

Superconductivity M2 ICFP 2025

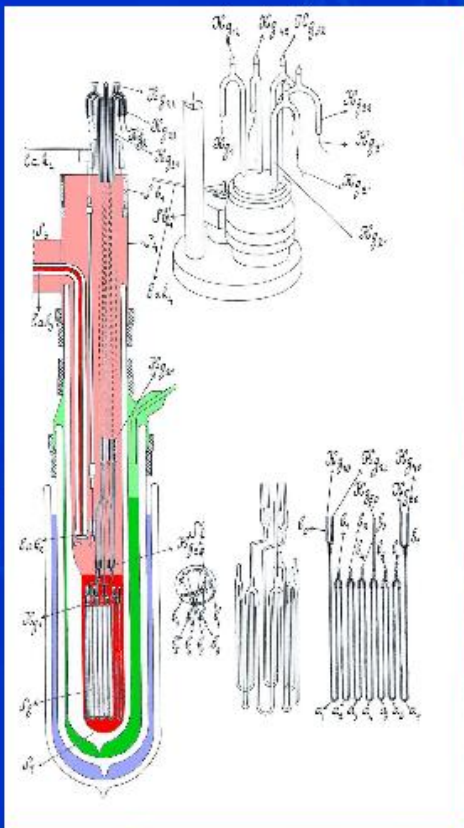
N.B. Here you will find what we saw and discussed during the lecture but also the additional information necessary for tutorials.

Content of Lecture 1:

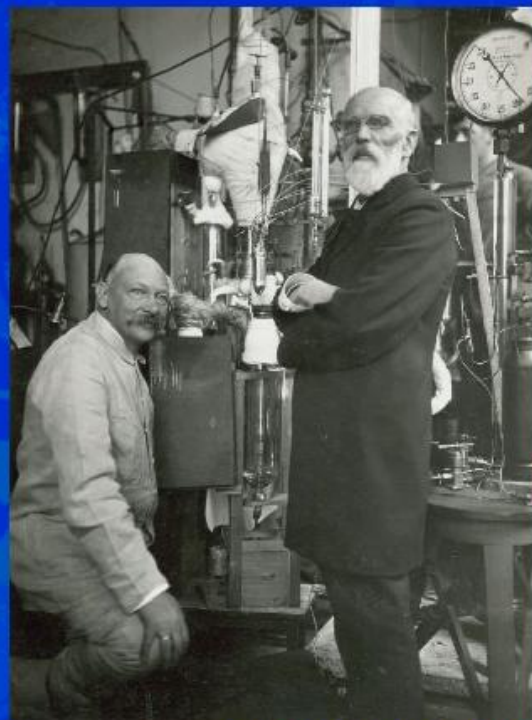
1. Discovery of superconductivity. Zero resistance. Meissner state. Idea of attractive interaction. Applications.
2. Reminder: How to measure transport and magnetic properties of solids.
3. Consequences of the Meissner-Ochsenfeld diamagnetism (1933). First TD considerations.
4. Idea of two-fluid model (London theory of superconductivity). London equations.
5. Meissner effect.
6. Non-local electrodynamics of superconductors
7. Quantum generalization of London's equations. Flux quantization.
8. Appendix 1 and 2.

1. Discovery of superconductivity. Main associated phenomena. Overview of theories, effects and applications.

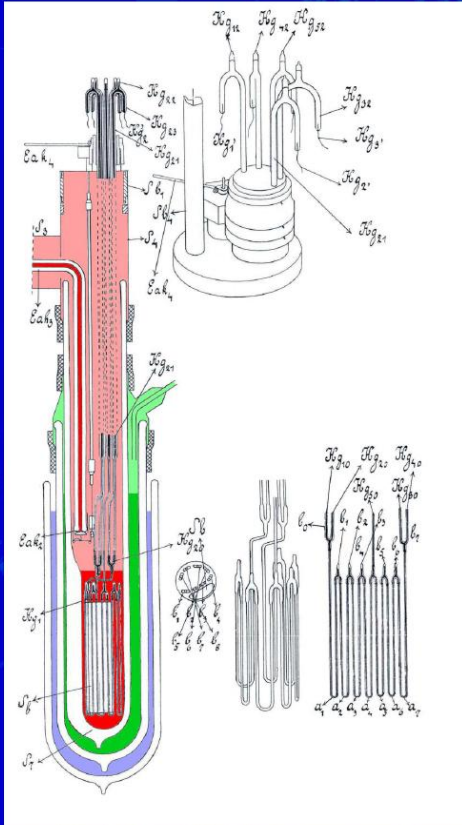
Power Point presentation and discussion .



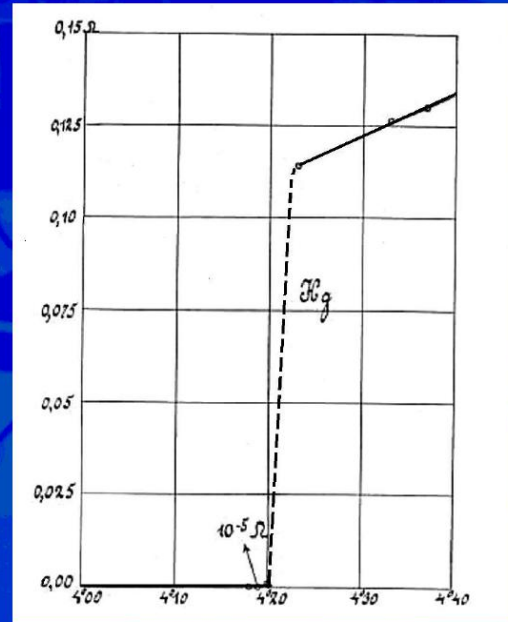
Liquefaction of He^4 : 1908



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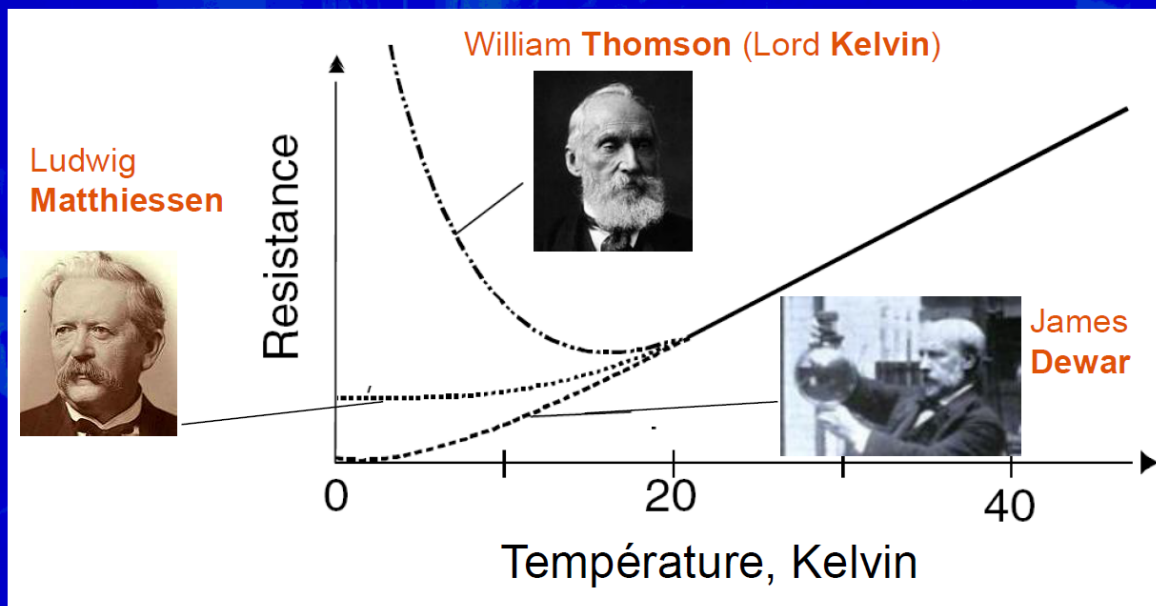


Experiment of 26 October 1911
with the historic plot showing the
resistance jump at 4.20 K.



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Resistance of a metal at low temperature



Crédit dessins et photos: Prof. P. Kes, Univ. Leiden

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Découvertes en cascade

22 Juin 1912 Le Mercure avec des impuretés (Au, Cd) est aussi supraconducteur !
Et même à une température plus élevée que le Mercure pur !

Automne 1912 Nouveaux supraconducteurs : Etain (Sn) et Plomb (Pb) (3,8K et 6K).

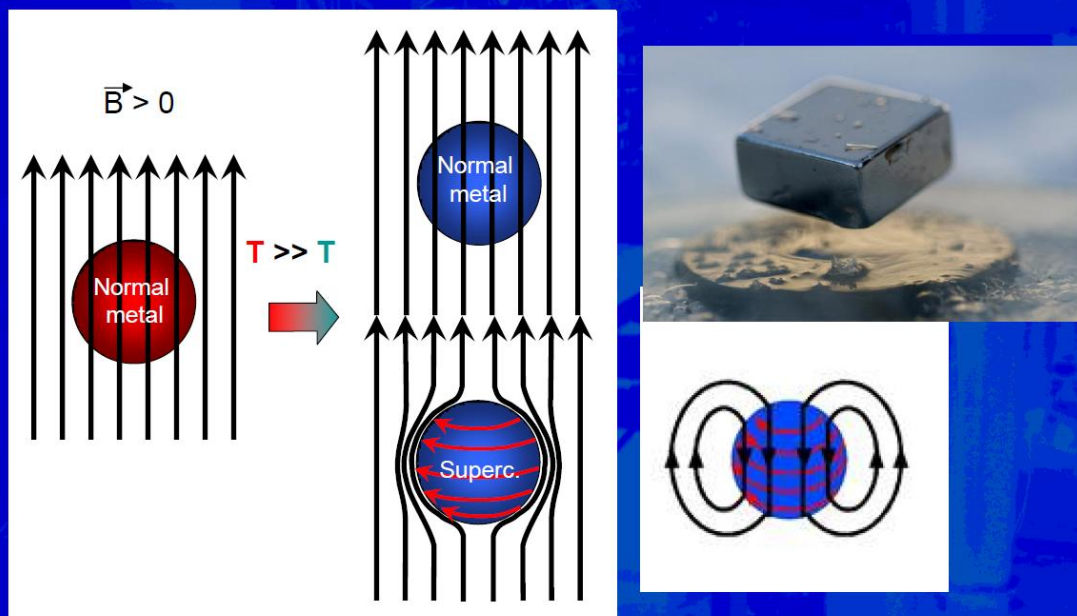
Décembre 1913 Grande déception : les supraconducteurs ne résistent pas
aux forts champs magnétiques ou aux forts courants !

