5. TERMODINAMICA SC E TEORIA DI GINSBURG-LANDAU

5.1 TERMODINAMICA DELLA TRANSIZIONE SUPERCONDUTTIVA

5.2 TEORIA DI GINSBURG-LANDAU

THERMODYNAMICS OF THE SC PHASE TRANSITION

SC : phase transition at T_c ; $n_B \to 0$ at T_c

In experiments T, p, B are fixed externally

London : no stationary state at $E \neq 0$ so we have $E = 0$.

Helmoltz Free energy

$$F_s(T, V, B) \quad ; \quad F_n(T, V, B)$$

$$\frac{\partial F}{\partial T} = -\underset{\substack{\uparrow \\ \text{entropy}}}{S} \quad ; \quad \frac{\partial F}{\partial V} = -p \quad ; \quad \frac{\partial F}{\partial B} = -V \underset{\substack{\uparrow \\ \text{magnetization density}}}{m}$$

In the bulk of the SC

$$B_{ext} + B_m = B + \mu_0 m = 0$$

(Ideal diamagnetism)
IInd London Eq.

$$\frac{\partial F_s}{\partial B} = + \frac{VB}{\mu_0} \implies F_s(B) = F_s(0) + \frac{VB^2}{2\mu_0}$$

Magnetic susceptibility of a normal (non magnetic) metal

$$|\chi_{m,n}| << 1 = |\chi_{m,s}|$$

therefore

$$F_n(B) \simeq F_n(0)$$

So we have

$$\begin{cases} F_s(T, V, B) = F_s(T, V, 0) + \dfrac{VB^2}{2\mu_0} \\[2ex] p(T, V, B) = p(T, V, 0) - \dfrac{B^2}{2\mu_0} \end{cases}$$

The ~~field~~ pressure a SC exerts on its surroundings reduces in an external field B. The field B implies a force per area

$$F = -n \frac{B^2}{2\mu_0}$$

on the surface of the SC with normal n.

The Free ~~en~~ Enthalpy (Gibbs Free Energy) G

at $B=0$

$$F_S(T,V,0) = G_S(T, p(T,V,0),0) - p(T,V,0)V$$

at $B \neq 0$

$$F_S(T,V,0) + \frac{VB^2}{2\mu_0} = F_S(T,V,B) =$$

$$= G_S(T, p(T,V,B), B) - p(T,V,B)\cdot V =$$

$$= G_S\left(T, \left[p(T,V,0) - \frac{B^2}{2\mu_0}\right], B\right) - p(T,V,0)V + \frac{VB^2}{2\mu_0}$$

which lead to

$$G_S(T, p(T,V,0),0) = G_S\left(T, \left[p(T,V,0) - \frac{B^2}{2\mu_0}\right], B\right)$$

or

$$G_S(T,p,B) = G_S\left(T, \left(p + \frac{B^2}{2\mu_0}\right), 0\right)$$

In agreement with the Free energy argument, the effect of B on G is a reduction of the pressure exerted on the surroundings by $B^2/2\mu_0$.

In the normal state

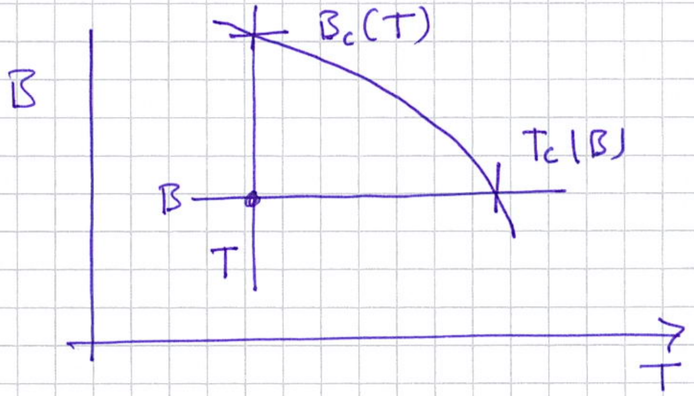
$$G_n(T,p,B) = G_n(T,p,0)$$

The critical temperature $T_c(p,B)$ is then given by

$$G_s\left(T_c,\ p + \frac{B^2}{2\mu_0}, 0\right) = G_n(T_c, p, 0)$$

and the critical field $B_c(T,p)$

$$G_s\left(T,\ p + \frac{B_c^2}{2\mu_0}, 0\right) = G_n(T, p, 0)$$



The thermodynamic critical field

The Free Enthalpy difference between n and s is usually small so that at $T<T_c$ the critical field $B_c(T)$ is also small

