (average) value of the quantity $F(\mathbf{r}, \mathbf{r})$ as in the 'pure' case. To recapitulate the argument, we write in that case

$$\Psi_{\text{BCS}} = \prod_n (u_n + v_n a_{n\uparrow} a_{\bar{n}\downarrow}) |\text{vac}\rangle \quad (2)$$

and the quantity $F(\mathbf{r}, \mathbf{r})$ takes the value

$$F(\mathbf{r}, \mathbf{r}) \equiv \langle \psi_\uparrow^\dagger(\mathbf{r}) \psi_\downarrow^\dagger(\mathbf{r}) \rangle = \sum_n u_n v_n \phi_n(\mathbf{r}) \phi_{\bar{n}}(\mathbf{r}) \quad (3)$$

but since $\phi_{\bar{n}}(\mathbf{r}) \equiv \phi_n^*(\mathbf{r})$ this becomes simply

$$F(\mathbf{r}, \mathbf{r}) = \sum_n u_n v_n |\phi_n(\mathbf{r})|^2 \quad (4)$$

and with an appropriate choice of the parameter $u_n v_n (= \Delta_n/2E_n)$ this can be made approximately as large (or larger) as its value for the pure case. Thus, the pair term in the potential energy, which for the simple contact potential considered is simply

$$\langle V \rangle_{\text{pair}} = V_0 \int |F(\mathbf{r})|^2 d\mathbf{r} \quad (5)$$

is also just as large as in the pure case.

For a system lacking time reversal invariance we cannot repeat this argument, because in general the eigenstates of the single-particle Hamiltonian no longer occur in pairs related by time reversal. We therefore have two obvious choices: (a) pair in eigenstates

of if \hat{H}_0 (which are not in general time-reversed) (b) pair in time reversed states (which are not in general eigenstates of \hat{H}_0). Of course, intermediate choices are also possible.

Before embarking on a quantitative calculation, let's try to consider the pros and cons of choices (a) and (b) qualitatively. If we make choice (a), then from the kind of general arguments developed in lecture 5 we would expect that the best choice is to pair eigenstates of \hat{H}_0 with nearly degenerate energies ϵ_n . (These will not of course in general be eigenstates of spin). Such a choice will lead to a depression of the quantity $F(\mathbf{r}, \mathbf{r})$, which is effectively equivalent to a suppression of the constant V_0 ; since T_c depends exponentially on V_0 , we expect it to be strongly depressed (except in very special circumstances, cf. below). So let's consider alternative (b) (which is (something like) what the system actually does, cf. below). We then lose little or nothing on the pairing contribution to $\langle V \rangle$, but the price is that we increase the kinetic energy; crudely speaking, we have to start our pairing from a "pseudo-Fermi sea" that is the Fermi sea that would describe the normal system subject to a Hamiltonian without the magnetic terms. What does it cost us to create this "pseudo-Fermi sea" from the true normal-groundstate (i.e., the groundstate of \hat{H}_0 including the magnetic impurities)? A back of envelope argument goes as follows: consider a spin (or more generally time-reversal) eigenstate made up out of eigenstates of \hat{H}_0 close to the Fermi energy. Such a state will have a width Γ ($\equiv \hbar/\tau_K$, see below) which tends to a constant near ϵ_F , i.e., it is made up of a packet of eigenstates of \hat{H}_0 which have spread $\sim \Gamma/2$. Thus, to reconstitute a "pseudo-Fermi sea" out of such spin eigenstates we need to supply an extra energy $\sim \Gamma/2$ to the number of states involved in the rearrangement, which is $\sim (dn/d\epsilon)\Gamma/2$. The total energy required is thus $\sim \frac{1}{4}(dn/d\epsilon)\Gamma^2 \equiv \frac{1}{2}N(0)\Gamma^2$. On the other hand, the condensation energy of the superconducting state relative to the "pseudo-Fermi sea" normal (pseudo-) groundstate is $\frac{1}{2}N(0)\Delta^2$ where Δ is the energy gap in the material without magnetic impurities. Thus, we expect superconductivity to become energetically unfavorable even at $T = 0$ (i.e. $T_c \rightarrow 0$) when $\Gamma \sim \Delta$. It is amusing that while the numerical factors in the above argument are clearly rather arbitrary, the exact criterion for the disappearance of superconductivity does in fact turn out to be $\Gamma = \Delta$ (see below). If for a pure material (in the absence of nonmagnetic impurities), we introduce the relaxation time τ_K against T -violating effects, so that $\Gamma \equiv \hbar/\tau_K$, and the corresponding mean free path $l_K \equiv v_F\tau_K$, and recall the definition of the Pippard coherence length ξ_0 , this criterion can be rewritten $l_K = \xi_0/\pi$.

