

Diamagnetism and Paramagnetism

Definitions:

Magnetization $M(H)$ in the presence of an uniform magnetic field H at $T=0$ is defined as:

$$M(H) = -\frac{1}{V} \frac{\partial E_0(H)}{\partial H}$$

where $E_0(H)$ is the ground state energy. Note that H is the magnetic field felt by the substance and not the applied magnetic field B ($B=\mu_0H$).

At finite temperature T , higher energy states may be occupied with finite probability, so net magnetization is the thermal equilibrium average of magnetization of each available state:

$$M(H, T) = -\frac{\sum_n M_n(H) e^{-\beta E_n(H)}}{\sum_n e^{-\beta E_n(H)}}; \beta = (k_B T)^{-1}$$

where

$$M_n(H) = -\frac{1}{V} \frac{\partial E_n(H)}{\partial H}$$

Can also write it as

$$M(H, T) = -\frac{1}{V} \frac{\partial F}{\partial H}$$

where the magnetic Helmholtz free energy is defined by:

$$e^{-\beta F(H)} = \sum_n e^{-\beta E_n(H)}; \beta = (k_B T)^{-1}$$

The magnetic susceptibility per unit volume is defined as

$$\chi = \mu_0 \frac{\partial M}{\partial H}$$

Magnetic moment of a free atom arises due to three main factors:

1. Spin of the electrons
2. Orbital momentum of electrons
3. Change of the orbital angular momentum of electrons due to applied magnetic field.

The first two give paramagnetic contribution, the last part is diamagnetic.

How does the Hamiltonian of an atom change in the presence of a magnetic field?

1. The kinetic energy of each electron is changed

$$\mathbf{p} \rightarrow \mathbf{p} + e\mathbf{A}$$

where \mathbf{A} is the vector potential defined through $\mathbf{H} = \nabla \times \mathbf{A}$; $\nabla \cdot \mathbf{A} = 0$

Usually take \mathbf{A} to be $\mathbf{A} = -\frac{1}{2} \mathbf{r} \times \mathbf{H}$

The kinetic energy of the nucleus remains almost unchanged due its large mass.

2. The interaction energy of electron spins with the external magnetic field is added to the hamiltoninan:

$$\Delta\mathcal{H} = g_0\mu_B\mathbf{H}\cdot\mathbf{S} = g_0\mu_BHS_z$$

assuming \mathbf{H} is along the z-axis and \mathbf{S} is the net electronic spin $\mathbf{S} = \sum_i \mathbf{s}_i$

$\mu_B = \frac{\hbar e}{2m} = 9.27 \times 10^{-24} \text{ J/T}$ is the *Bohr magneton*; $g_0 \sim 2$ is the *electronic g-factor*.

The total kinetic energy is now:

$$\begin{aligned} T &= \frac{1}{2m} \sum_i (\mathbf{p} + e\mathbf{A}(r_i))^2 = \frac{1}{2m} \sum_i \left(\mathbf{p} - \frac{e}{2} \mathbf{r}_i \times \mathbf{H} \right)^2 \\ &= \frac{1}{2m} \sum_i p^2 - \frac{e}{2m} \sum_i \mathbf{p} \times \mathbf{r}_i \cdot \mathbf{H} + \frac{e^2}{8m} H^2 \sum_i (x_i^2 + y_i^2) \\ &= T_0 + \mu_B \mathbf{L} \cdot \mathbf{H} + \frac{e^2}{8m} H^2 \sum_i (x_i^2 + y_i^2) \end{aligned}$$

Where, $\hbar\mathbf{L} = \sum_i \mathbf{r}_i \times \mathbf{p}$ is the total electronic orbital angular momentum.