$$G_n(T,p) = G_s(T,p) + \frac{B_c^2}{2\mu_0}\frac{\partial G_s}{\partial p} =$$

$$= G_s(T,p) + \frac{B_c^2}{2\mu_0} V(T,p,B=0)$$

Experiments show that at $B=0$ the transition is II$^{\text{nd}}$ order

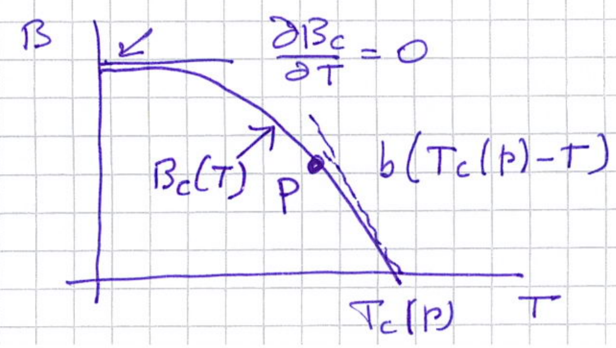
$$G_n(T,p) - G_s(T,p) = a\left(T_c(p) - T\right)^2$$

Hence

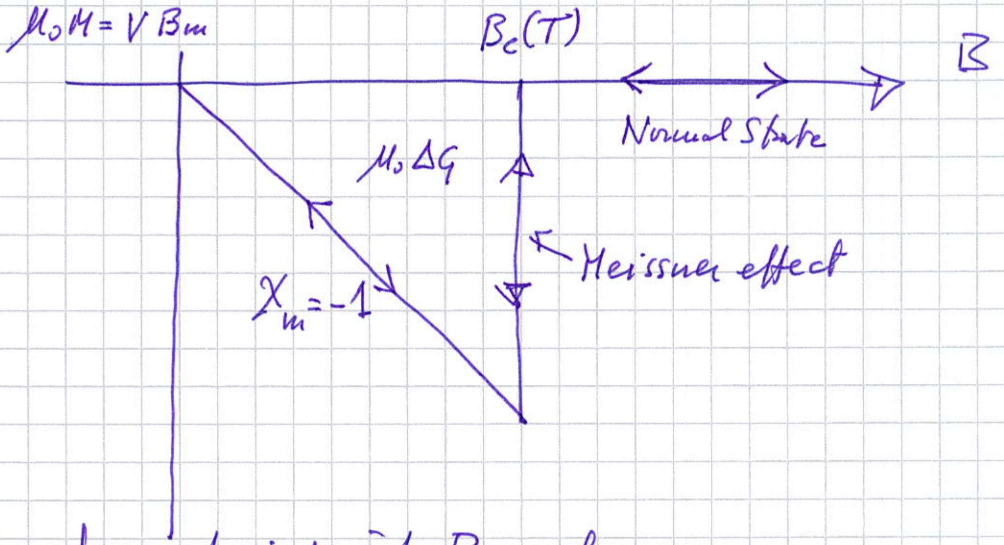
$$B_c(T,p) = b\left(T_c(p) - T\right)$$

where a is a constant and $b = \sqrt{2\mu_0 a / V}$

NB: $T_c(p)$ is meant at $B = 0$



Magnetization curve of a superconductor



At a transition point P we have

$$S_s(T,p,B) = -\frac{\partial G_s}{\partial T} = S_s\left(T,\left(p+\frac{B^2}{2\mu_0}\right);0\right)$$

$$V_s(T,p,B) = \frac{\partial G_s}{\partial p} = V_s\left(T,\left(p+\frac{B^2}{2\mu_0}\right);0\right)$$

