Approximation du champ central

$$\mathcal{H} = \underbrace{\sum_i \left[-\frac{\hbar^2}{2m}\nabla_i^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_i} + S(r_i) \right]}_{\mathcal{H}_{CF}}$$

$$\underbrace{+ \sum_{i<j} \frac{e^2}{4\pi\varepsilon_0 r_{ij}} - \sum_i S(r_i)}_{\mathcal{H}_I}$$

$\mathcal{H}_I \to 0$

$$\mathcal{H}_{CF}\, \psi_{nlm}(r,\theta,\phi) = E_{nl}\, \psi_{nlm}(r,\theta,\phi)$$

$n = n_r + l + 1 \qquad 0 \le l \le n-1$

$n_r = \#$ de zéros de $\underline{R_{nl}}$.

"Aufbau" atomique

pour le remplissage des orbitales

1s	2s	3s	4s	5s	6s
	2p	3p	4p	5p	6p
		3d	4d	5d	6d
			4f	5f	6f

états dégénérés : configurations électroniques

nl^{ν}

Li : $1s^2\ 2s^1$

Be : $1s^2 \quad 2s^2$

B = $1s^2 \quad 2s^2 \quad 2p^1$ ....

Dégénérescence

$\underbrace{\boxed{\uparrow}\boxed{\downarrow}\boxed{\ }\boxed{\ }\boxed{\ }}_{2l+1}$

$$g = \frac{[2(2l+1)]!}{\nu!\,[2(2l+1)-\nu]!} = \binom{2(2l+1)}{\nu}$$

Atomes alcalins

[gaz rare] ns^1 Spectre hydrogénoïde

$$E_{nl} = -\frac{Ry}{(n-\delta_{nl})^2}$$

$$\delta_{nl} \simeq \delta_l \xrightarrow[l\to\infty]{} 0$$

Comment construire les orbitales effectives (qui tiennent compte de l'écrantage) : Hartree-Fock

Déterminant de Slater à partir de N orbitales

$$\{\varphi_i(\vec{r}_j)\,\chi_i(\sigma_j)\} = A_{ij}$$

$$\psi(r_1\sigma_1, r_2\sigma_2, \dots, r_N\sigma_N) = \det(A)$$

$$= \begin{vmatrix} \psi_1(r_1)\chi_1(\sigma_1) & \psi_1(r_2)\chi_1(\sigma_2) & \dots & \psi_1(r_N)\chi_1(\sigma_N) \\ \vdots & & & \\ \psi_N(r_1)\chi_N(\sigma_1) & - & - & (\dots) \end{vmatrix}$$

Calcul auto cohérent des ~~fonct.~~ orbitales

<u>Fonctionnelle de HF</u>

$$E_{HF}[\psi_1\chi_1 \dots \psi_N\chi_N] =$$

$$\sum_{\sigma_1 \dots \sigma_N} \int d^3r_1 \dots \int d^3r_N \; \Psi^*(r_1\sigma_1, \dots, r_N\sigma_N)\, \mathcal{H}\, \Psi(r_1\sigma_1 \dots r_N\sigma_N)$$

$$- \lambda \sum_i \int d^3r \, |\psi_i(\vec{r})|^2$$

$$\frac{\delta E_{HF}}{\delta \psi_i^*} = 0$$

$$\frac{\delta}{\delta\psi^*(\vec{r})} \int d^3r' \, \psi^*(\vec{r}')\, O(\vec{r}')\, \psi(\vec{r}')$$

$$= O(\vec{r})\, \psi(\vec{r})$$

ex. deux particules

$$\Psi = \frac{1}{\sqrt{2}} \Big[\psi_a(r_1)\, \psi_b(r_2)\, \chi_a(\sigma_1)\, \chi_b(\sigma_2)$$

$$- \psi_b(r_1)\, \psi_a(r_2)\, \chi_b(\sigma_1)\, \chi_a(\sigma_2) \Big]$$

$$\left(-\frac{\hbar^2}{2m} \nabla_1^2 + \frac{Ze^2}{4\pi\epsilon_0 r_1} + \int d^3r_2 \frac{e^2}{4\pi\epsilon_0 r_{12}} |\psi_b(r_2)|^2 \right) \psi_a(r_1)$$