Print.-Été 1914 Les premières expériences de courants permanents.

La Première Guerre Mondiale → arrêt des expériences.

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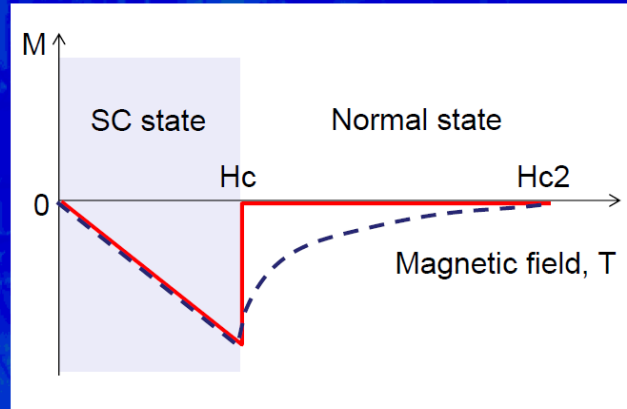
1933 : Meissner-Ochsenfeld effect : Perfect diamagnetism due to the supercurrents



1935 : Fritz London : Idea of a coherent macroscopic state!

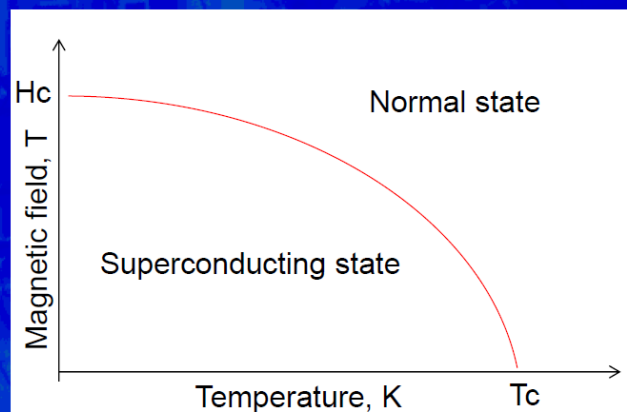
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Superconductivity : Perfect diamagnetism



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Superconductivity : Phase diagram



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1957: Microscopic Theory of Superconductivity (BCS) (Nobel prize: 1972)



John Bardeen

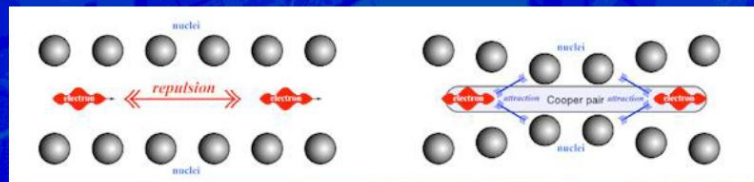


Leon Neil Cooper



John Robert Schrieffer

The Nobel Prize in Physics 1972 was awarded jointly to John Bardeen, Leon Neil Cooper and John Robert Schrieffer "for their jointly developed theory of superconductivity, usually called the BCS-theory".



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1960: Quantum Tunneling, Gap, Signatures of Electron-Phonon Interaction



Leo Esaki



Ivar Giaever



Brian Josephson

The Nobel Prize in Physics 1973 "for their experimental discoveries regarding tunneling phenomena in semiconductors and superconductors, respectively" and "for his theoretical predictions of the properties of a supercurrent through a tunnel barrier, in particular those phenomena which are generally known as the Josephson effects".

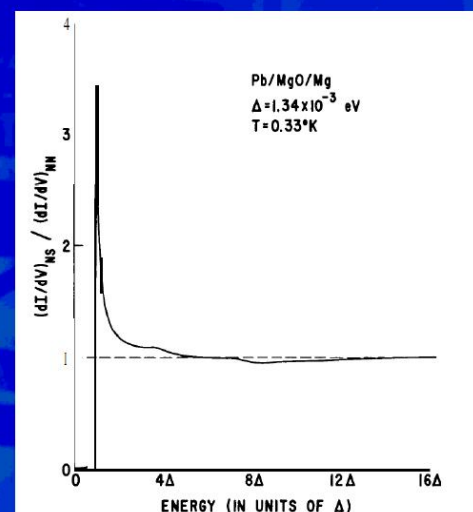
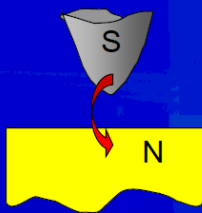


Fig. 12. A normalized derivative of the current with respect to voltage of a lead junction at low temperature. The simple BCS-theory predicts that the derivative should approach unity asymptotically as the energy increases. Instead several wiggles are observed in the range between 4Δ and 8Δ . These wiggles are related to the phonon spectrum in lead.

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Tunneling into a Superconductor

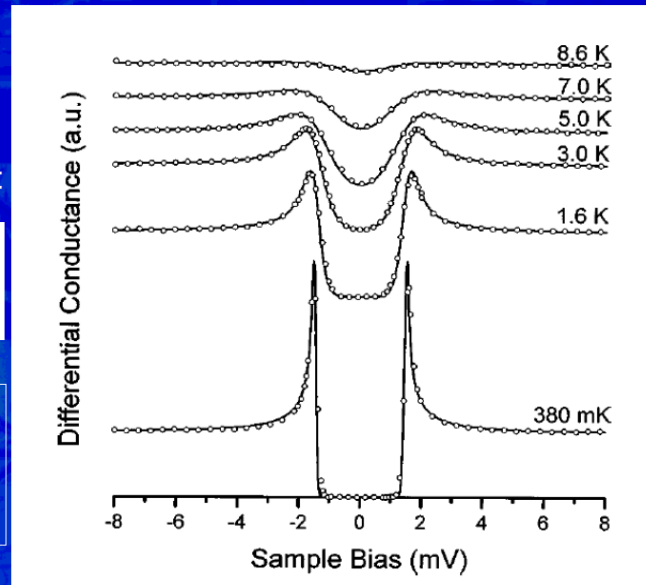
$$\frac{dI}{dV}(V) = -\frac{2\pi e^2 T}{\hbar} N_p \int_{-\infty}^{\infty} N_s(E+eV) \frac{\partial f}{\partial E}(E) dE$$

BCS-kind Superconductor:
Gap 2Δ in the excitation spectrum:

$$N_s(E) = N(0) \frac{E}{\sqrt{(E^2 - \Delta^2)}}$$

BCS

$$\frac{2 \Delta(0)}{k T_c} \approx 3.5$$



Pan, Davis, Univ. de Berkeley.(APL,1998)

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De la compréhension du piégeage de vortex à
l'optimisation des câbles fort courant



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Superconducting magnet 7T



Nb_3Sn : > 23 T

8000 sc magnets for
the LHC beam

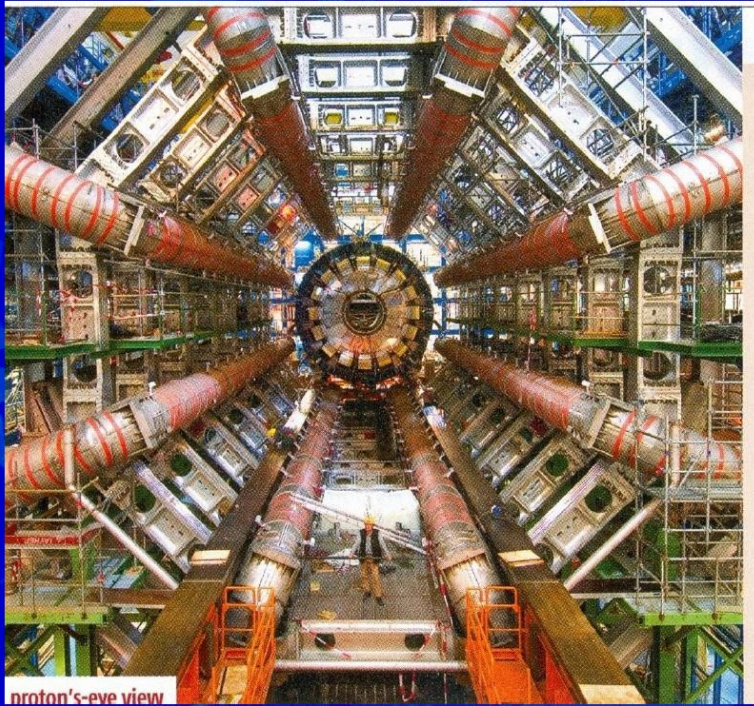
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Magnetic Resonance Imaging Magnet



Superconductivity+Spin
Magnetic Resonance Imaging

2006: Atlas Detector of LHC

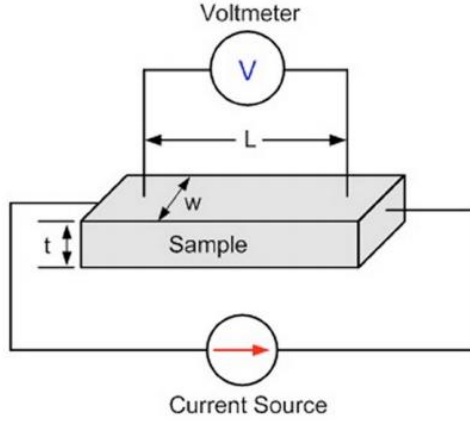


Atlas detector
Large Hadron Collider
4T field
21kA current
8pc 5x25m
6wk cooldown
1 GJ magnetic energy

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2. How to measure transport and magnetic properties of solids (reminder).

Reminder 2.1. Please revise how to measure correctly the electric resistivity of materials (make a difference between 2 terminal and 4 terminal methods). It will help you understanding the peculiar geometry of the pioneering experiment by Kamerlingh Onnes.