Now let us turn to a more exact calculation. In the general case, the presence of terms like $J_i S_i^x \sigma_x(\mathbf{r}_i)$, in the Hamiltonian means that the normal-state eigenfunctions are not in general eigenstates of spin, and the formulae then become rather messy: cf. de Gennes section 8.1. Let us therefore specialize to a rather artificial case which gives the essentials, namely one in which the impurity spins are constrained to lie along the z -axis, with however a random sign (and, still at random positions). Then the normal-state eigenfunctions can (indeed must) be chosen to be eigenstates of σ_z : we label them $\phi_{n\uparrow}(\mathbf{r})$, $\phi_{n\downarrow}(\mathbf{r})$. Since we wish the pair wave function $F(\mathbf{r}, \mathbf{r})$ to be as large as possible,

we pair with opposite spins; we write the BCS wave function in the form

$$\Psi_{\text{BCS}} = \prod_n (u_n + v_n a_{n\uparrow}^\dagger a_{\bar{n}\downarrow}^\dagger) |0\rangle \quad (6)$$

where the states n and \bar{n} are for the moment undetermined (and in particular are not necessarily energy eigenstates). We can then go through the standard derivation of the BdG equations as illustrated in lecture 11, with one important difference: the quantity u_n is associated with “spin up” and v_n with “spin down” and the relevant single-particle Hamiltonians are therefore different: in fact, the BdG eigenstates take the slightly modified form:

$$\begin{aligned} \hat{H}_{0,\uparrow} u_n(\mathbf{r}) + \Delta(\mathbf{r}) v_n(\mathbf{r}) &= E_n u_n(\mathbf{r}) \\ -\hat{H}_{0,\downarrow}^* v_n(\mathbf{r}) + \Delta(\mathbf{r}) u_n(\mathbf{r}) &= E_n v_n(\mathbf{r}) \end{aligned} \quad (7)$$

where we defined

$$\hat{H}_{0\sigma} \equiv \hat{p}^2/2m + V(r) + J \sum_i S_i^z \sigma(\mathbf{r} - \mathbf{r}_i) \quad (8)$$

with $V(\mathbf{r})$ the spin-independent part of the one-particle potential.

Note that $\hat{H}_{0\downarrow}$ is the time-reverse of $\hat{H}_{0\uparrow}$ i.e., formally, if \hat{K} is the time-reversal operator then $K^\dagger \hat{H}_{0\sigma} K = \hat{H}_{0,-\sigma}^*$.

In general the solution of equations (7) is complicated and may require numerical computation. However, in the limit $T \rightarrow T_c$ (so that $\Delta(\mathbf{r}) \rightarrow 0$) a very elegant method of solution is available¹. In the normal state, ($\Delta(\mathbf{r}) \equiv 0$) the solution of the equations (7) is simply

$$\begin{aligned} u_n^0(\mathbf{r}) = \phi_{n\uparrow}(\mathbf{r}), v_n^0(\mathbf{r}) = 0, (\epsilon_n > 0) & \quad E_n = \epsilon_{n\uparrow} \\ u_n^0(\mathbf{r}) = 0, v_n^0(\mathbf{r}) = \phi_{n\downarrow}(\mathbf{r}), (\epsilon_n < 0) & \quad E_n = \epsilon_{n\downarrow} \end{aligned} \quad (9)$$

where the sets $\phi_{n\uparrow}(\mathbf{r})$ and $\phi_{n\downarrow}^*(\mathbf{r})$ each form a complete set (provided we include the $\epsilon_n < 0$ solutions for $\phi_{n\uparrow}(\mathbf{r})$, etc.). We can then expand the first-order terms as²

$$\begin{aligned} u_n^1(\mathbf{r}) &= \sum_{m \neq n} e_{nm} \phi_{m\uparrow}(\mathbf{r}) \\ v_n^1(\mathbf{r}) &= \sum_{m \neq n} d_{nm} \phi_{m\downarrow}^*(\mathbf{r}) \end{aligned} \quad (10)$$

