Non-BCS Superconductivity: Diagnostics

The "classic" superconductors—that is, those whose behavior is well accounted for by the BCS theory, which essentially means all those known prior to 1986 with the exception of some "heavy-fermion" superconductors—have, or are believed to have, at least four general properties in common:

(1) The transition temperature T_c never exceeds 25K.

(2) The normal state appears to be well described by textbook (Fermi liquid) theory.

(3) The principal mechanism of formation of Cooper pairs is a phonon-induced attraction.

(4) The symmetry of the Cooper pairs is s-wave (or more precisely, the "simplest" representation of the appropriate crystal symmetry group).

In addition, most although not all of the classic superconductors have three other properties in common:

(5) The structure, although possibly anisotropic, is essentially 3-dimensional.

(6) The system is not particularly close to other types of ordering transition (e.g. magnetic ones).

(7) Superconductivity is not particularly sensitive to chemical stoichiometry (in the case of alloys).

All of the "exotic" classes of superconductors to be discussed in this part of the course (are believed to) fail to satisfy at least one of conditions (1)–(7): The cuprates fail *all* of them.

Clearly, the properties (1), (5), (6) and (7) can be read directly from experiment. What about (3) and (4)? (We will consider (2) in a later lecture.)

Property	⟵ Class ⟶							
	Classic	BKBO MgB_2	Heavy-fermions	Organics	Ruthenates	Fullerenes	Ferro-pnictides	Cuprates
$T_c < 25K$	(√)	×	√	√	√	×	×	×
FL normal state	√	√	×	×	×	√		×
No neighboring phase trans.	√	√	×	√	√	√		×
OP s-wave	√	√	?	?	×	×		×
Phonon mechanism	√	√	×	?	?	√		×
Crystal structure simple	√	×	√	×	×	×	×	×
Stoichiometry-insensitive	√	√	√	√	√	×		×

Diagnostics of non-phonon mechanism

A. (Absence of) isotope effect

We first recall the McMillan expression for T_c (bearing in mind that the specific form is derived for a particular choice of the phonon DOS, namely that characteristic of Nb):

$$T_c = \frac{\theta_{\rm D}}{1.45} \exp - \left\{ \frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.63\lambda)} \right\} \tag{1}$$

Here $\theta_{\rm D}$ is the phonon Debye frequency, λ the effective electron-phonon coupling constant defined by

$$\lambda \equiv 2 \int_0^{\omega_{\rm D}} \frac{\alpha^2(\omega) F(\omega) d\omega}{\omega} \tag{2}$$

where $F(\omega)$ is the phonon DOS and $\alpha^2(\omega)$ is a suitably averaged electron-phonon coupling constant, and finally μ^* is the effective (renormalized) Coulomb coupling constant, given by

$$\mu^* = N(0)\langle V_c \rangle (1 + N(0)\langle V_c \rangle \ln \left(\epsilon_{\rm F}/\theta_{\rm D} \right))^{-1} \tag{3}$$

It is clear that the only way in which μ^* depends on the isotopic mass M of the ions is through the cutoff $\theta_{\rm D}$ in the denominator. What is also crucially important is that the quantity λ is independent of M; this is most easily seen by noting that apart from an M-independent constant λ is simply the "local" compressibility of the lattice, a *static* quantity which, at least within the harmonic approximation, cannot depend on the ionic mass.

Suppose then that we calculate the dependence of T_c on isotopic mass M. If we were to neglect the dependence through μ^*, we would get $T_c \propto \theta_{\rm D} \propto M^{-1/2}$, or in terms of the conventionally defined isotope shift parameter $\alpha \equiv -\partial(\ln T_c)/\partial(\ln M)$, $\alpha = 1/2$; this is the original BCS result. If we take into account also the dependence via μ^*, we find

$$\alpha = \frac{1}{2} \left[1 - \frac{1.04(1 + \lambda(1+0.62\lambda)\mu^{*2}}{\left[\lambda - \mu^*(1+0.62\lambda)\right]^2} \right] \tag{4}$$

Note that even if μ^* is small, the correction to the BCS value $\alpha = 1/2$ may be appreciable if λ is also small.

Although many of the classic superconductors do show a value of α close to $1/2$, values right down to zero and occasionally even negative do occur: note that such negative values are not incompatible with eqn. (4). However, values of $\alpha > 1/2$ are not found.