Differentiating with respect to T

$$\frac{\partial}{\partial T} G_s\left(T,\left(p+\frac{B_c^2(T,p)}{2\mu_0}\right),B_c\right) = \frac{\partial}{\partial T} G_n(T,p,0 \text{ or } B_c)$$

$$-S_s(T,p,B_c) + \frac{V_s(T,p,B_c)}{2\mu_0}\frac{\partial}{\partial T} B_0^2(T,p) = -S_n(T,p,B_c)$$

$$\Delta S(T,p,B_c) = S_s(T,p,B_c) - S_n(T,p,B_c) =$$

$$= \frac{V_s(T,p,B_c)}{\mu_0} B_c(T,p) \frac{\partial B_c(T,p)}{\partial T}$$

but considering that $B_c(T,p) = b(T_c(p)-T)$

this difference is non-zero for $B_c \neq 0$ $(T < T_c(p))$.

For $B \neq 0$ this transition is first order with latent heat

$$Q = T\Delta S(T,p,B_c)$$

Heat Capacity Jump

For $B \simeq 0$, $T \simeq T_c(p)$ and using the Free Enthalpy expression to which we apply $-T\frac{\partial^2}{\partial T^2}$

$$\Delta C_p = C_{p,s} - C_{p,n} = -T\frac{\partial^2}{\partial T^2}\left(G_s(T,p) - G_n(T,p)\right) =$$

$$= \frac{TV(T,p)}{2\mu_0}\frac{\partial^2}{\partial T^2}B_c^2(T,p)$$

The thermal expansion $\partial V/\partial T$ gives a small contribution which can be neglected. Using

$$\frac{\partial^2}{\partial T^2}B_c^2 = \frac{\partial}{\partial T}2B_c\frac{\partial B_c}{\partial T} = 2\left(\frac{\partial B_c}{\partial T}\right)^2 + 2B_c\frac{\partial^2 B_c}{\partial T^2}$$

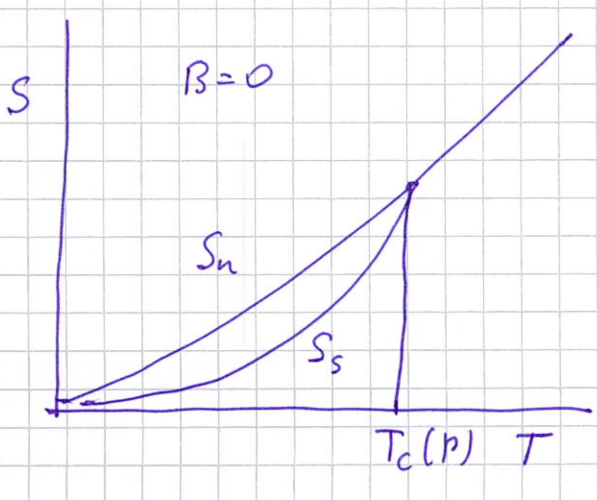
we obtain:

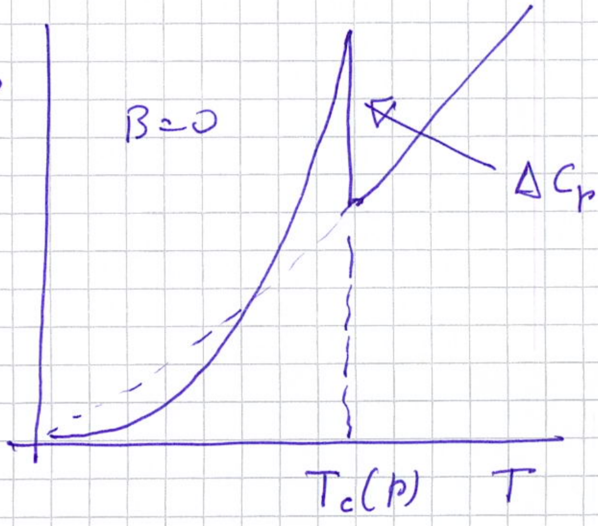
$$\Delta C_p = \frac{TV}{\mu_0}\left[\left(\frac{\partial B_c}{\partial T}\right)^2 + B_c\frac{\partial^2 B_c}{\partial T^2}\right]$$