Adding the spin energy to this gives the change in the Hamiltonian:

$$\Delta\mathcal{H} = \mu_B(\mathbf{L} + g_0\mathbf{S}) \cdot \mathbf{H} + \frac{e^2}{8m} H^2 \sum_i (x_i^2 + y_i^2) \quad --(1)$$

The energy shifts produced by (1) are $\sim 0.1\text{meV}$ and are very small as compared to atomic energy scales ($\sim \text{eV}$). So we can use perturbation theory to calculate the change in the energy of the system due to the magnetic perturbation. Using second order perturbation theory to get terms upto second order in H:

$$E_n \rightarrow E_n + \Delta E_n$$

where the energy change ΔE_n due to the magnetic field is:

$$\Delta E_n = \langle n | \Delta\mathcal{H} | n \rangle + \sum_{n \neq \dot{n}} \frac{|\langle n | \Delta\mathcal{H} | \dot{n} \rangle|^2}{E_n - E_{\dot{n}}} \quad --(2)$$

Combining (1) and (2) we get; to second order in H

$$\Delta E_n = \mu_B \mathbf{H} \cdot \langle n | (\mathbf{L} + g_0\mathbf{S}) | n \rangle + \sum_{n \neq \dot{n}} \frac{|\langle n | \mu_B(\mathbf{L} + g_0\mathbf{S}) \cdot \mathbf{H} | \dot{n} \rangle|^2}{E_n - E_{\dot{n}}} + \frac{e^2}{8m} H^2 \left\langle n \left| \sum_i (x_i^2 + y_i^2) \right| n \right\rangle \quad --(3)$$

From this energy expression we can get the susceptibility of individual atoms, ions or molecules and also of ionic and molecular solids.

Special cases:

1. ions/atoms with all shells filled - Larmor/Langevin diamagnetism:

In ground state the net spin, angular momentum are both zero; $\mathbf{L}|0\rangle = \mathbf{S}|0\rangle = 0$; so only the third term in (3) survives. The change in the ground state energy (and usually only the ground state is occupied to any appreciable probability):

$$\Delta E_0 = \frac{e^2}{8m} H^2 \left\langle 0 \left| \sum_i (x_i^2 + y_i^2) \right| 0 \right\rangle = \frac{e^2}{12m} H^2 \left\langle 0 \left| \sum_i r_i^2 \right| 0 \right\rangle$$

The magnetic susceptibility of N such ions is:

$$\chi = \mu_0 \frac{\partial M}{\partial H} = -\mu_0 \frac{1}{V} \frac{\partial^2 \Delta E_0}{\partial H^2} = -\frac{\mu_0 e^2}{6m} \frac{N}{V} \left\langle 0 \left| \sum_i r_i^2 \right| 0 \right\rangle$$

This is diamagnetic response, the magnetization is opposite to the external field – it opposes the external field like in Lenz's law.

2. Atoms/ions with unfilled shells – Curie paramagnetism:

The first term in (3) is of the order of $\mu_B H \sim 0.1 \text{ meV}$ for 1 Tesla field. The second term is substantially smaller than the first term. The third term can be shown to be about 10^{-5} times the first term. Thus if the first term is non-vanishing, it will dominate.

To calculate the first term we need to multiply the expectation value of $\mathbf{L} + g_0 \mathbf{S}$ with $\mu_B \mathbf{H}$. From atomic physics, $\mathbf{L} + g_0 \mathbf{S} = g \mathbf{J}$ where g is the Lande factor and $\hbar \mathbf{J}$ is the total angular momentum.

We calculate $\mu_B \mathbf{H} \cdot \mathbf{J}$ using statistical mechanics.

$$\Delta E_0 = \mu_B \mathbf{H} \cdot (\mathbf{L} + g_0 \mathbf{S}) = \mu_B g \mathbf{J} \cdot \mathbf{H}$$

The energy levels of the system are $E = \mu_B g m_j H$; where m_j are the azimuthal quantum numbers having $(2J+1)$ values $J, J-1, \dots, -J$.

