ATOMIC PHYSICS

The magnetic moment of an infinitesimal current loop is given by

$$\mathrm{d}\boldsymbol{\mu} = I\mathrm{d}\boldsymbol{S} \quad \rightsquigarrow \quad \boldsymbol{\mu} = I\int_\sigma \mathrm{d}\boldsymbol{S}$$

where I is the current and $\mathrm{d}\boldsymbol{S}$ is the area. Integrating over a surface σ gives us the total magnetic moment.

Magnetic moments of atoms

Atoms have magnetic moments, which can be decomposed into three constituents: A nuclear moment, and two electronic moments, one due to its spin and one due to its orbital momentum:

$$\boldsymbol{\mu} = \boldsymbol{\mu}_\mathrm{N} + \boldsymbol{\mu}_\mathrm{S} + \boldsymbol{\mu}_\mathrm{L} = \mu_N g_N \boldsymbol{S}_N + \mu_B g_s \boldsymbol{S} + \gamma\boldsymbol{L},\ \mu_B = \frac{e\hbar}{2m_e}$$

The orbital moment is demonstrated by the Einstein-de Haas effect, where the current through a coil with a ferromagnetic core is abruptly stopped causing a slight rotation of the core.

Classically applying a magnetic field to an orbital magnetic moment will cause a gyromagnetic precession, with frequency γB:

$$\begin{aligned} \text{torque} \equiv \boldsymbol{G} = \boldsymbol{\mu}\times\boldsymbol{B} = \frac{1}{\gamma}\dot{\boldsymbol{\mu}} \\ \rightsquigarrow \quad \boldsymbol{\mu}(t) = \boldsymbol{\mu}\cos(\Omega t + \phi_0) + \frac{\boldsymbol{\mu}\times\boldsymbol{B}}{B\cos(\theta)}\sin(\Omega t + \phi_0) \end{aligned}$$

where $\Omega = \gamma B$ is the Larmor precession frequency and θ is the angle between $\boldsymbol{\mu}$ and $\boldsymbol{B}$.

Magnetisation and field

The flux density is simply a linear combination of the applied field and the magnetisation:

$$\boldsymbol{B} = \mu_0\left(\boldsymbol{H} + \boldsymbol{M}\right)$$

where

$$\boldsymbol{M} = \chi\boldsymbol{H}, \quad M_i = \chi_{ij}H_j$$

where the former is for linear materials where $\chi_{ij} = M\delta_{ij}$ and the latter is for non-linear materials: in non-linear materials the magnetisation can point in a different direction than the applied field. For linear materials we have

$$\boldsymbol{B} = \mu_0(1+\chi)\boldsymbol{H} = \mu_0\mu_r\boldsymbol{H}$$

This course primarily uses the susceptibility χ rather than the relative permeability, μ_r.

The Bohr-van Leeuwen theorem

The total energy of a classical electron in a magnetic field is given by

$$E = \frac{\|\boldsymbol{p} + e\boldsymbol{A}\|^2}{2m}$$

This means that the partition function can be calculated

$$Z \sim \iint\cdots\int \exp\left(-\beta E(\boldsymbol{r}_i, \boldsymbol{p}_i)\right)\mathrm{d}\boldsymbol{r}_1\cdots\mathrm{d}\boldsymbol{r}_N\mathrm{d}\boldsymbol{p}_1\cdots\mathrm{d}\boldsymbol{p}_N$$

however as the momentum integral goes over entire $\mathbb{R}$ we can shift the momentum by $e\boldsymbol{A}$ resulting in an integral that is independent of $\boldsymbol{A}$ and hence all physical quantities are independent of $\boldsymbol{A}$ – there can exist no global magnetism, classically: this is the statement of the Bohr-van Leeuwen theorem.

Quantum mechanics of spin

The z-axis projection of the spin of a particle is measured using

$$s_z\left|s\ m_s\right\rangle = \hbar m_s\left|s\ m_s\right\rangle$$

The factors of $\hbar$ are often omitted. However, the x and y components are slightly more complicated, as $|s\rangle$ is not an eigenket to these operators. However, to make things easier we can define raising and lowering operators:

$$\begin{aligned} s_+ &= s_x + is_y \\ s_- &= s_x - is_y \end{aligned}$$

Which means that

$$\begin{aligned} s_x &= \frac{1}{2}\left(s_+ + s_-\right) \\ s_y &= \frac{1}{2i}\left(s_+ - s_-\right) \end{aligned}$$

which allows us to calculate what $\boldsymbol{s}\left|s\ m_s\right\rangle$ is:

$$\boldsymbol{s}\left|s\ m_s\right\rangle = \begin{pmatrix} \frac{\hbar}{2}\left(A_+\left|s\ m_s+1\right\rangle + A_-\left|s\ m_s-1\right\rangle\right) \\ \frac{\hbar}{2i}\left(A_+\left|s\ m_s+1\right\rangle - A_-\left|s\ m_s-1\right\rangle\right) \\ \hbar m_s\left|s\ m_s\right\rangle \end{pmatrix}$$

Where

$$A_\pm = \sqrt{(s\mp m_s)(s\pm m_s+1)}$$

Coupling of two spins

Let us consider two spin-1/2 particles that are coupled through a Hamiltonian:

$$\hat{H} = A\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 = \sum_i A S_1^i \otimes S_2^i$$

we use the direct product, because the two spins each live in their own Hilbert space, and the coupling of the operators couples the Hilbert space. We know that

$$\frac{1}{2} \otimes \frac{1}{2} = 0 \oplus 1$$

which implies that this system splits into a singlet (of spin zero) and a triplet (with spin 1). This can also be seen by rewriting $\boldsymbol{S}_1 \cdot \boldsymbol{S}_2$ out with conserved quantities:

$$\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 = \frac{1}{2}\left(S^2 - S_1^2 - S_2^2\right), \quad \boldsymbol{S} = \boldsymbol{S}_1 + \boldsymbol{S}_2$$

where $S \in \{0, 1\}$. In conclusion

$$\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 = \begin{cases} \frac{1}{4} & \text{triplets :} \quad \left|\uparrow\uparrow\right\rangle, \left|\downarrow\downarrow\right\rangle, \frac{1}{\sqrt{2}}\left(\left|\uparrow\downarrow\right\rangle + \left|\downarrow\uparrow\right\rangle\right) \\ \\ -\frac{3}{4} & \text{singlet :} \quad \frac{1}{\sqrt{2}}\left(\left|\uparrow\downarrow\right\rangle - \left|\downarrow\uparrow\right\rangle\right) \end{cases}$$

Generally

$$S_1 \otimes S_2 = |S_1 - S_2| \oplus (|S_1 - S_2| + 1) \oplus \cdots \oplus (S_1 + S_2)$$

ISOLATED MAGNETIC MOMENTS

By beginning with the Hamiltonian for an electron:

$$\hat{H} = \sum_i \left(\frac{\|\sigma \cdot (\boldsymbol{p}_i + e\boldsymbol{A}(\boldsymbol{r}_i))\|^2}{2m_e} + V_i \right)$$

you can show that

$$\hat{H} = \hat{H}_0 + \mu_B \left(\boldsymbol{L} + g_s \boldsymbol{S}\right) \cdot \boldsymbol{B} + \frac{e^2}{8m_e} \sum_i \left(\boldsymbol{B} \times \boldsymbol{r}_i\right)^2$$

in the symmetric gauge, where

$$\hat{H}_0 = \sum_i \left(\frac{p_i^2}{2m_e} + V_i \right)$$

The first term that is added to $\hat{H}_0$ is the paramagnetic term, and the second is the diamagnetic term.

Diamagnetism

The diamagnetic term has an expectation value of

$$E_{\text{dia}} = \frac{e^2 B^2}{8m} \sum_i \langle x_i^2 + y_i^2 \rangle = \frac{e^2 B^2}{12m} \sum_i \langle r_i^2 \rangle$$

where the final equality is only true if we assume spherical symmetry. The magnetisation is then given by

$$M = -\frac{\partial F}{\partial B} = -\frac{N}{V} \frac{\partial E_{\text{dia}}}{\partial B} = -\frac{N e^2 B}{6 m_e V} \sum_i \langle r_i^2 \rangle$$

For weak fields (or small susceptibilities) we can use $\chi = \frac{\partial M}{\partial H} \approx \mu_0 \frac{\partial M}{\partial B}$:

$$\chi = -\frac{N}{V} \frac{e^2 \mu_0}{6 m_e} \sum_i \langle r_i^2 \rangle$$

the sum $\sum_i \langle r_i^2 \rangle$ goes over all electrons in the atomic shell.

Paramagnetism

As we have seen, the magnetic moment of an atom is, primarily, associated with the total orbital angular momentum of the electrons:

$$\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$$

The partition function for the quantum mechanical description is

$$Z = \sum_{m_J = -J}^{J} \exp\left(\frac{m_J g_J \mu_B B}{k_B T} \right)$$

which gives us $\langle m_J \rangle$ under thermodynamic equilibrium, and hence

$$M = n g_J \mu_B \langle m_J \rangle = n k_B T \frac{\partial \ln Z}{\partial B}$$

Using the geometric series and defining the *Brillouin function*:

$$B_J(y) = \frac{2J+1}{2J} \coth\left(\frac{(2J+1)\, y}{2J} \right) - \frac{1}{2J} \coth\left(\frac{y}{2J} \right)$$

as well as the saturation magnetisation:

$$M_s = n g_J \mu_B J$$

it can be shown that

$$M = M_s B_J \left(\frac{g_J \mu_B J B}{k_B T} \right)$$

It is noteworthy that $B_{1/2}(y) = \tanh(y)$ and $B_\infty(y) = L(y)$, where

$$L(y) = \coth(y) - \frac{1}{y}$$

is the *Langevin function*, which is the semiclassical result.

