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(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 fields & 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. $\boldsymbol{B} = 0$. [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 ~25K (higher for HTS, etc.) For most elements & alloys, T_c ~ 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.).

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 they never will). In the periodic table of the elements, superconductivity occurs

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*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).

mainly in the middle: see AM p. 726, table 34.1, or Kittel (3rd edition), p. 338, table 2. Many intermetallic compounds, e.g. Nb_3, Sn, V_3, Ga, often with high T_c (~20K).

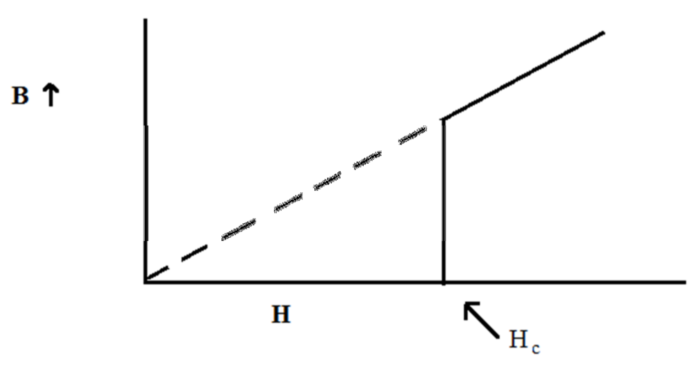
Superconductivity is not destroyed by <u>nonmagnetic</u> impurities, in fact T_c sometimes increases with alloying & there are thousands of superconducting alloys, including some with very high (20-25K) T_c. But <u>magnetic</u> impurities (i.e. impurities carrying electrons with nonzero total spin) are rapidly fatal: e.g. pure Mo is superconducting with T_c~1K, 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. <u>Normal state of superconductors</u>
   Almost all the classic superconductors are, above T_c, "textbook" normal metals: i.e. $C_v \sim T$, $\chi \sim$ const., $\rho \sim$const. + $f(T)$ ($f(T) \sim T$ for $T \gtrsim \theta_D$), $\kappa/\sigma T$ = const., etc.

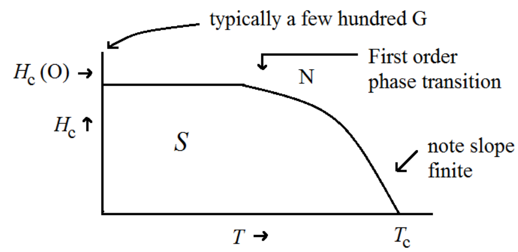
4. <u>Magnetic behavior of superconducting phase</u>
   For a given material, the magnetic behavior is in general a function of the shape of the sample: the simplest case to analyze is a (large) long cylinder parallel to the external field. In this case, there are 2 types of behavior, type-I and type-II. 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 ***H*** as the field due to external sources, and ***B*** as the total local field averaged over a few atomic distances. Thus, $\boldsymbol{B} = \mu_o \boldsymbol{H} + \boldsymbol{M}$ where ***M*** is the average magnetization due to macroscopic circulating currents. (Atomic-scale variations usually not considered)

The shape of $H_c(T)$ is approximately → [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

$$dE_{mag} = -\boldsymbol{M} \cdot d\boldsymbol{H}_{ext} \Rightarrow E_{mag} = +\tfrac{1}{2}\mu_o H^2{}_{ext} V \qquad \text{(S1 units)}$$

since $\boldsymbol{M}$ is <u>oppositely</u> directed to H_{ext} (diamagetism). ($B = 0 \Rightarrow M = -\mu_o H$) (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

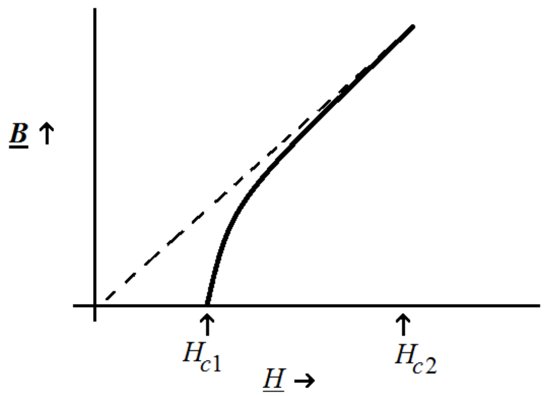
$$G_n(T) - G_s(T) = \tfrac{1}{2}\,\mu_o H^2 \equiv \tfrac{1}{2}\mu_o H^2{}_c(T) \qquad [\Rightarrow \text{transition } 1^{st} \text{ order}]$$

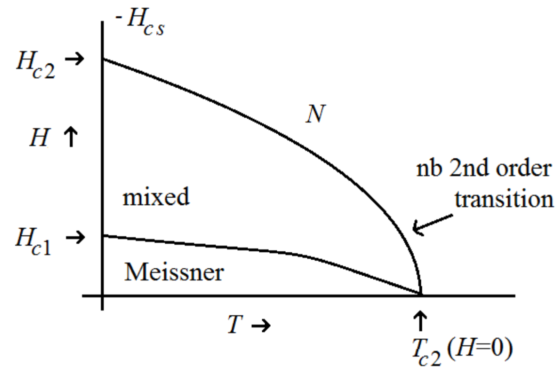
and this is a useful method of measuring the *LHS*. (See below (5)).