Reminder 2.2. Please revise how to measure $M(H)$:

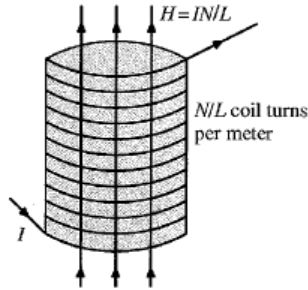


Fig. 3.6 Measurement of M as a function of H for a sample with solenoidal geometry. A long solenoid coil of N/L turns per metre leads to a uniform field $H = IN/L$ Amperes per metre inside the solenoid. The sample has magnetization, M , inside the solenoid, and the magnetic flux density is $B = \mu_0(H + M)$. Increasing the current in the coils from I to $I + dI$, by dI leads to an inductive e.m.f. $\mathcal{E} = -d\Phi/dt$ where $\Phi = NBA$ is the total magnetic flux threading the N current turns of area A . This inductive e.m.f. can be measured directly, since it is simply related to the differential self-inductance of the coil, $\mathcal{L}$, via $\mathcal{E} = -\mathcal{L}dI/dt$. Therefore, by measuring the self-inductance $\mathcal{L}$ one can deduce the B -field and hence M as a function of I or H .

For simplicity we shall usually assume that the sample is an infinitely long solenoid as sketched in Fig. 3.6. The external current flows in solenoid coils around the sample. In this case the field $\mathbf{H}$ is uniform inside the sample,

$$\mathbf{H} = I \frac{N}{L} \mathbf{e}_z \quad (3.27)$$

where I is the current flowing through the solenoid coil and there are N coil turns in length L . $\mathbf{e}_z$ is a unit vector along the solenoid axis.

Imposing the Meissner condition $\mathbf{B} = 0$ in Eq. 3.23 immediately leads to the magnetization

$$\mathbf{M} = -\mathbf{H}. \quad (3.28)$$

The magnetic susceptibility is defined by

$$\chi = \left. \frac{dM}{dH} \right|_{H=0} \quad (3.29)$$

and so we find that for superconductors

$$\chi = -1 \quad (3.30)$$

(or $-1/4\pi$ in cgs units!).

Solids with a negative value of χ are called diamagnets (in contrast positive χ is a paramagnet). Diamagnets screen out part of the external magnetic field, and so they become magnetized oppositely to the external field. In superconductors the external field is completely screened out. Therefore we can say that superconductors are **perfect diamagnets**.

Explication de l'expérience. Soit un long solénoïde de section S et de longueur L comportant le nombre N de spires. Une source externe fournit un courant électrique I qui produit le champ magnétique à $\mathbf{H} = I \frac{N}{L} \mathbf{e}_z$ l'intérieur du solénoïde. Si l'échantillon placé à l'intérieur du solénoïde a une magnétisation $\mathbf{M} = |M| \mathbf{e}_z$, alors le champ total (induction) à l'intérieur est $\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M})$.

Dans l'expérience, on augmente le courant (pendant un temps dt): $I \rightarrow I + dI$. Ceci augmente le champ du solénoïde, $H \rightarrow H + dI \frac{N}{L}$. Si l'échantillon est absent ou n'a aucune

magnétisation, $M = 0$, alors le flux magnétique $\Phi = NBS$ augmente, $\Phi \rightarrow \Phi + NSdB$, et une tension électrique $V = -d\Phi/dt$ apparaît aux bornes du solénoïde :

$$V = -NS\mu_0 \left(\frac{dH}{dt} + \frac{dM}{dt} \right) = -NS\mu_0 \frac{dH}{dt} \neq 0$$

Par contre, si l'échantillon montre le diamagnétisme parfait, $M = -H$, alors $\frac{dB}{dt} = \mu_0 \left(\frac{dH}{dt} + \frac{dM}{dt} \right) = \mu_0 \left(\frac{dH}{dt} - \frac{dH}{dt} \right) = 0$; ainsi la tension aux bornes reste $V = 0$. C'est comme si le solénoïde n'avait pas d'inductance ($V(t) = -\mathcal{L} \cdot \frac{dI}{dt} = 0$, avec $\frac{dI}{dt} \neq 0$).

Lors de ce processus, le travail total fourni par la source est $dW = -VIdt = \frac{d\Phi}{dt} \cdot Idt = dBNS \cdot HL/N = S \cdot L \cdot \mu_0(HdH + HdM)$. Le travail fourni par la source pour créer le champ H dans le solénoïde seul (s'il n'y avait pas d'échantillon) est $S \cdot L \cdot \mu_0(HdH)$. Cela veut dire que le travail $S \cdot L \cdot \mu_0(H \cdot dM)$ est fait sur l'échantillon pour augmenter sa magnétisation. Ainsi, par unité du volume, le travail fait sur le matériau pour augmenter sa magnétisation de dM est $\mu_0(H \cdot dM)$. Dans le cas d'un supraconducteur $M = -H$, et le travail est $-\mu_0(H \cdot dH)$. Ainsi, pour monter le champ de 0 à H , la source de courant « fournit » le travail additionnel négatif (par unité du volume du supraconducteur) de $W_s = \int_0^H -\mu_0(H \cdot dH) = -\mu_0 H^2/2$ (en effet, c'est le supraconducteur qui fournit ce travail en développant les courants d'écrantage).

3. Consequences of the Meissner-Ochsenfeld diamagnetism (1933). First TD considerations.

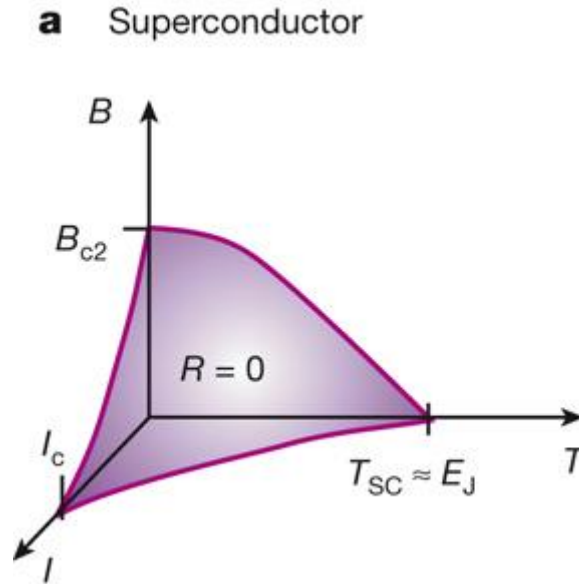


Figure. Typical phase diagram of a superconductor in field-current-temperature coordinates.

Condensation energy. The fact that the superconducting (SC) state appears when temperature is lowered below some critical temperature T_c witnesses that the SC state has a lower total energy than the normal (metallic) one. Moreover, the Meissner effect (i.e. complete and spontaneous expulsion of

the external magnetic field from the bulk of the SC) indicates that the externally applied magnetic field $\vec{H}_{ext}$ does some work to create the oppositely directed magnetization $\vec{M}$ inside superconductor:

$$\vec{B}_{int} = \mu_0(\vec{H}_{ext} + \vec{M}) \quad (\text{SI})$$

$$\vec{B}_{int} = \vec{H}_{ext} + 4\pi\vec{M} \quad (\text{SGS})$$

In the Meissner state, $\vec{B}_{int} = 0$, and we have $\vec{M} = -\vec{H}_{ext}$ (SI), or $\vec{M} = -\frac{1}{4\pi}\vec{H}_{ext}$ (SGS). Therefore, if the external magnetic field is increased from some value H to $H + dH$, the energy of the SC sample (per unit volume) will raise by

$$dA = -\mu_0 M dH = \mu_0 H dH \quad (\text{SI})$$

$$dA = -M dH = \frac{1}{4\pi} H dH \quad (\text{SGS})$$

because of perfect diamagnetism. This energy is provided by the external field source. Finally, the total work done by the magnetic field source to drive the SC sample from zero-field state to some field $\vec{H}_{ext} < H_C$ (i.e. the work to raise its diamagnetic moment from zero to $\vec{M} = -\vec{H}_{ext}$ (SI), or $\vec{M} = -\frac{1}{4\pi}\vec{H}_{ext}$ (SGS) is

$$A = \mu_0 \int_0^{H_{ext}} H dH = \mu_0 \frac{H_{ext}^2}{2} \quad (\text{SI})$$

$$A = \frac{1}{4\pi} \int_0^{H_{ext}} H dH = \frac{H_{ext}^2}{8\pi} \quad (\text{SGS})$$

Therefore, the maximum work can be done by increasing the field from 0 up to the critical field H_C (which is a function of temperature, $H_C = H_C(T)$), while keeping temperature T constant.

N.B. In the above calculation we considered that all work is done inside superconductor, i.e. the total energy would simply be A times the sample volume. This is only true in the case when there is no magnetic lines due to $\vec{M}$ outside superconductor, as otherwise we should also integrate over the outer space. Experimentally, the considered situation corresponds to a long cylindrical sample with the external magnetic field $\mu_0\vec{H}_{ext}$ directed parallel to its axis.

When the external field reaches $H_C(T)$ the material is right at the phase transition between the SC and normal state. The superconducting state and the normal state have at this point the same total (free) energies,

$$F_N(T, H_C) = F_S(T, H_C)$$

The energy of the superconducting state on the right side of this equation is just $F_S(T, H_C) = F_S(T, 0) + \mu_0 \frac{H_{ext}^2}{2}$ (SI). On the left side we have the free energy of the normal state. This energy does not depend significantly on magnetic field (as we deal with a non-magnetic metallic material), and therefore it is equal to the free energy of the same material in the normal state in zero-magnetic field, $F_N(T, H_C) = F_N(T, 0)$. By substituting the right and the left parts of the above equation we obtain

$$F_N(T, 0) = F_S(T, 0) + \mu_0 \frac{H_C(T)^2}{2}$$

, or yet the energy difference between the normal and superconducting states at zero-field,

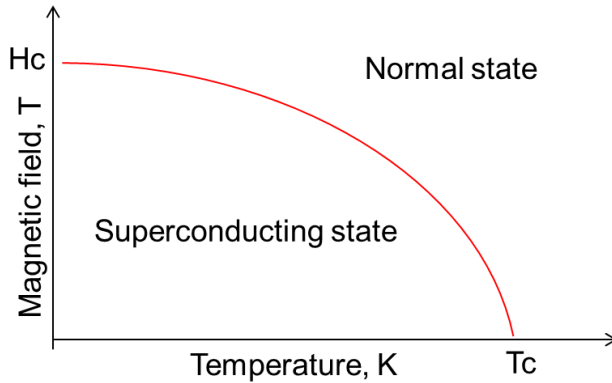
$$F_N(T, 0) - F_S(T, 0) = \mu_0 \frac{H_C(T)^2}{2}$$

We obtained, as expected, that the energy of the superconducting state is lower than the energy of the underlying (hypothetic) normal state. This is why from the TD perspective the system is in the SC and not in the normal state.