$$- \delta_{\chi_a \chi_b} \left(\int d^3r_2 \frac{e^2}{4\pi\epsilon_0} \frac{\psi_b^*(r_2)\, \psi_a(r_2)}{r_{12}} \right) \psi_b(r_1)$$

$$= \lambda_a \psi_a(r)$$

$$(a \leftrightarrow b)$$

Au delà de l'approximation de champ central

$$H_I = \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_i \delta(r_i)$$

perturbation

États dégénérés de la configuration électronique

$$|\{n_i l_i m_i\, m_{s_i}\}_i \; \{n\, l\, m_i, m_{s_i}\} \rangle$$

couches internes — couche externe

Matrice des perturbations

$$\langle \{n_j \ell_j m_j \ m_{s_j}\}_i \ \{n \ell m_i' \ m_{s_i}'\} | \underbrace{H_I} | \{n_j \ell_j m_j \ m_{s_j}\}, \{n \ell m_i' m_{s_i}'\} \rangle$$

$$[H_I, \vec{L}^2) = [H_I, L^z] = 0$$

$$\vec{L} = \sum_i \vec{l}_i$$

$$[\quad S^z] = [\quad S^z] = 0$$

$$|\gamma, LM, SM_S\rangle \qquad \gamma = \{n_i \ell_i\}$$

configuration électronique

H_I peut être diagonalisé sur la base de $\vec{L}^2, \vec{S}^2, L^z, S^z$

Schéma de "couplage LS" ou "Russell-Saunders"

Valeurs possibles de L, S reconstruites de façon constructive :

$$M = \sum_i m_i \qquad M_S = \sum_i m_{s_i}$$

$$= \sum_{i \in \text{couche externe}}' m_i \qquad M_S = \sum_i' m_{s_i}$$

L, S prennent contribution seulement des électrons sur la couche externe ...

Valeurs <u>LS possibles</u> : Termes spectroscopiques LS –

Ex. C : $1s^2\, 2s^2\, 2p^2$

$$\frac{6!}{2!\,4!} = \frac{6\times 5}{2} = 15$$

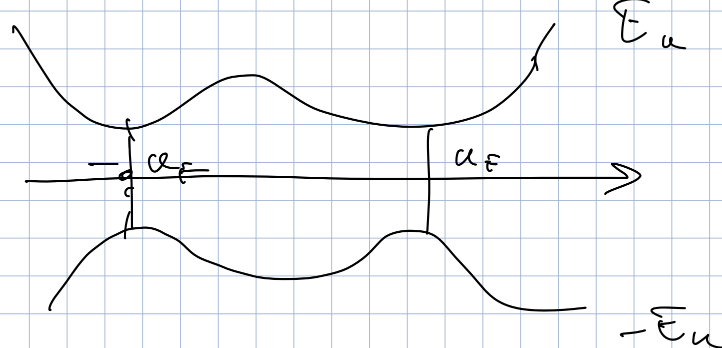
BCS theory of superconductivity

BCS free energy

$$F = \langle \mathcal{H} - \mu N \rangle - TS$$

$$= V \frac{|\Delta|^2}{V_0} - 2 k_B T \sum_{k} \log\left[2\cosh\left(\frac{\beta E_k}{2}\right)\right]$$

$$E_k = \sqrt{|\Delta_k|^2 + \xi_k^2}$$



$$= F(|\Delta|) \quad \text{even function}$$

$$= \text{const} + \frac{1}{2} A |\Delta|^2 + \frac{1}{4} B |\Delta|^4 + \cdots$$

