

(References: de Gannes chapters 1-3, Tinkham chapter 1)

Statements refer to “classic” (pre-1970) superconductors (Al, Sn, Pb, alloys...). Most but not all statements apply also to HTS, fullerenes, heavy-fermions, organics...

1. Definition of superconductivity

The superconducting state differs qualitatively from the normal (non-superconducting) state in 3 major respects:

- (a) d.c. conductivity (in zero magnetic field & for small enough current) effectively infinite (seen either in voltage-drop experiments, or in persistence of current in rings)
- (b) simply connected sample expels weak magnetic field (Meissner effect): perfect diamagnet, i.e. $\mathbf{B} = 0$. [convention for \underline{H} , \underline{B} later]
- (c) Peltier coefficient* vanishes, i.e. electrical current not accompanied by heat current (contrary to usual behavior in normal phase).

These three phenomena set in essentially discontinuously at a critical temperature T_c which may be anything from ~ 1 mK to ~ 25 K (higher for HTS, etc.) For most elements & alloys, $T_c \sim$ a few K. (Note: this is ~ 3 -4 orders of magnitude below T_F and ~ 1 -2 below θ_D) Onset is abrupt: no reliable way of telling, from N -state bulk measurements, whether superconductivity will set in at all, let alone at what temperature. (but cf. proximity-effect measurements on Cu etc.). For new HS compounds, at a pressure of 200 GPa, T_c can exceed 200K.

2. Occurrence

Superconductivity appears to occur only in materials which in the normal phase (i.e. above T_c) are metals or (occasionally, under extreme conditions) semiconductors: There is no clear case in which, as T is lowered, the system goes from an insulating to a S state[†]. In the case of the classic superconductors, N state is almost always a “textbook” metal (see (3) below).

However, the correlation between N -state conductivity σ and the occurrence of superconductivity is negative: the best N -state conductors (Cu, Ag, Au) do not become superconducting (at least down to 10 mK, and there is some reason to believe

*Peltier coefficient Π is defined as ratio of heat current to electric current for $\nabla T=0$: see Ziman, P. Th. Solids, pp. 201-2.

[†]Theoretically such a transition is predicted to be possible under extreme conditions. The experimental evidence is unconvincing for the classic superconductors and ambiguous for HTS: M.V. Sadovskii, Phys. Rev. 282, 226 (1997).

they never will). In the periodic table of the elements, superconductivity occurs mainly in the middle: see AM p. 726, table 34.1, or Kittel (3rd edition), p. 338, table 2. Many intermetallic compounds, e.g. Nb₃Sn, V₃Ga, often with high T_c (~20K).

Superconductivity is not destroyed by nonmagnetic impurities, in fact T_c sometimes increases with alloying & there are thousands of superconducting alloys, including some with very high (20-25K) T_c . But magnetic impurities (i.e. impurities carrying electrons with nonzero total spin) are rapidly fatal: e.g. pure Mo is superconducting with $T_c \sim 1\text{K}$, but a few ppm of Fe drives T_c to zero. No known case among classic superconductors where superconductivity coexists with any form of magnetic ordering. (but situation in “exotics” more complicated)

Isotope effect: in most though not all cases of classic superconductivity, $T_c \propto M^{-1/2}$. (crucial clue to mechanism)

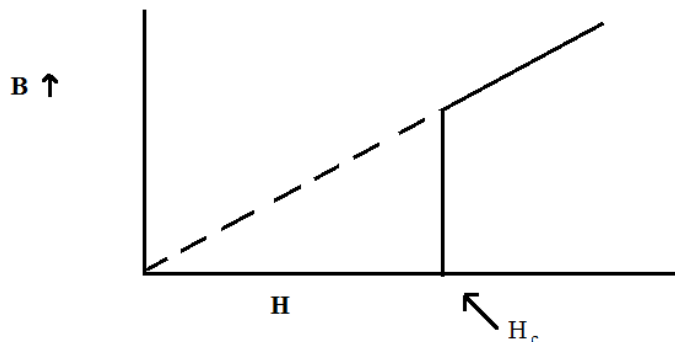
3. Normal state of superconductors

Almost all the classic superconductors are, above T_c , “textbook” normal metals: i.e. $C_v \sim T$, $\chi \sim \text{const.}$, $\rho \sim \text{const.} + f(T)$ ($f(T) \sim T$ for $T \gg \theta_D$), $\kappa/\sigma T = \text{const.}$, etc.