For weak fields[*], where we can treat the Brillouin as linear:

$$B_J(y) = \frac{(J+1)y}{3J} + \mathcal{O}(y^3)$$

we can calculate the susceptibility:

$$\chi = \frac{M}{H} \approx \frac{\mu_0 M}{B} = \frac{n\mu_0\mu_{\text{eff}}^2}{3k_BT}, \quad \mu_{\text{eff}} = g_J\mu_B\sqrt{J(J+1)}$$

and

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

We see that this model is in agreement with the Curie law, which predicts that $\chi \sim T^{-1}$.

Hund's rules and the ionic ground state

The non-relativistic limit of the Dirac equation gives us, among other terms, a term that couples the angular momentum to the spin of an electron: $\boldsymbol{L} \cdot \boldsymbol{S}$. This interaction leads to the fine structure of atoms. We treat this exactly how we treated the coupling of two spins:

$$\lambda\langle \boldsymbol{L} \cdot \boldsymbol{S}\rangle = \frac{\lambda}{2}\left(J(J+1) - S(S+1) - L(L+1)\right)$$

where $J = |L-S|, |L-S|+1, \dots, L+S \overset{S=1/2}{=} L \pm 1/2$. This leads to the *Landé interval rule*:

$$E_J - E_{J-1} = \lambda J$$

We see that depending on the sign of λ the ground state will either have $J_{\text{gs}} = \max\{J\}$ or $J_{\text{gs}} = \min\{J\}$: this is exactly what Hund's third rule says.

Hund's rule

For *equivalent electrons* the ground state is found by:

1. Maximising the spin-multiplicity and hence S of the shell.

2. Maximising the angular momentum of the shell

3. Minimising J if the shell is under half-filled and otherwise maximising J.

These rules do not always work, but usually give a good indication of what the ground state is.

For instance Dy^{3+} has an outer shell of $4f^9$. $f = 3$ therefore the Pauli exclusion principle doesn't allow for more than 7 spins to point upwards, therefore $S = 5/2$. The seven spin up electrons also have $L = 0$ therefore we maximise L by letting the two spin down electrons have $m_L = 3$ and $m_L = 2$, so $L = 5 = H$. The shell is over half-full so we maximise $J = 15/2$:

$$4f^9 \quad \rightsquigarrow \quad {}^6H_{15/2}$$

This only holds in the LS-coupling scheme, where S, L, J are good quantum numbers. For jj-coupling we would refer to levels using $(j_1, j_2)_J$ tuples. The LS-coupling scheme is valid when the spin-orbit coupling can be treated as a perturbation to the residual electrostatic interaction.

CRYSTAL FIELDS

In order to describe the magnetic properties of crystals it is necessary to investigate how magnetic moments interact with their surroundings. Particularly when the surrounding atoms are arranged in a crystal structure.

We will consider a d-orbital in both an octahedral and tetrahedral crystal structure. The former has atoms placed on the axes with respect to the atom we are looking at, which means that the d_z^2 and $d_{x^2-y^2}$ orbitals overlap (these point along the axes), whereas the remaining 3 orbitals do not overlap. We denote the orbitals that point along the axes as e_g and those that do not as t_{2g}. The energy splitting between e_g and t_{2g} will be given by some energy Δ, and $E(e_g) - E_{\text{free}} = 3\Delta/5$ whereas $E(t_{2g}) - E_{\text{free}} = -2\Delta/5$.

The tetrahedral splitting is similar, however now it is the t_{2g} that overlap, and hence $E(t_{2g}) - E_{\text{free}} = 2\Delta/5$, whereas $E(e_g) - E_{\text{free}} = -3\Delta/5$.

Orbital Quenching

For strong crystal fields (stronger than the spin-orbit interaction) the half-filled and filled orbitals have $L = 0$, this effect is due to orbital quenching. Assuming the ground state is non-degenerate, which is easily realised by the crystal-field splitting it is also a real function. $\hat{L}$ is an imaginary operator therefore $\langle \hat{L}\rangle = 0$.

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[*] The quantity $k_BT/\mu_B \sim 460$T at room temperature, so we're essentially always in the weak field limit.

The Jahn-Teller effect

The magnetic properties of a material can affect the structure of the material. A distortion of the crystal structure can decrease/increase the overlap of orbitals and therefore lower/increase the energy. Let us assume that this energy is linear in the distortion, and furthermore assume that the energy required to distort the crystal is quadratic in the distortion. This gives:

$$E(Q) = \pm AQ + \frac{1}{2}M\omega^2Q^2 \quad \rightsquigarrow \quad Q_{\text{min}} = \frac{\mp A}{M\omega^2}$$

This simple analysis implies that a distortion can cause the crystal structure to change, such that the energy goes from one local minimum to another: this is the Jahn-Teller effect.

INTERACTIONS

We would like to explain the long range order of ferro- and anti-ferromagnets, and will look at two interactions: the magnetic dipolar interaction, which is too small to be relevant at room temperature and the exchange interaction which is what causes magnetic ordering.

Magnetic dipolar interaction

The energy of the interaction between two magnetic dipoles is given by

$$E = \frac{\mu_0}{4\pi r^3}\left(\boldsymbol{\mu}_1\cdot\boldsymbol{\mu}_2 - \frac{3}{r^2}(\boldsymbol{\mu}_1\cdot\boldsymbol{r})(\boldsymbol{\mu}_2\cdot\boldsymbol{r})\right)$$

which for r of about one Angstrom is $E \sim 60\mu$eV and hence far too small to result in macroscopic ordering at room temperature. Note that $k_BT \approx 26$meV at room temperature which corresponds to the phononic energy.

Exchange interaction

Let us consider two identical atoms, that interact through the following Hamiltonian:

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{\text{int}}$$

where $\hat{H}_i\,|i\rangle = E_i\,|i\rangle$ and $\hat{H}_{\text{int}}$ is the interaction between the two atoms. This interaction can be treated with first order perturbation theory, which first of all gives us new wavefunctions:

$$|\psi_S\rangle\,\chi_A = \frac{1}{\sqrt{2}}\left(|\psi_1(\boldsymbol{r}_1)\psi_2(\boldsymbol{r}_2)\rangle + |\psi_1(\boldsymbol{r}_2)\psi_2(\boldsymbol{r}_1)\rangle\right)\chi_A$$

$$|\psi_A\rangle\,\chi_S = \frac{1}{\sqrt{2}}\left(|\psi_1(\boldsymbol{r}_1)\psi_2(\boldsymbol{r}_2)\rangle - |\psi_1(\boldsymbol{r}_2)\psi_2(\boldsymbol{r}_1)\rangle\right)\chi_S$$

where I have included the spin-wave functions that are required to make the total wave function antisymmetric under particle exchange, because electrons are fermions. This gives us two energies: the two isolated atoms split into two states, one where the electrons are in the triplet ordering (χ_S) and one where the electrons are in the singlet ordering (χ_A), *just* like what we saw with $\boldsymbol{S}_1\cdot\boldsymbol{S}_2$. Therefore, instead of writing a whole lot of integrals and complicated formulae for the exchange interaction, let us use $\boldsymbol{S}_1\cdot\boldsymbol{S}_2$ and some multiplicative constant that is calculated with the integrals:

$$\hat{H}_{\text{int}} = -2\mathtt{J}\boldsymbol{S}_1\cdot\boldsymbol{S}_2$$

where

$$\begin{aligned}\mathtt{J} &= \frac{\mathtt{V}-\mathtt{SU}}{1-\mathtt{S}^2}\\ \mathtt{U} &\equiv \int \mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2\hat{H}_{\text{int}}|\psi_1(\boldsymbol{r}_1)|^2|\psi_2(\boldsymbol{r}_2)|^2\\ \mathtt{V} &\equiv \int \mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2\hat{H}_{\text{int}}\psi_1^*(\boldsymbol{r}_2)\psi_2^*(\boldsymbol{r}_1)\psi_1(\boldsymbol{r}_1)\psi_2(\boldsymbol{r}_2)\\ \mathtt{S} &\equiv \int \mathrm{d}\boldsymbol{r}\psi_1^*(\boldsymbol{r})\psi_2(\boldsymbol{r})\end{aligned}$$

This is the interaction between two atoms, however, if there are many atoms in, for example, a crystal structure, one would want to include all interactions:

$$\hat{H} = -\sum_{ij}\mathtt{J}_{ij}\boldsymbol{S}_i\cdot\boldsymbol{S}_j$$

this is the **Heisenberg model**.

