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**University of
Zurich^{UZH}**

Department of Physics
University of Zurich
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Abstract

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Chapter 1

Charge Order

1.1 Peierl Transition

1.2 From Causality to Kramer-Kronig relation

Looking at a causal function $\tilde{\chi}(t)$, we can split it, like every analytical function, in an even $\chi_{even}(t)$ and an odd $\chi_{odd}(t)$ part.

$$\tilde{\chi}(t) = \begin{cases} 0 & t < t_0 \\ \chi(t) & t > t_0 \end{cases} \quad \text{University of Zurich}^{\text{UZH}}$$
$$\tilde{\chi}(t) = \frac{\tilde{\chi}(t) + \tilde{\chi}(-t)}{2} + \frac{\tilde{\chi}(t) - \tilde{\chi}(-t)}{2} = \chi_{even}(t) + \chi_{odd}(t) \quad (1.1)$$

Multiplying the even part of this function with the signum function yields,

$$\text{sign}(t) \cdot \chi_{even} = \text{sign}(t) \cdot \left\{ \frac{\tilde{\chi}(t)}{2} + \frac{\tilde{\chi}(-t)}{2} \right\} = \frac{\tilde{\chi}(t)}{2} - \frac{\tilde{\chi}(-t)}{2} = \chi_{odd}(t) \quad (1.2)$$

Using this relation to replace $\chi_{odd}(t)$ in Eq 1.1 .

$$\tilde{\chi}(t) = \chi_{even} + \chi_{odd} = (1 + \text{sign}(t)) \cdot \chi_{even}(t) = \sigma(t) \cdot \chi_{even}(t) \quad (1.3)$$

Onsager Relation

$$S \cdot \left(\frac{1}{B_{n+1}} - \frac{1}{B_n} \right) = \frac{2\pi e}{\hbar} \quad (1.4)$$

S is the Fermi surface ($S = \pi k_F^2$).

$$F \equiv \left(\frac{1}{B_{n+1}} - \frac{1}{B_n} \right)^{-1} \quad (1.5)$$

$$F = \frac{\Phi_0}{2\pi^2} \cdot S \quad (1.6)$$

where $\Phi_0 = \frac{h}{2e} = \text{Flux Quantum}$

Chapter 2

Second Quantization

2.1 1D-Chain

To have a first insight into second quantization, we look at a phonons emerging in a one dimensional chain of atoms

sketch 1D lattice chain

In the sketch above u_i refers to the distance from equilibrium of the i -th atom, p_i stands for the momentum of the i -th atom, K is the spring constant and the lattice constant a . The Hamiltonian of this system is given as

$$H_{\text{ph}} = \sum_{j_1}^N \left\{ \frac{1}{2M} p_j^2 + \frac{1}{2} K (u_j - u_{j-1})^2 \right\} \quad (2.1)$$

Since our problem has one dimension in real space it has also one dimension in the reciprocal space. We can introduce two length scales in the reciprocal space

1. The size of the one dim. unit cell defines the length of the reciprocal lattice vector \vec{G} which is equal to the size of the Brillouin zone: $G = 2\pi/a$
2. The length L of the chain of atoms in real space defines the lowest possible distance two points in reciprocal space can have $\Delta k_{\text{min}} = 2\pi/L$.

sketch 1D k-space

We now want to rewrite the Hamiltonian Eq 2.1 by replacing the distance from equilibrium and the momentum of the atoms by its Fourier transformations

$$p_j = \frac{1}{\sqrt{N}} \sum_{k \in \text{BZ}} P_k e^{ikR_j^0} \iff P_k = \frac{1}{\sqrt{N}} \sum_j p_j e^{-ikR_j^0} \quad (2.2)$$

$$u_j = \frac{1}{\sqrt{N}} \sum_{k \in \text{BZ}} U_k e^{ikR_j^0} \iff U_k = \frac{1}{\sqrt{N}} \sum_j u_j e^{-ikR_j^0} \quad (2.3)$$

Since it is a cumbersome procedure we look at the calculate the different terms from Eq 2.1 seperatly. We start with $\sum_i p_j^2$:

$$p_j = \frac{1}{\sqrt{N}} \sum_k P_k e^{ikR_j^0} = \frac{1}{2\sqrt{N}} \left\{ \underbrace{\sum_k P_k e^{ikR_j^0}}_A + \underbrace{\sum_{-k} P_{-k} e^{-ikR_j^0}}_B \right\} \quad (2.4)$$

The second equality sign holds because summing two times and sum and dividing by two gives the same result. Additionally in the second sum we replaced $k \rightarrow -k$. Now we can write

$$\begin{aligned} p_j^2 &= \frac{1}{4N} (A^2 + B^2 + 2AB) = \frac{2}{4N} \sum_j AB \\ &= \frac{1}{2N} \sum_j \sum_k \sum_{-k} P_k P_{-k} = \sum_k P_k P_{-k} \end{aligned} \quad (2.5)$$

is this correct?

To get to this result $\sum_j e^{ikR_j^0} = \delta(k)$ was used. For evaluating now $\sum_j (u_j - u_{j-1})^2$ we use

$$u_j = \left\{ \underbrace{\sum_k u_k e^{ikR_j^0}}_{A'} + \underbrace{\sum_{-k} u_{-k} e^{-ikR_j^0}}_{B'} \right\} \quad (2.6)$$

$$\begin{aligned} u_{j-1} &= \frac{1}{\sqrt{N}} \sum_k u_k e^{ikR_j^0} e^{-ika} \\ &= \frac{1}{2\sqrt{N}} \left\{ \sum_k u_k e^{ikR_j^0} e^{-ika} + \sum_{-k} u_{-k} e^{-ikR_j^0} e^{ika} \right\} \end{aligned} \quad (2.7)$$

To get the final expression for u_{j-1} we used $R_{j-1}^0 = r_j^0 - a$.

$$\begin{aligned}
\sum_j (u_j - u_{j-1})^2 &= \sum_j (u_j^2 + u_{j-1}^2 + 2u_j u_{j-1}) \\
&= \sum_k \left\{ u_k u_{-k} + u_k u_{-k} - 2u_k u_{-k} \frac{e^{-ika} + e^{ika}}{2} \right\} \\
&= \sum_k 2u_k u_{-k} \{1 - \cos(ka)\} \\
&= \sum_k 2u_k u_{-k} \sin^2(ka/2)
\end{aligned} \tag{2.8}$$

In the step where the summing over j changed to a summing over k the same arguments as for Eq 2.5 were used. As we already know from the *introduction to solid state physics* class, we can assign the argument of the sum in the final expression as the square of the phonon dispersion relation $\omega(k)$

$$\omega(k) = \omega_k = \sqrt{\frac{2K}{M}(1 - \cos(ka))} = \sqrt{\frac{4K}{M}} |\sin(ka/2)| \tag{2.9}$$

Plugging our solutions for $\sum_j p_j^2$ and $\sum_j (u_j - u_{j-1})^2$ into Eq 2.1 yields

$$H_{\text{ph}} = \sum_{j=1}^N \left\{ \frac{1}{2M} P_k P_{-k} + \frac{M\omega_k^2}{2} u_k u_{-k} \right\} \tag{2.10}$$