In attempting to compare eqn. (4) with the experimental data on (possibly) exotic superconductors, one must bear in mind that isotopic substitution could conceivably affect T_c in other ways, e.g. by changing the lattice structure (this is particularly true for substitution of H (^{1}H) by D (^{2}H)). However, crudely speaking, the occurrence of an isotope effect with α close to $1/2$ is prima facie evidence for a phonon mechanism, and conversely the absence of an isotope effect is at least some evidence for a non-phonon one.

B. (Absence of) "phonon" structure in tunneling I-V characteristics

Let's return for a moment to the Eliashberg formalism. There, one introduces a complex "gap" (off-diagonal self-energy) which is nearly independent of momentum but has a pronounced frequency dependence, which at $T = 0$ is given by the formula (cf. lecture 15 of part I):

$$\Delta(\omega) = \frac{1}{Z(\omega)} \int_0^\infty d\omega' \,\mathrm{Re}\quad \left\{ \frac{\Delta(\omega')}{\left(\omega'^2 - \Delta^2(\omega')\right)^{1/2}} \right\} \int_0^\infty d\Omega\, \alpha^2(\Omega) F(\Omega) \times$$
$$\frac{2(\omega' + \Omega)}{(\omega' + \Omega)^2 - \omega^2} - \frac{\mu^*}{Z(\omega)} \int_0^{\omega_c} d\omega' \,\mathrm{Re} \left\{ \frac{\Delta(\omega')}{\left(\omega'^2 - \Delta^2(\omega')\right)^{1/2}} \right\} \tag{5}$$

The second (Coulomb) term does not by itself give rise to any particularly sharp ω-dependence, and can be neglected in what follows. It can be shown[1] that in this generalized formalism the quantity which is measured in (Giaever) tunneling is a measure of the quantity $\Delta(\omega)$: quantitatively, for an S-I-N junction the ratio of $\partial I/\partial V$ in the superconducting ($T = 0$) and normal states is given by

$$(\partial I/\partial V)_s \,/(\partial I/\partial V)_n = \mathrm{Re} \left\{ \frac{\omega}{\sqrt{\omega^2 - \Delta^2(\omega)}} \right\}, \qquad \hbar\omega = eV. \tag{6}$$

(Note that the formula derived in lecture 8, for this ratio, namely $E/(\sqrt{E^2 - \Delta^2})$, is the special case of this result for $\Delta(\omega) = \mathrm{const} = \Delta$, and ω rewritten as E).

From (5) and (6) it is clear that the $I(V)$ characteristic in the superconducting state is sensitive to the structure of the phonon coupling function $\alpha^2(\omega)F(\omega)$, and computer programs have been devised by McMillan and others which allow one to work back trom the $I(V)$ characteristic and infer $\alpha^2(\omega)F(\omega)$. Since neutron scattering experiments measure $F(\omega)$ directly, and the coupling constants can be calculated with fair confidence, this means that one can check whether the values of $\alpha^2(\omega)F(\omega)$ obtained in these two quite different ways agree. Qualitatively, one would expect the phase of $\Delta(\omega)$ to change rapidly when ω is close to a value of Ω at which there is an anomously high phonon DOS (e.g. a van Hove singularity); this then gives rise to a sharp change with ω of the quantity $\mathrm{Re}\left\{\omega/\sqrt{\omega^2 - \Delta^2(\omega)}\right\}$. Consequently, the second derivative $\partial^2 I/\partial V^2$ is expected to show peaks whenever eV is close to such a value of Ω. For many of the classic superconductors such a correspondence has been established in a very convincing way (and I know of no case in which there is a serious discrepancy).

Thus, we can say that agreement of the spectrum $\alpha^2(\omega)F(\omega)$ obtained from the tunneling $I - V$ characteristics with that inferred from neutron scattering or other independent measurements on the phonons is very strong evidence for a phonon mechanism. Conversely, if peaks measured in the neutron scattering do not show up in the $I - V$

[1] Schrieffer et al., PRL **10**, 336 (1963).

characteristic (and there is no argument, e.g. from symmetry, that the relevant electron-phonon matrix element should vanish), that is a strong prima facie argument that the formation of the gap has nothing to do with phonons.