Consider first a single spin with $L=0$. Then $m_j = \pm \frac{1}{2}$ and $g = 2$. So the two levels have magnetic contribution to energies $\Delta E = \pm \mu_B H$. The lower energy $E_\downarrow = -\mu_B H$ is for spins aligned anti-parallel to the magnetic field, the higher energy $E_\uparrow = \mu_B H$ is for spins parallel to the magnetic field. If the total number of spins is N ; the occupation of the lower and upper levels are:

$$N_\uparrow = N \frac{e^{-\beta E_\uparrow}}{e^{-\beta E_\uparrow} + e^{-\beta E_\downarrow}} = N \frac{e^{-\beta \mu_B H}}{e^{-\beta \mu_B H} + e^{\beta \mu_B H}}$$

$$N_\downarrow = N \frac{e^{-\beta E_\downarrow}}{e^{-\beta E_\uparrow} + e^{-\beta E_\downarrow}} = N \frac{e^{\beta \mu_B H}}{e^{-\beta \mu_B H} + e^{\beta \mu_B H}}$$

The magnetic moment of each spin $\frac{1}{2}$ element is $\boldsymbol{\mu} = -g \mu_B \mathbf{J}$; hence the magnitude of its moment is $\mu = g \mu_B J = \mu_B$.

The total magnetization is:

$$M = N_\uparrow (-\mu_B) + N_\downarrow \mu_B = (N_\downarrow - N_\uparrow) \mu_B = N \mu_B \frac{e^{\beta \mu_B H} - e^{-\beta \mu_B H}}{e^{-\beta \mu_B H} + e^{\beta \mu_B H}} = N \mu_B \tanh(\beta \mu_B H)$$

For high temperatures, $\beta \mu_B H \ll 1$;

$$M = N \mu_B (\beta \mu_B H) = N \frac{\mu_B^2 H}{k_B T}$$

This is the magnetization of a gas of N spins at high temperatures. The magnetic susceptibility per unit volume will be:

$$\chi = \frac{\mu_0}{V} \frac{\partial M}{\partial H} = \frac{N \mu_0 \mu_B^2}{V k_B T} = C/T$$

For the general case of N ions with angular momentum \mathbf{J} , the allowed energy values are $E = \mu_B g m_J H$. So the free energy is

$$e^{-\beta F(H)} = \sum_n e^{-\beta E_n(H)} = \sum_{m_J=-J}^J e^{-\beta \mu_B g m_J H}$$

Using the summation rule:

$$\sum_{k=m}^n x^k = \frac{x^m - x^{n+1}}{1-x}$$

$$e^{-\beta F(H)} = \frac{e^{\beta \mu_B g H (J + \frac{1}{2})} - e^{-\beta \mu_B g H (J + \frac{1}{2})}}{e^{\beta \mu_B g H / 2} - e^{-\beta \mu_B g H / 2}}$$

The magnetization is then

$$M(H, T) = -\frac{N}{V} \frac{\partial F}{\partial H} = \frac{N}{V} \mu_B g J B_J(\beta \mu_B g J H)$$

where the Brillouin function $B_J(x)$ is defined as

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

For high temperatures, $\beta \mu_B g J H \ll 1$; we can expand $\coth(x) \sim 1/x + (1/3)x + \text{terms}(x^3)$ and hence

$$B_J(x) \sim \frac{J+1}{3J} x + \text{terms}(x^3)$$

Hence at high T,

$$M(H, T) = \frac{N (g \mu_B)^2}{V} \frac{J(J+1)}{3 k_B T} H$$

and

$$\chi = \mu_0 \frac{\partial M}{\partial H} = \mu_0 \frac{N (g \mu_B)^2}{V} \frac{J(J+1)}{3 k_B T} = C/T$$

This is Curie's law of paramagnetic susceptibility, valid at high temperatures for substances with an atomic moment whose alignment is favoured by magnetic field but disrupted by the temperature. The value of paramagnetic susceptibility for an ion with non-zero \mathbf{J} is about 10^3 times larger than Larmor diamagnetism.