This expression is similar to the Hamiltonian from the harmonic oscillator. We therefore define the latter operators b_k and b_k^\dagger

$$b_k = \frac{1}{\sqrt{2}} \left(\frac{u_k}{l_k} + i \frac{p_k}{\hbar/l_k} \right) \tag{2.11}$$

$$b_k^\dagger = \frac{1}{\sqrt{2}} \left(\frac{u_k}{l_k} - i \frac{p_k}{\hbar/l_k} \right) \tag{2.12}$$

and rewrite H_{ph} as

$$H_{\text{ph}} = \sum_k \hbar \omega_k (b_k^\dagger b_k + 1) \tag{2.13}$$

This analogy between the Hamiltonian from the harmonic oscillations and Eq 2.10 emphasises that we can describe the state of excited phonons in a solid as a combination of different modes similar to the different modes of oscillations of an excited harmonic oscillator. Further we can use the latter operators applied to the vacuum state to describe the excited states mathematically.

picture single atom phonon dispersion relation picture two atom basis phonon dispersion relation ...if going down in temperature peierl transition occurs - kohn anomaly

why is neutron scattering good for probing accoustic bands? - check lecture notes for explanation

...neutrons only probe lattice and neglect electronic structure

Second quantization: Free electron gas

Hamiltonian of a free electron gas can be written as.

$$H = \sum_{k\sigma} \frac{(\hbar k)^2}{2m} c_{k\sigma}^\dagger c_{k\sigma} \quad (2.14)$$

The ground state at $T = 0K$ is create by applying the electron-creation operators $c_{k_i\uparrow}$ of the i - th electron $e_{i\uparrow}$ to the vacuum state $|0\rangle$ for every electron that is present in the electron gas.

$$|\text{FS}\rangle = c_{k_{N/2}\uparrow} c_{k_{N/2}\downarrow} \dots c_{k_1\uparrow} c_{k_1\downarrow} |0\rangle = \quad (2.15)$$

To get the total number of electrons N the number operator $\hat{N} = \sum_{k\sigma} c_{k\sigma}^\dagger c_{k\sigma}$ can be applied on the ground state to the ground state $|\text{FS}\rangle$

$$N = \langle \text{FS} | \hat{N} | \text{FS} \rangle = \langle \text{FS} | \sum_{k\sigma} c_{k\sigma}^\dagger c_{k\sigma} | \text{FS} \rangle \quad (2.16)$$

This expression is equivalent to a step function

Second Quantization: Free Electron Gas

$$k_F^3 = 3\pi^2 n$$

$$E_0 = \frac{3}{5} N \epsilon_{F0}$$

$$\text{Bohr Radius: } a_0 = \frac{\hbar}{me^2}$$

$$\frac{3\pi^2}{k_F^3} = \frac{1}{n} = \frac{V}{N} = \frac{4\pi}{3} (r_S a_0)^3 \Rightarrow r_S = \left(\frac{9\pi}{4} \right)^{1/3} \frac{1}{a_0 k_F}$$

$$\frac{E_0}{N} = \frac{2.21}{r_S^2} \frac{e^2}{2a_0}$$

Electron Interaction

$$\frac{E_1}{N} = \frac{\langle FS | V_{el-el} | FS \rangle}{N} = -\frac{e^2}{2} \frac{V}{N} \frac{k_F^4}{2\pi^3} = -\frac{0.916}{r_S} \frac{e^2}{2a_0}$$

plot - energy minimum at r_S

$$V_{\text{el-el}} = \frac{1}{2V} \sum_{\sigma_1 \sigma_2} \sum_{k_1 k_2 q} V_q c_{k_1+q}^\dagger c_{k_2-q}^\dagger c_{k_2} c_{k_1} \quad (2.17)$$

Electron Tight Binding Model

Chapter 3

Magnetism

3.1 Paramagnetism

Magnetic Moment

insert picture - magnetic moment

If \vec{A} is the area inside the loop and I the current, the magnetic moment can be written as

$$\vec{\mu} = I\vec{A} \quad (3.1)$$

Example: Hydrogen Atom

insert picture - hydrogen atom and orbiting electron

The magnetic moment of a hydrogen atom can be described semi-classically by assuming the electron to be on a fixed trajectory orbiting the hydrogen nucleus with constant radius r and velocity v . The current I produced by the moving electron can be written as $I = -e/\tau$ with the orbital period $\tau = 2\pi r/v$. For the loop area we use the formula $A = \pi r^2$. This leads the magnetic moment to be

$$\mu = \frac{-ev\pi r^2}{2\pi r} = \frac{-evr}{2} = \frac{-emvr}{2m} \quad (3.2)$$

We can identify the classical definition of the angular momentum $\vec{l} = \vec{r} \times m\vec{v}$ in the numerator. Taking the quantisation of angular momentum $|\hat{l}| = n\hbar$ in quantum mechanics into account we can rewrite expression 3.2 for $n = 1$

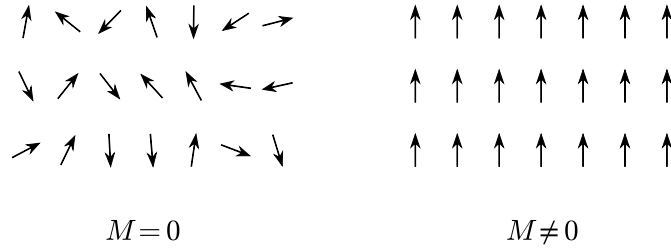


Figure 3.1: hohohoh

$$\mu \simeq \frac{-e\hbar}{2m} \equiv -\mu_B \quad (3.3)$$

Which we define as the Bohr magneton μ_B .

Magnetic Moment of Atoms

The total angular momentum in an atom is given as the sum of total orbital angular Momentum \hat{L} and total spin angular momentum \hat{S}

$$\hat{J} \simeq \hat{L} + \hat{S} \quad (3.4)$$

Magnetisation

Considering a solid with N atoms each having a magnetic moment $\vec{\mu}$. We define the magnetization as

$$\vec{M} \equiv \frac{\text{Magnetic moment}}{\text{Volume}} \quad (3.5)$$

Magnetic Moment in a \vec{B} -Field

From classical electrodynamics we know that the potential energy E of a magnetic moment $\vec{\mu}$ in a magnetic field \vec{B} is described as

$$E = -\vec{\mu} \cdot \vec{B} \quad (3.6)$$

To get a feeling for the order of magnitudes of magnetic energy of atomic scale we

$$\mu_B \times 1\text{Tesla} \simeq 0.05\text{meV}$$

This is comparable to the energy one has to put into a system to increase its temperature by 1 K ($k_B \cdot 1\text{K} \simeq 0.084\text{meV}$).

Magnetic susceptibility

$$\chi \simeq \frac{\mu_0 \vec{M}}{\vec{B}} \quad (3.7)$$

We can look at the magnetic susceptibility χ as response function. χ describes the response of the system \vec{M} when exposed to an external changing field \vec{B} . To simplify things in the calculations we will make the following constraints on \vec{B} .

$$\begin{aligned} \vec{B} \text{ is static} &\Rightarrow \text{no time dependence} \\ \vec{B} \text{ is homogeneous} &\Rightarrow \text{no dependence on } \vec{r} \end{aligned}$$

The definition of the susceptibility allows us now to classify materials depending on how they respond to an external magnetic field. We call materials to be *paramagnetic* if they align their spin parallel to the applied \vec{B} -Field. This is the case if $\chi > 0$. On the contrary we refer to materials as *diamagnetic* if their inner magnetic moments align anti-parallel in respect to an applied field \vec{B} . This results in a negative value for the susceptibility $\chi < 0$.