Finally, we should remark that just as the electron behavior in tunneling reflects the effects of phonons, the converse should also be true: the phonon spectrum should show some effects of the onset of superconductivity in the electron system. These effects should be small, of the order of the dimensionless attenuation due to phonon-electron collisions in the normal phase, i.e. $c_s/v_{\rm F} \sim 10^{-2}$ where c_s is the phonon (sound) velocity, however they should be outside the experimental error. In particular, one would expect an anomalous contribution to the ultrasound attenuation when the frequency ω is close to the gap edge $\omega = 2\Delta$), c.f. lecture 8 of part I. While the existence of such anomalous attention does not unambiguously establish a phonon mechanism for superconductivity, its absence would tend to indicate that the coupling of phonons to electrons is very weak and thus to cast doubt on such a mechanism.

Diagnostics of non-s-wave pairing.

In BCS theory as described in part I of the course, it is assumed that the "pseudomolecular" wave function $\varphi(\mathbf{r}_1\mathbf{r}_1\sigma_1\sigma_2)$ which enters the many-body wave function

$$\Psi(\mathbf{r}_1\sigma_1\mathbf{r}_2\sigma_2\ldots) = \mathcal{N}\,\mathcal{A}\,\{(\varphi(\mathbf{r}_1\mathbf{r}_1\sigma_1\sigma_2)\varphi(\mathbf{r}_3\mathbf{r}_4\sigma_3\sigma_4)\ldots\} \tag{7}$$

can be factorized into a spin part which is a singlet and an orbital part:

$$\varphi(\mathbf{r}_1\mathbf{r}_1\sigma_1\sigma_2) = 2^{-1/2}\,(\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2)\cdot\tilde{\varphi}(\mathbf{r}_1\mathbf{r}_1) \tag{8}$$

It then follows that the "pair wave function" F has the same structure, i.e. $\langle\psi_\uparrow(\mathbf{r}_1)\psi_\downarrow(\mathbf{r}_2)\rangle = -\langle\psi_\downarrow(\mathbf{r}_1)\psi_\uparrow(\mathbf{r}_2)\rangle \equiv F(\mathbf{r}_1\mathbf{r}_2)$, $\langle\psi_\alpha(\mathbf{r}_1)\psi_\alpha(\mathbf{r}_2)\rangle \equiv 0$. Furthermore, $F(\mathbf{r}_1\mathbf{r}_2)$ is assumed, in the free-space case, to correspond to center of mass at rest (in thermal equilibrium) so that $F(\mathbf{r}_1\mathbf{r}_2) = F(\mathbf{r}_1 - \mathbf{r}_2)$, and finally to correspond to isotropic (s-wave) internal structure of the pair, i.e. $F(\mathbf{r}_1 - \mathbf{r}_2) = F(|\mathbf{r}_1 - \mathbf{r}_2|)$ with no dependence on the direction of $\mathbf{r}_1 - \mathbf{r}_2$. In the presence of a crystalline lattice we have to modify the last couple of statements slightly: although $F(\mathbf{r}_1\mathbf{r}_2)$ is not in general now simply a function of $|\mathbf{r}_1 - \mathbf{r}_2|$, it is invariant under all operations of the crystal symmetry group (crystal translations and point-group operations).[2]

We cannot assume that this simple state of affairs will hold for all possible systems in which Cooper pairs form (in fact, as early as the 70's it was established not to hold in superfluid ^{3}He). Let us define a generalized "pair wave function" by

$$F_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) \equiv \langle\psi_\alpha(\mathbf{r}_1)\psi_\beta(\mathbf{r}_2)\rangle. \tag{9}$$

[2]In the simplest case, we can use a Bloch-wave basis and assume that only one band intersects the Fermi surface. Then we can introduce the quantity $F_{\mathbf{k}} \equiv \langle a^\dagger_{\mathbf{k}\uparrow}\, a^\dagger_{-\mathbf{k}\downarrow}\rangle$, where the $a^\dagger_{\mathbf{k}}$ are Bloch-wave creation operators) and the statement is that $F_{\mathbf{k}}$ is invariant under transformations $\mathbf{k} \to \mathbf{k}'$ induced by the point group of the crystal.