N.B. We expressed the energy difference in terms of the external field; it does not mean however that the magnetic field is a relevant microscopic parameter of superconductivity.

This amount of energy density (energy per unit of volume) is called “condensation energy”. We will justify this term later when studying the microscopic BCS theory of superconductivity.

Experimentally, most of (type I) superconductors have a specific $H_C = H_C(T)$ dependence :



Starting from the known $H_C = H_C(T)$ function and the above expression for $F_N(T, 0) - F_S(T, 0)$ we can find several interesting results.

The entropy of the SC state. First, considering the free energy, $F = U - TS$, and

$$dF = dU - SdT - TdS$$

Since our processes are reversible, we have $TdS = \delta Q$, (where δQ is the amount of the heat related to dS). At the same time, $\delta Q = -\delta W + dU$ (since the internal energy is $dU = \delta W + \delta Q$) where δW is the amount of external work done by the SC. If such a work is not done,

$$\delta W = 0$$

And therefore, $\delta Q = dU$. Now by putting this to the above expression for dF we get

$$dF = \delta Q - \delta Q - SdT = -SdT$$

Thus, we can express the entropy as

$$S = - \left(\frac{dF}{dT} \right)_{W,V=cte}$$

While we do not know the free energy of SC and normal state separately, we know their difference. We can write

$$S_S - S_N = \left(\frac{dF_N}{dT} \right) - \left(\frac{dF_S}{dT} \right) = \mu_0 H_C \frac{dH_C}{dT}$$

By analysing $H_C(T)$ dependence one sees that:

- 1) $\frac{dH_C}{dT}(T \rightarrow 0) = 0$, and therefore $S_S(T \rightarrow 0) \rightarrow 0$. This is fine as at $T = 0$:
 $S_S(T = 0) = S_N(T = 0) = 0$.
- 2) $\frac{dH_C}{dT}(0 < T < T_C) < 0$; and therefore $S_S - S_N < 0$,

i.e. **the SC state is more ordered as compared to the normal one !**

- 3) A $T \rightarrow T_C$ and zero-field $H = 0$ the difference $S_S - S_N \rightarrow 0$ since $H_C = 0$. There is no latent heat; we have a 2nd order phase transition.
- 4) A $T < T_C$ the S-N transition takes place in a magnetic field; in a magnetic field we have $S_S(H_C, T < T_C) < S_N(H_C, T < T_C)$, and the transition to the normal state is of the 1st order phase transition.

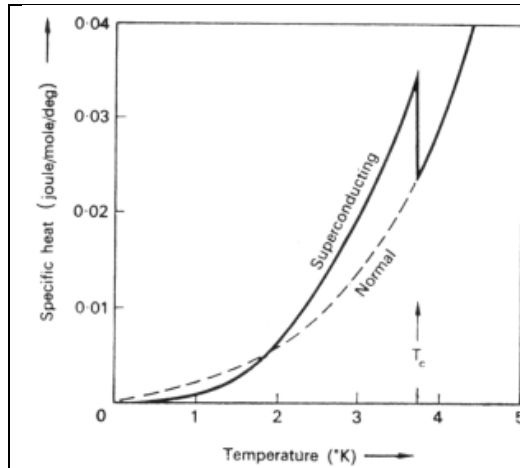
Specific heat. The knowledge of the specific heat is very important in physics and chemistry as it enables one in detecting and following different phase transitions. By definition, the specific heat is : $c = \frac{\delta Q}{dT} = T(dS/dT)$ (reversible processes). By putting in this formula the result for the entropy difference $S_S - S_N$ found in the previous section, we can calculate the difference between the specific heats of the SC and normal states

$$c_S - c_N = \mu_0 T \left[\left(\frac{dH_C}{dT} \right)^2_{W,V=cte} + H_C \frac{d^2 H_C}{dT^2} \right]$$

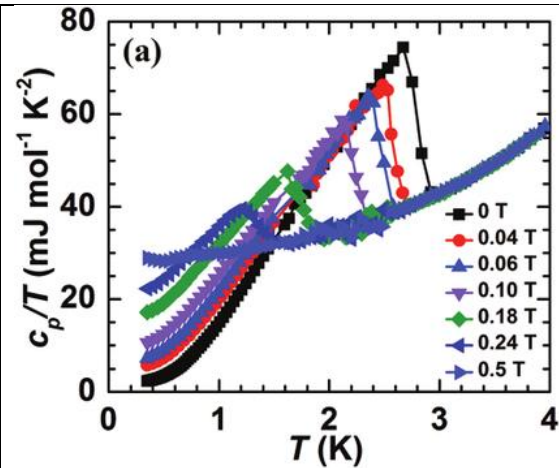
At the critical temperature $T = T_C$ and $H_C = 0$,

$$c_S - c_N = \mu_0 T_C \left(\frac{dH_C}{dT} \right)^2_{T_C}$$

i.e. one expect a finite height jump of $c_S - c_N$ at T_C . This effect is experimentally observed:



Theoretic $c_p(T)$ curve



Experimental $c_p/T(T)$ curves measured in $\text{AlPd}_{15}\text{B}_7$

4. Idea of two-fluid model (London theory of superconductivity). London equations.

Global TD considerations are not sufficient to describe local characteristics of superconductors such as currents or magnetic field distributions. The London brothers were first who suggested combining the electron energy considerations with Maxwell equations. The first London's hypothesis was that at $0 < T < T_c$ there are normal (resistive, Drude-like) electrons and the superconducting electrons

$$n = n_n + n_s$$

When $T \rightarrow 0$ $n \rightarrow n_s$, and when $T \rightarrow T_c$ $n \rightarrow n_n$, which seems reasonable.

First London equation. The first London equation simply comes from the classical motion equation for the SC electrons which (unlike Drude electrons) move without any dissipation:

$$n_s m \frac{d\vec{v}_s}{dt} = n_s e \vec{E}$$

where m is the SC electron mass, e is their charge, $\vec{v}_s$ is the superfluid velocity. Since by definition $\vec{J}_s = n_s e \vec{v}_s$ we have :

$$E = \frac{d}{dt} (\Lambda \vec{J}_s)$$

where $\Lambda = \frac{m}{n_s e^2}$. This is just the 2nd Newton's law: in the stationary state $\vec{J}_s = cte(t)$, and without dissipation there is no electric field inside the sample. Since the electric field is zero, the remaining n_n (Drude) electrons do not move.

N.B. This is only valid if the chemical potential is constant. However, in heterojunctions (junctions containing different materials) the chemical potential may vary locally, thus generating an electric field. Such effects exist near interfaces of S-N junctions.

Second London equation. The London found the relation between the superconducting currents and the local magnetic field. They explained the Meissner effect. Let us consider the free energy of a superconductor (in a form of a long cylinder) in the magnetic field

$$F = \int F_S d^3r + E_{cin} + E_{mag}$$

where F_S is the free energy of non-moving superconducting electrons (energy of the ground state) per unit of volume, E_{cin} is the kinetic energy of super-currents, E_{mag} is the magnetic energy. If the currents in point $\vec{r}$ are

$$j_S(\vec{r}) = en_S v(\vec{r})$$

their kinetic energy is

$$E_{cin} = \int n_S \frac{1}{2} m v(\vec{r})^2 d^3r$$

Finally we can express the magnetic energy through the magnetic induction

$$E_{mag} = \int \frac{B^2}{8\pi} d^3r \text{ (en SGS)}$$

$$E_{mag} = \int \frac{B^2}{2\mu_0} d^3r \text{ (en SI)}$$

(where $\vec{B} = \vec{B}(\vec{r})$ is the magnetic induction in $\vec{r}$)

Now let us link the super-currents to the magnetic induction via Maxwell equations:

$$\text{rot}(\vec{B}(\vec{r})) = \frac{4\pi}{c} \vec{j}_S(\vec{r}) \quad (\text{SGS})$$

$$\text{rot}(\vec{B}(\vec{r})) = \mu_0 \vec{j}_S(\vec{r}) \quad (\text{SI})$$

Putting all terms in the expression for free energy we get

$$F = \int F_S d^3r + \frac{1}{8\pi} \int [B^2 + \lambda_L^2 |\text{rot}(\vec{B})|^2] d^3r \quad (\text{SGS})$$

$$F = \int F_S d^3r + \frac{1}{2\mu_0} \int [B^2 + \lambda_L^2 |\text{rot}(\vec{B})|^2] d^3r \quad (\text{SI})$$

, several parameters which combine into a single parameter having the dimension of a length

$$\lambda_L = \left[\frac{mc^2}{4\pi n_S e^2} \right]^{1/2} \text{ (en SGS)}$$

$$\lambda_L = \left[\frac{m}{\mu_0 n_S e^2} \right]^{1/2} \text{ (en SI)}$$

This parameter is called « London penetration depth ». Note that at $T = 0$ $n_S = n$, and it becomes possible to calculate λ_L directly ($\lambda_L \sim 50 - 200 \text{ nm}$).

The TD stable state corresponds to the minimum free energy among all possible configurations. To find the TD stable configuration we can calculate a small variation δF of free energy F which now depends only on magnetic induction B . At the minimum of F , δF should be $\delta F = 0$.