For $T \to T_c(p)$; $B_c \to 0$ the jump in the specif. heat is

$$\boxed{\Delta C_p = \frac{T_c V}{\mu_0}\left(\frac{\partial B_c}{\partial T}\right)^2 = \frac{T_c V}{\mu_0}b^2}$$

It is given by the slope of $B_c(T)$ at $T_c(p)$





THE GINSBURG-LANDAU THEORY

The basic idea is to make a phenomenological theory of phase transitions in the vicinity of the transition point.

A key concept is the introduction of the order parameter, a quantity which is $\neq 0$ in the low symmetry state.

In our case this could be Δ or the SC density written as

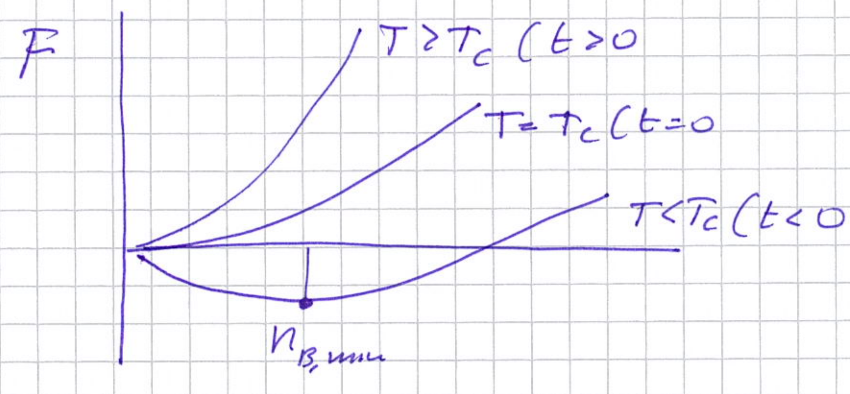
$$n_B = |\Psi|^2$$

For $n_B > 0$ the electrochemical potential ϕ has a certain value which breaks the global gauge invariance by fixing the time derivative of the phase θ of Ψ

<u>NB:</u> This L-G approach is very general (phenomenological) and has been applied to a variety of phase transitions

The Free Energy is the <u>minimum</u> of the Free Energy Functional

$$F(T,V) = \min_{\Psi} \mathbb{F}(T,V,|\Psi|^2)$$



Close to the transition, for

$$t = \frac{T - T_c}{T_c} \qquad |t| << 1$$

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the order parameter is small and $\mathcal{F}$ can be expanded

$$\mathcal{F}(t|\Psi|^2) \simeq \mathcal{F}_n(t) + A(t)|\Psi|^2 + \frac{1}{2}B(t)|\Psi|^4 + \dots$$

NB: Odd terms would lead to Ist order transitions

From the Figure we see that

$$A(t) \gtreqless 0 \quad \text{for} \quad t \gtrless 0 \qquad B(t) > 0$$

Since $|t| \ll 1$ we put

$$A(t) \simeq \alpha t V \qquad ; \quad B(t) \simeq \beta V$$

Then we have

$$F_n(t) = \mathcal{F}_n(t) \quad \text{for } t \geq 0$$

and

$$\frac{1}{V}\frac{\partial \mathcal{F}}{\partial |\Psi|^2} = \alpha t + \beta |\Psi|^2 = 0$$

$$|\Psi|^2 = -\frac{\alpha t}{\beta} \qquad F_s(t) = F_n(t) - \frac{\alpha^2 t^2}{2\beta} V \quad \text{for } t < 0$$

Small changes in free energy and free enthalpy are equal

[see before] $\longrightarrow$ $$\underset{V}{\Delta} C_p = \frac{T_c V}{\mu_0}\left(\frac{\partial B_c}{T_c \partial t}\right)^2 = \frac{V}{T_c}\frac{\alpha^2}{\beta}$$ (critical field)