Above analysis is for a "large" sample. Actually, there is a characteristic length λ (cf. below) over which field penetrates. Thus, for sample sizes **<** λ, 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) <u>Type-II</u>: 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 $\boldsymbol{M}$ is negative but $|\boldsymbol{M}| < \mu_o \boldsymbol{H}$, so $B > 0$. As $\boldsymbol{H}$ further increased, $\boldsymbol{M}$ 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. <u>Resistance</u>

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 <u>total</u> resistance even of a thin wire is a quite complicated function of current*. For a single wire (dimensions ≫ λ) in zero external magnetic field the resistance is zero up to a critical current $I_c(T)$ defined by Silsbee's rule, i.e.

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

As I is increased beyond $I_c(T)$, the resistance jumps discontinuously to a value ~ 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 <u>local</u> 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)

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

[effect of pinning]

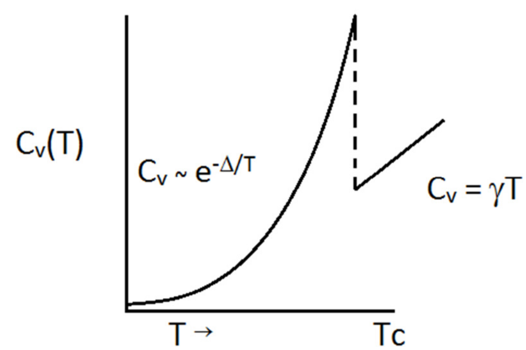
* See Tinkham section 3-5.

Again, in a thin wire resistance first develops when $I_c = H_{c2}(T)a/2$ and tends to the normal value asymptotically as $I \to \infty$.
The above all refers to d.c. resistance. The a.c. resistance is finite 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) <u>Specific heat C_v</u>. (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 $T \to 0$ follows

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

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 $S_n - S_s = -\mu_o H_c \frac{\partial H_c}{\partial T} \to$ 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 $T \to T_c$ ($H_c \to 0$) we have

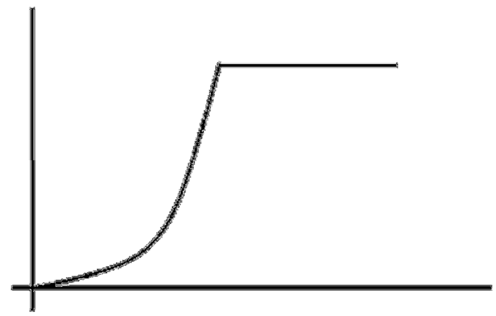
$$c_n(T_c) - c_s(T) = -T\mu_o\left(\frac{\partial H_c}{\partial T}\right)^2_{T_c}$$

† Note the fact that $c_s \sim c_n$ indicates only electrons with $\in \sim k_B T_c$ (much) affected by S.

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

(b) <u>Pauli susceptibility χ</u> (Type – I)

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



(c) <u>Ultrasound attenuation</u> (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.

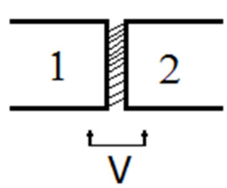
(d) <u>Thermal conductivity</u> (κ)

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 $\to 0$ for $T \to 0$. (For low enough T, phonons may again dominate).

(e) <u>Nuclear relaxation rate T_1^{-1}</u>

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 $\to 0$ as $T \to 0$.

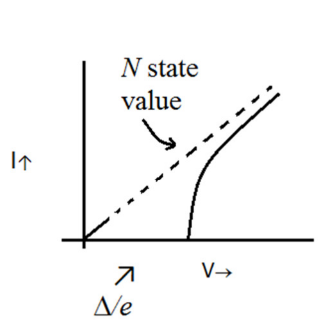
EM absorption (as seen e.g. in reflectivity): lower than in N state at low ω, rises sharply at $\omega \sim 2\Delta$, when Δ is "gap" observed in c_v.

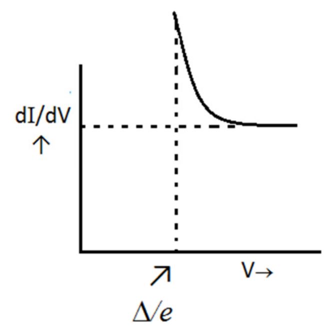


(f) Tunneling.

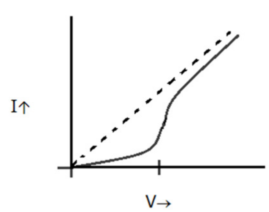
The tunneling current between two N metals, whether the same or different, is usually proportional to the voltage applied across the barrier, so dI/dV = const. When one metal is a S and the other a N metal, no current flows for either polarity until $e|V|=\Delta$, where Δ is the same quantity as appears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

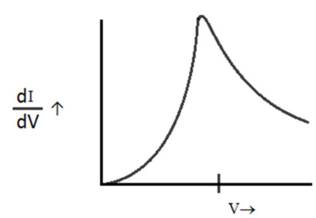
(T=0)





At finite $T < T_c$:



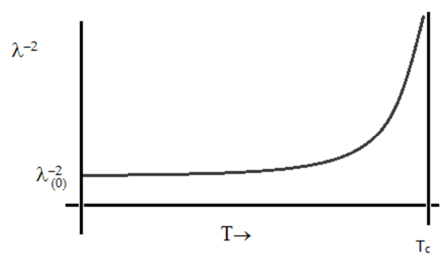


If both metals are S, we get qualitatively similar behavior, with however Δ replaced by the sum $\Delta_1 + \Delta_2$.

[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 ~Δ/kT.