If the local magnetic induction $B(\vec{r})$ varies by $\vec{\delta b}(\vec{r})$, the free energy varies by δF ,

$$\delta F = \frac{1}{4\pi} \left\{ \frac{1}{\mu_0} \right\} \int [\vec{B} \vec{\delta b} + \lambda_L^2 \text{rot}(\vec{B}) \text{rot}(\vec{\delta b})] d^3r = \frac{1}{4\pi} \left\{ \frac{1}{\mu_0} \right\} \int [\vec{B} + \lambda_L^2 \text{rot}(\text{rot}(\vec{B}))] \vec{\delta b} d^3r$$

N.B. Here the second term inside the integral $\text{rot}(\vec{B}) \text{rot}(\vec{\delta b})$ is due to the fact that the variation of this term is $|\text{rot}(\vec{B} + \vec{\delta b})|^2 - |\text{rot}(\vec{B})|^2 = 2\text{rot}(\vec{B}) \text{rot}(\vec{\delta b}) + |\text{rot}(\vec{\delta b})|^2 \approx 2\text{rot}(\vec{B}) \text{rot}(\vec{\delta b})$ (as $\vec{\delta b}$ is very small). Moreover, since $\vec{a} \text{rot}(\vec{b}) = \vec{b} \text{rot}(\vec{a}) - \text{div} [\vec{a} \times \vec{b}]$, in our case we have: $\text{rot}(\vec{B}) \text{rot}(\vec{\delta b}) = \vec{\delta b} \text{rot}(\text{rot}(\vec{B})) - \text{div} [\text{rot}(\vec{B}) \times \vec{\delta b}]$. The term with $\text{div} [\text{rot}(\vec{B}) \times \vec{\delta b}]$ does not contribute to the integral since $\int \text{div} [\text{rot}(\vec{B}) \times \vec{\delta b}] d^3r = \oint [\text{rot}(\vec{B}) \times \vec{\delta b}] d\vec{S}$ and, since at the surface of the SC the magnetic field is fixed, $\vec{B}_{\text{surface}} = \vec{B}_{\text{ext}} = \text{cte}$, and thus cannot be varied, $\vec{\delta b} = 0$ there.

The condition of minimum of free energy is then

$$\vec{B} + \lambda_L^2 \text{rot}(\text{rot}(\vec{B})) = 0$$

This is the second London equation. It is possible to rewrite it in a more useful form. By using $\vec{B} = \text{rot}(\vec{A})$ and $\text{rot}(\vec{B}(\vec{r})) = \frac{4\pi}{c} \vec{J}_S(\vec{r})$ ($\text{rot}(\vec{B}(\vec{r})) = \mu_0 \vec{J}_S(\vec{r})$) one obtains:

$$\text{rot}(\vec{J}_S) = -\frac{c}{4\pi\lambda_L^2} \text{rot}(\vec{A}) \quad (\text{SGS})$$

$$\text{rot}(\vec{J}_S) = -\frac{1}{\mu_0\lambda_L^2} \text{rot}(\vec{A}) \quad (\text{SI})$$

Moreover, if we use a specific (London) gauge for $\vec{A}$, $\text{div}(\vec{A}) = 0$; $(\vec{A}, \vec{S}) = 0$, we can write:

$$\vec{J}_S = -\frac{c}{4\pi\lambda_L^2} \vec{A}$$

$$\vec{J}_S = -\frac{1}{\mu_0\lambda_L^2} \vec{A}$$

i.e. in London gauge the supercurrents circulate owing the vector-potential $\vec{A}$. In this gauge : no vector-potential – no currents!

N.B.1. En fait, la démonstration ci-dessus de la deuxième équation de London, même s'elle donne le bon résultat, n'est pas exacte. Les courants circulant dans le supraconducteur ne génèrent pas le champ $\vec{B}$ mais seulement le champ « diamagnétique » $\mu_0 \vec{M}$ car le champ constant $\mu_0 \vec{H}_{\text{ext}}$ est produit par la bobine externe seule. En effet, $\text{rot}(\vec{B}(\vec{r})) = \mu_0 [\vec{J}_S(\vec{r}) + \vec{J}_{\text{bobine}}(\vec{r})] = \text{rot}(\mu_0 \vec{H}_{\text{ext}} + \mu_0 \vec{M}(\vec{r}))$.

L'énergie magnétique totale à l'intérieur du supraconducteur est bien $E_{\text{mag}} = \int \frac{B^2}{2\mu_0} d^3r$, mais une

partie de cette énergie, $E_{sol} = \int \frac{\mu_0 \vec{H}_{ext}^2}{2\mu_0} d^3r$ est produite par le solénoïde seul. Ainsi, l'augmentation de l'énergie magnétique due au supraconducteur est

$$E_{mag} - E_{sol} = \frac{1}{2\mu_0} \int \left[\vec{B}^2 - (\mu_0 \vec{H}_{ext})^2 \right] d^3r$$

L'énergie cinétique due aux électrons supraconducteurs est $E_{cin} = \int n_s \frac{1}{2} m v_s(\vec{r})^2 d^3r = \frac{1}{2\mu_0} \int \lambda_L^2 |rot(\mu_0 \vec{M})|^2 d^3r$

En mettant les ingrédients dans F :

$$F = \int F_S d^3r + \frac{1}{2\mu_0} \int \left[\vec{B}^2 - (\mu_0 \vec{H}_{ext})^2 + \lambda_L^2 |rot(\mu_0 \vec{M})|^2 \right] d^3r$$

Puisque la bobine produit le champ extérieur spatialement homogène, $rot(\mu_0 \vec{M}(\vec{r})) = rot(\vec{B}(\vec{r}))$.

L'énergie libre s'exprimée en fonction du champ $\vec{B}$ est donc :

$$F = \int F_S d^3r + \frac{1}{2\mu_0} \int \left[(\vec{B}^2 - (\mu_0 \vec{H}_{ext})^2) + \lambda_L^2 |rot(\vec{B})|^2 \right] d^3r$$

En appliquant la méthode variationnelle par rapport au champ $\vec{B}$, $\vec{B} \rightarrow \vec{B} + \delta \vec{b}$, on obtient :

$$\delta F = \frac{1}{\mu_0} \int [\vec{B} \delta \vec{b} + \lambda_L^2 rot(\vec{B}) rot(\delta \vec{b})] d^3r = \frac{1}{\mu_0} \int [\vec{B} + \lambda_L^2 rot(rot(\vec{B}))] \delta \vec{b} d^3r$$

Et donc, la deuxième équation de London est bien :

$$\vec{B} + \lambda_L^2 rot(rot(\vec{B})) = 0$$

ou, pour le vecteur de magnétisation produite par les courants,

$$\vec{M} + \lambda_L^2 rot(rot(\vec{M})) = \vec{H}_{ext}$$

Si on définit les axes (x, y) coïncident avec la surface, le champ extérieur orienté vers l'axe x et l'axe z dirigé vers l'intérieur du supraconducteur, on a, à la surface du supraconducteur, $\vec{B}(z=0) = (\mu_0 |\vec{H}_{ext}|, 0, 0)$. Ceci donne bien

$$\vec{B}(z) = (\mu_0 |\vec{H}_{ext}|, 0, 0) \exp\left(-\frac{z}{\lambda_L}\right)$$

et

$$\vec{M}(z) = (|\vec{H}_{ext}|, 0, 0) \left[\exp\left(-\frac{z}{\lambda_L}\right) - 1 \right]$$

i.e. à l'intérieur de l'échantillon, loin des bords ($z \gg \lambda_L$), $\vec{B}(z) = 0$ et $\vec{M}(z) = -\vec{H}_{ext}$ (effet Meissner).

Les courants supraconducteurs sont $\vec{j}_s(\vec{r}) = \text{rot}(\vec{M}(\vec{r})) = \frac{1}{\mu_0} \text{rot}(\vec{B}(\vec{r}))$ car $\vec{H}_{ext}$ est constant. Ceci donne, dans nos coordonnées,

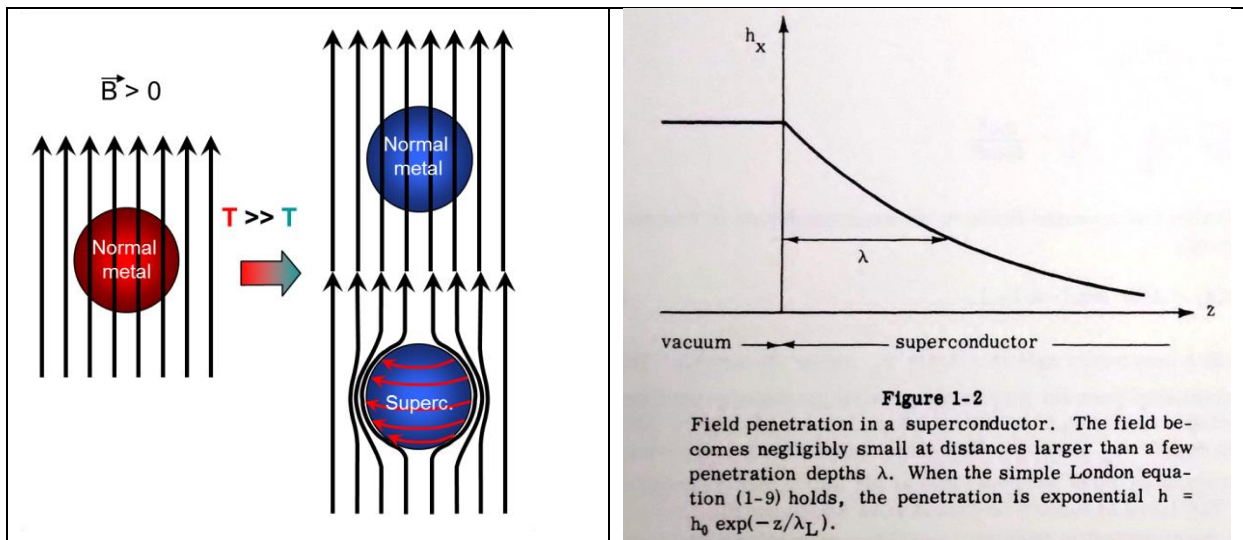
$$\vec{j}_s(z) = (0, -\frac{1}{\lambda_L} \vec{H}_{ext}, 0) \exp(-\frac{z}{\lambda_L})$$

i.e. les courant Meissner circulent dans la direction y et décroissent exponentiellement à l'intérieur du supraconducteur.