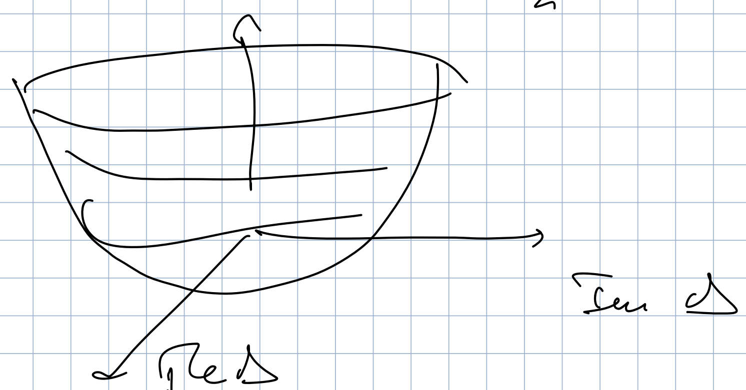
$$0 = \frac{\partial F}{\partial |\Delta|} = A|\Delta| + B|\Delta|^3 + \ldots$$

$$|\Delta| = \sqrt{-\frac{A}{B}} \sim |T_c - T|^{1/2}$$

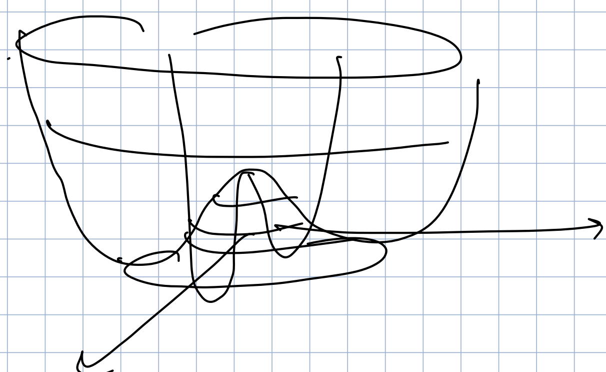
$$A = a(T - T_c)$$

$$F(|\Delta|) = \text{const.} + \frac{1}{2} a (T - T_c) |\Delta|^2 + \frac{b}{4} |\Delta|^4 + \ldots$$

$T > T_c$

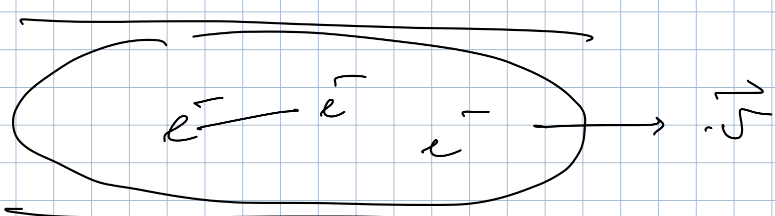


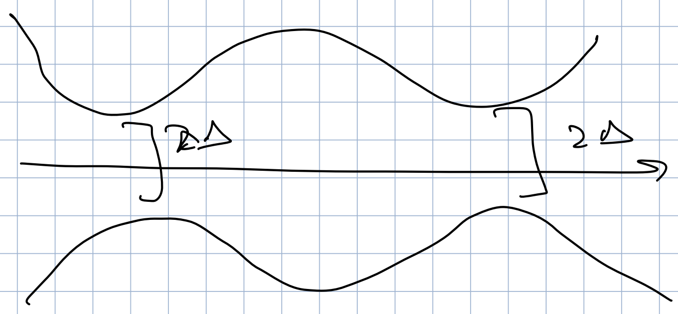
$T < T_c$



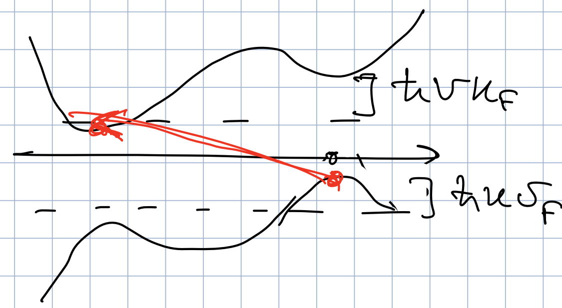
$T < T_c$

From gap to superconductivity





fluid frame



lab frame

$$E_k \to E_k + \hbar \vec{k}\cdot\vec{v}$$

If $\underline{\hbar k_F v > \Delta}$ $\quad v > \frac{\Delta}{\hbar k_F} = v_c$

<u>depairing velocity</u>

pairs can break as quasi-particles are scattered

$$\gamma^{\dagger}_{k_F+}\, \gamma_{k_F-} \,|\Psi_0\rangle$$

Below this velocity, nothing can scatter quasi-particles => <u>The whole electron gas is superconducting</u>.