Let us insert $u_n^1(\mathbf{r})$ into the first BdG equation, multiply by $\phi_{m\uparrow}^*(\mathbf{r})$ and integrate. In this way we obtain

$$(|\epsilon_{n\uparrow}| - \epsilon_{m\uparrow}) e_{nm} = \int \Delta(\mathbf{r}) \phi_{m\uparrow}^*(\mathbf{r}) v_n^0(\mathbf{r}) d\mathbf{r} \quad (11)$$

¹For the next four pages, I follow closely the discussion in de Gennes sections 7.1 and 8.1–2, with minor variations. For an alternative derivation which does not use the BdG equations, see AJL QL §5.9

²The diagonal terms e_{mm} can always be chosen zero by a suitable phase choice for u_n^0 .

and similarly for the second equation, multiplying by $\phi_{m\downarrow}(\mathbf{r})$ and integrating,

$$(|\epsilon_{n\uparrow}| + \epsilon_{m\uparrow})d_{nm} = \int \Delta(\mathbf{r})\phi_{m\downarrow}^*(\mathbf{r})u_n^0(\mathbf{r})d\mathbf{r} \quad (12)$$

Now, the self-consistency equation for Δ has the form

$$\Delta(\mathbf{r}) = V_0 \sum_n u_n(\mathbf{r})v_n^*(\mathbf{r}) \tanh \beta E_n/2 \quad (13)$$

Where we substitute the form (10) of $u_n(\mathbf{r})$ and $v_n(\mathbf{r})$ in the RHS, the zeroth-order term gives zero since we automatically have $u_n^0(\mathbf{r})v_n^0(\mathbf{r}) = 0$. The terms linear in Δ give an expression of the form $\int K(\mathbf{r}, \mathbf{r}')\Delta(\mathbf{r}')d\mathbf{r}'$, where $K(\mathbf{r}, \mathbf{r}')$ is given after a little algebra by the expression

$$K(\mathbf{r}, \mathbf{r}') = V_0 \sum_{nm} \left\{ \frac{u_n^0(\mathbf{r})u_n^{0*}(\mathbf{r}')\phi_{m\downarrow}^*\phi_{m\downarrow}(\mathbf{r})(\mathbf{r}') \tanh \beta|\epsilon_{n\uparrow}|/2}{|\epsilon_{n\downarrow}| + \epsilon_{m\uparrow}} + \frac{v_n^{0*}(\mathbf{r})v_n^0(\mathbf{r}')\phi_{m\uparrow}^*\phi_{m\uparrow}(\mathbf{r}) \tanh \beta|\epsilon_{n\downarrow}|/2}{|\epsilon_{n\downarrow}| - \epsilon_{m\uparrow}} \right\} \quad (14)$$

which is a generalization of de Gennes equation (7.8). Using the fact that the second term only exists for $\epsilon_{n\downarrow} < 0$ and so $\tanh \beta|\epsilon_{n\downarrow}|/2 \equiv -\tanh \beta\epsilon_{n\downarrow}/2$, and interchanging n and m in the second term, we can write this in a more compact form:

$$K(\mathbf{r}, \mathbf{r}') = V_0/2 \sum_{nm} \left\{ \frac{\tanh(\beta\epsilon_{n\uparrow}) + \tanh(\beta\epsilon_{m\downarrow})}{\epsilon_{n\uparrow} + \epsilon_{m\downarrow}} \times \phi_{n\uparrow}(\mathbf{r})\phi_{m\downarrow}(\mathbf{r})\phi_{m\downarrow}^*(\mathbf{r}')\phi_{n\uparrow}^*(\mathbf{r}') \right\} \quad (15)$$

$K(\mathbf{r}, \mathbf{r}')$ is the kernel of the linearized gap equation

$$\Delta(\mathbf{r}) = \int K(\mathbf{r}, \mathbf{r}')\Delta(\mathbf{r}')d\mathbf{r}' \quad (16)$$

it is expressed entirely in terms of the normal-state eigenfunctions $\phi_{m\sigma}(\mathbf{r})$. In the ‘‘pure BCS’’ case, where the eigenstates are mutually orthogonal plane waves, we may take $\Delta(\mathbf{r}) = \text{const}$, and it may be straightforwardly verified that the only contribution to the integral over \mathbf{r}' in equation (16) comes from $m \equiv \mathbf{k}$, $n \equiv -\mathbf{k}$; we thus recover the BCS equation for T_c . A slight generalization of this argument applies to the case of nonmagnetic disorder.