However, for many materials $\langle r\rangle < d$ where d is the interatomic spacing, which implies that $\mathtt{S}\approx 0$. Furthermore the large interatomic distance would imply that $\hat{H}_{\text{int}}$ is negligible and hence $\mathtt{V}\approx 0$: we cannot explain the magnetic properties of some solids due to the direct exchange[†]. In many materials it is necessary to consider some kind of indirect exchange interaction.

Superexchange

[†] exchange between neighbouring atoms

In a number of ionic solids there is an indirect exchange, where the electrons "communicate"non-locally: superexchange. Non-neighbouring ions experience the exchange interaction, because the electrons delocalise to increase their kinetic energy. Let us consider a simple cubic crystal structure that has two atoms in the unit cell, say O and Mn. Mn has a single unpaired electron and O has a pair of electrons. Due to this superexchange it is beneficial for the next-neighbouring Mn atoms to have anti-aligned spins, such that their electrons can delocalise without the Pauli exclusion principle "acting". The oxygen atom mediates the interaction between the unpaired electrons on the manganese atoms.

Indirect exchange in metals

In metals the conduction electrons mediate the exchange interaction between metallic ions. This is the RKKY interaction (also known as the itinerant exchange). We will show later that

$$\mathrm{J} \sim r^{-3}\cos(2k_F r)$$

ORDER AND MAGNETIC STRUCTURES

Ferromagnetism

For a ferromagnet in a magnetic field the Hamiltonian is

$$\hat{H} = -\sum_{ij} \mathrm{J}_{ij} \boldsymbol{S}_i \cdot \boldsymbol{S}_j + g\mu_B \sum_j \boldsymbol{S}_j \cdot \boldsymbol{B}$$

For magnetic ordering we would require that the nearest neighbour exchange constant is positive. The first term is very difficult to evaluate, however, for ferromagnetism we can use the Weiss model, which defines an effective molecular field at the i-th site:

$$\boldsymbol{B}_{\mathrm{mf}} = -\frac{2}{g\mu_B}\sum_j \mathrm{J}_{ij}\boldsymbol{S}_j$$

Which simplifies the Hamiltonian to

$$\hat{H} = g\mu_B \sum_i \boldsymbol{S}_i \cdot (\boldsymbol{B} + \boldsymbol{B}_{\mathrm{mf}})$$

The molecular field is due to the alignment of magnetic moments, and therefore we can assume that $\boldsymbol{B}_{\mathrm{mf}} = \lambda\boldsymbol{M}$. The analysis in the book ignores L until now. But it is clear that S and L behave the same way in a magnetic field, therefore we can replace $\boldsymbol{S}_i \rightsquigarrow \boldsymbol{J}_i$. This brings us back to the Brillouin function:

$$M = M_s B_J(y), \quad y \equiv \frac{g_J\mu_B J(B+\lambda M)}{k_B T}$$

This can only be solved numerically. However, suppose that the magnetic energy is much smaller than the thermal energy: $\mu_B(B+\lambda M) \ll \frac{k_B T}{g_J J}$ and hence we can use the first order approximation of the Brillouin function:

$$M \approx M_s \frac{g_J\mu_B(J+1)(B+\lambda M)}{3k_B T}$$

above the Curie-temperature, $T \geq T_C$, where

$$T_C = \frac{g_J\mu_B(J+1)\lambda M_s}{3k_B}$$

hence

$$M \approx \frac{T_C}{T}\left(\frac{B}{\lambda} + M\right) \quad \rightsquigarrow \quad M = \frac{T_C B}{\lambda(T-T_C)}$$

For small B it holds that $\chi = \frac{\mu_0 M}{B}$, which implies that

$$\chi \sim \frac{1}{T-T_C}, \quad T > T_C$$

which is the **Curie-Weiss** law.

Plotting the numerical solution to M/M_s as a function of T/T_C will give a graph that looks similar to the first quadrant of the unit circle (though not quite circular)[‡]. This shows that the magnetisation will decrease as a function of T/T_C, and reach zero at $T = T_C$. The magnetisation is zero for $T \geq T_C$, which hints toward the fact that the magnetisation is an order parameter for magnetism.

Origin of the molecular field

The molecular field is what gives rise to spontaneous magnetisation, and hence ferromagnetism. Weiss could not obtain a large enough value of λ to describe nature, because he only considered dipole fields. It is, as we've seen, the exchange interaction that drives the spontaneous magnetisation. Using our description above we can show that

$$\lambda = \frac{2z\mathrm{J}}{ng^2\mu_B^2}$$

where z is the number of neighbouring atoms, which implies that

$$T_C = \frac{2z\mathrm{J}J(J+1)}{3k_B}$$

Antiferromagnetism

[‡] See Figure 5.3 in the book

The description of antiferromagnetism requires us to overlay two ferromagnetic lattices.

$$B_\pm = -|\lambda| M_\mp$$

Assuming the sub-lattices are identical we have that $|M_+| = |M_-| = M$, and hence

$$M = M_s B_J \left(\frac{g_J \mu_B J |\lambda| M}{k_B T} \right)$$

just like before. However, due to the opposite sign of λ, which now is negative, we must switch the sign of T_C everywhere: let us define the **Néel Temperature** as $T_N = -T_C$ for anti-ferromagnets:

$$\chi \sim \frac{1}{T + T_N}$$

This leads to a generalisation, where we instead use the *Weiss temperature*, θ:

$$\chi \sim \frac{1}{T-\theta}, \quad \theta \begin{cases} > 0 : & \text{ferromagnetism} \\ = 0 : & \text{paramagnetism} \\ < 0 : & \text{anti}-\text{ferromagnetism} \end{cases}$$

Ferrimagnetism

This is very similar to anti-ferromagnetism, however now the sublattices are not equivalent, and hence the atoms can have different magnetic moments. This means that the magnetisation can be non-zero, even though there are as many magnetic moments pointing upwards as there are moments pointing downwards.

Helical Order

In many rare earth metals the atoms lie in planes, which can lead to helical order, where the ferromagnetic planes are rotated an angle θ with respect to one another:

$$\cos\theta = -\frac{\mathrm{J}_1}{4\mathrm{J}_2}$$

where J_1 is the nearest neighbour coupling and J_2 is the next-to-nearest neighbour coupling.

LANDAU THEORY

Landau theory is a mean-field theory[§] that describes the Helmholtz free energy, F, as a polynomial expansion.

Let us first discuss the Helmholtz free energy and why a system will minimise it. We know from thermodynamics that

$$\mathrm{d}S_{\text{universe}} = \mathrm{d}S_{\text{system}} + \mathrm{d}S_{\text{surroundings}} \geq 0$$

For constant volume and particle number this gives us that

$$\mathrm{d}S_{\text{universe}} = \mathrm{d}S_{\text{system}} - T^{-1}\mathrm{d}U_{\text{system}} = -T^{-1}\mathrm{d}F_{\text{system}}$$

Thus for constant temperature, we maximise the universe's entropy by minimising the system's free energy.

In the case of ferromagnetism the order parameter is the magnetisation, M. The Helmholtz free energy is invariant under time-reversal, therefore we can conclude that the expansion only includes even terms of M. The simplest expansion that produces a *global* minimum that is non-trivial is

$$F = F_0 + aM^2 + bM^4$$

where $a = a_0(T - T_C)$ and $b > 0$: this ensures that F has a global minimum below the Curie-temperature, which will allow for magnetic ordering: non-zero magnetisation. The linear expansion of $a(T)$ naturally only holds near the Curie-temperature. Equation is minimised for:

$$M \in \left\{ 0, \pm\sqrt{\frac{a_0(T_C - T)}{2b}} \right\}$$

In order to evaluate which of these minima are the global minimum we must calculate the free energy:

$$F(M=0) = F_0, \quad F(\pm M_0) = F_0 - \frac{a_0^2}{4b}(T - T_C)^2$$

thus the non-zero minima are equally favourable. The system has to spontaneously choose a magnetisation direction.

Using this theory we can also find an expression for the susceptibility of ferromagnets, by including another term[¶]:

$$F = F_0 + aM^2 + bM^4 - HM$$

which has different minima above and below the Curie-temperature:

$$\chi = \begin{cases} \frac{1}{2a_0(T-T_C)} & T > T_C \\ \frac{1}{4a_0(T_C-T)} & T < T_C \end{cases}$$

[§] A macroscopic model that doesn't consider the microscopic information about the field, such as individual magnetic moments.

[¶] This corresponds to $\boldsymbol{J} \cdot \boldsymbol{B}$ in our Hamiltonian: the free energy is minimised if the magnetisation points in the same direction as the applied field

The entropy under constant volume and applied field is given by

$$S = -\frac{\partial F}{\partial T} = \begin{cases} S_0 & T > T_C \\ S_0 - \frac{a_0^2(T_C - T)}{2b} & T < T_C \end{cases}$$

and from here we can calculate the heat capacity:

$$c = T\frac{\partial S}{\partial T} = \begin{cases} c_0 \\ c_0 + \frac{a_0^2 T}{2b} \end{cases}$$

This is a second order phase transition, because there is a discontinuity in the second derivative of the Helmholtz free energy.

A first order transition can be described by including

$$F = F_0 + aM^2 + bM^4 + cM^6$$

and we now require $c > 0$ and that b changes sign at some temperature. At this temperature there will be a first order transition.