The only generic requirement on F is that it respects the Fermi statistics, i.e. that

$$F_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) = -F_{\beta\alpha}(\mathbf{r}_2, \mathbf{r}_1) \tag{10}$$

but this still leaves many possibilities. It is convenient to restrict ourselves, as above, to the case where the Fermi surface is intersected only by a single band, and to assume that the center of mass is at rest. Then we have a more compact description in terms of the Fourier-transformed pair wave function in the Bloch-wave basis:

$$F_{\alpha\beta}(\mathbf{k}) \equiv \langle a^\dagger_{\mathbf{k}\alpha} a^\dagger_{-\mathbf{k}\beta} \rangle = -F_{\beta\alpha}(\mathbf{k}) \tag{11}$$

We can classify possible forms[3] of $F_{\alpha\beta}(\mathbf{k})$ by their parity, i.e. by whether $F_{\alpha\beta}(\mathbf{k}) = +$ or $-F_{\alpha\beta}(-\mathbf{k})$ [note spin indices are in the *same* order!], corresponding to even or odd parity respectively. It follows at once[4] from (10) (or (10)) that even-parity solutions must be spin singlet (i.e. odd in $\alpha \rightleftharpoons \beta$ and odd-parity ones spin triplet (even in $\alpha \rightleftharpoons \beta$). In the singlet case $F_{\alpha\beta}$ is manifestly just a product of spin and orbital functions:

$$F_{\alpha\beta}(\mathbf{k}) = F_{\alpha\beta}(-\mathbf{k}) = (i\sigma_y)_{\alpha\beta} F(\mathbf{k}) \tag{12}$$

while for the triplet case $F_{\alpha\beta}(\mathbf{k})$ may in general be a superposition of three different functions associated with the three Zeeman substates $S_z = 1, 0, -1$. In the latter case it is convenient to characterize $F_{\alpha\beta}(\mathbf{k})$ by a vector $\mathbf{d}(\mathbf{k})$ (in general complex) defined by

$$\mathbf{d}(\mathbf{k}) \equiv (i\sigma_y \boldsymbol{\sigma})_{\alpha\beta} F_{\beta\alpha}(\mathbf{k}) \tag{13}$$

In the (common) case where $\mathbf{d}(\mathbf{k})$ is a real vector, its physical significance is that there exists for any given $\mathbf{k}$ a direction along which the spin state of the relevant pair is $S = 1, S_z = 0$ ($\frac{1}{\sqrt{2}}(\uparrow_1\downarrow_2 + \downarrow_1\uparrow_2)$), and the direction of $\mathbf{d}$ is just this direction (while its magnitude is a measure of the amplitude of the pair wave function, just as in the singlet case). In this case (real $\mathbf{d}$) if we choose any axis in the plane *perpendicular* to $\mathbf{d}$, the pairs appear to be formed in a linear superposition of $S_z = 1$ ($\uparrow_1\uparrow_2$) and $S_z = -1$ ($\downarrow_1\downarrow_2$) states, with a relative phase that depends on the specific choice.[5]

Diagnostics of spin triplet (odd-parity) states.

1. Knight shift

The most obvious difference between spin, triplet and spin singlet Cooper pairs is that the former, unlike the latter, can co-exist with a substantial spin polarization even in the

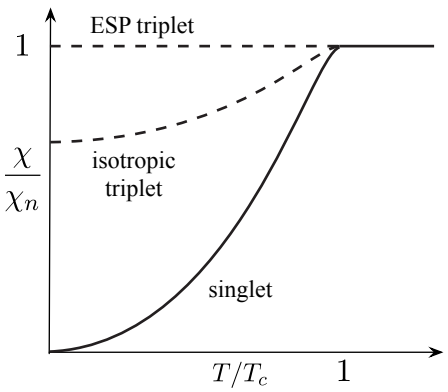
[3] Superpositions of even- and odd-parity states can in principle occur, but the conditions for such a solution to be stable are extremely stringent and there is no evidence for them in any known (pure) Cooper-paired system.

[4] (11) itself follows strictly only because the operators $a^\dagger_{\mathbf{k}\alpha} a^\dagger_{-\mathbf{k}\beta}$ are evaluated at the same time. It is in principle possible to consider a scenario in which $\langle a^\dagger_{\mathbf{k}\alpha}(t) a^\dagger_{-\mathbf{k}\beta}(t') \rangle$ is *odd* in the time variable $t - t'$ and thus vanishes for $t = t'$: then the "spin-parity connection" can be broken.