While ΔC_p can be measured, this is not so obvious for B_c

We can rewrite

$$n_B(t) = \frac{\alpha}{\beta}|t| \quad ; \quad B_c^2(t) = \frac{\alpha^2 t^2 \mu_0}{\beta}$$

and

$$\beta = \frac{B_c^2(t)}{\mu_0 n_B^2(t)} \quad ; \quad \alpha = \frac{B_c^2(t)}{\mu_0 |t| n_B(t)}$$

In addition to previous page

For small changes $\Delta F \sim \Delta G$ therefore

$$\Delta F = \frac{\alpha^2 t^2}{2\beta} V \approx \Delta G \text{ (previous section)} = \frac{B_c^2}{2\mu_0} V$$

therefore

$$\frac{\alpha^2 t^2}{2\beta} = \frac{B_c^2}{2\mu_0}$$

and

$$B_c(t) = \alpha |t| \sqrt{\frac{\mu_0}{\beta}}$$

$$\frac{\partial B_c(t)}{\partial t} = \frac{\alpha^2 \mu_0}{\beta}$$

$$\Delta C_p = \frac{T_c V}{\mu_0} \left(\frac{\partial B_c}{T_c \partial t} \right)^2 = \frac{V}{T_c} \frac{\alpha^2}{\beta}$$

We can also rewrite

$$n_B(t) = \frac{\alpha}{\beta} |t| \quad ; \quad B_c^2(t) = \frac{\alpha^2 t^2 \mu_0}{\beta}$$

and

$$\beta = \frac{B_c^2(t)}{\mu_0 n_B^2(t)} \quad ; \quad \alpha = \frac{B_c^2(t)}{\mu_0 |t| n_B(t)}$$

Since

$$B_c(T, p) = b\,(T_c(p) - T) \sim t$$

it follows

$$\boxed{n_B \sim t}$$

Bosonic density goes to zero ~~at~~ as $T_c - T$

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Since $B_c \sim t$ then it follows

$$n_B \sim t \propto (T_c - T)$$

G-L Equations

We want to include B in the Free Energy function
- B causes supercurrents $J_s \sim \frac{\partial \Psi}{\partial r}$ and these create an internal field B_{in}, then the energy contribution of Ψ must be related to the Schrödinger eq.

$$\frac{1}{2m_B}\left(\frac{\hbar}{i}\frac{\partial}{\partial r} - qA\right)^2 \Psi + qU\Psi = (E - \mu_B)\Psi$$

$\phi = \mu_B + qU$ is the electrochemical potential

μ_B: chem pot.

$$\begin{cases} q = -2e \\ m_B = 2m_e \end{cases}$$

~~In a homogeneous SC~~

$$F(t, B, \Psi) = F_n(t) +$$

$$+ \int_0^\infty d^3r \frac{B_{in}^2}{2\mu_0} + \int_V d^3r \left\{ \frac{\hbar^2}{4m}\left|\left(\frac{\partial}{\partial r} + \frac{2ie}{\hbar}A\right)\Psi\right|^2 + \alpha t|\Psi|^2 + \frac{\beta}{2}|\Psi|^4 \right\}$$

Field energy of the field B_{in} created by Ψ including the field outside V where $|\Psi| = 0$

$$\frac{\partial}{\partial r} \times A = B + B_{in}$$

The Free Energy is obtained by minimizing F with respect to $\Psi(r)$ and $\Psi^*(r)$. It is convenient to rewrite (by parts)

$$\int_V dr^3 \left[\left(\frac{\partial}{\partial r} + \frac{2ie}{\hbar}A\right)\Psi\right]\left[\left(\frac{\partial}{\partial r} - \frac{2ie}{\hbar}\right)\Psi^*\right] =$$

$$= -\int_V d^3r\, \Psi^*\left(\frac{\partial}{\partial r} + \frac{2ie}{\hbar}A\right)^2 \Psi + \int_{\delta V} d^2n\, \Psi^*\left(\frac{\partial}{\partial r} + \frac{2ie}{\hbar}A\right)\Psi$$

$$\int_V d^3r \left|\left(\frac{\partial}{\partial r} + \frac{2ie}{\hbar}A\right)\psi\right|^2 =$$