@ $T=0$

$j_c = -e n v_c$ critical current

$j_c = -e\, n_s(T)\, v_c(T)$ $\quad \hookrightarrow \quad \Delta = \Delta(T)$

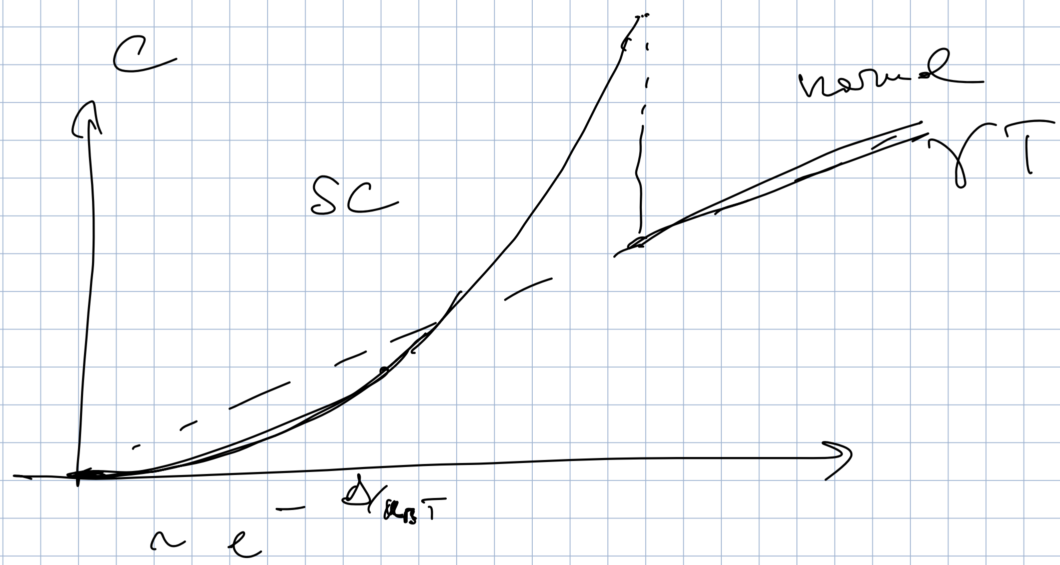
number of "superfluid" charge carriers decreases, pairs break thermally.

Specific Heat:

$$S = -k_B \sum_{\vec k} \Big[n^{(+)}_{\vec k} \log n^{(+)}_{\vec k} + \big(1-n^{(+)}_{k}\big)\log\big(1-n^{(+)}_{k}\big) + (+ \to -) \Big]$$

$$c = T\frac{\partial S}{\partial T} = -\beta \frac{\partial S}{\partial \beta}$$

discontinuity because of dropping gap



From the SC gap to the macroscopic wavefunction

$$\langle \psi_\downarrow(\vec r)\, \psi_\uparrow(\vec r\,')\rangle = \sqrt{n_0}\,\chi_0(\vec r\downarrow, \vec r\,'\uparrow)$$

(from the $G^{(2)}$ function)

$\vec r\,' = \vec r$

$$\langle \psi_\downarrow(\vec r)\, \psi_\uparrow(\vec r)\rangle = \frac{1}{V}\sum_{\vec k \vec k'} \langle c_{\vec k\downarrow}\, c_{k'\uparrow}\rangle\, e^{i(\vec k+\vec k')\cdot\vec r}$$

$$= \frac{1}{V}\sum_{\vec k}{}' \underbrace{\langle c_{-\vec k\downarrow}\, c_{+\vec k\uparrow}\rangle} = \frac{\Delta}{V_0}$$

$$\Delta = \frac{V_0}{V} \sum_{\vec{k}}' \langle c_{-\vec{k}\downarrow} \, c_{\vec{k}\uparrow} \rangle$$