4. Magnetic behavior of superconducting phase

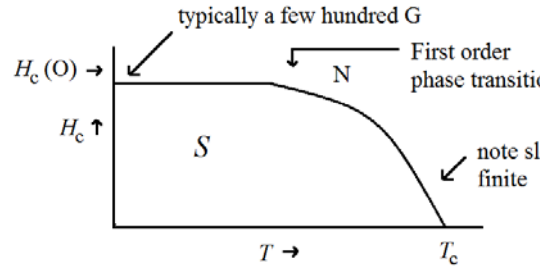
For a given material, the magnetic behavior is in general a function of the shape of the sample: the simplest case to analyze is a (large) long cylinder parallel to the external field. In this case, there are 2 types of behavior, type-I and type-II. Most pure elemental superconductors are type-I (exception: pure Nb): compounds and alloys tend to be type-II, and this is the case for virtually all the highest- T_c materials.

(a) **Type-I:** At any given $T < T_c(0)$, if we gradually raise H , system remains perfectly superconducting up to a definite critical field $H_c(T)$, at which point it goes over discontinuously (by a first-order transition) to the normal phase and readmits the magnetic field completely. In terms of the $B(H)$ relation*:



*It is conventional in the theory of superconductivity to define \mathbf{H} as the field due to external sources, and \mathbf{B} as the total local field averaged over a few atomic distances. Thus, $\mathbf{B} = \mu_0 \mathbf{H} + \mathbf{M}$ where \mathbf{M} is the average magnetization due to macroscopic circulating currents. (Atomic-scale variations usually not considered)

The shape of $H_c(T)$ is approximately \rightarrow [actually more curved at low T] and is well fit by the formula $(1-(T/T_c)^2)$



The reason for the existence and behavior of the critical field $H_c(T)$ is a straightforward thermodynamic one: the S state has a negative (condensation) energy relative to the N state, but since it excludes the magnetic field entirely, this costs an (extra) energy

$$dE_{mag} = -\mathbf{M} \cdot d\mathbf{H}_{ext} \Rightarrow E_{mag} = + \frac{1}{2}\mu_0 H_{ext}^2 V \quad (\text{SI units})$$

since \mathbf{M} is oppositely directed to \mathbf{H}_{ext} (diamagnetism). ($B = 0 \Rightarrow \mathbf{M} = -\mu_0 \mathbf{H}$) (This is essentially the energy necessary to “bend” the field lines so as to avoid the sample) (levitation). In the normal phase, excluding small atomic-level magnetic effects, the extra energy is zero. Thus it becomes energetically advantageous to switch to the N phase at the point

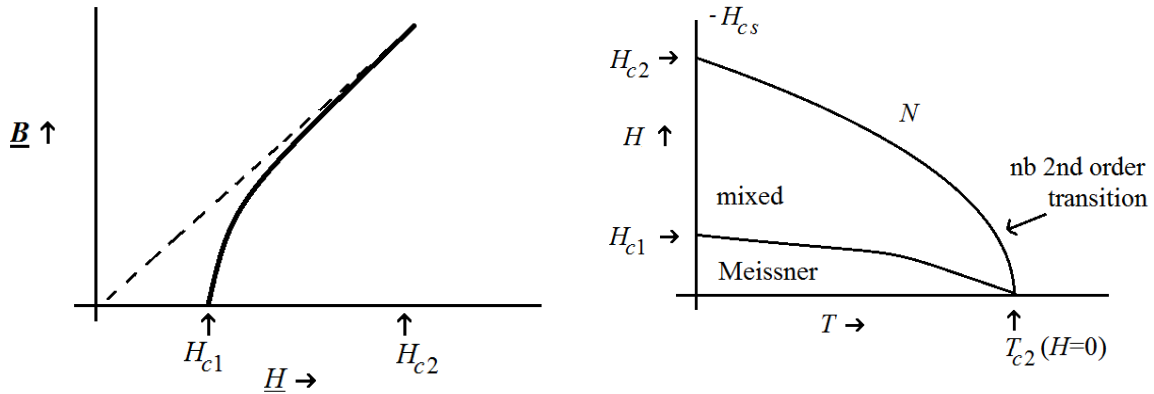
$$G_n(T) - G_s(T) = \frac{1}{2} \mu_0 H^2 \equiv \frac{1}{2}\mu_0 H_c^2(T) \quad [\Rightarrow \text{transition 1}^{st} \text{ order}]$$

and this is a useful method of measuring the LHS . (See below (5)).

Above analysis is for a “large” sample. Actually, there is a characteristic length λ (cf. below) over which field penetrates. Thus, for sample sizes $< \lambda$, we expect the thermodynamic critical field to be higher, and this is indeed seen.

Note also that for samples of less convenient shape may get a break-up into N and S regions (intermediate state: distinguish from “mixed” state, below).