MEAN-FIELD THEORY

As we discussed previously, we can simplify the Heisenberg model, by assuming that the spin-spin interaction can be described using a mean field, B_{mf}:

$$\hat{H} = -\mathrm{J}\sum_{\langle ij\rangle} \boldsymbol{S}_i \cdot \boldsymbol{S}_j \approx -\frac{2\mathrm{J}zM}{g\mu_B n}\sum_i S_i^z$$

where we've let $\boldsymbol{B}_{\text{mf}} \parallel \hat{\boldsymbol{z}}$ and z is the number of nearest neighbours. The mean field is given by

$$B_{\text{mf}} = -\frac{2\mathrm{J}zM}{ng^2\mu_B^2}$$

and hence we once again get a self-consistent equation:

$$M = \frac{g\mu_B n}{2}\tanh\left(\frac{\beta \mathrm{J}zM}{ng\mu_B}\right)$$

Let us now solve this equation up to third order:

$$M = \frac{g\mu_B n}{2}\left(\frac{\beta \mathrm{J}zM}{ng\mu_B} - \frac{1}{3}\left(\frac{\beta \mathrm{J}zM}{ng\mu_B}\right)^3\right)$$
$$\rightsquigarrow \quad M = \frac{ng\mu_B T}{2T_C}\sqrt{\frac{3(T_C - T)}{T_C}}$$

This predicts $M \sim \sqrt{T_C - T}$ near the Curie-temperature, just as Landau theory did. Using the magnetisation we can now calculate the partition function, and from there other thermodynamic quantities. For instance:

$$\langle E\rangle = -\frac{k_B T M}{M_s}\tanh\left(\frac{T_C M}{T M_s}\right), \quad M_s = \frac{g\mu_B n}{2}$$

and

$$c = k_B\left(\frac{T_C M}{M_s}\right)^2 \operatorname{sech}^2\left(\frac{T_C M}{T M_s}\right)$$

An interesting side note is that using the mean-field Hamiltonian in the partition function gives us the free energy, whose minimum is exactly when Equation holds.

Goldstone modes and the energy dispersion

Let us solve the Heisenberg Hamiltonian for a 1D chain, using the Fourier transformation. Let us consider a 1D chain of N moments, and furthermore let $|j\rangle = S_j^- |0\rangle$: we excited the ferromagnetic ground state by lowering a spin at the j-th site. First we need that

$$S^- |SS\rangle = \sqrt{2S}\,|SS-1\rangle$$
$$S^+ |SS-1\rangle = \sqrt{2S}\,|SS\rangle$$

and defining the Fourier transform of $|j\rangle$:

$$|q\rangle = \frac{1}{\sqrt{N}}\sum_j e^{iqr_j}|j\rangle$$

we get that

$$H|q\rangle = 2\mathrm{J}S\left(-NS + 2(1-\cos(qa))\right)|q\rangle$$

The long wave spin waves that emerge for small q are **Goldstone modes:**

> **Goldstone modes** are long wavelength modes that appear when a continuous symmetry is broken spontaneously.

Our continuous symmetry is the rotational symmetry of M, which is broken spontaneously when the material "chooses"a magnetisation direction.

The particle that carries the spin waves is the **magnon**, which is a boson** Therefore the relevant distribution function for magnons is the Bose-Einstein distribution

---

** Most likely because $\frac{1}{2} \otimes \frac{1}{2} = 0 \oplus 1$ and only 1 has spin.

function, from which we can calculate the total density of magnons:

$$n_{\text{magnon}} = \int_0^\infty \frac{g(\omega)\mathrm{d}\omega}{\exp\left(\frac{\hbar\omega}{k_BT}\right) - 1}$$

Converting this integral into a dimensionless integral:

$$n_{\text{magnon}} = \left(\frac{k_BT}{\hbar}\right)^{3/2} \int_0^\infty \frac{x^{1/2}}{e^x - 1} \sim T^{3/2}$$

Each magnon reduces total magnetisation by $g_s\mu_B$ (they are bosons, remember), therefore:

$$\frac{M(0) - M(T)}{M(0)} \sim T^{3/2}$$

which is **Bloch's $T^{3/2}$ law**.

MAGNETISM IN METALS

If we ignore electron-electron interactions we can describe the electrons in metals using the **nearly free electron model**, which treats the lattice as a perturbation to the free electron Hamiltonian.

In 3D the density of states is:

$$g(k)\mathrm{d}k = \left(\frac{L}{2\pi}\right)^3 8\pi k^2\mathrm{d}k = \frac{Vk^2}{\pi^2}\mathrm{d}k$$

where the additional factor two comes from spin degeneracy. From here we can calculate the dependence of N on the fermi energy at $T = 0$:

$$N = \int_0^{k_F} \mathrm{d}k g(k) = \frac{Vk_F^3}{3\pi^2} \quad \rightsquigarrow \quad k_F^3 = 3\pi^2 n$$

Naturally

$$E_F = \frac{\hbar^2 k_F^2}{2m} \quad \rightsquigarrow \quad g(E_F) = \frac{3}{2}\frac{n}{E_F} = \frac{3}{2}\frac{k_F^3}{3\pi^2 E_F}$$

For $T > 0$ the implicit Heaviside function used in the integral for N becomes a Fermi-Dirac distribution function:

$$f_{\text{FD}}(E, \mu) = \frac{1}{e^{(E - \mu)/k_BT} + 1}$$

where $\lim_{T\to 0}\mu(T) = E_F$. When $f_{\text{FD}}(E, \mu) \approx \Theta(\mu - E)$, which is nearly always the case for metals that are below their melting temperature, it is said that the electrons are in the *degenerate limit.* In the non-degenerate limit, which corresponds to $(E - \mu) \gg k_BT$ the Fermi-Dirac distribution becomes asymptotic to the Boltzmann distribution $e^{-(E - \mu)/k_BT}$. The Fermi energy, E_F is equal to the chemical potential at $T = 0$, but for non-zero temperatures we must use the Sommerfeld approximation to find that:

$$\mu(T) = E_F\left(1 - \frac{\pi^2}{12}\left(\frac{k_BT}{E_F}\right)^2 + \mathcal{O}\left(\left(\frac{k_BT}{E_F}\right)^4\right)\right)$$

Pauli Paramagnetism

Electrons are negatively charged and therefore their magnetic moments point opposite their spin. Which means that if the magnetic moment aligns with the magnetic field, then the spin anti-aligns. Let the magnetic field point "downwards"so that it is favourable for spins to point upwards. Therefore the application of a magnetic field will move some spins from the down state to the up state:

$$n_\uparrow = \frac{1}{2}\int_0^\infty g(E + \mu_B B) f_{\text{FD}}(E)\mathrm{d}E$$

$$n_\downarrow = \frac{1}{2}\int_0^\infty g(E - \mu_B B) f_{\text{FD}}(E)\mathrm{d}E$$

The magnetisation is

$$M = \mu_B(n_\uparrow - n_\downarrow) \approx \mu_B^2 B \int_0^\infty \frac{\mathrm{d}g}{\mathrm{d}E} f_{\text{FD}}(E)\mathrm{d}E$$

where we have used that B is small. Now, using integration by parts and the fact that the boundary terms are equal to zero we get

$$M \approx -\mu_B^2 B \int_0^\infty \frac{\mathrm{d}f}{\mathrm{d}E} g(E)\mathrm{d}E$$

In the degenerate limit $-f' = \delta(E - E_F)$:

$$\chi = \frac{\mu_0 M}{B} = \mu_0\mu_B^2 g(E_F)$$

whereas in the non-degenerate limit:

$$-\frac{\mathrm{d}f}{\mathrm{d}E} = \frac{f}{k_BT}$$

and hence

$$\chi = \frac{n\mu_0\mu_B^2}{k_BT}$$

following the Curie-law.

Spontaneously split bands

Let us consider a ferromagnetic material, where the molecular field is given by λM. Blundell argues that this molecular field will magnetise the material further, which may lead to spontaneous ferromagnetism. Blundell continues to try and establish whether (or how) a ferromagnetic system can save energy by being in the ferromagnetic state.