N.B.2. As demonstrated, this equation does not distinguish between the behavior of a superconductor or an « ideal metal » upon cooling in a spatially homogeneous magnetic field.

5. Meissner effect (from De Gennes « Superconductivity of metals and alloys »).

Using London equations we can derive now the Meissner effect



To do this let us consider an border of a macroscopically large SC sample in contact with vacuum. Let this surface coincide with (X,Y) plane ; positive Z-direction will go inside superconductor, negative Z – to vacuum. Let us consider different directions of the magnetic field.

Case 1: imagine $\vec{B}$ directed parallel to Z (towards the bulk of the SC sample, $\vec{B} = (0,0,B)$). The 2nd Maxwell equation gives $\frac{dB}{dz} = 0$, i.e. the amplitude of the magnetic field is constant inside the SC material. Then, the 1st Maxwell equation gives $j_s(\vec{r}) = 0$. Finally, since $j_s(\vec{r}) = 0$ the London equation gives $\vec{B} = 0$. Thus, in the considered limit of low fields and currents, it is impossible to have a non-zero magnetic field (or a component of it) directed perpendicularly to the surface of a SC material.

Case 2: consider now $\vec{B}$ parallel to X (i.e. perpendicular to Z). The 1st Maxwell equation gives the supercurrent directed in Y-direction,

$$\frac{dB}{dz} = \frac{4\pi}{c} j_s(\vec{r}) \quad (\text{SGS})$$

$$\frac{dB}{dz} = \mu_0 j_s(\vec{r}) \quad (\text{SI})$$

The second London equation becomes

$$\frac{d^2 B}{dz^2} = \frac{B}{\lambda_L^2}$$

The solution inside the superconductor (positive Z-direction) is

$$B(z) = B(0) \exp\left(-\frac{z}{\lambda_L}\right)$$

where $B(0) = B_{\text{Surface}}$ is the magnetic field at the sample surface (equal to the externally applied field), and $\lambda_L = \left[\frac{mc^2}{4\pi n_s e^2}\right]^{1/2}$ (SGS).

It means that **the magnetic field exponentially decays inside the SC material on a scale of the London penetration depth.**

We can also find the supercurrent distribution

$$\frac{d j_s}{dz} = \frac{n_s e^2}{mc} B \quad (\text{SGS})$$

By integrating this equation we obtain the exponential decay of screening super-currents inside the superconductor:

$$j_s = \frac{c}{4\pi\lambda_L} B_{\text{Surface}} \exp\left(-\frac{z}{\lambda_L}\right) \quad (\text{SGS})$$

$$j_s = \frac{1}{\mu_0\lambda_L} B_{\text{Surface}} \exp\left(-\frac{z}{\lambda_L}\right) \quad (\text{SI})$$

i.e. **the screening supercurrents circulate only near the surface of the superconductor where $B(z) \neq 0$.**

In the second London equation, the only important parameter is $\lambda_L = \lambda_L(n_s)$. Therefore this parameter is expected to depend on temperature, since $n_s(T \rightarrow T_c) \rightarrow 0$. It means that, approaching T_c from the superconducting side ($T < T_c$), the magnetic field will start to penetrate deeper and deeper the material; at T_c the penetration is full as no Meissner currents circulate.

Experimentally, by studying the diamagnetic response of SC samples as a function of temperature, researchers had elaborated the following empiric formula:

$$\lambda_L(T) = \frac{\lambda_L(0)}{\left(1 - \left(\frac{T}{T_c}\right)^4\right)^{1/2}}$$

Let us estimate λ_L . At $T = 0$ all the electrons are « superconducting », i.e. $n_s \sim 10^{22} \text{ cm}^{-3}$. Putting this number into the formula for λ_L we obtain $\lambda_L(0) \sim 60 \text{ nm}$. This is indeed a very good estimation for simple type I superconductors: $\lambda_L(\text{Al}) = 50 \text{ nm}$, $\lambda_L(\text{Hg}) = 44 \text{ nm}$, $\lambda_L(\text{In}) = 64 \text{ nm}$, $\lambda_L(\text{Nb}) = 47 \text{ nm}$, $\lambda_L(\text{Pb}) = 39 \text{ nm}$, $\lambda_L(\text{Sn}) = 51 \text{ nm}$, $\lambda_L(\text{Tl}) = 92 \text{ nm}$. Unfortunately, for type II SC materials it does not work!

6. Non-local electrodynamics of superconductors.

The London equation is local in sense that the current $\vec{J}_s(\vec{r})$ depend only on the local value of the vector-potential $\vec{A}(\vec{r})$

$$\vec{J}_s(\vec{r}) = -\frac{c}{4\pi\lambda_L^2} \vec{A}(\vec{r})$$

Pippard argued (Pippard A.B. Proc.Roy.Soc., 1953, A215, 547) that this is not very reasonable since the superconducting electron wave packet should have a certain spatial extend ξ_0 (for instance, Drude electrons are characterized by their mean free path $l = v_F \tau$). If $\vec{A}(\vec{r})$ varies on the scale of ξ_0 then the superconducting electron wave packet is affected by $\vec{A}(\vec{r})$ over ξ_0 . (Note that for clean simple metals (like superconducting Al) the local London description does not work, since $\xi_0^{Al} \approx 10^3 \text{ nm}$, and $\lambda_L^{Al} \approx 10 - 100 \text{ nm}$, i.e. indeed $\vec{A}(\vec{r})$ varies strongly on the scale of ξ_0^{Al} .)

Pippard suggested considering a non-local link between $\vec{J}_s(\vec{r})$ and $\vec{A}(\vec{r})$ via convolution with a space averaging operator

$$\vec{J}_s(\vec{r}) = \int d\vec{r}' \hat{Q}(\vec{r} - \vec{r}') \vec{A}(\vec{r}')$$

Where is space “averaging” operator $\hat{Q}(\vec{r} - \vec{r}')$ on $\vec{A}(\vec{r}')$ on the scale of ξ_0 . Pippard suggested to take it in the form

$$\hat{Q}(\vec{r} - \vec{r}') \vec{A}(\vec{r}') = -\frac{3n_s e^2}{4\pi m c \xi_0} \frac{(\vec{r} - \vec{r}')}{(\vec{r} - \vec{r}')^4} ((\vec{r} - \vec{r}'), \vec{A}(\vec{r}')) \exp\left(-\frac{|\vec{r} - \vec{r}'|}{r_0}\right)$$

with $\frac{1}{r_0} = \frac{1}{\xi_0} + \frac{1}{l}$. The expression for r_0 reflects the fact that the superconducting electron wave packet is always limited to its normal mean free path.

In the non-local case, the decay of the magnetic field inside the superconductor is not simply exponential. Nevertheless one can define the penetration depth as

$$\lambda_p = \frac{1}{B_{ext}} \int_0^\infty dz B$$

Where H_{ext} is the external parallel field at the SC surface, and the integration is done inside the superconductor in the perpendicular direction z . In practice, the decay is quite exponential and, therefore it is possible to introduce the effective Pippard penetration depth λ_p . In the “very” unlocal limit $\lambda_p \ll \xi_0$ it is easy to obtain the estimate for λ_p

$$\lambda_p \approx (\lambda_L^2 \xi_0)^{1/3}$$

However, in most of superconductors local (London) electrodynamics work well since $\lambda > \xi$.

7. Quantum generalization of London's equations. Flux quantization.

In 1934-45, Fritz London suggested that the superconducting state could be a macroscopic quantum state. If so, one could imagine to describe it by a wave function $\psi(r)$. At zero temperature one could imagine to have $\psi(r) = (n_s/2)^{1/2} \exp(i\theta(\vec{r}))$, in order to obtain the total density $n_s/2$ of superconducting electron pairs.

In QM the probability current j due to the wave function $\psi(r, t)$ describing a particle of a mass $2m$ is :

$$j = \frac{\hbar}{2(2m)i} (\psi^* \vec{\nabla} \psi - \psi \vec{\nabla} \psi^*)$$

In the case of a non-zero magnetic field

$$\frac{\hbar}{i} \vec{\nabla} \rightarrow \frac{\hbar}{i} \vec{\nabla} + \frac{2e}{c} \vec{A} \text{ (SGS)}$$

$$\frac{\hbar}{i} \vec{\nabla} \rightarrow \frac{\hbar}{i} \vec{\nabla} + 2e \vec{A} \text{ (SI)}$$

And the current,

$$\vec{j} = \frac{1}{2(2m)} \left[(\psi^* (-i\hbar \vec{\nabla} \psi) - \psi (-i\hbar \vec{\nabla} \psi^*)) - 2 \frac{2e}{c} \vec{A} |\psi|^2 \right] \text{ (SGS)}$$

$$\vec{j} = \frac{1}{2(2m)} \left[(\psi^* (-i\hbar \vec{\nabla} \psi) - \psi (-i\hbar \vec{\nabla} \psi^*)) - 4e \vec{A} |\psi|^2 \right] \text{ (SI)}$$

Putting the expression for ψ we obtain:

$$\vec{j} = \frac{1}{2(2m)} \left[2 \frac{n_s}{2} \hbar \vec{\nabla} \theta - 2 \frac{2e}{c} \vec{A} \frac{n_s}{2} \right]$$

$$\vec{j} = \frac{1}{2(2m)} \left[2 \frac{n_s}{2} \hbar \vec{\nabla} \theta - 4e \vec{A} \frac{n_s}{2} \right]$$

At the same time the current of particles is $\vec{j} = \frac{n_s}{2} \vec{v}_s$, that gives for the electric supercurrent $\vec{j}_s = 2e \vec{j}$:

$$j_s = \frac{en_s}{2m} \left[\hbar \vec{\nabla} \theta - \frac{2e}{c} \vec{A} \right] = \frac{n_s e^2}{cm} \left[\frac{\hbar c}{2e} \vec{\nabla} \theta - \vec{A} \right] = \frac{n_s e^2}{cm} \left[\frac{\Phi_0}{2\pi} \vec{\nabla} \theta - \vec{A} \right] \text{ (SGS)}$$

$$j_s = \frac{en_s}{2m} \left[\hbar \vec{\nabla} \theta - 2e \vec{A} \right] = \frac{n_s (2e)^2}{4m} \left[\frac{\hbar}{2e} \vec{\nabla} \theta - \vec{A} \right] = \frac{n_s (2e)^2}{4m} \left[\frac{\Phi_0}{2\pi} \vec{\nabla} \theta - \vec{A} \right] \text{ (SI)}$$

with $\Phi_0 = \frac{\hbar c}{2e} = 2.07 \cdot 10^{-7} \text{ Gauss} \cdot \text{cm}^2$ (SGS) or $\Phi_0 = \frac{\hbar}{2e} = 2.07 \cdot 10^{-15} \text{ Wb}$ (SI). The value Φ_0 is the superconducting flux quantum.