- (b) Type-II: start with $T < T_c(H = 0)$, turn up field H . For sufficiently small field behaves as type-I, i.e. expels flux completely (“Meissner state”). Above a “lower critical field” H_{c1} , flux begins to penetrate, so \mathbf{M} is negative but $|\mathbf{M}| < \mu_0 \mathbf{H}$, so $B > 0$. As \mathbf{H} further increased, \mathbf{M} becomes smaller until at an “upper critical field” H_{c2} it vanishes (in the bulk) & system switches to normal state. Apart from this, in the “mixed” state between H_{c1} and H_{c2} system behaves in a typically superconducting way (though cf below for resistive behavior).



Anticipate: in mixed state, magnetic field punching through in form of vortices (cores effectively normal), while bulk remains superconducting.

Can define $H_c(T)$ for type-II as above from $G_n - G_s$. Then, to an order of magnitude $H_{c1} \cdot H_{c2} \sim H_c^2$. Typically $H_{c1} \sim$ a few G , $H_{c2} \sim$ several T . (30T for V_3Ga)

5. Resistance

One can make one simple statement about the d.c. resistance R of a superconductor: For any bulk type-I superconductor when the field (including that generated by the current) is everywhere less than $H_c(T)$, or for a bulk type-II superconductor when it is less than $H_{c1}(T)$, the effective resistance is zero. It is also true that for a type-I superconductor, those parts which are in a field $< H_c(T)$ have local resistivity zero: however, because any current will generate a spatially varying field, the total resistance even of a thin wire is a quite complicated function of current*. For a single wire (dimensions $\ll \lambda$) in zero external magnetic field the resistance is zero up to a critical current $I_c(T)$ defined by Silsbee's rule, i.e.

$$I_c(T) = H_c(T)a/2, \quad a = \text{radius of wire}$$

As I is increased beyond $I_c(T)$, the resistance jumps discontinuously to a value $\sim 0.7 - 0.8$ of the normal-state value, and for $I \gg I_c(T)$ approaches the latter.

For type-II superconductors situation is even more complicated, because in general in the mixed phase even local resistivity is not zero, (due to the possibility of flux flow). A formula which often describes the behavior in this region quite well is (cf. Tinkham section 5.5.1)

$$\rho/\rho_n \cong B/\mu_0 H_{c2}$$

[effect of pinning]

* See Tinkham section 3-5.

Again, in a thin wire resistance first develops when $I_c = H_{c2}(T)a/2$ and tends to the normal value asymptotically as $I \rightarrow \infty$.

The above all refers to d.c. resistance. The a.c. resistance is nonzero even when all regions of the superconductor are in the Meissner phase: generally speaking, R increases as some power of ω

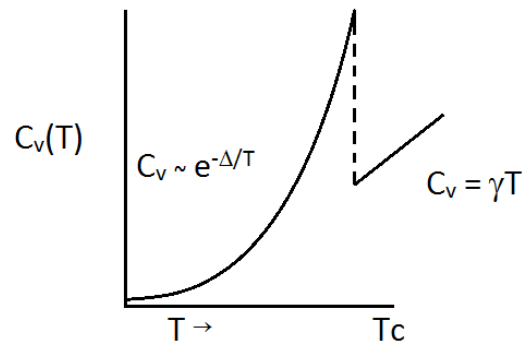
6. Microscopic properties of the superconducting phase

(a) Specific heat C_v . (after subtraction of phonon terms)

This is $\propto T$ in the N phase. There is a jump[†] at T_c , such that $\Delta C_v / C_v^{(n)} \cong 1.4$ (or sometimes a little greater, up to 2.65 for Pb). For $T \ll T_c$ C_v drops below the N state value, and as $T \rightarrow 0$ follows

$$C_v|_{T \rightarrow 0} \sim \exp - \Delta / \kappa T$$

where Δ is a constant of the order of $k_B T_c$.



A very useful relation between the specific heat and the thermodynamic critical field $H_c(T)$ can be obtained by differentiating twice the relation $G_n - G_s = 1/2 \mu_o H_c^2(T)$, namely

$$c_n - c_s = -T \frac{d^2}{dT^2} \left(\frac{1}{2} \mu_o H_c^2(T) \right)$$

(and $S_n - S_s = -\mu_o H_c \frac{\partial H_c}{\partial T} \rightarrow$ transition 1st order in finite H) Although in this relation c_n and c_s should strictly speaking be evaluated at $H = H_c(T)$, it is usually adequate to insert the $H = 0$ values. In particular as $T \rightarrow T_c$ ($H_c \rightarrow 0$) we have

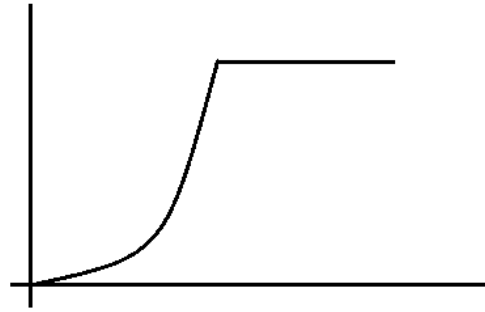
$$c_n(T_c) - c_s(T) = -T \mu_o \left(\frac{\partial H_c}{\partial T} \right)_{T_c}^2$$

[†] Note the fact that $c_s \sim c_n$ indicates only electrons with $\epsilon \sim k_B T_c$ (much) affected by the onset of superconductivity.