The potential energy is

$$\Delta V = -\int_0^M \mu_0 \lambda M' \mathrm{d}M' = -\frac{1}{2}\mu_0 \lambda M^2 = -\frac{1}{2}\mu_0 \mu_B^2 \lambda (n_\uparrow - n_\downarrow)^2$$

Let us write that as

$$\Delta V = -\frac{1}{2} U g^2(E_F) \delta E^2$$

where U is a measure of the Coulomb interaction and δE is the energy gained by spin flipping. The "kinetic"energy is

$$\Delta T = \frac{1}{2} g(E_F) \delta E^2$$

Thus the total change in energy is

$$\Delta E = \frac{1}{2} g(E_F) \delta E^2 \left(1 - U g(E_F)\right)$$

therefore spontaneous ferromagnetism is beneficial if $Ug(E_F) > 1$, which is known as the **Stoner criterion**. From this energy shift we can calculate the susceptibility:

$$\chi = \frac{\chi_{\mathrm{P}}}{1 - Ug(E_F)}$$

For $0 < 1 - Ug(E_F) < 1$ we have a so-called *Stoner enhancement.*

LANDAU LEVELS

Let us consider a free electron in a magnetic field. Using the Landau gauge, the vector potential for a field pointing along the z axis is:

$$\boldsymbol{A} = Bx\hat{\boldsymbol{y}}$$

thus the Schrödinger Equation is:

$$\frac{1}{2m_e}\left(-\hbar^2 \frac{\partial^2}{\partial x^2} + \left(-i\hbar \frac{\partial}{\partial y} + eBx\right)^2 - \hbar^2 \frac{\partial^2}{\partial z^2}\right)\psi = E\psi$$

We still have that $[p_y, H] = 0$ and $[p_z, H] = 0$, therefore we can write our wavefunction as

$$\psi = u(x) e^{i(k_y y + k_z z)}$$

which means

$$\hat{H} = \frac{p_x^2}{2m_e} + \frac{1}{2} m \omega_c^2 (x - x_0)^2 + \frac{\hbar^2 k_z^2}{2m_e}$$

where we've defined

$$\omega_c = \frac{eB}{m_e}, \quad x_0 = -\frac{\hbar k_y}{eB}$$

This is the dispersion of a free electron and a harmonic oscillator:

$$E = \left(\ell + \frac{1}{2}\right)\hbar\omega_c + \frac{\hbar^2 k_z^2}{2m_e}, \quad \ell \in \mathbb{N}^0$$

It is not visible in this formula, but the system has cylindrical symmetry: the states form Landau tubes, parallel to the magnetic field in reciprocal space.

Landau Diamagnetism

The density of states for Landau levels is

$$g(E) = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{\hbar\omega_c}{2} \sum_{n=0}^{n_{\max}} \left(E - \left(n + \frac{1}{2}\right)\hbar\omega_c\right)^{-1/2}$$

Using this in $E = \int \varepsilon g(\varepsilon) \mathrm{d}\varepsilon$ we get that

$$E = \frac{3NE_F}{5} - \frac{V}{24\pi^2} e^2 B^2 \frac{k_F}{2m_e}$$

which in turn gives us a *negative* contribution to the susceptibility:

$$\chi_{\mathrm{Landau}} = \frac{\mu_0}{V}\frac{\partial^2 E}{\partial B^2} = -\frac{\mu_0 e^2 k_F}{3m_e}\frac{1}{4\pi^2} = -\frac{\mu_0 \mu_B^2}{3} g(E_F)$$

precisely one third of the value of the Pauli susceptibility.

Momentum-dependent susceptibility

Let us apply a sinusoidal magnetic field to an itinerant gas:

$$\boldsymbol{H}(\boldsymbol{r}) = \boldsymbol{H}_{\boldsymbol{q}} \cos(\boldsymbol{q} \cdot \boldsymbol{r})$$

Leading to a perturbation:

$$\hat{H}' = \pm \frac{g\mu_0\mu_B}{2} |\boldsymbol{H}_{\boldsymbol{q}}| \cos(\boldsymbol{q} \cdot \boldsymbol{r})$$

The first order correction to the wave function is

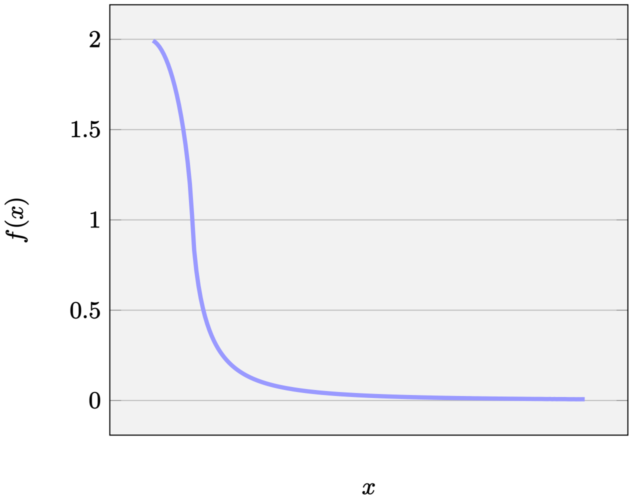
$$\frac{1}{\sqrt{V}}\left(e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \pm \frac{g\mu_0\mu_B H_{\boldsymbol{q}}}{4}\right)\left(\frac{e^{i(\boldsymbol{k}+\boldsymbol{q})\cdot\boldsymbol{r}}}{E_{\boldsymbol{k}+\boldsymbol{q}} - E_{\boldsymbol{k}}} + \frac{e^{i(\boldsymbol{k}-\boldsymbol{q})\cdot\boldsymbol{r}}}{E_{\boldsymbol{k}-\boldsymbol{q}} - E_{\boldsymbol{k}}}\right)|\pm\rangle$$

this can be used to get an expression for the magnetisation – the norm squared of the spin up and spin down electrons is proportional to the density. Finally we integrate over $\boldsymbol{k}$-space, which removes the k-dependence, and we end up with a susceptibility:

$$\chi_{\boldsymbol{q}} = \chi_P f\left(\frac{q}{2k_F}\right)$$

where

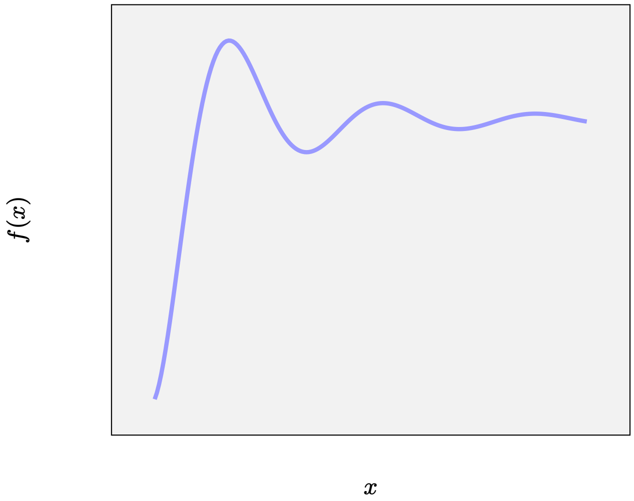
$$f(x) = \frac{1}{2}\left(1 + \frac{1-x^2}{2x}\log\left|\frac{1+x}{1-x}\right|\right)$$



RKKY-INTERACTION

We have the susceptibility's behaviour in reciprocal space, so let us calculate the inverse Fourier transform:

$$\begin{aligned}\chi(\boldsymbol{r}) = \mathcal{F}^{-1}\left\{\chi_{\boldsymbol{q}}\right\} &= \frac{1}{(2\pi)^3}\int \mathrm{d}^3\boldsymbol{q}\ \chi_{\boldsymbol{q}} e^{i\boldsymbol{q}\cdot\boldsymbol{r}} \\ &= \frac{2k_F^3\chi_P}{\pi}F(2k_F r)\end{aligned}$$



Spin density waves

Just like for the electron gas treated with q-independent excitations, the q-dependent susceptibility experiences a Stoner enhancement:

$$\chi_{\boldsymbol{q}} = \frac{\chi^0_{\boldsymbol{q}}}{1-\alpha\chi^0_{\boldsymbol{q}}}$$

where $\chi^0_{\boldsymbol{q}}$ is the expression we found previously. It may happen that $\chi^0_{\boldsymbol{q}}$ has a maximum at a non-zero value of $\boldsymbol{q}$, in which case it is possible for spontaneous magnetisation to appear in the sample and we would expect spiral spin-density waves in the wave vector, $\boldsymbol{q}$. The derivation of the q dependence of $\chi_{\boldsymbol{q}}$ can be repeated in 1D and 2D: the 1D susceptibility diverges at $q = 2k_F$, which is the **Kohn anomaly**, which shows that one-dimensional electron gases are unstable to the formation of density waves with wave vector $2k_F$. This is associated with the fact that the modulation opens up a gap at the Fermi surface, which allows states with $q = 2k_F$ to lower their energy, which is an opportunity to drive the formation of a density wave, which causes it to diverge.

Kondo Effect

Below some temperature, the **Kondo temperature**, T_K, electrons screen the magnetic moments of nuclei/ions. This shields any magnetic properties of the material, and also creates quasi-bound states. These bound states increase the scattering area, which means that the resistivity has a term $-|\mathrm{J}|\ln T$ which diverges at low temperatures.

Hubbard Model

In some materials the electron-nucleus binding energy is so strong, that electrons cannot be treated as (nearly) free electrons. In this case we must use the Hubbard model, where we treat the electrons as excitations of each site, with hopping amplitudes, such that the electrons can move through the material if the Pauli-exclusion principle allows this.

$$\hat{H} = -t \sum_{\sigma,\langle ij\rangle} \left(c^\dagger_{i\sigma} c_{j\sigma} + c^\dagger_{j\sigma} c_{i\sigma} \right) + U \sum_i \left(n_{i\uparrow} + n_{i\downarrow} - 1 \right)^2$$
$$- \mu \sum_i (n_{i\uparrow} + n_{i\downarrow})$$

The first term is hopping between sites, and the second term is the Coulomb energy, which will try to move the electrons away from each other. Setting $\mu = 0$ and treating the first term as a perturbation of the second term, you can show that the effective Hamiltonian (second order) can be written as

$$H_{eff} = \frac{4t^2}{U} \sum_{\langle ij\rangle} \left(\boldsymbol{S}_i \cdot \boldsymbol{S}_j - \frac{1}{4} \right)$$

SUPERCONDUCTIVITY

For conductive (linear) materials

$$\boldsymbol{j} = \sigma \boldsymbol{E}, \quad \leftrightsquigarrow \quad \boldsymbol{E} = \rho \boldsymbol{j}$$

Generally $\rho(T)$ is an increasing function, because phononic excitations make the crystal lattice "less uniform"which increases scattering rates. For superconductors there exists a critical temperature, T_C, where

$$\rho(T) = 0, \quad T < T_C$$

However, this is not the *defining* characteristic, because there exist ideal conductors that have $\rho = 0$ without expelling magnetic flux. The defining characteristic of superconductors is the **Meissner effect**, which will be described in further detail shortly. The supercurrents in the surface of the superconductor shield any exterior magnetic field, such that $\boldsymbol{B}_{\text{int}} = 0$. This implies that $\chi = -1$. However, there exists a critical field, $\boldsymbol{H}_c$ where the superconductor begins to behave like a normal conductor again.