We now ask: is it possible to relate $K(\mathbf{r}, \mathbf{r}')$, and hence the gap equation, more generally to some experimentally measurable properties of the normal phase? Actually, this is a question of rather general interest, for example in cases where the physical conditions, and hence $\Delta(\mathbf{r})$, vary substantially in space: in fact, in such cases analysis of equation (15) recovers for us the GL equation, with an identification of the parameters entering it: see de Gennes sections 7.1–2. However, we are interested in the case where the impurity distribution, while microscopically random, is on average homogenous. To

analyze this, and some other similar cases, it is useful to transform the expression for $K(\mathbf{r}, \mathbf{r}')$ somewhat.

Step 1 is to note that because of the identity

$$\tanh \beta\epsilon/2 = 2k_{\text{B}}T \sum_n \frac{1}{\epsilon - i\hbar\omega_n} \quad (17)$$

where $\omega \equiv (n + 1/2)2\pi k_{\text{B}}T$ and the sum runs over all positions or negative integers, we can write the expression involving the ϵ 's as

$$2k_{\text{B}}T \sum_{\omega_m} \frac{1}{\epsilon_{n\uparrow} - i\hbar\omega_m} \frac{1}{\epsilon_{m\downarrow} + i\hbar\omega_m} \quad (18)$$

We can then introduce continuous variables of integration ϵ, ϵ' such that $\sum_n \rightarrow \int d\epsilon N(0)$, and a quantity

$$Q(\epsilon, \epsilon' : \mathbf{r}, \mathbf{r}') \equiv \sum_n \sum_m \delta(\epsilon_{n\uparrow} - \epsilon) \delta(\epsilon_{m\downarrow} - \epsilon') \phi_{n\uparrow}(\mathbf{r}) \phi_{m\downarrow}(\mathbf{r}) \phi_{m\downarrow}^*(\mathbf{r}') \phi_{n\uparrow}^*(\mathbf{r}') \quad (19)$$

Then

$$K(\mathbf{r}, \mathbf{r}') = V_0 k_{\text{B}}T \sum_{\omega} \int d\epsilon \int d\epsilon' \frac{Q(\epsilon\epsilon' : \mathbf{r}\mathbf{r}')}{(\epsilon - i\hbar\omega)(\epsilon' + i\hbar\omega)} \quad (20)$$

Step 2. (this is the trickiest): We now argue that since the states near the Fermi energy in the normal phase are in no way “special,” the quantity $Q(\epsilon\epsilon' : \mathbf{r}\mathbf{r}')$ is very insensitive to the “center of mass” variable $(\epsilon + \epsilon')/2$, and thus we can replace³ the quantity $\sum_n \sum_m \delta(\epsilon_{n\uparrow} - \epsilon) \delta(\epsilon_{m\downarrow} - \epsilon')$ by $(\epsilon - \epsilon')^{-1} \sum_{mn} (1 - f_{n\uparrow}) f_{m\downarrow} \delta(\epsilon_{n\uparrow} - \epsilon_{m\downarrow} - (\epsilon - \epsilon'))$, where the f 's are Fermi functions. Thus

$$Q(\epsilon, \epsilon' : \mathbf{r}, \mathbf{r}') = Q(\epsilon - \epsilon' : \mathbf{r}, \mathbf{r}') = \sum_{nm} f_{m\downarrow} (1 - f_{n\uparrow}) \delta(\epsilon_{n\uparrow} - \epsilon_{m\downarrow} - (\epsilon - \epsilon')) / (\epsilon - \epsilon') \\ \times \phi_{m\downarrow}(\mathbf{r}) \phi_{m\downarrow}^*(\mathbf{r}') \phi_{n\uparrow}^*(\mathbf{r}') \phi_{n\uparrow}(\mathbf{r}) \quad (21)$$