[5] For further details on the $\mathbf{d}$-vector notation, see e.g. AJL, RMP **47**, 331 (1975).

absence of "FFLO" or similar sophisticated effects: this is clear from the fact that now the electrons with momenta k and $-\mathbf{k}$ have *the same* spin and thus a weak polarization does not affect the pairing at all. Consequently, *provided* the pairs form in the states $\uparrow\uparrow, \downarrow\downarrow$ with respect to the field, i.e. with $\mathbf{d} \perp \mathbf{H}$, the Pauli susceptibility χ is unaffected by the superconducting transition (to a good approximation), and consequently the spin part of the Knight shift, and hence the total shift, should be unchanged below T_c.

If, however, for some reason $\mathbf{d}$ lies parallel to $\mathbf{H}$ ($S = 1, S_z = 0$ state), the situation is the same as in the singlet state and we expect the relevant part of the Knight shift to be described roughly by the Yosida function, falling to 0 as $T \to 0$. If $\mathbf{d}(\mathbf{k})$ varies over the Fermi surface, then we expect the reduction of χ to be proportional to the average of $(\mathbf{d} \cdot \hat{\mathbf{H}})^{\mathbf{2}}$, which gives the "weight" of the $S_z = 0$ component.



2. Absence of CC limit on upper critical field.

For a variety of reasons (not necessarily connected) almost all the "exotic" superconductors to be discussed in this part of the course are extreme type-II, and thus have very short coherence lengths ξ_0. Under these conditions the "Meissner" upper critical field, which we recall is defined by $H_{c2} = \phi_0/2\pi\xi^2$, may be very large, and the actual field that the superconducting state can tolerate may be limited by the Pauli effects discussed in Part I, lecture 12. We saw there that for the usual spin singlet case (in the absence of FFLO-type solutions, etc.) Pauli effects give the Chandrasekhar-Clogston limit, $H_c(0) = \Delta(0)/(\sqrt{2}\mu_{\mathrm{B}})$ (or more generally $g\mu_{\mathrm{B}}$). By an argument exactly analogous to that on the Knight shift, this limit should also apply for a triplet state with $\mathbf{d} \parallel \mathbf{H}$, while for a triplet state with $\mathbf{d} \perp \mathbf{H}$ Pauli paramagnetism should not limit the field at all and $\mathbf{H}_{c2}$ should take the Meissner value.

3. Absence of HS (coherence) peak just below $\mathbf{T_c}$?

The occurrence of an HS peak in an isotropic s-wave superconductor requires two things:

(1) a singularity ($\propto (E^2 - \Delta^2)^{-1/2}$ for the s-wave case) in the single-particle DOS at the gap edge, and

(2) the *absence* of a cancelling factor $\propto (E^2 - \Delta^2)$ due to coherence factors in the matrix element.

In general, as we shall see in a triplet-paired superconductor it is likely (though not required) that there is no DOS singularity (or that it is much weaker than in the s-wave case). However, even when there is, the question arises whether it would be cancelled by coherence effects. The answer is no, because the terms in $\Delta_{\mathbf{k}}\Delta^*_{\mathbf{k}'}$, now vanish when

averaged over the *direction* of $\mathbf{k}$: cf. below. So if the DOS retains a singularity, we still expect an HS peak.

Diagnostics of non-s-wave orbital states[6]

Let's start with the simple case that the spin configuration of the pairs is a singlet, then the orbital configuration is characterized by a single scalar order parameter $F_{\mathbf{k}} \equiv \langle a^\dagger_{\mathbf{k}\downarrow} a^\dagger_{-\mathbf{k}\uparrow} \rangle$, which is in general complex and must have even parity ($F_{\mathbf{k}} = +F_{-\mathbf{k}}$). Equivalently, we can work in terms of the "gap parameter" $\Delta_{\mathbf{k}}$, which is related to $F_{\mathbf{k}}$ by

$$F_{\mathbf{k}} = \Delta_{\mathbf{k}}/2E_{\mathbf{k}}, \qquad E_{\mathbf{k}} \equiv \left(\epsilon^2_{\mathbf{k}} + |\Delta_{\mathbf{k}}|^2\right)^{1/2} \tag{14}$$