N.B. With respect to the classical case we see an additional term in current-field equation, due to the gradient of the quantum wave function. This term is needed to describe experimentally observed phenomena. This need demonstrates the quantum coherent nature of superconductivity, as we see below.

(from V.V.Shmidt "The Physics of Superconductors : Introduction to Fundamentals and Applications")

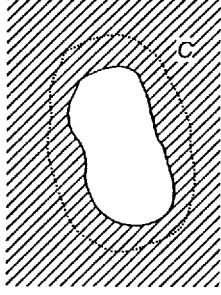


Fig. 2.2. Solid superconductor (dashed area) contains a hole. The contour C goes around the hole through the interior of the superconductor

Let us consider a macroscopic superconductor with a hole drilled inside. Let us choose a closed loop inside the material far from the hole ($\gg \lambda_L$). From London equation we get on the loop

$$j_s^{loop} = 0, H^{loop} = 0$$

Let us take an integral from both parts of the $j_s = \frac{n_s e^2}{cm} \left[\frac{\Phi_0}{2\pi} \vec{\nabla} \theta - \vec{A} \right]$ over the loop. We get

$$\frac{\Phi_0}{2\pi} \oint d\vec{s} \vec{\nabla} \theta = \oint d\vec{s} \vec{A} = \Phi$$

But

$$\oint d\vec{s} \vec{A} = \int d\vec{S} \text{rot}(\vec{A}) = \int d\vec{S} \vec{B} = \Phi$$

Therefore

$$\frac{\Phi_0}{2\pi} \oint d\vec{s} \vec{\nabla} \theta = \Phi$$

The flux Φ is the magnetic flux across the loop. One immediately sees that θ is not uni-defined, but as it changes but $\psi(\vec{r})$ should be. Finally, if the phase accumulation along the loop is $2\pi n$, then $\psi(r, \theta + 2\pi n) = |\psi| e^{i(\theta + 2\pi n)} = |\psi| e^{i\theta} = \psi(r, \theta)$, i.e. the wave function is uni-evaluated. It means that

$$\Phi = n\Phi_0$$

NB 3.3. Experimentally, magnetic flux quantization was discovered in 1961 almost simultaneously in the USA (B. Deaver and W. Fairbank) and in Germany (R. Doll and M. Nabauer) (refs: B.S. Deaver, Jr., W.M. Fairbank: Phys. Rev. Lett. 7, 43 (1961) and R. Doll, M. Nabauer: Phys. Rev. Lett. 7, 51 (1961)). It is interesting to note that F. London, who predicted the flux quantization, believed that the flux quantum should be $\frac{hc}{e}$, that is, he predicted a value twice as large as Φ_0 . But that is not surprising because he believed that the charge of an elementary supercurrent carrier was equal to the electron charge e . Experiment confirmed the validity of $\Phi_0 = \frac{hc}{2e}$. Thus the experiments that detected the quantization of magnetic flux also provided direct evidence that the supercurrent is carried by pairs of electrons.

Appendix 1.

(from J.F. Annett “Superconductivity, Superfluids and Condensates”)

4.1 Introduction

The superconducting state and the normal metallic state are separate thermodynamic phases of matter in just the same way as gas, liquid, and solid are different phases. Similarly, the normal Bose gas and Bose–Einstein Condensate (BEC), or normal liquid He⁴ and superfluid He II are separated by a thermodynamic phase transitions. Each such phase transition can be characterized by the nature of the singularities in specific heat and other thermodynamic variables at the transition, T_c . We can therefore examine the problems of superfluidity and superconductivity from the point of view of the thermodynamics of phase transitions.

The theory of superconductivity introduced by Ginzburg and Landau in 1950 describes the superconducting phase transition from this thermodynamic point of view. It was originally introduced as a phenomenological theory, but later Gor’kov showed that it can be derived from full the microscopic Bardeen Cooper Schrieffer (BCS) theory in a suitable limit.¹

In this chapter we shall first discuss the superconducting phase transition from the point of view of equilibrium thermodynamics. Then we gradually build up toward the full Ginzburg–Landau (GL) model. First we discuss spatially uniform systems, then spatially varying systems and finally systems in an external magnetic field. The Ginzburg–Landau theory makes many useful and important predictions. Here we focus on just two applications: to flux quantization, and to the Abrikosov flux lattice in type II superconductors.

The GL theory as originally applied to superconductors was *par excellence* a **mean-field theory** of the thermodynamic state. However, in fact, one of its most powerful features is that it can be used to go beyond the original mean-field limit, so as to include the effects of thermal fluctuations. We shall see below that such fluctuations are largely negligible in the case of conventional “low- T_c ” superconductors, making the mean-field approximation essentially exact. However, in the newer high T_c superconductors these fluctuations lead to many important phenomena, such as flux flow, and the melting of the Abrikosov vortex lattice.

4.2 The condensation energy

We already have enough information about superconductivity to derive some important thermodynamic properties about the superconducting phase

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¹In fact, the Ginzburg–Landau model is very general and has applications in many different areas of physics. It can be modified to describe many different physical systems, including magnetism, liquid crystal phases, and even the symmetry breaking phase transitions, which took place in the early universe as matter cooled following the big bang!

transition. We can analyze the phase diagram of superconductors in exactly the same manner as one would consider the well known thermodynamics of a liquid–gas phase transition problem, such as given by the van der Waals equation of state. However, for the superconductor instead of the pair of thermodynamic variables P, V (pressure and volume) we have the magnetic variables $\mathbf{H}$ and $\mathbf{M}$ as the relevant thermodynamic parameters.

Let us first briefly review the basic thermodynamics of magnetic materials. This is covered in several undergraduate text books on thermodynamics such as Mandl (1987) or Callen (1960), Blundell (2001). If we consider a long cylindrical sample in a solenoidal field, as shown in Fig. 3.6, then the magnetic field $\mathbf{H}$ inside the sample is given by

$$\mathbf{H} = \frac{N}{L} I \mathbf{e}_z, \quad (4.1)$$

where the coil has N/L turns per meter, I is the current and $\mathbf{e}_z$ is a unit vector along the axis of the cylinder. The total work done, dW , on increasing the current infinitesimally from I to $I + dI$ can be calculated as

$$\begin{aligned} dW &= -N\mathcal{E} I dt, \\ &= +N \frac{d\Phi}{dt} I dt, \\ &= +NI d\Phi, \\ &= +NAI dB, \\ &= +NV\mathbf{H} \cdot d\mathbf{B}, \\ &= +\mu_0 V (\mathbf{H} \cdot d\mathbf{M} + \mathbf{H} \cdot d\mathbf{H}), \end{aligned} \quad (4.2)$$

where A is the cross sectional area of the coil, $V = AL$ is its volume, $\mathcal{E} = -d\Phi/dt$ is the e.m.f. induced in the coil by the change in the total magnetic flux, Φ , through the sample. We also used the identity $\mathbf{B} = \mu_0(\mathbf{M} + \mathbf{H})$ in writing the last step in Eq. 4.2.

This analysis shows that we can divide the total work done by increasing the current in the coil into two separate parts. The first part,

$$\mu_0 \mathbf{H} \cdot d\mathbf{M}$$

per unit volume, is the **magnetic work** done on the sample. The second part,

$$\mu_0 \mathbf{H} \cdot d\mathbf{H}$$

is the work per unit volume which would have been done even if no sample had been present inside the coil; it is the work done by the **self-inductance** of the coil. If the coil is empty, $\mathbf{M} = 0$ and so $\mathbf{B} = \mu_0 \mathbf{H}$ and one can easily see that the work done is exactly the change in the vacuum field energy of the electromagnetic field

$$E_B = \frac{1}{2\mu_0} \int B^2 d^3r \quad (4.3)$$

due to the change of current in the solenoid coils. By convention² we shall not include this vacuum field energy, as work done “on the sample.” Therefore we define the magnetic work done on the sample as $\mu_0 \mathbf{H} \cdot d\mathbf{M}$ per unit volume.

²Unfortunately there is no single standard convention used by all books and papers in this field. Different contributions to the total energy are either included or not, and so one must be very careful when comparing similar looking equations from different texts and research papers. Our convention follows Mandl (1987) and Callen (1960).

With this definition of magnetic work the first law of thermodynamics for a magnetic material reads

$$dU = T dS + \mu_0 V \mathbf{H} \cdot d\mathbf{M}, \quad (4.4)$$

where U is the total internal energy, TdS is the heat energy with T the temperature and S the entropy. We see that the magnetic work is analogous to the work, $-PdV$, in a gas. As in the usual thermodynamics of gases the internal energy, U , is most naturally thought of as a function of the entropy and volume: $U(S, V)$. The analog of the first law for a magnetic system, Eq. 4.4, shows that the internal energy of a magnetic substance is most naturally thought of as a function of S and $\mathbf{M}$, $U(S, \mathbf{M})$. In terms of this function the temperature and field $\mathbf{H}$ are given by

$$T = \frac{\partial U}{\partial S} \quad (4.5)$$

$$\mathbf{H} = \frac{1}{\mu_0 V} \frac{\partial U}{\partial \mathbf{M}}. \quad (4.6)$$

However, S and $\mathbf{M}$ are usually not the most convenient variables to work with. In a solenoidal geometry such as Fig. 3.6 it is the H -field which is directly fixed by the current, not $\mathbf{M}$. It is therefore useful to define magnetic analogs of the Helmholtz and Gibbs free energies

$$F(T, \mathbf{M}) = U - TS \quad (4.7)$$

$$G(T, \mathbf{H}) = U - TS - \mu_0 V \mathbf{H} \cdot \mathbf{M}. \quad (4.8)$$

As indicated, the Gibbs free energy G is naturally viewed as a function of T and $\mathbf{H}$ since,

$$dG = -S dT - \mu_0 V \mathbf{M} \cdot d\mathbf{H}. \quad (4.9)$$

In terms of G one can calculate the entropy and magnetization,

$$S = -\frac{\partial G}{\partial T}, \quad (4.10)$$

$$\mathbf{M} = -\frac{1}{\mu_0 V} \frac{\partial G}{\partial \mathbf{H}}. \quad (4.11)$$

$G(T, \mathbf{H})$ is usually the most convenient thermodynamic quantity to work with since T and $\mathbf{H}$ are the variables which are most naturally controlled experimentally. Furthermore from $G(T, \mathbf{H})$ one can also reconstruct the free energy, $F = G + \mu_0 V \mathbf{H} \cdot \mathbf{M}$ or the internal energy $U = F + TS$.