Equation (21) looks very reminiscent of the imaginary part of a correlation function. In fact, let us for orientation consider the case where \hat{H}_0 is real and thus the $\phi_{m\uparrow, \downarrow}(\mathbf{r})$ can be chosen real. Then we can, trivially, add and remove complex conjugation, and thus rewrite Q in the form

$$Q(\epsilon - \epsilon' : \mathbf{r}, \mathbf{r}') = \sum_{mn} f_{m\downarrow} (1 - f_{n\uparrow}) \phi_{n\uparrow}^*(\mathbf{r}) \phi_{m\downarrow}^*(\mathbf{r}) \phi_{m\downarrow}(\mathbf{r}') \phi_{n\uparrow}(\mathbf{r}') \delta(\epsilon_{n\uparrow} - \epsilon_{m\downarrow} - (\epsilon - \epsilon')) / (\epsilon - \epsilon') \quad (22)$$

But the expression on the RHS is simply the imaginary part of the normal-state correlation function $\langle\langle S_+(\mathbf{r}) S_-(\mathbf{r}') \rangle\rangle(\omega)$ for $\omega = \epsilon - \epsilon'$! The great advantage of this result is that we can now use our phenomenological knowledge of the behavior of such correlation functions in the normal phase to calculate Q and hence the kernel $K(\mathbf{r}, \mathbf{r}')$.

³This follows because in the latter comparison in view of its antisymmetry with respect to $\epsilon - \epsilon'$, can replace $(1 - f_{n\uparrow}) f_{m\downarrow}$ by $\frac{1}{2} \{ (1 - f_n) f_m - (m \rightleftharpoons n) \} = \frac{1}{2} (f_n - f_m)$ and $\int_0^\infty f(E + \omega) - f(E - \omega) = 2\omega$

At this point, it is convenient to make the ansatz that $\Delta(\mathbf{r})$ is approximately constant in space; this is likely to be true if the distribution of impurity potentials, magnetic and nonmagnetic, is homogeneous and there are no other sources of inhomogeneity. Substituting into the linearized gap equation,

$$\Delta(\mathbf{r}) = \int K(\mathbf{r}, \mathbf{r}') \Delta(\mathbf{r}') d\mathbf{r}' \quad (23)$$

and integrating over \mathbf{r} and \mathbf{r}' , we see that it becomes ($\omega \rightarrow \omega_m$ in the Matsubara sum to avoid confusion)

$$\begin{aligned} 1 &= \frac{1}{v} \iint K(\mathbf{r}\mathbf{r}') d\mathbf{r}d\mathbf{r}' \quad (v \equiv \text{volume}) \\ &= \frac{1}{v} V_0 k_B T \sum_{\omega_m} \iint \frac{d\epsilon d\epsilon'}{(\epsilon - i\hbar\omega_m)(\epsilon' + i\hbar\omega_m)} \iint Q(\epsilon - \epsilon' : \mathbf{r}, \mathbf{r}') d\mathbf{r}d\mathbf{r}' \\ &= V_0 k_B T \sum_{\omega_m} \iint \frac{d\epsilon d\epsilon'}{(\epsilon - i\hbar\omega_m)(\epsilon' + i\hbar\omega_m)} \frac{1}{v} \text{Im} \langle \langle S_+ S_- \rangle \rangle (\epsilon - \epsilon') / (\epsilon - \epsilon') \end{aligned} \quad (24)$$

where $\langle \langle S_+ S_- \rangle \rangle(\omega)$ is now the correlation function of the total spin of the system. This quantity is exactly conserved in the absence of spin-flip scattering. In the presence of such scattering, an obvious ansatz is simple exponential relation, $S_+(t) = S_+(0) \exp(-t/\tau_s)$ where τ_s is the spin relaxation time. This gives (in the “electron-gas” model of the normal state).

$$\langle \langle S_+ S_- \rangle \rangle(\omega) = \frac{N(0)}{1 + i\omega\tau_s} \quad (25)$$

so that $\text{Im} \langle \langle S_+ S_- \rangle \rangle(\omega) / \omega = \frac{\tau_s N(0)}{1 + \omega^2 \tau_s^2}$. Hence the gap equation becomes

$$1 = V_0 N(0) k_B T \sum_{\omega} \iint \frac{d\epsilon d\epsilon'}{(\epsilon - i\hbar\omega)(\epsilon' + i\hbar\omega)} (\tau_s / (1 + (\epsilon - \epsilon')^2 \tau_s^2)) \quad (26)$$