Choosing the London Gauge, $\nabla \cdot \boldsymbol{A} = 0$, we can write

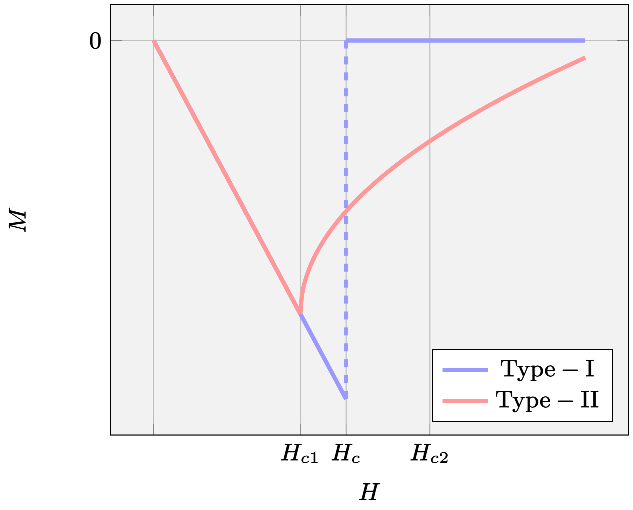
$$\boldsymbol{j} = -\frac{n_e e^2}{m} \boldsymbol{A} \quad \rightsquigarrow \quad \mathcal{L}\{\} B = \frac{1}{\lambda_L^2} \boldsymbol{B}, \quad \lambda_L \equiv \sqrt{\frac{m}{\mu_0 n_s e^2}}$$

λ_L is the penetration depth of the superconductor. The current carriers in superconductors are not electrons, but Cooper pairs, which are bosons[††]

Thermodynamics of Superconductors

$$\boldsymbol{B} = \mu_0(\boldsymbol{H} + \boldsymbol{M}) = 0 \quad \rightsquigarrow \quad \chi = -1$$

However, this only holds up to the critical field. Type-I superconductors have a discontinuity in χ at $H = H_c$, where the susceptibility abruptly falls to zero. Type-II superconductors have two critical fields: H_{c1} where χ transitions away from perfect diamagnetism continuously, and H_{c2} where superconductivity is destroyed. Above H_{c1}, M decays in the "mixed region"where there are parts that are superconducting and parts that are in the normal state.



Figur 1: *Schematic drawing of the magnetisation as a function of applied field for type-I and type-II superconductors. In the region $H_{c1} < H < H_{c2}$ vortices can exist in the type-II superconductors.*

For an *isothermal* type-I superconductor:

$$G = -\mu_0 \int_0^H M(H')\mathrm{d}H' + G_0$$

thus

$$G_\text{s}(T, H) = G_\text{s}(T, 0) + \frac{\mu_0 H^2}{2}$$

[††] $\frac{1}{2} \otimes \frac{1}{2} = 0 \oplus 1$... Although, technically, they are hard-core bosons (not to be confused with hardcore bosons).

The phase transition occurs at $H = H_c$, therefore at this applied field we have that

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

which just reflects that it is more beneficial to be in the superconducting phase below the critical field.

The phase transition is a second order transition, because the discontinuity is in the specific heat:

$$c_s - c_n\big|_{T=T_c} = 4\mu_0 \frac{H_c^2}{T_c}$$

Due to this discontinuity it is sometimes easier to find the phase transition using c, than to find where $\rho \to 0$.

Ginzburg-Landau Theory

The order parameter for superconductivity is $\psi(r) = |\psi(r)|e^{i\phi(r)}$, which can be thought of as a kind of macroscopic wave function. The free energy density is then:

$$\begin{aligned} f_s = f_n &+ \alpha(T)|\psi(r)|^2 + \frac{1}{2}\beta|\psi(r)|^4 \\ &+ \frac{1}{2m^*}\left|\left(-i\hbar\nabla + e^*\boldsymbol{A}\right)\psi\right|^2 + \frac{B^2}{2\mu_0} \end{aligned}$$

This free energy is symmetric under Gauge Transformations:

$$\{\psi(r), \boldsymbol{A}(r)\} \quad \rightsquigarrow \quad \left\{\psi(r)e^{i\theta(r)}, \boldsymbol{A} + \frac{\hbar}{e^*}\nabla\theta(r)\right\}$$

This symmetry is broken spontaneously below the critical temperature: the superconductor "picks"a specific phase.

$|\psi|$ is proportional to the density of Cooper-pairs.

Let us set $B = 0$ and minimise the free energy and only consider the homogeneous case:

$$\delta f_s = \left(\alpha(T)\psi(r) + \beta|\psi(r)|^2\psi\right)\delta\psi^* + \cdots$$

which gives us

$$|\psi|^2 = \frac{-a_0(T - T_c)}{\beta}$$

Using this and the result for the Gibbs energy difference above, we can show that

$$H_c(T) = \frac{a_0}{\sqrt{\mu_0 b}}(T_c - T)$$

near T_c. For the non-homogenous case, we have the ∇ term, which just adds on to the equation, making it look similar to a Schrödinger equation, except that it is non-linear:

$$-\frac{\hbar^2}{2m^*}\mathcal{L}\{\psi\}(r) + a(T)\psi(r) + b|\psi(r)|^2\psi(r) = 0$$

This is the **first Ginzburg-Landau equation**. For instance, this tells us about the attenuation of the order parameter close to the interface to (let us say) a vacuum:

$$\psi(x) = \psi_0 \tanh\left(\frac{x}{\sqrt{2}\xi(T)}\right), \quad \text{for} \quad x \geq 0$$

where the constant, ξ, is the *coherence length* or *healing length*.

$$\xi(T) = \sqrt{\frac{\hbar^2}{2m^*|a(T)|}}$$

For $B \neq 0$ we can just replace $\hat{\boldsymbol{p}}$ with $\hat{\boldsymbol{p}} + e^*\boldsymbol{A}$. However, we can additionally require that the free energy is minimised with respect to A, in which case we get the **second Ginzburg-Landau equation**:

$$\boldsymbol{j}_s = \frac{\hbar e^*}{2m^* i}\left(\psi\nabla\psi^* - \psi^*\nabla\psi\right) - \frac{(e^*)^2}{m^*}|\psi|^2\boldsymbol{A}$$

this looks exactly like the quantum mechanical current, however it describes a macroscopic quantity. For any shape that is topologically equivalent to a ball, if we assume that $|\psi| = \text{const.}$ and that there is a steady state, in which case $\nabla \cdot \boldsymbol{j}_s = 0$, we get that

$$\boldsymbol{j}_s = -\frac{(e^*)^2}{m^*}|\psi|^2\boldsymbol{A}$$

Another interesting artefact of superconductivity is **flux quantisation**. Consider a doughnut geometry and again assume the order parameter only varies in its phase, then it can be shown that

$$F_s = F_s^0 + \Gamma\left(\Phi - n\Phi_0\right)^2 + \Omega\Phi^2, \quad n \in \mathbb{Z}, \quad \Phi_0 = \frac{h}{2e}$$

which is minimised for $\Phi = n\Phi_0, \quad n \in \mathbb{Z}$: exactly when the flux is an integer multiple of the flux quantum. Another way of approaching the description of flux quantisation is through the London Equation:

$$\oint \boldsymbol{j}_s \cdot \mathrm{d}\boldsymbol{\ell} = \frac{e^*}{m^*}|\psi|^2 \oint \left(\hbar\nabla\phi - e^*\boldsymbol{A}\right) \cdot \mathrm{d}\boldsymbol{\ell}$$

Inside the doughnut $\boldsymbol{j}_s = \boldsymbol{0}$, so

$$\oint \boldsymbol{A} \cdot \mathbf{d}\boldsymbol{\ell} = \frac{h}{4\pi e}\oint \nabla\phi \cdot \mathrm{d}\boldsymbol{\ell} = n\left(\frac{h}{2e}\right) = n\Phi_0, \quad n \in \mathbb{Z}$$

Assuming that ϕ is single valued.