In reality, the response of systems is composed of multiple different responses which can have different origins.

$$\chi_{total} \simeq \chi_{paramagnetic} + \chi_{diamagnetic} + \dots \quad (3.8)$$

Paramagnetism and diamagnetism can also have different origins. For example:

$$\begin{aligned} \chi_{paramagnetic} &\simeq \chi_{Langevin} + \chi_{Van Vleck} + \chi_{Pauli} + \dots \\ \chi_{diamagnetic} &\simeq \chi_{electronic} + \chi_{superconductivity} + \dots \end{aligned}$$

Diamagnetism

insert picture - loop current to illustrate Lenz law

To symbolize diamagnetic behaviour we recall Lenz law. It states, that a changing magnetic field induces a current which creates for itself a magnetic field that points in the opposite

direction as the initial magnetic field change. In that way the system tries to compensate the externally induced field changes.

To describe that, we use 3.1, with the area $\vec{A} = \pi \langle r^2 \rangle$ and the current $I = -Ze/\tau$ with the number of electrons Z per atom and the orbit period τ . expression the orbit period in terms of the *cyclotron frequency* $\omega = eB/2m$ shows the dependency on the magnetic field.

$$\tau = \frac{2\pi}{\omega} = \frac{4\pi m}{eB} \quad (3.9)$$

Putting everything together we get the following expression to approximate the magnetic moment of a diamagnet

$$\vec{\mu} = -\frac{Ze^2 B}{4\pi m} \pi \langle r^2 \rangle = -\frac{Ze^2 B}{4m} \langle r^2 \rangle \quad (3.10)$$

The magnetisation of a macroscopic material can be written as the sum over all the magnetic moments of its atoms resulting in

$$\vec{M} = \mu_0 N \vec{\mu} \quad (3.11)$$

where N denotes the number of atoms per volume. Recalling 3.7, we find for the diamagnetic susceptibility caused by electrons

compare formula with wikipedia. probably wrong by a prefactor

$$\chi_{\text{Diamagnetic}} = -\frac{\mu_0 N e^2 \langle r^2 \rangle Z}{4m} \quad (3.12)$$

Simplest Case: e^- only

Consider a system consisting of atoms with only one electron

$$\rightarrow \hat{L} = 0, \quad \hat{S} \simeq 1/2 \quad \Rightarrow \quad \hat{J} = 1/2 \quad (3.13)$$

Further more we assume for the spin g-factor $g \simeq 2$ (not proved). This system has only two states: *spin-up* and *spin-down*.

Consider the energy of these two states leads to

$$E = -\vec{\mu} \cdot \vec{B} = \pm \mu_B \cdot |\vec{B}| \quad (3.14)$$

vector diagram energy consideration of magnetic moment in B-field

As stated before, the Energy resulting from magnetic moments of the order of magnitude of a bohr magneton μ_B to magnetic fields to several Tesla are in the same energy range of some Kelvin (some $k_B T$). Therefore we use Boltzmann statistics to describe the **population distribution** of the system. The probability of energy level E_1 to be populated can be written as

$$p_\alpha = \frac{e^{\beta E_\alpha}}{\mathcal{Z}} = \frac{e^{\beta E_\alpha}}{e^{\beta E_1} + e^{\beta E_2}}, \quad \text{with } \alpha = \{1, 2\} \quad (3.15)$$

where $\beta = 1/k_B T$ and the partition function $\mathcal{Z} = \sum_i e^{\beta E_i}$.

$$p_1 = \frac{e^{\beta E_1}}{e^{\beta E_1} + e^{-\beta E_1}}, \quad p_2 = \frac{e^{-\beta E_1}}{e^{\beta E_1} + e^{-\beta E_1}} \quad (3.16)$$

This has to be equal to $p_1 = N_1/N$ and $p_2 = N_2/N$ with N_1 (N_2) being the number of electrons in the energy state E_1 (E_2) and $N = N_1 + N_2$ being the total number of electrons in the system. Furthermore we substitute $\bar{x} = \beta E_1 = \mu_B b / k_B T$.

plots energy level population

The magnetisation M can now be written as the difference in the number of electrons with opposite magnetic moment

$$\begin{aligned} M &= (N_1 - N_2)\mu_B = N\mu_B\left(\frac{N_1}{N} - \frac{N_2}{N}\right) = N\mu_B\left(\frac{e^{\bar{x}} - e^{-\bar{x}}}{e^{\bar{x}} + e^{-\bar{x}}}\right) \\ M &= N\mu_B \tanh(\bar{x}) \end{aligned} \quad (3.17)$$

Looking at the case $\bar{x} \ll 1$, which stands for having large Temperatures and/or low magnetic fields. We get for the magnetisation

$$M \simeq N\mu_B \bar{x} = N \frac{\mu_B^2 B}{k_B T} \quad (3.18)$$

With the help of this equation we can now write down an expression for the paramagnetic susceptibility for (large temperature or low magnetic fields)

$$\chi_{\text{paramagnet}} = \frac{N\mu_B^2}{k_B T} \quad (3.19)$$

We refer to this formula as *Curie law* and we call the introduced constant $C = N\mu_B^2/k_B$ *Curie-constant*.

3.1.1 How to fill the valence shell

Hund's rules

The Hund's rules provide simply rules which give an idea about the total spin-, total orbital- and total angular momentum of an atom in its ground state

1. Maximize S to minimize the Coulomb energy
2. Maximize L to minimize Coulomb repulsion
3. $J = |L - S|$ for less than half filling and $J = |L + S|$ for more than half filling.

Crystal field effects

Atoms arranged in a lattice feel the presence of the atoms around. This happens in a way, that the valence electrons of the atom under consideration are experiencing the electric field from the ligands surrounding the atom. That causes the energy degeneracy, apparent in a free atom, to be lifted. This splitting of energy levels has impact on the occupation of the different orbitals when "filling" the atom with electrons. For studying this effect now we will consider the valence electrons to partially fill the $3d$ -orbital because this is also the case in a variety of materials in nature. Partially filled $3d$ -bands can especially be found in the *Transition metals*. We now exemplify that at systems with ligands arranged octahedrally and tetragonal.