In the following I shall assume that $\Delta_{\mathbf{k}}$ is not appreciably a function of the *magnitude* of $\mathbf{k}$, at least over a range $\epsilon_{\mathbf{k}} \sim k_{\mathrm{B}}T_c$. Thus, it is the variation of $\Delta_{\mathbf{k}}$, with direction on the Fermi surface that is of interest in the following. The quantity which is of primary interest for diagnostics of the orbital pairing state is the single-particle DOS in the superconducting state at $T = 0$,

$$N_s(E) \equiv \sum_{\mathbf{k}} \delta(E - E_{\mathbf{k}}). \tag{15}$$

It is clear that this quantity is sensitive to the variation of $\Delta_{\mathbf{k}}$ over the Fermi surface; in particular, if $\Delta_{\mathbf{k}}$ is everywhere bounded below by some minimum value $\Delta_{\min}$, then $N_s(E) \equiv 0$ for $E < \Delta_{\min}$. If on the contrary $\Delta_{\mathbf{k}}$ has one or more nodes, i.e. tends to zero at one or more point or line on the Fermi surface, then $N_s(E)$ will be finite for finite E. Let us make this a little more quantitative: The total number of states $N_s(< E)$ with energies *less* than E is the number for which $(\epsilon^2_{\mathbf{k}} + |\Delta(\hat{\mathbf{n}})|^2) \leq E^2$, and hence it is (almost) intuitively obvious that the density of states $dN_s(< E)/dE$ is proportional to the area of that part of the Fermi surface that has $|\Delta(\hat{\mathbf{n}})| < E$. Formally, we can see this by writing

$$N_s(E) \equiv \sum_{\mathbf{k}} \delta(E - E_{\mathbf{k}}) = N(0) \int \frac{d\Omega}{4\pi} \int dE\, \delta\big(E - E(\epsilon, \hat{\mathbf{n}})\big) \tag{16}$$

$$\equiv N(0) \int \frac{d\Omega}{4\pi} \int \frac{d\epsilon(E', \hat{\mathbf{n}})}{dE'}\, dE'\, \delta(E - E') \equiv N(0) \int \frac{d\Omega}{4\pi}\, \frac{d\epsilon(E', \hat{\mathbf{n}})}{dE'}$$

Since $\epsilon(E, \hat{\mathbf{n}}) = (E^2 - |\Delta(\hat{\mathbf{n}})|^2)^{1/2}$, this becomes

$$N_s(E) = N(0) \int_{\Delta(\hat{\mathbf{n}}) \leq E} \frac{d\Omega}{4\pi}\, \frac{E}{\sqrt{E^2 - |\Delta(\hat{\mathbf{n}})|^2}} \tag{17}$$

and thus, apart from a numerical constant that depends on the form of the node, is indeed proportional to the area for which $|\Delta(\hat{\mathbf{n}})| < E$. Thus we have, for point and line nodes in 3D and point nodes (the only possibility) in 2D, the results

[6] Ref. Kuramoto & Kitaoka, Dynamics of Heavy Electrons, Sections 5.1–3.

$$\begin{aligned}&\text{3D, point: } N_s(E) \propto E^2\\ &\text{3D, line: } \quad N_s(E) \propto E\\ &\text{2D, point: } N_s(E) \propto E.\end{aligned}$$

So far we discussed explicitly the spin singlet case. The triplet case is a bit more complicated, but simplifies considerably in the so-called unitary case in which the vector $\mathbf{d}(\hat{\mathbf{n}})$ describing the OP is real. In that case, for any particular direction of $\hat{\mathbf{n}}$ (and its opposite $-\hat{\mathbf{n}}$) we can always choose our spin axis so that the spin state is pure $S = 1, S_z = 0$ $\left(\frac{1}{\sqrt{2}}(\uparrow_1\downarrow_2 + \downarrow_1\uparrow_2)\right)$ and the pairing can thus be described by a single complex number $F_{\mathbf{k}}$ (or $\Delta_{\mathbf{k}}$), the only difference with the singlet case being that $F_{\mathbf{k}}$ (or $\Delta_{\mathbf{k}}$) must now have odd parity ($F_{\mathbf{k}} = -F_{-\mathbf{k}}$). The above formulae for the density of states, expressed in terms of the quantity $|\Delta(\hat{\mathbf{n}})|$ (which is of course invariant under the choice of axes) are then unchanged. In the nonunitary case we have in general two different gaps for a given $\hat{\mathbf{n}}$, and must then sum the two densities of states resulting from them to get a total DOS.