Type-I and Type-II superconductivity

The two scale lengths

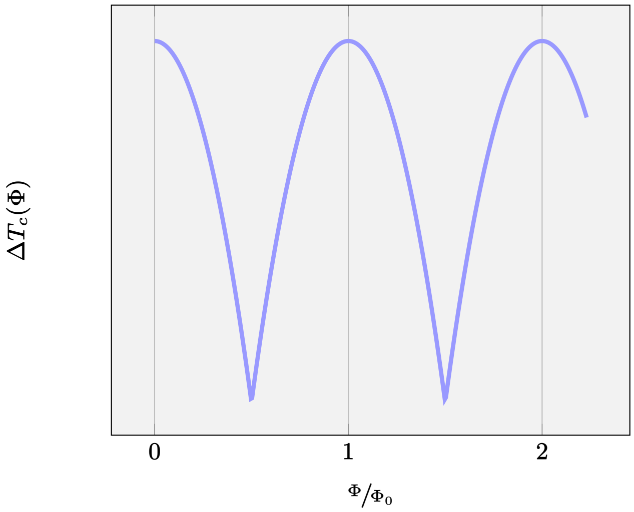
$$\lambda_L = \sqrt{\frac{m^*\beta}{\mu_0(e^*)^2 a_0(T_c - T)}}$$
$$\xi = \sqrt{\frac{\hbar^2}{2ma_0(T_c - T)}}$$

are sufficient to distinguish the two types of superconductors:

$$\kappa \equiv \frac{\lambda_L}{\xi} \begin{cases} < \frac{1}{\sqrt{2}} & \mathrm{type-I} \\ > \frac{1}{\sqrt{2}} & \mathrm{type-II} \end{cases}$$

Little-Parks Experiment

The experiment studies a thin superconducting ring, where the thickness, $d \approx \lambda_L, \xi$. The critical temperature oscillates:



Figur 2: *Change in critical temperature as a function of magnetic flux in the Little-Parks experiment. The amplitude of the oscillation is approximately* 1mK.

This result can be explained with Ginzburg-Landau theory. Consider the current in the superconductor:

$$\boldsymbol{j}_s = \frac{e^*}{m^*}|\psi|^2(\hbar\nabla\theta - e^*\boldsymbol{A}) = en_s\boldsymbol{v}_s$$

The movement of Cooper pairs corresponds to a kinetic energy, which should be included in the free energy:

$$f_s = f_n + \alpha|\psi|^2 + \frac{\beta}{2}|\psi|^4 + |\psi|^2 2m^*\|\boldsymbol{v}_s\|^2 + \frac{\|\boldsymbol{B}\|^2}{2\mu_0}$$

At equilibrium ($\delta f_s = 0$) and hence

$$|\psi|^2 = -\frac{\alpha + 2m^*\|\boldsymbol{v}_s\|^2}{\beta} = |\psi_0|^2\left(1 - \frac{2m^*\|\boldsymbol{v}_s\|^2}{|\alpha|}\right)$$

for $T < T_c$. By plugging this into the old expression for the free energy and comparing to the term above, we see that

$$v_s = \frac{\hbar}{2m^*R}\left(n - \frac{\Phi}{\Phi_0}\right)$$

Additionally we have that

$$\boldsymbol{j}_s = 2e^*|\psi_0|^2\left(1 - \frac{2m^*\|\boldsymbol{v}_s\|^2}{|\alpha|}\right)\boldsymbol{v}_s$$

at equilibrium

$$-|\alpha| = a_0(T - T_c) = -\frac{\hbar^2}{2m^*R^2}\left(n - \frac{\Phi}{\Phi_0}\right)^2$$

Interface & Surface Energies

The normal and superconducting phases can mix, or not mix, depending on whether the surface energy is positive or negative. The positive case means that the surface keeps to itself, separate from the superconducting phase, whereas negative surface energy implies that the surface states are mixed into the superconductor. The latter is type-II superconductivity.

The Gibbs free energy can be obtained with a Legendre transformation:

$$G = F - HB$$

according to Ginzburg-Landau theory, this would imply that

$$\begin{aligned} g_n(T,H) =& f_n(T,0) + \frac{1}{2\mu_0}B^2 - HB \\ =& f_n(T,0) - \frac{1}{2}\mu_0 H^2 \end{aligned}$$

because the order parameter vanishes in the normal state. For superconducting state, however, it is:

$$\begin{aligned} g_s(T,H) =& f_n(T,0) + \alpha(T)|\psi|^2 + \frac{\beta}{2}|\psi|^4 \\ &+ \frac{1}{2m^*}\left|\left(\frac{\hbar}{i}\nabla + e^*\boldsymbol{A}\right)\psi\right|^2 + \frac{1}{2\mu_0}B^2 - HB \end{aligned}$$

This implies that the "surface energy", σ_{ns}, which is the difference between G_n and G_s is at $H = H_c$:

$$\begin{aligned}\sigma_{ns} &= \int_{-\infty}^{\infty} \Delta G \mathrm{d}x \\ &= \int_{-\infty}^{\infty} \alpha(T)|\psi|^2 + \frac{\beta}{2}|\psi|^4 + \frac{1}{2m^*}\left|\left(\frac{\hbar}{i}\nabla + e^*\boldsymbol{A}\right)\psi\right|^2 \\ &+ \frac{(B-\mu_0 H_c)^2}{2\mu_0}\mathrm{d}x\end{aligned}$$

However it turns out that there are a few terms that integrate to zero, which simplifies to

$$\sigma_{ns} = \int_{-\infty}^{\infty}\left(-\frac{1}{2}\beta|\psi|^4 + \frac{(B-\mu_0 H_c)^2}{2\mu_0}\right)\mathrm{d}x$$

If the first term dominates, the surface energy is negative, which implies that we have a type-II superconductor and it is energetically beneficial to disperse surfaces within the sample. Note that this is at $H = H_c$. At $H < H_c$ we'd expect positive surface energies in type-I and in type-II we'd expect positive surface energies for $H < H_{c1}$.

Type-II Superconductors

For strong H $|\psi|^2 \ll 1$, because the strong magnetic field is in the process of destroying the superconductivity. This means we can linearise the Ginzburg Landau equation:

$$\frac{1}{2m^*}\left(\frac{\hbar}{i}\nabla + e^*\boldsymbol{A}\right)^2\psi = -\alpha\psi$$

For $B \parallel z$ and using the Landau gauge, in which case $\boldsymbol{A} = Bx\hat{\boldsymbol{y}}$, this becomes the equation for a harmonic oscillator. Therefore we conclude that

$$a_0(T - T_c) = \hbar\omega_c\left(n + \frac{1}{2}\right) + \frac{\hbar^2 k_z^2}{2m^*}, \quad \omega_c = \frac{e^* B}{m^*}$$

This implies that

$$B = \frac{-\alpha m^*}{e^*\hbar\left(n + \frac{1}{2}\right)}$$

which is maximised for $n = 0$: the superconductor can't support a stronger magnetic field and it goes into the normal state. Thus

$$H_{c2} = \frac{B}{\mu_0} = -\frac{\alpha m^*}{\hbar e^* \mu_0} = \frac{1}{\mu_0}\frac{\Phi_0}{2\pi\xi^2}, \quad \xi^2 = \frac{\hbar^2}{2m^* a_0(T_c - T)}$$

The first critical field is a bit more difficult to calculate. Let us calculate the energy of a single vortex. The current, just like the flux, is quantised, therefore we expect that the momentum is quantised such that

$$\oint \boldsymbol{p}\cdot\mathrm{d}\boldsymbol{\ell} = nh \quad \rightsquigarrow v_s = \frac{n\hbar}{m^* r}$$

Now consider the kinetic energy in the region where the supercurrent is correcting for the rogue field, i.e $\xi < r < \lambda_L$[‡‡] giving us

$$E_{\text{vortex}} = n_s^*\int_{\xi}^{\lambda_L}\frac{\pi n^2\hbar^2}{m^* r}\mathrm{d}r = \frac{\pi n_s^*\hbar^2}{m^*}\ln\kappa$$

The first vortex appears where

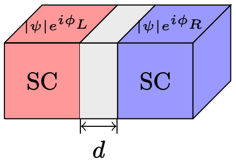
$$H_{c1}\Phi_0 = E_{\text{vortex}}$$

and hence

$$H_{c1} = \frac{\Phi_0^2}{4\pi\mu_0\lambda_L^2}\ln\kappa$$

Josephson junction:

Let us consider two superconductors separated by an insulator of thickness, d.



Figur 3: *The grey area is an insulator situated between two superconductors with order parameters $|\psi|e^{i\phi_L}$ and $|\psi|e^{i\phi_R}$.*

The dimensionless (first) Ginzburg-Landau equation is

$$\xi^2 f'' + f - f^3 = 0$$

but let us include a factor d^{-2}:

$$\left(\frac{\xi}{d}\right)^2 f'' + d^{-2}f - d^{-2}f^3 = 0$$

for $d \ll \xi$ the first term dominates, giving us a Laplace equation, the solution to which can be approximated to

$$f(x) \approx \left(\frac{1}{2} - \frac{x}{d}\right)e^{i\phi_L} + \left(\frac{1}{2} + \frac{x}{d}\right)e^{i\phi_R}$$

[‡‡] Yes in that order, because this is a type-II superconductor.

as this is a solution to the Laplace equation. Now, inserting this expression into the second Ginzburg-Landau equation for $B = 0$ gives us

$$j = \frac{2e\hbar|\psi_0|^2}{m^*\alpha}\sin\left(\phi_R - \phi_L\right)$$

This implies that if we have two superconductors separated by an insulating layer and these superconductors have order parameters that only differ by a phase factor, then current will pass through the insulating layer, *even* when the voltage difference is zero.