Octahedral crystal environment

Tetrahedral crystal environment

Variation of crystal field environment

Jahn-Teller Distortion

complete this subsection with infos from lecture notes

Resonant inelastic x-ray scattering (RIXS)

3.2 Ferromagnetism

3.2.1 H₂ Molecule

Wave Function Considerations

$$\Psi^{Total}(2 \text{ Electrons}) \rightarrow \text{Antisymmetric} \quad (3.20)$$

$$\Psi^{Total}(\vec{r}_1, \vec{r}_2) = -\Psi^{Total}(\vec{r}_2, \vec{r}_1) \quad (3.21)$$

$$\Psi_A = \psi_\alpha(\vec{r}_1)\psi_\beta(\vec{r}_2) - \psi_\alpha(\vec{r}_2)\psi_\beta(\vec{r}_1) \quad (3.22)$$

$$\Psi_S = \psi_\alpha(\vec{r}_1)\psi_\beta(\vec{r}_2) + \psi_\alpha(\vec{r}_2)\psi_\beta(\vec{r}_1) \quad (3.23)$$

Consider now spin wave function:

$$\chi_S = \chi_{Symmetric} = \begin{cases} |\uparrow_\alpha \downarrow_\beta\rangle & |1, 1\rangle \\ (|\uparrow \downarrow\rangle + |\downarrow \uparrow\rangle) / \sqrt{2} & |1, 0\rangle \\ |\downarrow_\alpha \uparrow_\beta\rangle & |1, -1\rangle \end{cases} \quad (3.24)$$

$$\chi_A = \chi_{Antisymmetric} = (|\uparrow \downarrow\rangle - |\downarrow \uparrow\rangle) / \sqrt{2} \quad |0, 0\rangle \quad (3.25)$$

Where to the χ_S is referred to as **Triplet state** and to the wave function χ_A is referred to as **Singlet state**.

Quantum mechanical Spin-Operators

Recalling that $\hat{S}^2|S, m\rangle = S(S+1)|S, m\rangle$ we get for the eigenvalues of \hat{S}_α^2 and \hat{S}_β^2

$$\hat{S}_\alpha^2|S_\alpha, m\rangle = S_\alpha(S_\alpha + 1)|S_\alpha, m\rangle = 3/4 \quad (3.26)$$

$$\hat{S}_\beta^2|S_\beta, m\rangle = S_\beta(S_\beta + 1)|S_\beta, m\rangle = 3/4 \quad (3.27)$$

$$\hat{S} = \hat{S}_\alpha + \hat{S}_\beta \Rightarrow \hat{S}^2 = \hat{S}_\alpha^2 + \hat{S}_\beta^2 + 2\hat{S}_\alpha \hat{S}_\beta \Rightarrow \hat{S}_\alpha \cdot \hat{S}_\beta = \frac{\hat{S}^2 - \hat{S}_\alpha^2 - \hat{S}_\beta^2}{2} \quad (3.28)$$

Calculating $\langle \hat{S}_\alpha \cdot \hat{S}_\beta \rangle$ leads to 1/4 for χ_S and -3/4 for the χ_A case.

Consider weak Coulomb interaction

$$H = H_{\text{single-H}} + H_{\text{int}} = H_0 + H_{\text{int}} \quad (3.29)$$

Where the interaction Hamiltonian H_{int} includes the proton-proton, electron-electron, proton 1 - electron 2 and electron 1 - proton 2 interactions.

$$H_{\text{int}} = \frac{e^2}{d_{pp}} + \frac{e^2}{d_{ee}} - \frac{e^2}{d_{ep}} - \frac{e^2}{d_{pe}} \quad (3.30)$$

Here d_{pp} stands for the proton-proton distance, d_{ee} for the electron-electron distance. Furthermore contains $H_{\text{single-H}}$ both Hamiltonians of the single hydrogen atoms

$$H_{\text{single-H}} = H_{H_1} + H_{H_2} = \frac{\hbar}{2m} (\nabla_\alpha^2 + \nabla_\beta^2) - \left(\frac{e^2}{d_{p_\alpha e_\alpha}} + \frac{e^2}{d_{p_\beta e_\beta}} \right) \quad (3.31)$$

$$E_+ = E_S = \langle \Psi_S | H_{\text{int}} | \Psi_S \rangle = \int (\psi_\alpha \psi_\beta + \psi_\beta \psi_\alpha)^* \overbrace{H_{\text{int}} (\psi_\alpha \psi_\beta + \psi_\beta \psi_\alpha)}^{\substack{J_1 \\ J_2}} d^3r \quad (3.32)$$

$$E_- = E_A = \langle \Psi_S | H_{\text{int}} | \Psi_S \rangle = \int (\psi_\alpha \psi_\beta - \psi_\beta \psi_\alpha)^* \overbrace{H_{\text{int}} (\psi_\alpha \psi_\beta - \psi_\beta \psi_\alpha)}^{\substack{J_1 \\ J_2}} d^3r \quad (3.33)$$

By defining $C \equiv C_1 + C_2$ and $J \equiv J_1 + J_2$ one can write the the two energies as

$$E_\pm = C \pm J \quad (3.34)$$

Furthermore for the difference of the singlett- and triplett energy we get

$$E_+ - E_- = 2J \int \psi_\alpha^* \psi_\beta^* H_{\text{int}} \psi_\alpha \psi_\beta d^3r \quad (3.35)$$

From this equatoin we can associate the introduced variable J as the **Exchange Integral**.

$$J = \frac{E_+ - E_-}{2} = \int \psi_\alpha^* \psi_\beta^* H_{\text{int}} \psi_\alpha \psi_\beta d^3r \quad (3.36)$$

What is $H^{\text{Spin}}_{\text{int}}$

$$E_{\pm} = C \pm J = C + J/2 + 2J + \langle \hat{S}_{\alpha} \cdot \hat{S}_{\beta} \rangle = \text{constant} + 2J \langle \hat{S}_{\alpha} \cdot \hat{S}_{\beta} \rangle \quad (3.37)$$

The constant contribution to the energies E_{\pm} can be neglected since absolute energies values are arbitrary. The interesting term for us is the second one on the right-most side. It gives us a quantitative measure of how large the energy difference between the two spin configurations is

$$\Rightarrow H^{\text{Spin}}_{\text{int}} = -2J \hat{S}_{\alpha} \cdot \hat{S}_{\beta} \quad \begin{cases} J > 0 & \Rightarrow E_S > E_A \\ J < 0 & \Rightarrow E_A < E_S \end{cases} \quad (3.38)$$

From the upper formula we see that J if χ_S or χ_A is preferred. Therefore it can be seen as an indication if ferro- or antiferromagnetism is present in a material.

Ferromagnetism

$$\begin{aligned} H &= - \sum_{ij} J_{ij} \vec{S}_i \cdot \vec{S}_j + g\mu_B \cdot \sum_j \vec{S}_j \cdot \vec{B} \\ &= - \sum_j \sum_i J_{ij} \vec{S}_i \cdot \vec{S}_j + g\mu_B \sum_j \vec{S}_j \cdot \vec{B} \\ &= g\mu_B \sum_j \vec{S}_j \cdot \left(\underbrace{\vec{B}_{mf}}_{\text{internal}} + \underbrace{\vec{B}}_{\text{external}} \right) \end{aligned} \quad (3.39)$$

Using a mean field approximation we rewrite the interaction from all spins on \vec{S}_j from the first term as with a mean magnetic field \vec{B}_{mf} whereas we defined $\vec{B}_{mf} \equiv -2/g\mu_B \sum_i J_{ij} \vec{S}_i$.