It is clear that the occurrence of gap nodes on the Fermi surface will have a profound effect on the behavior at low temperatures of those properties that involve the normal component: crudely speaking, the density of the latter vanishes exponentially as $T \to 0$ for a gap that is everywhere finite, but only as a power of T if there are nodes. Specifically, if the DOS vanishes as E^n for $E \to 0$, then for the asymptotic behavior of various physical quantities simple scaling arguments predict the following[7]:

$$\begin{aligned}&c_v \propto T^{n+1}\\ &\lambda(T) - \lambda(0) \propto T^n\\ &T_1^{-1} \propto T^{2n+1}\\ &K_s \propto T^n \quad \text{(spin singlet case).}\end{aligned} \tag{18}$$

I now turn more briefly to the way in which the symmetry of the order parameter affects the presence or not of gap nodes and hence the low-energy DOS. In the 3D freespace case things are relatively straightforward: for spin singlet pairing, barring pathologies[8], the form of the OP must correspond to either a single spherical harmonic Y_m^l or to a combination of Y_m^l for the same l, where l = even because of the necessity for even parity. The case $l = 0$ (s-wave) is the simple BCS case and has a gap that is constant over the Fermi surface. For $l \geq 2$ it is impossible to form a state that does not have, at least, point nodes, so the low-energy DOS is power law. For spin triplet pairing, again the only possibility is that the vector $\mathbf{d}(\hat{\mathbf{n}})$ has components each of which is some combination of spherical harmonics Y_m^l with the same (odd) l. For $l = 1$ this allows states in which the total gap magnitude $|\Delta(\hat{\mathbf{n}})|$ is finite for all $\hat{\mathbf{n}}$ (e.g. the "Balian-Werthamer" state $\mathbf{d}(\hat{\mathbf{n}}) = \text{const } \hat{\mathbf{n}}$); for $l \geq 3$ no such state is possible and again one must have at least point nodes. The situation is different in 2D, where nodeless states are possible for any l (e.g. $\Delta(\hat{\mathbf{n}}) \propto \exp il\varphi$).

[7] K_s is the Knight shift (relative to its $T = 0$ value).

[8] Mixtures of spherical harmonics with different l are in principle possible but require very stringent conditions on the coupling constants.

In the presence of a crystal lattice the situation is considerably more complicated[9]: I will not discuss it in full generality here (but will discuss the special case relevant to the cuprates in a later lecture). An important difference from the free-space case is that it is not excluded that a form of the OP (or gap) that belongs to the "trivial" representation of the crystal point group (the analog of the s-wave state) nevertheless has nodes on the Fermi surface (a state of this type is sometimes called "extended s-wave"). Consequently, the fact that in a given superconductor the quantities c_v, Δ, λ, etc. have a powerlaw behavior at low T cannot be regarded as by itself irrefutable evidence for an "exotic" pairing state. Rather similar considerations hold for the question of the HS peak: Although a non-s-wave state cannot (except by pathology) have a DOS that diverges as $(E^2 - \Delta^2)^{-1/2}$, a weaker divergence for E close to the gap maximum Δ_0 is possible and in fact occurs for $l \neq 0$ in free space. However, in a crystalline environment the same kind of singularity can and often does occur for s-wave-type pairing (and in both cases may be smeared by lifetime effects etc.). Thus, the presence or absence of an HS peak is not a particularly good test of the pairing state.

One further possible diagnostic of "exotic" pairing should be mentioned briefly (again, it will be taken up more systematically in the context of the cuprates): Generally speaking, any pairing state that does not belong to the trivial representation of the crystal point group is expected to be very strongly suppressed by nonmagnetic as well as magnetic impurities, so that even a small concentration of either is enough to suppress superconductivity entirely. By contrast, an "extended s-wave state" is expected to have its T_c lowered by nonmagnetic impurities, but not driven to zero. We will investigate the reason for this behavior later.

[9] Ref: Sigrist & Ueda, RMP **83** 239 (1991).