$$\langle \psi_\downarrow(\vec{r}) \, \psi_\uparrow(\vec{r}') \rangle = \Phi_0\left(\vec{R} = \frac{\vec{r}+\vec{r}'}{2}, \; \vec{r}-\vec{r}'\right)$$

$$\Phi_0(\vec{R} = \vec{r}, 0) = \frac{\Delta}{V_0}$$

$$= \Psi_0(\vec{R}) \, \varphi_0(\vec{\rho})$$

separation of variables

$$\lambda_0 = \int d^3R \, d^3\rho \; |\Psi_0|^2 \, |\varphi_0(\vec{\rho})|^2$$

$$= \int d^3R \, |\Psi_0|^2$$

$$\Psi_0(\vec{R}) \sim \frac{\Delta}{V_0}$$ macroscopic wavefunction

Inhomogeneous superconductors (over $l \gg \xi = \frac{\hbar v_F}{\Delta}$)

$$\Psi_0(\vec{R}) \approx \frac{\Delta}{V_0} e^{i\vec{k}\cdot\vec{R}}$$ finite mom. pairs

$$E_{kin} = \lambda_0 \frac{\hbar^2 k^2}{2m} = \int d^3R \, \Psi_0^* \left(-\frac{\hbar^2 \nabla^2}{2m^*}\right) \Psi_0(\vec{R})$$

by parts

$$= \int d^3R \, \frac{\hbar^2}{2m^*} \left| \vec{\nabla} \Psi_0 \right|^2$$

Effective free energy of a moving condensate of Cooper pairs:

$$F = \text{const} + \frac{1}{2}\tilde{a}(T-T_c)\int d^3R\, |\Psi_0(R)|^2 + \frac{\tilde{b}}{4}\int d^3R\, |\Psi_0(\vec{R})|^4 + \int d^3R\, \frac{\hbar^2}{2m}|\nabla\Psi_0|^2 A \ldots$$

Adding a vector potential

$$-i\hbar\vec{\nabla} \to -i\hbar\vec{\nabla} + 2e\vec{A} = -i\hbar\left(\vec{\nabla} + i\frac{2e}{\hbar}\vec{A}\right)$$

GL functional

$$F[\Psi_0, \Psi_0^*]$$

$$= \text{const.} + \int d^3r \Big[\frac{\hbar^2}{2m^*}\left|\left(\vec{\nabla} + i\frac{2e}{\hbar}\vec{A}\right)\Psi_0\right|^2 + \left(\frac{1}{2}\tilde{a}(T-T_c) - 2eV(\vec{r})\right)|\Psi_0|^2 + \frac{\tilde{b}}{4}|\Psi_0|^4 + \ldots \Big]$$

Useful phenomenological theory to study inhomogeneities and electrodynamics

$$F = F[\Psi_0, \Psi_0^*; \vec{A}] = F + \int d^3r \frac{(\vec{\nabla}\times\vec{A})^2}{2\mu_0}$$

$$\frac{\delta F}{\delta \Psi_0^*} \Rightarrow = -\frac{\hbar^2}{2m^*}\left(\vec{\nabla} + i\frac{2e}{\hbar}\vec{A}\right)^2\Psi_0 + \frac{1}{2}\tilde{a}(T-T_c)\Psi_0$$

$$+\frac{b}{2}\,|\Psi_0|^2\Psi_0 + \dots$$

1st GL equation

$$\vec\nabla\times\vec B = \mu_0\,\vec J$$

$$\frac{\delta F}{\delta\vec A} = 0 = \vec J + \frac{\delta}{\delta\vec A}F_0$$

$$\vec J = -2e\left[\frac{\hbar}{2m^* i}\left(\Psi_0^*\vec\nabla\Psi_0 - \Psi_0\vec\nabla\Psi_0^*\right) + \frac{2e}{m^*}|\Psi_0|^2\vec A\right]$$

$$\Psi_0(\vec r) = |\Psi_0|\,e^{i\phi_0} \qquad \vec v_s = \frac{\hbar}{m^*}\vec\nabla\phi$$

$$\vec J = -2e\,|\Psi_0|^2\left[\vec v_s + \frac{2e}{m^*}\vec A\right]$$

$$\vec\nabla\times\vec v_s = 0 \qquad |\Psi_0|^2 \text{ uniform}$$

$$\vec\nabla\times\vec J = -\frac{(2e)^2}{m^*}|\Psi_0|^2\,\vec B \qquad \text{London equation}$$