$$= \int_V d^3r \left[\left(\frac{\partial}{\partial r} - \frac{2ie}{\hbar}A\right)\psi^*\right]\left[\frac{\partial}{\partial r} + \frac{2ie}{\hbar}A\right]\psi\Big] =$$

$$= \int_V d^3r \left\{ \frac{\partial}{\partial r}\psi^*\left[\frac{\partial}{\partial r} + \frac{2ie}{\hbar}A\right]\psi - \frac{2ie}{\hbar}\overbrace{A}^{\psi^*}\left(\frac{\partial}{\partial r} + \frac{2ie}{\hbar}A\right)\psi = \right.$$

$$\left[\int_V u\,dv = [uv]_\sigma - \int_V v\,du \right]$$

$$= \int_S d^2n\, \psi^*\left(\frac{\partial}{\partial r} + \frac{2ie}{\hbar}A\right)\psi -$$

$$- \int_V d^3r\, \cancel{\frac{\partial}{\partial r}}\psi^* \frac{\partial}{\partial r}\left(\frac{\partial}{\partial r} + \frac{2ie}{\hbar}A\right)\psi + \frac{2ie}{\hbar}\overbrace{A}^{\psi^*}\left(\frac{\partial}{\partial r} + \frac{2ie}{\hbar}A\right)\psi =$$

$$= \int_S (\cdots) - \int_V d^3r\, \psi^*\left(\frac{\partial}{\partial r} + \frac{2ie}{\hbar}A\right)^2\psi$$

Performing now the variation

$$\psi^* \to \psi^* + \delta\psi^*$$

$$0 = \delta F = \int_V d^3r\, \delta\psi^* \left\{ -\frac{\hbar^2}{4m}\left(\frac{\partial}{\partial r} + \frac{2ie}{\hbar}A\right)^2 + \alpha t + \beta|\psi|^2 \right\}\psi +$$

$$+ \int_S d^2n\, \delta\psi^* \frac{\hbar^2}{4m}\left(\frac{\partial}{\partial r} + \frac{2ie}{\hbar}A\right)\psi$$

Integral of the surface currents which is zero if the SC is not connected but anyhow it is a small surface term.

$\mathcal{F}$ is stationary for variations of $\delta\Psi^*$ if

$$\boxed{\frac{1}{4m}\left(\frac{\hbar}{i}\frac{\partial}{\partial r}+2eA\right)^2\Psi-\alpha|t|\Psi+\beta|\Psi|^2\Psi=0}$$

and
$$n\left(\frac{\hbar}{i}\frac{\partial}{\partial r}+2eA\right)\Psi=0$$

The connection of Ψ with B_m must be that of Ampere's law

$$\left(\frac{\partial}{\partial r}\right)\times B_m=\mu_0 j_s$$
↖ supercurrent density

Since in thermodynamic equilibrium there are no supercurrents then $\left(\frac{\partial}{\partial r}\right)\times B=0$. So we have

$$\frac{\partial}{\partial r}\times B_{tot}=\mu_0 j_s \qquad B_{tot}=B+B_m=\frac{\partial}{\partial r}\times A$$

$$j_s=\frac{ie\hbar}{2m}\left(\Psi^*\frac{\partial}{\partial r}\Psi-\Psi\frac{\partial}{\partial r}\Psi^*\right)-\frac{2e^2}{m}\Psi^*A\Psi$$

The G-L. functional can be considered as an effective Hamiltonian for the fluctuations of the fields Ψ and A near the phase transition

From the surface equation one can conclude that

$$n.\,j_s=0$$

there is no supercurrent passing through the surface of a superconductor into the non SC volume.

The G–L parameter

Taking the curl of ~~the~~ the eq. for B leads to (as before)

$$\frac{\partial^2 B_{tot}}{\partial r^2} = \frac{B_{tot}}{\lambda^2} \qquad \lambda^2 = \frac{m}{2\mu_0 e^2 |\Psi|^2} = \frac{m\beta}{2\mu_0 e^2 \alpha |t|}$$

λ is the Ginzburg Landau penetration depth, near T_c it diverges like $\lambda \sim |t|^{-1}$. If T_c is approached from below, the external field penetrates more and more and at T_c the diamagnetism vanishes.