Conjecture

By making an educated guess one could assume, that the mean magnetic field \vec{B}_{mf} can be approximated macroscopically with the following expression.

$$\vec{B}_{mf} \simeq \lambda \cdot \vec{M} \quad (3.40)$$

Solution

Solution can be adapted from the results about paramagnetism we gained last week. By focusing on the case $\vec{B} = 0$ we get

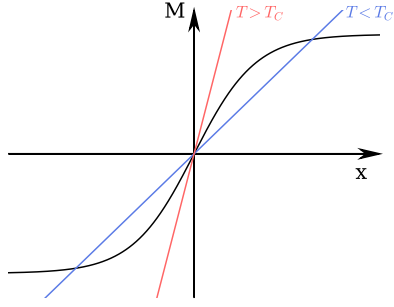


Figure 3.2: Illustration of the graphical solution of 3.41. the straight lines refer to different values of T .

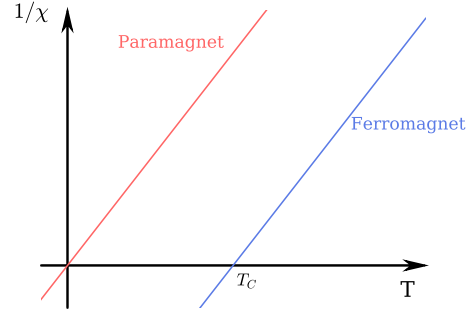


Figure 3.3: Illustration of susceptibility χ of a Para- and Ferromagnet.

$$M \simeq N\mu_B \tanh(x) \quad \text{with} \quad x = \frac{\mu_B}{k_B T}(\vec{B} + \lambda \vec{M}) \quad (3.41)$$

Since the argument of the tangent hyperbolicus depends also on the magnetisation \vec{M} we have a implicit equation. A solution of this equation is illustrated in ?? as the crossing point between the hyperbolic tangent and the straight line. In this graph it is also visible, that above a certain Temperature $T > T_C$ there only exists one solution for of the implicit equation which can be associated with the paramagnetic phase of the material. On the other hand for $T < T_C$ we see that there are exists multiple solution of 3.41 which is in accordance with the magnetisation curve of a ferromagnet. We can determine the Transition temperature T_C by comparing the slopes of the two curves at the origin

$$\frac{d}{dx} N\mu_B \tanh(x) = \frac{d}{dx} \frac{k_B T}{\mu_B \lambda} x \Rightarrow T_C = \frac{\lambda N \mu_B^2}{k_B} = \lambda \cdot C \quad (3.42)$$

Looking at the limit $x \ll 1$

$$\left. \begin{aligned} M &= CB/T \\ \chi &\equiv M/B = C/T \end{aligned} \right\} \rightarrow \left. \begin{aligned} M &= \frac{C(B + \lambda M)}{T} \\ \chi &\equiv \frac{C}{T} + \frac{\lambda}{T} \chi \end{aligned} \right\} \Rightarrow \chi = \frac{C}{T - \lambda C} = \frac{C}{T - T_C}$$

Checking the magnetisation $M(T)$ at zero field $\vec{B} = 0$. Using 3.41 with zero field and the definitinos $m = M/N\mu_B$ and $t = k_B T/N\mu_B^2 \lambda = T/T_C$ we get

$$m = \tanh\left(\frac{m}{t}\right) \quad (3.43)$$

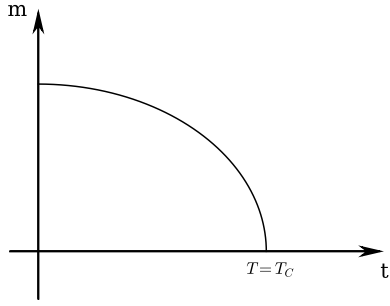


Figure 3.4: Temperature dependence of magnetisation.

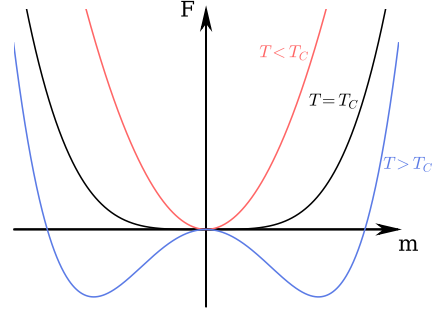


Figure 3.5: Free Energy dependence on the order parameter m for the 3 cases $T < T_C$, $T = T_C$ and $T > T_C$.

Landau Theory

According to the Landau theory of phase transisiton the free energy F can be expressed

$$F = F_0 + a(T)m^2 + bm^4 + \dots \quad (3.44)$$

Were the parameter a and b has to meet the conditions

$$a(T) = a_0(T - T_C) \quad \text{and} \quad b > 0 \quad (3.45)$$

We find the thermodynamical state of our system by minimizing the free energy

$$\frac{dF}{dm} = m(2a(T) + 4bm^2) = 0 \quad \Rightarrow \quad m = \begin{cases} 0 \\ \pm \sqrt{\frac{a_0(T-T_C)}{2b}} \end{cases} \quad (3.46)$$

3.2.2 Exchange Interaction J

Analog to the susceptibility of ferromagnets $\chi_{FM} = C/(T - T_C)$, we can define the susceptibility for anti-ferromagnets

$$\chi_{AFM} = \frac{C}{T + T_N} \quad (3.47)$$

Where we refer to the Transition Temperature T_N as Neel-Temperature.

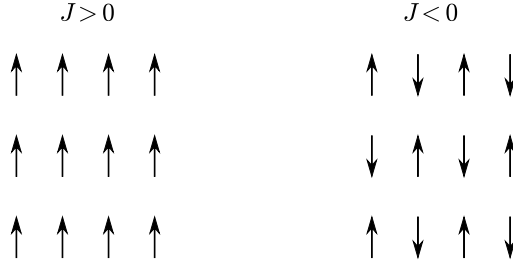


Figure 3.6: hohoho

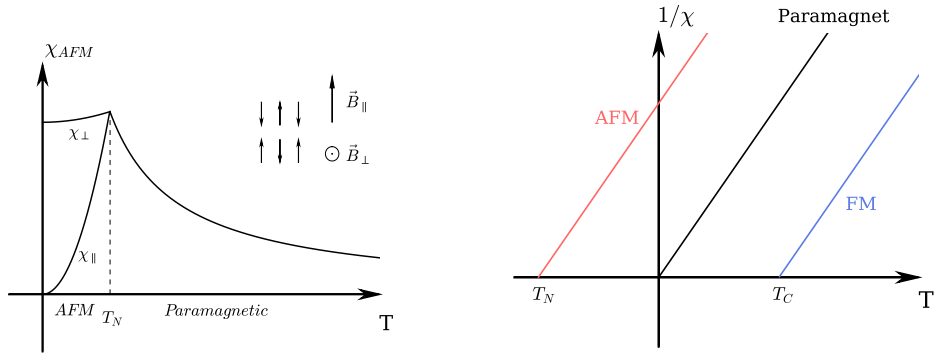


Figure 3.7: Temperature dependence of magneti-

Figure 3.8: Free Energy dependence on the order parameter m for the 3 cases $T < T_C$, $T = T_C$ and $T > T_C$.