3. Pauli paramagnetism of metals:

The magnetic moment and energy of spin $1/2$ elements:

Spin direction	Magnetic moment $\boldsymbol{\mu} = -g\mu_B\mathbf{S}$	Energy in field \mathbf{H} $E = -\boldsymbol{\mu} \cdot \mathbf{H} = g\mu_B\mathbf{S} \cdot \mathbf{H}$	No. per unit volume	Density of states
+1/2	$-\mu_B$	$\mu_B H$	n_+	$g_+(E) = \frac{1}{2}g(E - \mu_B H)$
-1/2	μ_B	$-\mu_B H$	n_-	$g_-(E) = \frac{1}{2}g(E + \mu_B H)$

For spin parallel to \mathbf{H} , the contribution to magnetization is $-\mu_B$ while for spin anti-parallel to \mathbf{H} , the contribution is μ_B . So the net magnetization per unit volume is:

$$M = -\mu_B(n_+ - n_-)$$

The density of states in the absence of field is

$$g_{\pm}(E) = \frac{1}{2}g(E)$$

In presence of field, the energy levels of +1/2 spins go up by $\mu_B H$. So the number of levels with energy E in presence of field is the same as the number of levels with energy $(E - \mu_B H)$ at zero field.

$$g_+(E) = g(E - \mu_B H)$$

Since all the action happens near E_F which is very large compared to $\mu_B H$, we can expand

$$g_+(E) = \frac{1}{2}g(E - \mu_B H) = \frac{1}{2}g(E) - \frac{1}{2}\mu_B H g'(E)$$

The number density of up spin electrons is then:

$$n_+(E) = \int dE f(E) g_+(E) = \frac{1}{2} \int dE f(E) g(E) - \frac{\mu_B H}{2} \int dE f(E) \frac{\partial g(E)}{\partial E}$$

Similarly, number of down -spin electrons is:

$$n_-(E) = \int dE f(E) g_-(E) = \frac{1}{2} \int dE f(E) g(E) + \frac{\mu_B H}{2} \int dE f(E) \frac{\partial g(E)}{\partial E}$$

Thus the magnetization per unit volume is:

$$\begin{aligned} M &= -\mu_B(n_+ - n_-) \\ M &= -\mu_B \left[\frac{1}{2} \int dE f(E) g(E) - \frac{\mu_B H}{2} \int dE f(E) \frac{\partial g(E)}{\partial E} - \frac{1}{2} \int dE f(E) g(E) \right. \\ &\quad \left. + \frac{\mu_B H}{2} \int dE f(E) \frac{\partial g(E)}{\partial E} \right] \\ M &= \mu_B^2 H \int dE f(E) \frac{\partial g(E)}{\partial E} \end{aligned}$$

Integrating by parts:

$$M = \mu_B^2 H \int g(E) \left(-\frac{\partial f}{\partial E}\right) dE$$

At low temperatures, $-\frac{\partial f}{\partial E} = \delta(E - E_F)$; and $\int g(E) \left(-\frac{\partial f}{\partial E}\right) dE = g(E) \delta(E - E_F) = g(E_F)$

Thus, low temperature magnetization density is:

$$M = \mu_B^2 H g(E_F)$$

And the Pauli susceptibility of conduction electrons in metals is:

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

independent of temperature.

From Sommerfeld semi-classical model $g(E_F) = \frac{3n}{2E_F}$; hence the Pauli susceptibility in this case becomes:

$$\chi = \frac{3N \mu_0 \mu_B^2}{2V E_F}$$

Compare this with the case of Curie susceptibility of spin-1/2 particles:

$$\chi = \frac{N \mu_0 \mu_B^2}{V k_B T}$$

In case of Pauli susceptibility, Fermi energy plays the role of temperature. Since E_F is hundreds of times larger than typical $k_B T$; the Pauli susceptibility of metals is very small in magnitude as compared to Curie paramagnetism for ionic/molecular solids. This is a reflection of the fact that Fermi statistics is much better at preventing alignment of all spins than temperature is.