There is also a second length parameter.

For $A=0$ and for small Ψ, $|\Psi|^2 \ll \alpha |t| / \beta$ and one gets

$$\frac{\partial^2 \Psi}{\partial r^2} = \frac{\Psi}{\xi^2} \quad ; \quad \xi^2 = \frac{\hbar^2}{4m\alpha|t|}$$

This is the Ginzburg–Landau coherence length ξ which describes the modulations of the order parameter near T_c.
It has the same T dependence as λ and

$$\kappa = \frac{\lambda}{\xi} = \sqrt{\frac{2m^2\beta}{\hbar^2 \mu_0 e^2}} \qquad \text{Ginzburg-Landau parameter}$$

Dimensionless parameters

$x = r/\lambda \qquad \Psi = \Psi / \sqrt{\frac{\alpha|t|}{\beta}}$

$b = B_{tot} / \sqrt{2}\, B_c(t) = B_{tot} / \left(\alpha |t| \sqrt{\frac{2\mu_0}{\beta}}\right)$

$i_s = j_s \left(\lambda \mu_0 / \sqrt{2}\, B_c(t)\right)$

$a = A / \left(\sqrt{2}\, \lambda B_c(t)\right)$

Dimensionless Ginzburg Landau equations

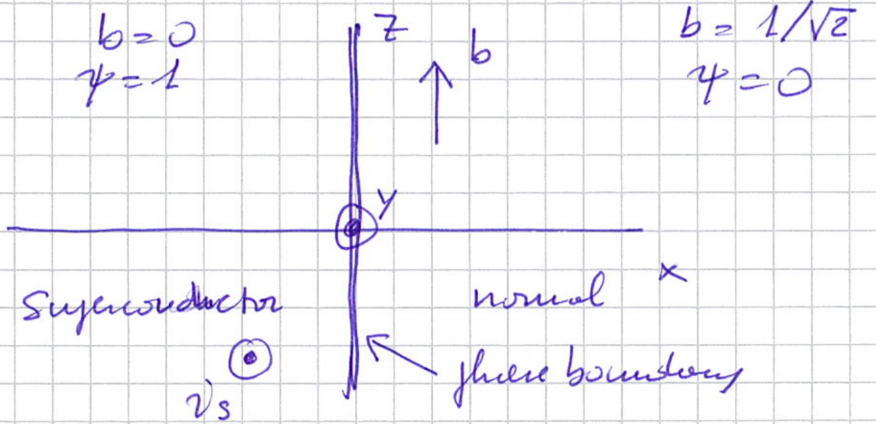
$$\begin{cases} \left(\frac{1}{i\kappa}\frac{\partial}{\partial x}+a\right)^2\psi-\psi+|\psi|^2\psi=0 \\ \frac{\partial}{\partial x}\times b = i_s \qquad i_s=\frac{i}{2\kappa}\left(\psi^*\frac{\partial}{\partial x}\psi-\psi\frac{\partial}{\partial x}\psi^*\right)-\psi^* a\psi \end{cases}$$

which depend only on the parameter κ.

The phase boundary

Consider a homogeneous SC at $T \lesssim T_c$ in a homogeneous external field $B \simeq B_c(T)$ in z-direction.

Phase boundary in the y-z plane



$$\psi=\psi(x) \qquad b_z=b(x) \qquad b_x=b_y=0$$

$$a_y=a(x) \qquad a_x=a_z=0 \qquad b(x)=a'(x)$$

The supercurrent flows in the y direction and the phase ψ depends on y. Consider $y=0$ and take ψ as real.
As a gauge constant we may fix $a(-\infty)=0$.
Then the G-L eqs reduce to

$$-\frac{1}{\kappa^2}\psi''+a^2\psi-\psi+\psi^3=0 \qquad a''=a\psi^2$$

Consider $\kappa \ll 1$. For large negative x we have $a \simeq 0$ and $\psi \simeq 1$. We put $\psi = 1 - \varepsilon(x)$