3.2.3 Ferromagnetic Magnons

Consider a linear FM chain $|\text{FM}\rangle = |\uparrow\uparrow\uparrow \dots\rangle$. Applying the latter operator s_j^- onto this expression leads to

$$|j\rangle = s_j^- |\text{FM}\rangle = |\uparrow\uparrow \dots \underbrace{\uparrow\downarrow}_j \uparrow \dots\rangle \quad (3.48)$$

Defining

$$|q\rangle = \frac{1}{\sqrt{N}} \sum_j e^{iqR_j} |j\rangle \quad (3.49)$$

The Hamilton is given as

$$\begin{aligned}
H &= -\sum_{ij} J_{ij} \hat{S}_i \cdot \hat{S}_j = -2J \sum_i \hat{S}_i \cdot \hat{S}_{i+1} \\
&= -2J \sum_i \left\{ \hat{S}_i^z \hat{S}_{i+1}^z + \frac{1}{2} [\hat{S}_i^+ \hat{S}_{i+1}^- + \hat{S}_i^- \hat{S}_{i+1}^+] \right\}
\end{aligned} \tag{3.50}$$

By taking only nearest neighbour interactions into account we get the The second equality sign holds if we only take nearest neighbour interactions into account. To get the final expression we used the substitution

$$\hat{S}^2 = \hat{S}^{z^2} + \frac{1}{2} [\hat{S}_i^+ \hat{S}_{i+1}^- + \hat{S}_i^- \hat{S}_{i+1}^+] \tag{3.51}$$

$$H|\text{FM}\rangle = -2JNS^2|\text{FM}\rangle = E_0|\text{FM}\rangle \tag{3.52}$$

$$H|j\rangle = -2J \{ (N-4)S^2|j\rangle + S[|j+1\rangle + |j-1\rangle] \} \tag{3.53}$$

$$\begin{aligned}
H|q\rangle &= \frac{1}{\sqrt{N}} \sum_j e^{iqR_j} \{ NS^2|j\rangle - 2S^2|j\rangle + S|j+1\rangle + S|j-1\rangle \} \\
&= -2JNS^2|q\rangle - 2J \{ -2S^2 + (e^{iqa} + e^{-iqa}) \} |q\rangle \\
&= E_0|q\rangle + 2JS \{ 1 - \cos(qa) \} |q\rangle
\end{aligned} \tag{3.54}$$

Since we are considering an infinite long 1D chain of spin states we can rewrite the expression

$$H|q\rangle = E_0|q\rangle + 2JS \{ 2 - 2\cos(qa) \} |q\rangle \tag{3.55}$$

which leads to

$$H|q\rangle = E(q)|q\rangle \quad \text{with} \quad E(q) \simeq E_0 + 2JS(2 - 2\cos(qa)) \tag{3.56}$$

This is the dispersion relation for ferromagnets. For anti-ferromagnets we have a similar relation (not derived)

$$\hbar\omega = 2J|\sin(qa)| \tag{3.57}$$

Chapter 4

Superconductivity

4.1 Conventional superconductors

4.1.1 Link ρ & Meissner Effect

As we know, superconductors are characterised by vanishing resistivity ($\rho = 0$) for undergoing a critical temperature T_C (Fig.4.1). Recalling Ohm's law,

$$\vec{j} = \sigma \vec{E} \quad (4.1)$$

which relates the electron current density \vec{j} and the electric field inside a conductor \vec{E} by introducing the material dependent conductivity σ .

Looking at the case of superconductors, we can emphasize, by rearranging Ohm's law, that the electric field vanishes.

$$\vec{E} = \frac{1}{\sigma} \vec{j} = \rho \vec{j} \simeq 0 \quad (4.2)$$

By using one of the Maxwell equations $\nabla \times \vec{E} = -d\vec{B}/dt$ we can conclude, that for a vanishing electric field $\vec{E} = 0$ there can't be a change of the magnetic field over time $d\vec{B}/dt = 0$.

diagram vanishing B-field

4.2 London Equation

The London equation is a macroscopic theory that was one of the first theories which allowed to describe effects like the Meissner-Ochsenfeld effect quantitatively. We now want

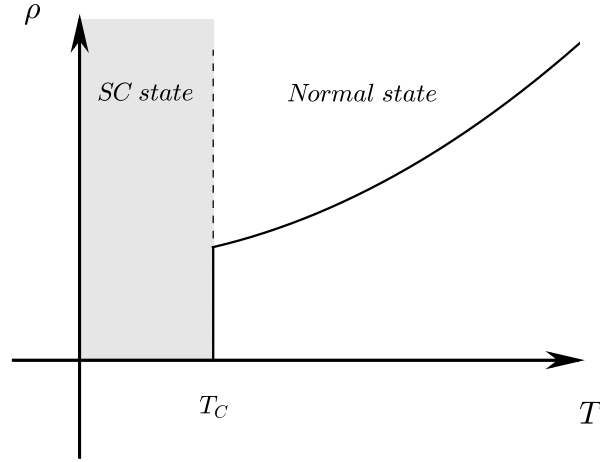


Figure 4.1: hohoho

to qualitatively derive the London equation. For that consider a current oscillating with the frequency ω

$$\vec{j}e^{-i\omega t} = \sigma(\omega)\vec{E}e^{-i\omega t} \quad (4.3)$$

Using the expression for the conductivity $\sigma(\omega)$ from the Drude model for a time-dependent electric field

$$\sigma(\omega) = \frac{\vec{j}}{\vec{E}} = \frac{ne^2\tau}{m} \frac{1}{1 - i\omega\tau} \quad (4.4)$$

From this we get, as already proven in a previous exercise, that the real part of the conductivity can be written in the limit of $\tau \rightarrow \infty$ as

$$\text{Re}(\sigma(\omega)) = \frac{\pi ne^2}{m} \delta(\omega) \quad (4.5)$$

This can also be made clear, when looking at the limits

$$\text{Re}(\sigma(\omega)) = \frac{ne^2}{m} \frac{\tau}{1 + \omega^2\tau^2} \xrightarrow{\omega \rightarrow 0} \frac{ne^2\tau}{m} \quad (4.6)$$

$$\sigma(\omega) \xrightarrow{\tau \rightarrow \infty} -\frac{ne^2}{im\omega} = \text{Im}(\sigma(\omega)) \Rightarrow \text{Re}(\sigma(\omega)) = 0 \quad \text{for } \omega \neq 0 \quad (4.7)$$

From Eq.4.5 , we see that in the regime of very large mean free times τ between ionic collisions, the real part of the conductivity $\sigma(\omega)$ is only different from zero for vanishing oscillations of the electric field.

To derive the London equation, the following two assumptions have to be made

1. $\tau \rightarrow \infty$, which is given since there are no collisions between electrons and lattice ions in the superconducting state.
2. We have to split up the conductivity in a part $\sigma_N(\omega)$ of normal state electrons and a conductivity contribution due to *super electrons* σ_S : $\sigma(\omega) = \sigma_N(\omega) + \sigma_S(\omega)$, where only $\sigma_S(\omega) \neq 0$ in the superconducting state

Taking the curl of the oscillating current

$$\begin{aligned}\nabla \times (\vec{j} e^{-i\omega t}) &= -\sigma(\omega) \nabla \times (\vec{E} \cdot e^{-i\omega t}) = -\sigma(\omega) \frac{d}{dt} (\vec{B} \cdot e^{-i\omega t}) \\ &= -\frac{n_S e^2}{m} \vec{B} \cdot e^{-i\omega t}\end{aligned}\quad (4.8)$$

Here we used Eq.4.3 in the first and faradays law ($\nabla \times \vec{E} = d/dt \vec{B}$) in the second step. Furthermore is only the *super electron* density n_S contributing to the conductivity $\sigma(\omega)$. From this equation we can deduce that

$$\nabla \times \vec{j} \propto \vec{B} \quad \text{and thereof} \quad \vec{j} = -\frac{n_S e^2}{m} \vec{A} \quad (4.9)$$

with \vec{A} being the vector potential. The equation describing this proportionality between the current density \vec{j} and the vector potential \vec{A} is the London equation.