The Gibbs free energy allows us to calculate the free energy difference between the superconducting state and the normal state. Consider the H, T phase diagram of a type I superconductor, as sketched above in Fig. 4.1. We can evaluate the change in Gibbs free energy in the superconducting state by integrating along the vertical line drawn. Along this line $dT = 0$, and so, clearly,

$$G_s(T, H_c) - G_s(T, 0) = \int dG = -\mu_0 V \int_0^{H_c} \mathbf{M} \cdot d\mathbf{H},$$

where the subscript s implies that $G(T, \mathbf{H})$ is in the superconducting state. But for a type I superconductor in the superconducting state we know from the

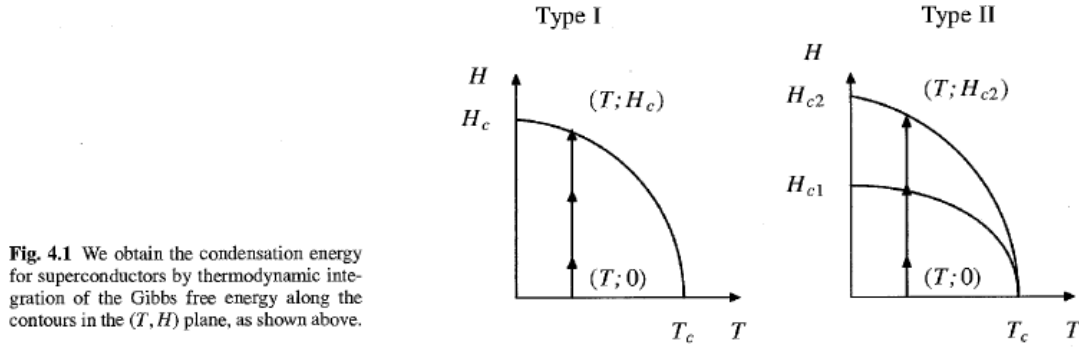


Fig. 4.1 We obtain the condensation energy for superconductors by thermodynamic integration of the Gibbs free energy along the contours in the (T, H) plane, as shown above.

Meissner–Ochsenfeld effect that $\mathbf{M} = -\mathbf{H}$ and thus,

$$G_s(T, H_c) - G_s(T, 0) = \mu_0 \frac{H_c^2}{2} V.$$

Now, at the critical field H_c in Fig. 4.1 the normal state and the superconducting state are in thermodynamic equilibrium. Equilibrium between phases implies that the two Gibbs free energies are equal:

$$G_s(T, H_c) = G_n(T, H_c).$$

Furthermore, in the normal state $M \approx 0$ (apart from the small normal metal paramagnetism or diamagnetism which we neglect). So if the normal metal state had persisted below H_c down to zero field, it would have had a Gibbs free energy of,

$$G_n(T, H_c) - G_n(T, 0) = \int dG = -\mu_0 V \int_0^{H_c} M dH \approx 0.$$

Putting these together we find the difference in Gibbs free energies of superconducting and normal states at zero field:

$$G_s(T, 0) - G_n(T, 0) = -\mu_0 V \frac{H_c^2}{2}. \quad (4.12)$$

The Gibbs potential for the superconducting state is lower, so it is the stable state.

We can also write the above results in terms of the more familiar Helmholtz free energy. Using $F = G - \mu_0 V \mathbf{H} \cdot \mathbf{M}$ and substituting $\mathbf{H} = \mathbf{M} = 0$ we can see that the difference in Helmholtz free energies $F(T, \mathbf{M})$ is the same as for the Gibbs potentials, and hence

$$F_s(T, 0) - F_n(T, 0) = -\mu_0 V \frac{H_c^2}{2}. \quad (4.13)$$

The quantity $\mu_0 H_c^2/2$ is the **condensation energy**. It is a measure of the gain in free energy per unit volume in the superconducting state compared with the normal state at the same temperature.

As an example let's consider niobium. Here $T_c = 9 \text{ K}$, and $H_c = 160 \text{ kA m}^{-1}$ ($B_c = \mu_0 H_c = 0.2 \text{ T}$). The condensation energy $\mu_0 H_c^2/2 = 16.5 \text{ kJ m}^{-3}$. Given that Nb has a bcc crystal structure with a 0.33 nm lattice constant we can work

out the volume per atom and find that the condensation energy is only around $2 \mu\text{eV}/\text{atom}$! Such tiny energies were a mystery until the BCS theory, which shows that the condensation energy is of order $(k_B T_c)^2 g(E_F)$, where $g(E_F)$ is the density of states at the Fermi level. The energy is so small because $k_B T_c$ is many orders of magnitude smaller than the Fermi energy, ϵ_F .

The similar thermodynamic arguments can also be applied to calculate the condensation energy of type II superconductors. Again the magnetic work per unit volume is calculated as an integral along a contour, as shown in the right panel of Fig. 4.1,

$$G_s(T, H_{c2}) - G_s(T, 0) = \mu_0 V \int_0^{H_{c2}} \mathbf{M} \cdot d\mathbf{H}. \quad (4.14)$$

The integral is simply the area under the curve of M as a function of H drawn in Fig. 3.8 (assuming that $\mathbf{M}$ and $\mathbf{H}$ have the same vector directions). Defining the value of H_c for a type II superconducting from the value of the integral

$$\frac{1}{2} H_c^2 \equiv \int_0^{H_{c2}} \mathbf{M} \cdot d\mathbf{H} \quad (4.15)$$

we again can express the zero field condensation energy in terms of H_c ,

$$F_s(T, 0) - F_n(T, 0) = -\mu_0 V \frac{H_c^2}{2}. \quad (4.16)$$

Here H_c is called the **thermodynamic critical field**. Note that there is no phase transition at H_c in a type II superconductor. The only real transitions are at H_{c1} and H_{c2} , and H_c is merely a convenient measure of the condensation energy.

We can also calculate the entropy of the superconducting state using the same methods. A simple calculation (Exercise 4.1) shows that in a type I superconductor there is a finite change in entropy per unit volume between the normal and superconducting states at H_c ,

$$s_s(T, H_c) - s_n(T, H_c) = -\mu_0 H_c \frac{dH_c}{dT}. \quad (4.17)$$

This shows that the phase transition is generally **first-order**, that is, it has a finite latent heat. But, in zero external field, at the point $(T, H) = (T_c, 0)$ in Fig. 4.1, this entropy difference goes to zero, and so in this case the phase transition is **second-order**.

Appendix 2. Latent heat Calculations

- (4.1) (a) For a type I superconductor $H_c(T)$ is the boundary between normal metal and superconductor in the H, T phase diagram. Everywhere on this boundary thermal equilibrium requires

$$G_s(T, H) = G_n(T, H).$$

Apply this equation and $dG = -SdT - \mu_0 VMdH$ to two points on the $H - T$ phase boundary (T, H) and $(T + \delta T, H + \delta H)$, as illustrated in Fig. 4.12. Hence show that:

$$-S_s\delta T - \mu_0 VM_s\delta H = -S_n\delta T - \mu_0 VM_n\delta H$$

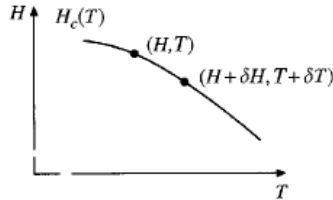


Fig. 4.12 Exercise 4.1. Consider the Gibbs free energy at the points shown on the normal-superconducting phase boundary of a type I superconductor (T, H) and $(T + \delta T, H + \delta H)$. At both points equilibrium requires that both normal and superconducting Gibbs free energies must be equal: $G_n(T, H) = G_s(T, H)$.

when δT and δH are small, and where $S_{s/n}$ $M_{s/n}$ are the superconducting and normal state entropy and magnetization, respectively.

- (b) Using part (a), and $M_n = 0$, and $M_s = -H$ show that the latent heat per unit volume for the phase transition, $L = T(s_n - s_s)$, is given by

$$L = -\mu_0 TH_c \frac{dH_c(T)}{dT}$$

where the phase boundary curve is $H_c(T)$. (This is exactly analogous to the Clausius-Claperyon equation in a gas-liquid phase change except H replaces P and $-\mu_0 M$ replaces V . See Mandl 1987, p. 228.)

- (4.2) Find $|\psi|^2$, the free energy $F_s - F_n$, the entropy and the heat capacity of a superconductor near T_c , using the bulk Ginzburg-Landau free energy. Sketch their variations with temperature assuming that $a = \hat{a} \times (T - T_c)$ and $\hat{a}$ and b are constant near T_c .

- (4.3) (a) Show that for one-dimensional problems, such as the surface discussed in Section 4.5, the Ginzburg-Landau equations for $\psi(x)$ can be rewritten as:

$$-\frac{d^2}{dy^2}f(y) - f(y) + f(y)^3 = 0,$$

where $\psi(x) = \psi_0 f(x/\xi)$, $y = x/\xi$ and $\psi_0 = \sqrt{|a|/b}$.

- (b) Verify that

$$f(y) = \tanh(y/\sqrt{2})$$