Meissner effect (1933)

SC

$$\vec B_0 = \mu_0\vec H$$

$\vec{\nabla}\times\vec{j}$

$\mu_0\vec{j} = \vec{\nabla}\times\vec{B}$

$n_s = |\Psi_0|^2$

Cooper pair density

$$= \frac{\vec{\nabla}\times(\vec{\nabla}\times\vec{B})}{\mu_0} = \frac{1}{\mu_0}\left(\vec{\nabla}\left(\cancelto{0}{\vec{\nabla}\cdot\vec{B}}\right) - \nabla^2\vec{B}\right) = -\frac{(2e)^2 n_s}{m^*}\vec{B}$$

$$\nabla^2\vec{B} = \frac{1}{\lambda_L^2}\vec{B}$$

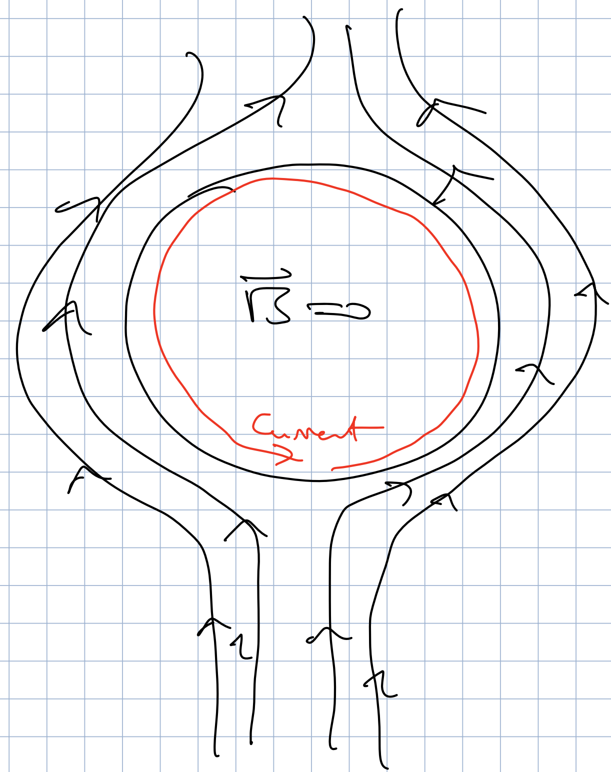
$$\lambda_L = \sqrt{\frac{m}{2\mu_0 n_s e^2}}$$

London penetration depth

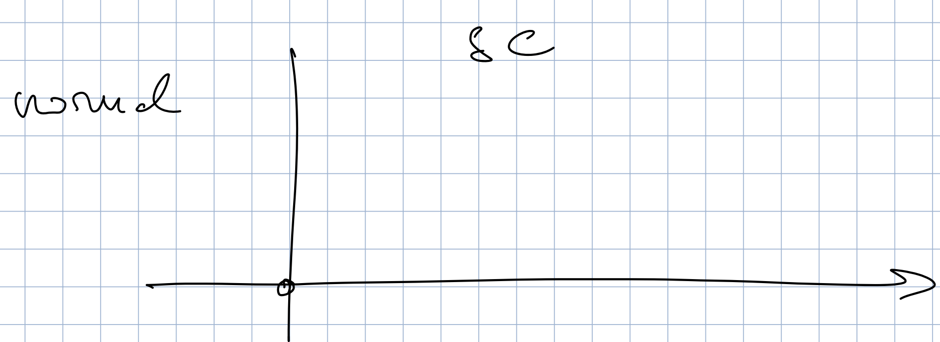
$$\frac{d^2\vec{B}}{dx^2} = \frac{1}{\lambda_L^2}\vec{B}$$

$$\vec{B} = B_0 e^{-x/\lambda_L}$$

Perfect diamagnetism



GL coherence length



$$\varepsilon(T-T_c) = a(T)$$

$$-\frac{\hbar^2}{2m}\nabla^2\Psi_0 + \frac{a}{2}\Psi_0 + \frac{b}{2}|\Psi_0|^2\Psi_0 = 0$$