4. Van Vleck paramagnetism:

If $J=0$ (as for shells one short of being half filled); the linear term vanishes. Then the energy shift of the ground state is:

$$\begin{aligned} \Delta E_0 &= \frac{e^2}{8m} H^2 \left\langle 0 \left| \sum_i (x_i^2 + y_i^2) \right| 0 \right\rangle + \sum_{\dot{n}} \frac{|\langle 0 | \mu_B (\mathbf{L} + g_0 \mathbf{S}) \cdot \mathbf{H} | \dot{n} \rangle|^2}{E_0 - E_{\dot{n}}} \\ &= \frac{e^2}{8m} H^2 \left\langle 0 \left| \sum_i (x_i^2 + y_i^2) \right| 0 \right\rangle - \sum_{\dot{n}} \frac{|\langle 0 | \mu_B (\mathbf{L} + g_0 \mathbf{S}) \cdot \mathbf{H} | \dot{n} \rangle|^2}{E_{\dot{n}} - E_0} \end{aligned}$$

The susceptibility of a solid with N such atoms is:

$$\chi = \mu_0 \frac{\partial M}{\partial H} = -\mu_0 \frac{N}{V} \frac{\partial^2 E_0}{\partial H^2} = -\mu_0 \frac{N}{V} \left[\frac{e^2}{4m} \left\langle 0 \left| \sum_i (x_i^2 + y_i^2) \right| 0 \right\rangle - 2\mu_B^2 \sum_{\dot{n}} \frac{|\langle 0 | (\mathbf{L} + g_0 \mathbf{S}) | \dot{n} \rangle|^2}{E_{\dot{n}} - E_0} \right]$$

The first term is Larmor diamagnetic response. The second term represents *Van Vleck* paramagnetism. The total magnetization is thus a competition between diamagnetic and paramagnetic responses.

Ferromagnetism

Weiss theory of molecular fields:

Ferromagnets have a finite magnetic moment even at zero magnetic fields below a certain temperature. Weiss postulated that the effective magnetic field acting on the moments in a ferromagnet is not the applied field \mathbf{H} but rather, $\mathbf{H} + \lambda \mathbf{M}$ where \mathbf{M} is the magnetization, λ is a proportionality factor independent of temperature. $\lambda \mathbf{M}$ is called the 'molecular field'. The typical values of the molecular field are of the order of 10^3 T, much larger than experimentally achievable fields.

(It was shown quantum mechanically that this molecular field is due to the ‘exchange interaction’ term in the Hamiltonian arising due to the overlap of the orbital wave functions – more on this later. At this point we note that it is a predominantly electron spin effect.)

The paramagnetic magnetization density due to spin $1/2$ elements was found to be at high temperatures:

$$M = n \frac{\mu_B^2 H}{k_B T}$$

where $n=N/V$ is the number density of spins.

In this we include the molecular field term, $M = n \frac{\mu_B^2 (H + \lambda M)}{k_B T}$

Solving for M; $M = n \frac{\mu_B^2 H}{(k_B T - \lambda n \mu_B^2)}$

Susceptibility is: $\chi = \mu_0 \frac{\partial M}{\partial H} = n \frac{\mu_0 \mu_B^2}{(k_B T - \lambda n \mu_B^2)} = \frac{C}{T - T_C}$

where $T_C = \lambda n \mu_B^2 / k_B$ is called the Curie temperature – the temperature at which susceptibility diverges. Below T_C the system is in ferromagnetic phase.