This can be checked experimentally, and is often used to determine c_s more accurately. Note that since $c_s \rightarrow 0$ as $T \rightarrow 0$ while $c_n \propto T$, the form of H_c^2 (hence also of H_c) in this limit is $H_c(T) \cong H_c(0)(1-(T/T^*)^2)$ where $T^* \sim T_c$.

(b) Pauli susceptibility χ (Type – I)

This can often be measured from the Knight shift. We find χ drops off sharply for $T < T_c$ and as $T \rightarrow 0$ tends exponentially to zero, like c_v .



(c) Ultrasound attenuation (α)

The longitudinal attenuation remains proportional to ω as in the normal phase, but the coefficient drops off sharply. (roughly as $(T/T_c)^4$) The transverse ultrasonic attenuation has a discontinuous drop at T_c (consequence of Meissner effect), thereafter drops similarly.

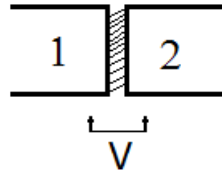
(d) Thermal conductivity (κ)

The thermal conductivity in the N phase for $T \sim T_c$ is usually dominated by electrons rather than phonons. Generally speaking it has no discontinuity in the superconducting phase, but drops similarly to the ultrasonic attenuation and $\rightarrow 0$ for $T \rightarrow 0$. (For low enough T , phonons may again dominate).

(e) Nuclear relaxation rate T_1^{-1}

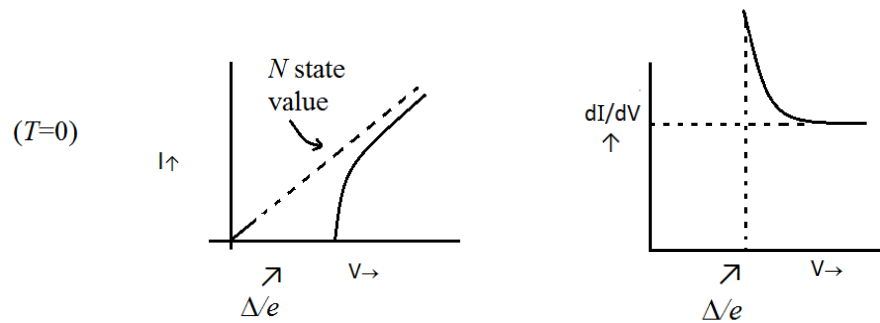
In the N state $\Gamma \equiv T_1^{-1}$ is roughly $\propto T$. (Korringa law). As T falls below T_c , Γ first rises (the famous Hebel-Slichter peak) then falls, roughly similar to χ , and $\rightarrow 0$ as $T \rightarrow 0$.

EM absorption (as seen e.g. in reflectivity): lower than in N state at low ω , rises sharply at $\omega \sim 2\Delta$, when Δ is “gap” observed in c_v .



(f) Tunneling.

The tunneling current between two N metals, whether the same or different, is usually proportional to the voltage applied across the barrier, so $dI/dV = \text{const}$. When one metal is a S and the other a N metal, no current flows for either polarity until $e|V| = \Delta$, where Δ is the same quantity as appears in the low-temperature specific heat. If we plot dI/dV rather than $I(V)$



At finite $T < T_c$:

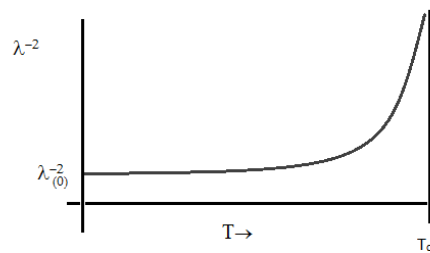


If both metals are S , we get qualitatively similar behavior, with however Δ replaced by the sum $\Delta_1 + \Delta_2$.

[Also: Josephson tunneling]

(g) Penetration depth. λ

This is one quantity which is not defined in the N phase: it is the depth to which, in the Meissner phase, an EM field penetrates into the surface of the superconductor. It turns out to be more convenient to plot $\lambda^{-2}(T)$, which as we shall see has a direct physical interpretation:



λ tends exponentially to its $T=0$ limit as $T \rightarrow 0$, again with an exponent $\sim \Delta/kT$, and diverges in the limit $T \rightarrow T_c$, as $(1 - T/T_c)^{-1/2}$.