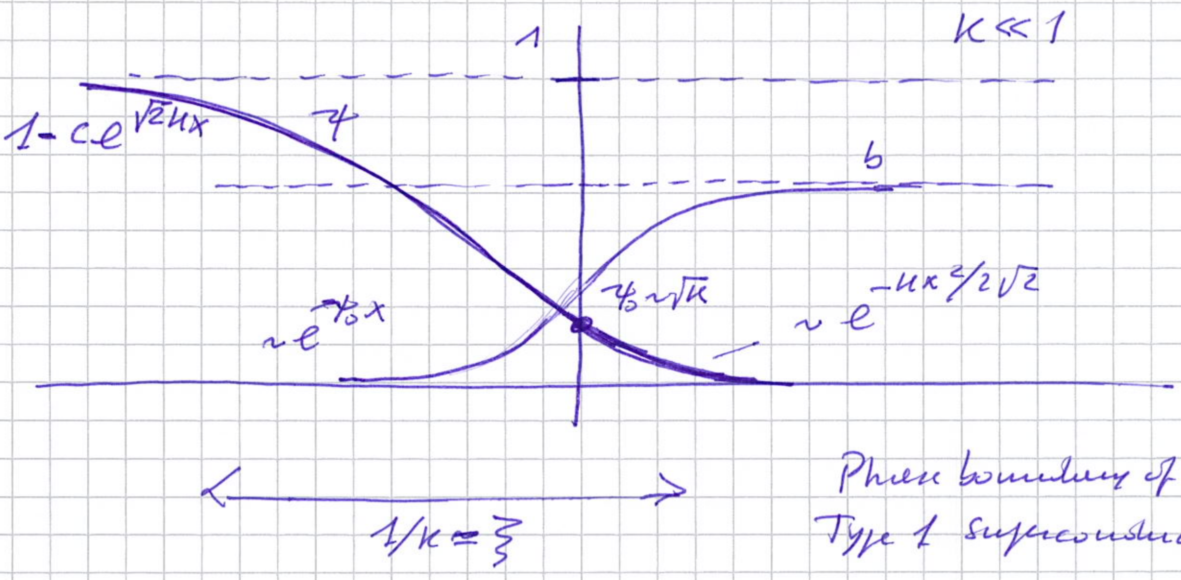
$$\varepsilon'' \simeq \kappa^2(1-\varepsilon-1+3\varepsilon) = 2\kappa^2\varepsilon$$

$$\varepsilon \sim e^{\sqrt{2}\kappa x} \quad ; \quad x \lesssim \kappa^{-1}$$

For large positive x we have $b = 1/\sqrt{2}$, $a = x/\sqrt{2}$, $\psi \ll 1$

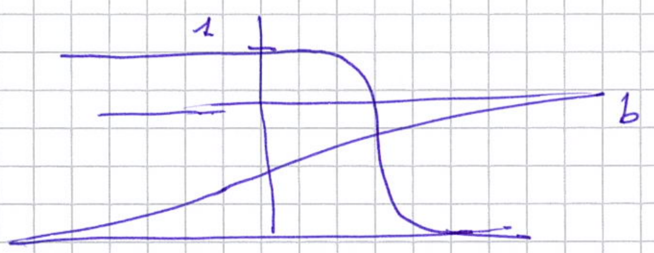
$$\psi'' \simeq \frac{\kappa^2 x^2}{2}\psi \quad , \quad \psi \sim e^{-\kappa x^2/2\sqrt{2}} \quad , \quad \kappa x^2 \gg 1$$

this leads to a penetration depth $\sim \psi_0^{-1}$ where ψ_0 is the field where the field drops



Phase boundary of a Type 1 superconductor

In the opposite case $\kappa \gg 1$ ψ falls off ~~fast~~ for $x \gtrsim 1$ where $b = \frac{1}{\sqrt{2}}$, $a \simeq x/\sqrt{2}$ and for $x \gg 1$ $\psi'' \simeq \kappa^2 x^2 \psi/2$



Type 2 superconductor

$\rightarrow$ Applications