Together with Ampere's law ($\nabla \times \vec{B} = \mu_0 \vec{j}$) allows us the London equation (Eq.4.9) now to set up a differential equation for the magnetic field \vec{B} .

$$\nabla \times \nabla \times \vec{B} = -\frac{1}{\lambda^2} \vec{B}, \quad \text{where } \lambda = \sqrt{\frac{m}{\mu_0 n_S e^2}} \quad (4.10)$$

This equation can also be written as

$$\nabla^2 \cdot \vec{B} = \frac{1}{\lambda^2} \vec{B} \quad (4.11)$$

To exemplify the solution of this differential equation we look at it in one dimension. Then Eq.4.11 becomes $d^2/dx^2 B_z(x) = 1/\lambda^2 B_x$.

To exemplify the solution of this differential equation we look at a situation where we have a superconductor filling the space for all values $x \geq 0$ corresponding to that we have vacuum

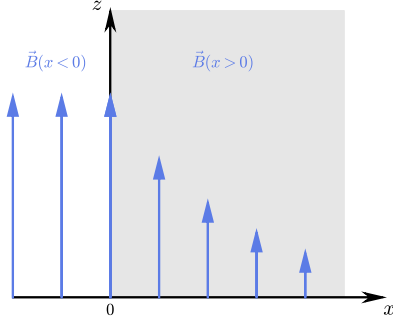


Figure 4.2: Illustration of the magnetic field decrease inside the superconductor according to Eq.4.13 . The magnetic field is pictorially drawn as blue vectors. Adapted from redKittel - include citation

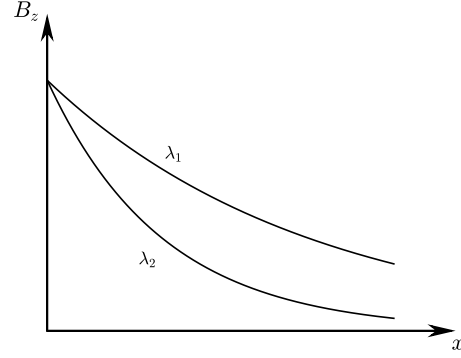


Figure 4.3: Illustration of Eq.4.13 for two different values for the london penetration depth.

at $x < 0$. Applying now a magnetic field in the vacuum region aligned along the z-axis $\vec{B} = (0, 0, B_0)$. in this case the differential equation Eq.4.11 simplifies to

$$\frac{d^2}{dx^2} B_z(x) = \frac{1}{\lambda^2} B_z(x) \quad (4.12)$$

Using the boundary conditions $B_z(x) \xrightarrow{x \rightarrow \infty} 0$ (Meissner Effect) and $B_z(x \rightarrow 0) = B_0$ leads to the solution

$$B_z(x) = B_0 e^{-x/\lambda} \quad (4.13)$$

This solution describes an exponentially decreasing magnetic field inside the the superconductor close to the surface. From this formula one can also recognize that $\lambda = \sqrt{m/\mu_0 n_S e^2}$ introduced a characteristic length scale over which the magnetic penetrates the superconductor. For that reason λ is referred to as *London penetration depth*. In 4.7 we see Eq.4.13 plotted for two different values of lambda $\lambda_1 > \lambda_2$. Looking at the definition of the London penetration depth we see that $n_{S_1} < n_{S_2}$, which means that the higher the charge density the more is the penetrating magnetic field $B_z(x)$ diminished.

4.3 Coherence Length

Another lengthscale that helps us to classify the different types of superconductors is the *coherence length* ξ . The coherence length is a measure of the distance within which the superconducting electron concentration cannot change drastically in a spatially-varying magnetic field.

$$\xi = \frac{\hbar v_F}{\pi \Delta} \quad (4.14)$$

Where v_F stands for the fermi velocity and Δ for superconducting gap being present at the fermi surface in the SC state. ξ is a parameter in the *Ginzburg-Landau Theory* and can be derived there.

The two length scales, penetration depth and coherence length, allow us now, to categorize the superconductors in the groups *Type 1* and *Type 2*. This goes as follows:

By defining $\kappa \equiv \xi/\lambda$ we say a Superconductor contains to the group of *Type 1* (*Type 2*) if $\kappa < (>) 1/\sqrt{2} \simeq 0.707$.

Values of κ for some materials are given in [length scale table](#). The classification of SC into Type 1 and Type 2 does not fully coincide with the classification of conventional and unconventional. Although a lot of the conventional (elementary) superconductors are of Type 1, there are also some exceptions like Niobium (Nb) which is a conventional Type 2 Superconductor.

[include table from PPP](#)

4.4 Ginzburg-Landau Theory

The Landau Theory of Phase Transition can also be used in the case of the transition from normal to superconducting state. The free energy per volume of the system in the superconducting state is given as

$$f_{SC} = f_{NS} + a(T)|\psi(T)|^2 + \frac{1}{2}b(T)|\psi(T)|^4 + \dots \quad (4.15)$$

$|\psi|$ is treated as the order parameter. To find the temperature dependence of the free energy per volume we make the following assumptions: near the transition temperature T_C has a to be linear in temperature ($a(T) = a_0(T - T_C) + \dots$) and b given as $b(T) = b_0 + \dots$ with a_0, b_0 being constant and larger than zero.

Looking for the extrema of $(f_{SC} - f_{NS})$

$$\frac{d(f_{SC} - f_{NS})}{d|\psi|} = 2|\psi| \{a(T) + b(T)|\psi|^2\} \stackrel{!}{=} 0 \quad (4.16)$$

We find the following condition for $|\psi|$ to minimize $(f_{SC} - f_{NS})$

$$|\psi| = \begin{cases} 0, & T > T_C \\ \pm\sqrt{-a(T)/b(T)}, & T < T_C \end{cases} \quad (4.17)$$

Plugging Eq.4.17 into Eq.4.16 leads to

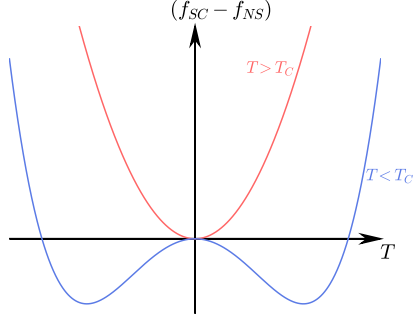


Figure 4.4: Difference of the free energy per volume between the normal- and superconducting state.