The double integral turns out to be simply $2\pi / (2|\omega| + 1/\tau_s)$. Hence, finally,

$$(N(0)V_0)^{-1} = \pi k_B T \sum_{\omega} \frac{1}{2|\omega| + 1/\tau_s} \quad (27)$$

It is possibly instructive to rewrite the Matsubara sum as an explicit integral over energy. By evaluating the integral $\int_{-\infty}^{\infty} \frac{\tanh \beta\epsilon/2}{\epsilon + i\Gamma} d\epsilon$ by contour integration, we find that the relevant form is ($\Gamma = 1/2\tau_s$)

$$(N(0)V_0)^{-1} = \text{Re} \int_0^{\epsilon_0} \frac{\tanh \beta\epsilon/2}{\epsilon + i/(2\tau_s)} d\epsilon \quad (28)$$

so that the energies which occur on the RHS are effectively “broadened” by an amount $1/2\tau_s$. This corresponds, intuitively, to the fact that on average the difference between the mean energy of an up and down spin in a given orbital state is of this order.

In the literature, it is conventional to subtract from equation (27) the $\tau_s = \infty$ gap equation (with transition temperature T_{c0}) and express the result in the form

$$\ln(T_{c0}/T_c) = \psi\left(1/2 + \frac{\hbar}{4\pi\tau_s k_B T_c}\right) - \psi(1/2) \quad (29)$$

where $\psi(1/2)$ is the so called "digamma function" defined by ($\Gamma(z) \equiv$ Euler Γ -function)

$$\psi(z) \equiv \Gamma'(z)/\Gamma(z) = -0.577 + \sum_{v=1}^{\infty} \left(1/v - 1/(v+z)\right) - z^{-1} \quad (30)$$

Note that the equation for the relative reduction of T_c is expressed entirely in terms of the single dimensionless parameter $\alpha \equiv \hbar/(2\pi\tau_s k_B T_c)$.

A particularly simple result holds for the value of \hbar/τ_s which completely destroys superconductivity. This is most easily obtained by evaluating the RHS of expression (28) for $\beta \rightarrow \infty$ and comparing with the $\tau_s = \infty$, $T = 0$ gap equation to obtain

$$\text{Re} \int_0^{\epsilon_c} d\epsilon/(\epsilon + i/2\tau_s) = \int_0^{\epsilon_c} d\epsilon/\sqrt{\epsilon^2 + \Delta^2} \quad (31)$$

which for large ϵ_c yields $1/2\tau_s = \Delta(0)$.

The general behavior of T_c as a function of \hbar/τ_K is as shown. For small impurity concentration the slope is given approximately by $k_B(T_{c0} - T_c) \cong \pi\hbar/2\tau_K$. The region just below the N-S transition temperature which is shaded in the figure is very interesting. As shown by Abrikosov and Gor'kov in their original paper, in this regime that superconductor is gapped, that is, there exist Bogoliubov quasiparticles of arbitrarily low energy. I follow the discussion of de Gennes (Section 8.2):

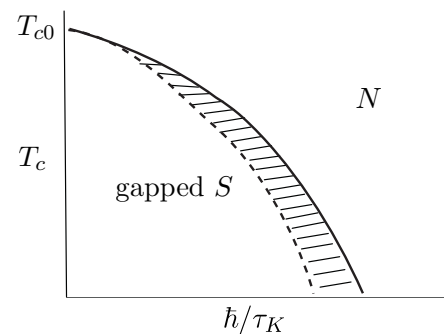
Consider for definiteness the case $T = 0$, but with a concentration of impurities close to critical; then we may reasonably assume that the "gap" Δ is small, and work as above to lowest order in it. To order Δ we have for the energy eigenvalues

$$E_n = |\epsilon_n| + |\Delta|^2 \mathcal{P} \sum_m \frac{|\langle n|K|m\rangle|^2}{|\epsilon_n| + |\epsilon_m|}, \quad \mathcal{P} = \text{principal part} \quad (32)$$