Achievements of this simple theory:

1. Linear dependence of the inverse susceptibility above T_C on temperature.

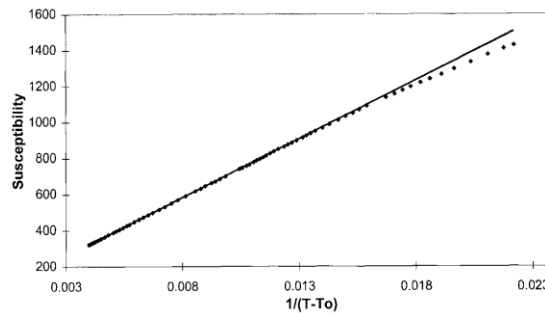


Figure 1: Susceptibility of SrTiO₃

2. Estimate of the saturation magnetization – universal curve

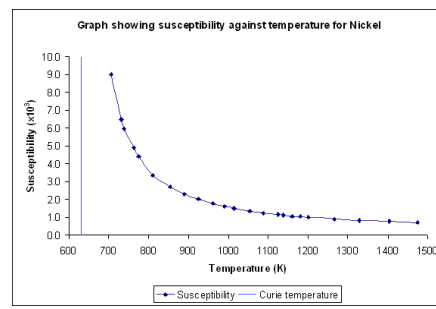
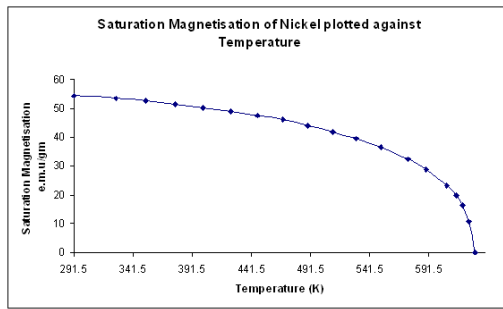
At any general temperature below T_C , the magnetization is:

$$M = N \mu_B \tanh(\beta \mu_B (H + \lambda M)) \sim N \mu_B \tanh(\beta \mu_B \lambda M)$$

We write it as;

$$m = \frac{M}{N \mu_B} = \tanh(m/t)$$

where $m = \frac{M}{N \mu_B}$ is the ratio of saturation magnetization to magnetization at zero temperature (when all moments are aligned); $t = T/T_C$ is the reduced temperature. This is a universal curve independent of any material parameters - valid for all ferromagnetic materials.



Physical explanation of ‘molecular field’:

The exchange interaction occurs due to the *Pauli Exclusion Principle*; if two electrons have different spins then they can occupy the same orbital (angular momentum state), hence be closer to each other and they will therefore have a stronger Coulomb repulsion. If the electrons have the same spin then they will occupy different orbitals and therefore have less Coulomb repulsion as they will be further apart. In this way, the exchange energy (the energy due to the repulsion between the two electrons) is minimised. Therefore the Coulomb repulsion force, under certain conditions, favours the parallel alignment of all the electron spins as the exchange energy is minimised. This term appears in the Hamiltonian as an additional potential energy relating to the coupling of the two spins:

$$V_{ij} = -2J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j$$

where J_{ij} is the *exchange integral* and \mathbf{S}_i is the total spin angular momentum of atom i . Positive J_{ij} favours parallel aligning of nearest neighbours – ferromagnetic interaction; while negative J_{ij} leads to anti-ferromagnetic arrangement.

Domains:

If molecular field is so large as compared to external field, why does the magnetization of ferromagnet change at all with application of external field? The answer is in domains – small spontaneously magnetized regions that are randomly oriented. External magnetic field either moves the walls between them to form bigger domains (at weaker fields) or reorients the domains (at higher fields) to face in the same direction thus increasing the net magnetization.

Domains are also related to the hysteresis shown in the B-H loops of ferromagnetic samples.

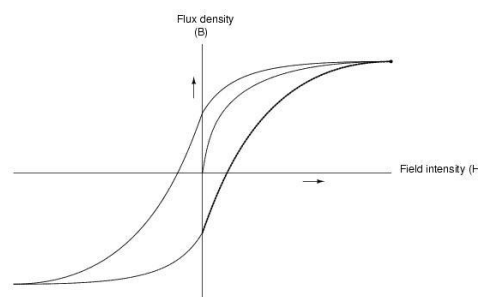


Figure 2: Hysteresis in B-H plot