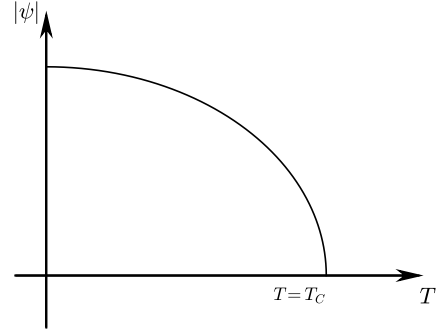


Figure 4.5: Temperature dependence of the order parameter $|\psi|$.

$$(f_{\text{SC}} - f_{\text{NS}}) = -\frac{a^2(T)}{b(T)} + \frac{1}{2} \frac{a^2(T)}{b(T)} = -\frac{1}{2} \frac{a_0^2 (T - T_C)^2}{b_0} \quad (4.18)$$

Since f_{SC} is the free energy, we can write

$$S \equiv -\frac{df}{dT} \quad \text{and} \quad C \equiv T \cdot \frac{dS}{dT} \quad (4.19)$$

This gives for the difference in the heat capacity

$$\Delta C \equiv C_{\text{SC}} - C_{\text{NS}} = -T \frac{d^2(f_{\text{SC}} - f_{\text{NS}})}{dT^2} = T \frac{a_0^2}{b_0} \quad (4.20)$$

Evaluating Eq.4.20 at the transition Temperature gives us the jump in specific heat at the phase transition

$$\Delta C(T_C) = \frac{a_0^2}{b_0} T_C \quad (4.21)$$

4.4.1 Orderparameter in the Ginzburg-Landau Model

To point out the connection between the penetration depth resulting from the London Equation and the Ginzburg-Landau Theory, we look a bit closer at the order parameter $|\psi|$. Before we defined the term of the super electrons n_s in the London's theory. In BCS-Theory this quantity is referred to as density of cooper pairs.

$$n_S = \begin{cases} \text{\#super electrons} & \leftarrow \text{London Theory} \\ \text{\#cooper pairs} & \leftarrow \text{BCS Theory} \end{cases}$$

Here we assign

$$n_S = 2|\psi|^2 = 2\frac{a_0(T_C - T)}{b_0} \quad (4.22)$$

This allows us now to express the penetretion depth λ from Eq.4.10 as explicitly temperature dependent

$$\lambda(T) = \sqrt{\frac{b_0 m}{2\mu_0 e^2 a_0 (T_C - T)}} \quad (4.23)$$

4.5 Classification of different superconductors

4.6 Vorteces

To define the appearance of vorteces from Type 2 Superconductors into into our formalism we define the free energy per volumne as

$$f_{SC} - f_{NS} \simeq a(T)|\psi(r)|^2 + b(T)|\psi(r)|^4 + \frac{\hbar^2}{2m}\nabla|\psi|^2 \quad (4.24)$$

To get the total Free energy we integrate Eq.4.24 over all space

$$F_{SC} - F_{NS} = \int d^3r (f_{SC} - f_{NS}) \quad (4.25)$$

We are interested now in finding the wavefunction $\psi(r)$ for which the Free energy is minimized. Since $\psi(r)$ is a function, this condition is formulated in a functional of the following form

$$\frac{\delta F_{SC}}{\delta \psi(r)} \stackrel{!}{=} 0 \quad (4.26)$$

This is a differential equation for $\psi(r)$. In one dimnesion this DEG looks like the following

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + a(T)\psi(x) + b(T)\psi^3(x) = 0 \quad (4.27)$$

A solution to this differential equation is

$$\psi(x) = \psi_0 \tanh\left(\frac{x}{\sqrt{2}\xi(T)}\right) \quad (4.28)$$

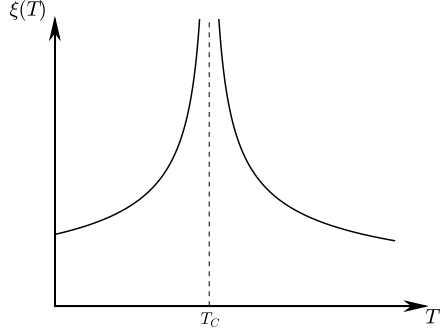


Figure 4.6: Coherence length $\xi(T)$ plotted over Temperature according to Eq.?? . Noteworthy is the diverging of ξ when going close to T_C .

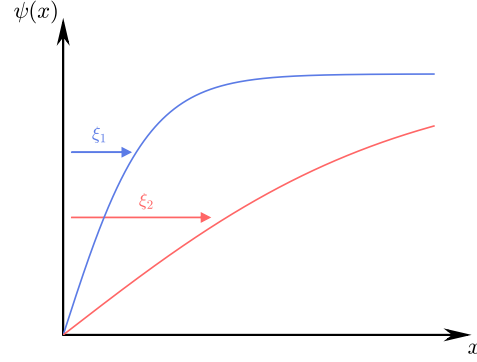


Figure 4.7: Wavefunction in one dimension according to Eq.4.28 . Comparing the the blue and red curve shows that the wave function gets *pushed down* for increasing coherence length ($\xi_2 > \xi_1$).

The coherence length $\xi(T)$ introduces a temperature dependent length scale and is given as

$$\xi(T) = \left(\frac{\hbar}{2m|a(T)|} \right)^{1/2} = \xi_0 t^{-1/2} \quad \text{with} \quad t = \frac{T - T_C}{T_C} \quad (4.29)$$

Here we used the same expression for $a(T)$ as in the ginzburg-Landau Theory.

We can now use our expressions for the penetration depth (Eq.4.23) and the coherence length (Eq.4.29) to express the Ginzburg-Landau paramater κ as

$$\kappa \equiv \frac{\lambda(T)}{\xi(t)} \quad (4.30)$$

Since the temperature dependence of both characteristic length scales cancels out, κ **is independent of T** .

Each vortex has one flux quantum Φ_0 . The diameter of a vortex is given by the coherence length ξ . Looking at a cut through a superconductor with edge length L , we can define the total surface of the material covered by vorteces as

$$2\pi\xi^2 N = A_{\text{vortex}} \quad (4.31)$$

where N is the number of vorteces in the material an. Looking for the situation where $A_{\text{vortex}} = L$ we can say, that the superconducting state is fully repressed by the vortex inherent magnetic field. The magnetic field inside the superconductor can then be written as

$$H = \frac{N\Phi_0}{L^2} \quad (4.32)$$

This allows us to set up a relation between the upper critical field H_{c_2} for which the superconducting state is entirely suppressed and the coherence length, which defines the vortex diameter

$$H_{c_2} \simeq \frac{\Phi_0}{2\pi\xi^2} \quad (4.33)$$

Since one vortex has exactly one flux quantum, we can set up a relation between the penetration depth λ and a lower critical field H_{c_1} . This lower critical field marks the point when vortices start to be *produced* at the materials surface. We assume, that the magnetic field penetration the superconductor has at least to be as strong as one flux quantum to be able to create a vortex

$$\pi\lambda^2 H \stackrel{!}{=} \Phi_0 \quad \Rightarrow \quad H_{c_1} = \frac{\Phi_0}{\pi\lambda} \quad (4.34)$$

sketch - vortices in the material

sketch - condition for creating one vortex

$$\mathcal{F}\{p, u\} \quad (4.35)$$

$$\mathcal{F}\{p, u\} \quad (4.36)$$

$$\mathcal{F}^{pu} \quad (4.37)$$

$$F^p_u \quad (4.38)$$

$$f_{pu} \quad (4.39)$$

$$\psi\pi v \quad (4.40)$$

Bibliography