If the one-electron part of the Hamiltonian is invariant under time reversal, then the only state m occurring in the sum is degenerate with ϵ_n , so that

$$E_n = |\epsilon_n| + |\Delta|^2/(2|\epsilon_n|) \quad (33)$$

This is the beginning of an expansion in $\Delta/|\epsilon_n|$: it clearly works for $|\epsilon_n| \rightarrow \infty$ but fails for $|\epsilon_n| \rightarrow 0$. If the system is not invariant under K , then the second term is not



singular as $|\epsilon_n| \rightarrow 0$ and the perturbation theory may work. Suppose in particular K relaxes exponentially to zero with time constant τ_K , then

$$\begin{aligned} E_n &= |\epsilon_n| + |\Delta|^2 \mathcal{P} \int d\epsilon' \operatorname{Im} \chi_K(\epsilon_n - \epsilon') / (\epsilon_n + \epsilon') \\ &= |\epsilon_n| + |\Delta|^2 \mathcal{P} \int d\epsilon' \frac{\tau_K}{1 + (\epsilon_n - \epsilon')^2 \tau_K^2} \frac{1}{\epsilon_n + \epsilon'} \\ &= |\epsilon_n| + \frac{2|\Delta|^2 |\epsilon_n|}{(2\epsilon_n)^2 + (\hbar/\tau_K)^2} \end{aligned} \quad (34)$$

If now we take $|\epsilon_n| \ll \hbar/\tau_K$, this tends to

$$E_n = |\epsilon_n| (1 + 2(\Delta\tau_K/\hbar)^2) \quad (35)$$

which can be arbitrarily small. The density of states is

$$N_s(\epsilon) = N(0) d\epsilon/dE \cong \left\{ 1 + 2(\Delta/\hbar)^2 \frac{(2\epsilon)^2 - (\hbar/\tau_K)^2}{(2\epsilon)^2 + (\hbar/\tau_K)^2} \right\} \quad (36)$$

so for $\epsilon < \hbar/\tau_K$ is less than the N-state value but for $\epsilon > \hbar/\tau_K$ greater. [cf. de Gennes Fig. 8.5.]

The above considerations work for most kinds of pair-breaking effects. However, we should always bear in mind that solutions we have obtained are at most variational ansatz, and we cannot exclude that there may exist other solutions which as it were differ by a finite amount from the simple perturbation-theoretic ones. As an example, consider the case of a constant finite Zeeman field (assumed to act only on the spins and not on the orbital degrees of freedom). We could follow through the above calculation, but now the spectrum of S_+ is a δ -function at $\epsilon - \epsilon' = 2\mu_B \mathcal{H}$, the energy necessary to flip a spin. Correspondingly, the zero- T linearized gap equation becomes

$$(N(0)V_0)^{-1} = \int_0^{\epsilon_c} \frac{d\epsilon}{\epsilon + \mu_B \mathcal{H}} \cong \ln(\epsilon_c/\mu_B \mathcal{H}) \quad (37)$$

(where in the last equality we assume ϵ_c is large). The zero-field $T = 0$ gap Δ satisfies the relation

$$(N(0)V_0)^{-1} = \int_0^{\epsilon_c} \frac{d\epsilon}{\sqrt{\epsilon^2 + \Delta^2}} \cong \ln(2\epsilon_c/\Delta) \quad (38)$$

and thus the critical field at $T = 0$ should apparently be given by $\mu_B \mathcal{H} = \Delta/2$.

However, this conclusion is not correct. To see this, let us compare the energies of the normal state in field \mathcal{H} , and the paired state obtained by refusing to let the particles polarize in the field and then proceeding as if in field 0. Relative the normal state in zero field, the first has energy $-(1/2)\mu_B^2 \mathcal{H}^2 (dn/d\epsilon) = -\mu_B^2 \mathcal{H}^2 N(0)$, while the second has energy (cf. Lecture 6) $-(1/2)\Delta^2 N(0)$. Thus the second is stable for $\mu_B \mathcal{H} < \Delta/\sqrt{2}$, i.e. beyond the limit given by the perturbation calculation. The latter is actually the limit of metastability of the N phases, i.e. the ‘‘supercooling’’ field. cf. Maki and Tsuneto, Prog. Theor. Phys. 21, **945** (1964).

(A further complication: FFLO state).