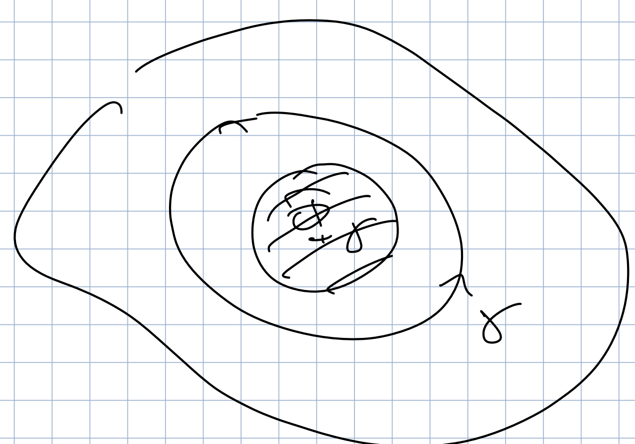
$$\Psi_0(x) = \Psi_0(\infty)\tanh\left(\frac{x}{\sqrt{2}\,\xi_{GL}}\right)$$

$$\xi_{GL} = \sqrt{\frac{\hbar}{m^*|a(T)|}} \sim \frac{1}{|T-T_c|^{1/2}}$$

Flux quantization

$$\vec{J} = -(2e)|\Psi_0|^2\left[\frac{\hbar}{m^*}\vec{\nabla}\phi + \frac{2e}{m^*}\vec{A}\right]$$

@ equilibrium $\vec{J} = 0$

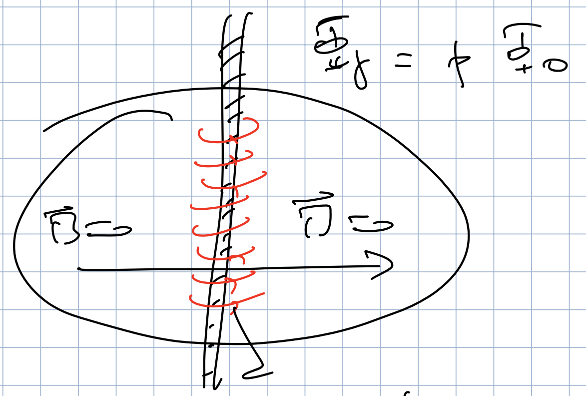


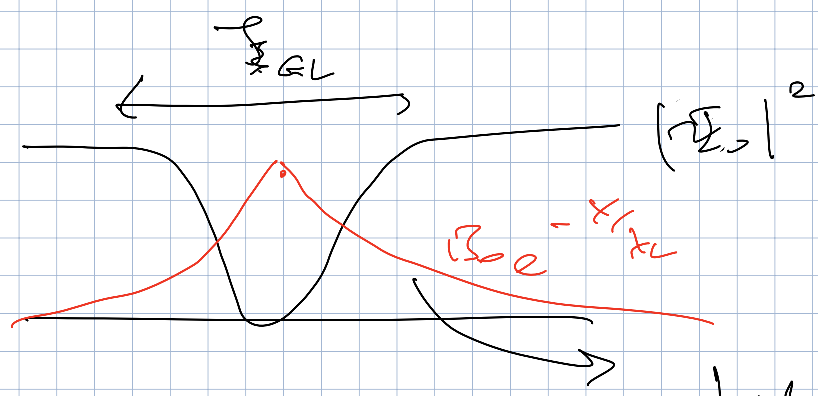
$$0 = \int d\vec{l}\cdot\vec{J} = -(2e)|\Psi_0|^2\frac{\hbar}{m^*}\left[\overbrace{\oint d\vec{l}\cdot\vec{\nabla}\phi}^{2\pi p} + \left(\frac{2e}{\hbar}\right)\underbrace{\oint\vec{A}\cdot d\vec{l}}_{\Phi_\gamma}\right]$$