This effect is more closely described using Feynman's method, where we use that it is the chemical potential that sets the time-evolution of ψ[§§]:

$$-\frac{\hbar}{i}\frac{\partial\psi}{\partial t} = \mu\psi$$

However, now it is the case that the left and right order parameters are coupled. Let us couple them phenomenologically, using a first order approximation:

$$-\frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix}\psi_L \\ \psi_R\end{pmatrix} = \begin{pmatrix}\mu_L & T \\ T & \mu_R\end{pmatrix}\begin{pmatrix}\psi_L \\ \psi_R\end{pmatrix}$$

We get (by setting in and looking at the real and imaginary parts separately)

$$\frac{\partial|\psi_L|}{\partial t} = \frac{1}{\hbar}T|\psi_R|\sin(\phi_R - \phi_L)$$

This tells us about the current from the one side to the other:

$$\begin{aligned} j &= -e^*\frac{\partial|\psi_L|^2}{\partial t} = -2e^*|\psi_L||\dot{\psi}_L| \\ &= -\frac{2e^*T}{\hbar}|\psi_L||\psi_R|\sin(\phi_L - \phi_R) \end{aligned}$$

The time evolution can also be calculated from this "Schrödinger"equation:

$$\frac{\partial}{\partial t}\left(\phi_R - \phi_L\right) = \frac{1}{\hbar}\left(\mu_L - \mu_R\right)$$

which is constant when $\Delta V = 0$.

Non-zero voltage difference

In the case that $\Delta V \neq 0$ we instead get

$$\frac{\partial}{\partial t}\left(\phi_R - \phi_L\right) = \frac{2e\Delta V}{\hbar} \quad\rightsquigarrow\quad \Delta\phi = \Delta\phi_0 + \frac{2e\Delta V}{\hbar}t$$

which in turn implies that

$$j_s = j_0\sin\left(\Delta\phi_0 + \frac{2e\Delta V}{\hbar}t\right)$$

This is a very high frequency:

$$\frac{2e\Delta V}{\hbar} = \frac{\Delta V}{0.33\text{mV}}\text{THz}$$

Josephson junction in magnetic field

Consider a setup as before, but we now apply a magnetic field, parallel to the z-axis. The magnetic field attenuates exponentially within the superconductors, but remains constant in the insulating region. Suppose the interface is the yz-plane. Let $\boldsymbol{A} = A(x)\hat{\boldsymbol{y}}$.

Far inside the superconductor the current is zero, hence

$$\nabla\phi = -\frac{e^*}{\hbar}\boldsymbol{A}$$

This implies that the phase difference between two point within the same superconductor (still far inside) is given by:

$$\phi(L_2) - \phi(L_1) = \int_{L_1}^{L_2}\nabla\phi\cdot\mathrm{d}\boldsymbol{\ell} = -\frac{e^*}{\hbar}\int_{L_1}^{L_2}\boldsymbol{A}\cdot\mathrm{d}\boldsymbol{\ell}$$

And similarly far inside the right superconductor. Suppose line connecting L_i and R_i is parallel to the x-axis, and hence $\boldsymbol{A}\cdot\mathrm{d}\boldsymbol{\ell} = 0$. This implies we can add this quantity to the integral, without cost, hence:

$$\frac{e^*}{\hbar}\oint\boldsymbol{A}\cdot\mathrm{d}\boldsymbol{\ell} = 2\pi\frac{\Phi}{\Phi_0}$$

Let L_1 and R_1 be at $y = 0$ and L_2 and R_2 be at $y = y$, hence

$$\Delta\phi(y) - \Delta\phi(0) = 2\pi\frac{\Phi(y)}{\Phi_0}, \quad \Phi(y) = B(d + \lambda_L + \lambda_R)y$$

This means the current becomes y-dependent:

$$J_x(y) = J_0\sin\left(\Delta\phi_0 + 2\pi\frac{\Phi(y)}{\Phi_0}\right)$$

Integrating over y:

$$I_J = I_y\sin(\delta\phi_0)\frac{\sin\left(\pi{}^{\phi}\!/_{\phi_0}\right)}{\pi{}^{\Phi}\!/_{\Phi_0}}$$

SQUIDs

Creating a loop that links two superconductors at two points, with two insulators creates a SQUID. This device is very sensitive to magnetic flux due to the interference pattern. Thus this device measures flux in units of the flux quantum!

[§§] Is it a kind of time-dependent Ginzburg-Landau theory?

LANDAU LEVELS: REVISITED

As described by Hamiltonian mechanics (and quantum mechanics), the application of a magnetic field to an electronic gas, corresponds to the transformation:

$$-i\hbar\nabla \to -i\hbar\nabla + e\boldsymbol{A}$$

Let us consider free electrons in a box, and apply a magnetic field $\boldsymbol{B} \parallel \hat{\boldsymbol{z}}$. This can be solved in both the Landau and the symmetric gauge. We focussed on the Landau gauge:

$$\boldsymbol{A} = Bx\hat{\boldsymbol{y}}$$

This, as before, leads to a harmonic oscillator:

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{1}{2}m\omega_c^2(x-x_0)^2 + \frac{\hbar^2k_z^2}{2m}$$

and an energy of

$$E = \left(\ell + \frac{1}{2}\right)\hbar\omega + \frac{\hbar^2k_z^2}{2m}$$

k_y only decides the equilibrium position and hence does not influence the energy: degenerate in k_y. However, x_0 must be inside the sample:

$$0 < x_0 = \frac{\hbar k_y}{eB} < L_x$$

but the free electron gas has

$$k_y = \frac{2\pi n}{L_y}$$

and hence

$$n \in \mathbb{N}, \quad N = \left\{ n \in \mathbb{N} : n < \frac{L_xL_yeB}{h} \right\}$$

Ignoring boundary subtleties, note that $L_xL_yB = \Phi$ and $\Phi_0 = h/e$, so

$$N_P = \frac{\Phi}{\Phi_0}$$

where $N_P = \left\lfloor \frac{L_xL_yeB}{h} \right\rfloor$ is the degeneracy and $\Phi_0 = h/e$ for single electrons. Thus adding one state to the degenerate space corresponds to adding a flux quantum to the flux.

Density of states

The n-th Landau subband has N_n states, which is N_p multiplied by the number of k_z values. The number of k_z values between k_z and $k_z + \mathrm{d}k_z$ is $L_z/2\pi\,\mathrm{d}k_z$, and therefore

$$\mathrm{d}N_n = L_xL_yL_z\frac{2eB}{(2\pi)^2\hbar}\mathrm{d}k_z = \frac{2VeB}{(2\pi)^2\hbar}\mathrm{d}k_z$$

where the extra factor two is due to spin degeneracy. Substituting for $\mathrm{d}k_z$:

$$\mathrm{d}N_n = \frac{2VeB}{(2\pi)^2\hbar}\frac{\sqrt{2m}}{\hbar}\left(E - \left(n + \frac{1}{2}\right)\hbar\omega_c\right)^{-1/2}\mathrm{d}E$$

Now the additional factor two is because k can be negative, but E is strictly positive. So

$$g_n(E) = \frac{1}{V}\frac{\mathrm{d}N_n}{\mathrm{d}E} = \frac{\sqrt{2m}}{2\pi^2\hbar^2}eB\left(E - (n + 1/2)\,\hbar\omega_c\right)^{-1/2}$$

Summing

$$g(E) = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\frac{\hbar\omega_c}{2}\sum_{n=0}^{n_{\max}}\left(E - (n + 1/2)\,\hbar\omega_c\right)^{-1/2}$$

In reciprocal space the states of a free electron form a filled circle. When we apply a magnetic field it changes into rings, with Φ/Φ_0 states per ring.

The magnetic field slices the Fermi surface

INTEGER QUANTUM HALL EFFECT

Classically we had that

$$E_i = \rho_{ij}j_i$$

where the resistivity tensor is

$$\rho_{ij} = \rho_0\delta_{ij} + \varepsilon_{ijk}H_k, \quad \rho_0 = \frac{m}{ne^2\tau}, \quad H_k = \frac{B_k}{ne}$$

however, in the quantum limit (so low energy limit), we measure a quantisation of these quantities, that follow:

$$\rho_{xy} = \frac{h}{\xi e^2}, \quad \xi \in \mathbb{N}$$

and ρ_{xx} has a narrow spike every time ρ_{xy} transitions from one ξ to another. This implies that the Hall coefficient, H_k is quantised for low energies:

$$H_k = \frac{B_k}{ne} = \frac{h}{\xi e^2}$$

this is because $n_e = \frac{\xi N_p}{L_xL_y}$ for Landau levels, thus the transition from one step to another corresponds to the filling of a new Landau level.

This is in fact the case: every time the energy of a Landau level approaches the fermi energy it is possible for electrons to scatter across the sample, from the edge states that are going in the one direction to the edge states that are going in the other direction. The Landau levels are inert, so conduction only occurs in the edge states where the energy bands curl upwards and *cross* the fermi level.

The scattering *across* the sample causes a current drop, giving a higher on-diagonal resistivity.