$$\Phi_\gamma = \frac{\hbar}{2e} 2\pi p = p\, \Phi_0$$

$$\Phi_0 = \frac{h}{2e} = \text{sc flux quantum}$$

sc vortices : flux penetration





London equation holds

$$\boxed{\lambda_L \gtrsim \xi_{GL}}$$

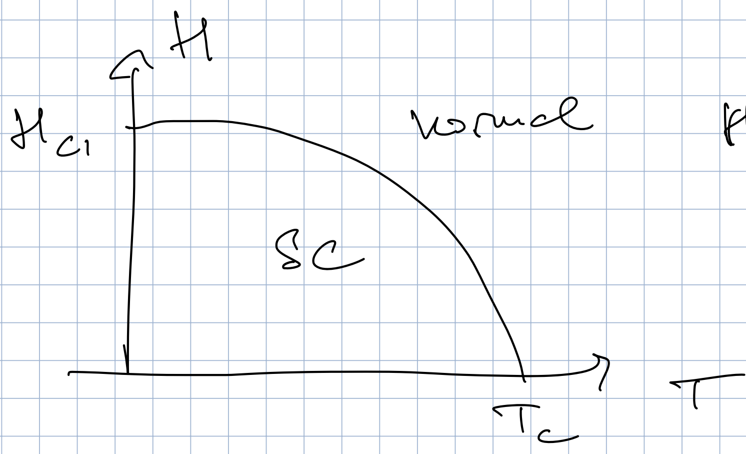
$$\kappa = \frac{\lambda_L}{\xi_{GL}} \gtrsim 1 \qquad \lambda_L = \sqrt{\frac{m^*}{(2e)^2 \mu_0 |\Psi_0|^2}}$$

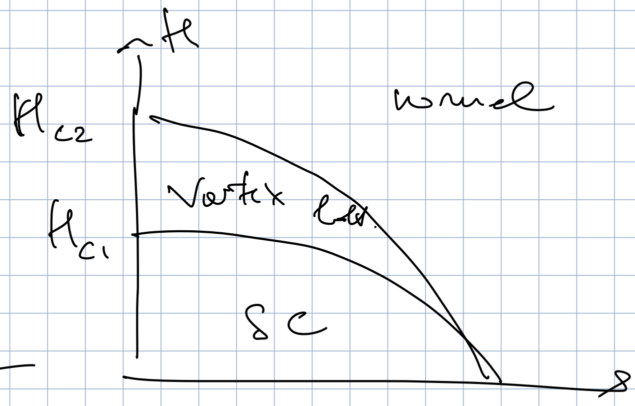
$$\sim \Delta^2 \sim |T - T_c|$$

in fact $\boxed{\kappa > \frac{1}{\sqrt{2}}}$ $\qquad \sim \frac{1}{|T-T_c|^{1/2}}$

for the formation of vortices

Phase diagram





type I SC

$\kappa < \frac{1}{\sqrt{2}}$

type

$\kappa > \frac{1}{\sqrt{2}}$

$$E_{\text{vortex}} \simeq \frac{\Phi^2 L}{4\pi\mu_0\lambda_L^2}\ln\left(\frac{\lambda_L}{\xi}\right)$$

$\Phi = \Phi_0 p$

$p=1$ minimizes energy $\Rightarrow$ vortex lattice

magnetic energy $-\Phi_0 H \simeq \frac{dE}{dz}$

$$\Phi_0 H \simeq \frac{\Phi^2}{4\pi\mu_0\lambda_L^2}$$

$$\Phi = \frac{\mu_0 H}{S}$$

$$H \geq H_{c1} \simeq \frac{\Phi_0}{4\pi\mu_0\lambda_L^2}$$

Φ

$H \geq H_{c2} \sim \frac{\Phi_0}{\mu_0\xi_{GL}^2} = \frac{M\Phi_0}{\mu_0 M\xi_{GL}^2}$ length of vortices

$\rightarrow$ system

$M\mathfrak{g}_{G_2}$