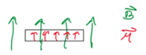
Lecture 19 – Paramagnetism

Tuesday, December 21, 2021 8:00 AM

Review

1. Macroscopic properties of magnetism



$B = \mu_0(H + M)$

$\mu_0 = 4\pi \cdot 10^{-7}\,\frac{H}{m}$ (vacuum permeability, magnetic field constant)

H: Magnetic field strength [A/m]
M: Magnetization [A/m]
B: Magnetic Flux Density [T]

$$M = \chi \cdot H = \frac{m}{V}$$

χ: magnetic susceptibility (how susceptible is my solid to H e.g. $\chi = 0 \rightarrow$ no reaction to H)

→ Connects H and M
→ Could be written as a second order tensor (direction dependence)
→ Is unitless (can be given as molar susceptibility $\chi_m = \chi \cdot V_m\ [\frac{m^3}{mol^{-1}}]$
Or mass susceptibility $\chi_\rho = \chi \cdot \rho\ [\frac{m^3}{kg}]$

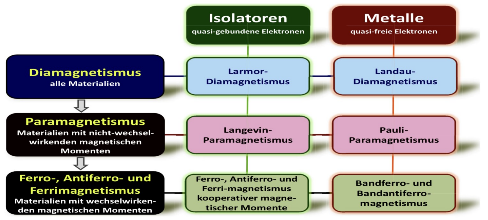
$\chi < 0$: diamagnetism (dia = through; induced magnetic moments [Lenz law])
$\chi > 0$: paramagnetism (para = at, next; already existing moments which align)

Magnetic order

Ferromagnetism: ↑↑↑↑↑↑

Antiferromagnetism: ↑↓↑↓↑↓

Ferrimagnetism: ↑ ↓ ↑ ↓ ↑ ↓



2.2 Atoms in a homogeneous magnetic field

- Consider a system of atoms; non-interacting

$$H = \underbrace{\frac{1}{2m}\left[\vec{p} + eA\right]^2}_{\text{kinetic part } T} + V(\vec{r})$$

↳ electrostatic potential "crystal"

↳ $\vec{B} \parallel \hat{z} \rightarrow B = \begin{pmatrix} 0 \\ 0 \\ B_z \end{pmatrix}$ $\quad \vec{A} = -\frac{1}{2}\vec{r} \times \vec{B}$ (Coulomb-gauge)

$$T = \frac{1}{2m}\sum_{i \atop \text{all } i}\left[\vec{p}_i - \frac{e}{2}\vec{r}_i \times \vec{B}\right]^2 = \underbrace{\frac{1}{2m}\sum_i \vec{p}_i^{\,2}}_{T_0} + \underbrace{\frac{e\hbar}{2m}}_{\mu_B}\sum_i \underbrace{\frac{(\vec{r}_i \times \vec{p}_i)_z}{\hbar}}_{\frac{L_z}{\hbar}} B_z + \frac{e^2 B_z^2}{8m}\sum_i (x_i^2 + y_i^2)$$

$$T = T_0 + \mu_B \cdot \frac{L_z}{\hbar} B_z + \frac{e^2 B_z^2}{8m}\sum_i (x_i^2 + y_i^2) := T_0 + \Delta H_e$$

$L_z = \sum_i L_{z,i}$

↳ orbital contributions

- Equivalently, spin contribution: → $\Delta H_s = g_s \mu_B \sum_i \frac{\vec{S}_i}{\hbar} \cdot \vec{B}_{ext}$

$$= g_s \mu_B \frac{S_z}{\hbar} \cdot B_z \qquad S_z = \sum_i S_{z,i}$$

$$\Delta H = \Delta H_e + \Delta H_s = \underbrace{\frac{\mu_B}{\hbar}\left(L_z + g_s S_z\right) \cdot B_z}_{\text{Langevin paramagnetism}} + \underbrace{\frac{e^2 B_z^2}{8m}\sum_i (x_i^2 + y_i^2)}_{\text{Larmor diamagnetism}}$$

↳ 2nd order perturbation theory (because magnetic interaction is much smaller than the electronic energies of the atomic levels E_n)

$$\Delta E_n = \langle n | \Delta H | n \rangle + \sum_{n \neq n'} \frac{|\langle n | \Delta H | n' \rangle|^2}{E_n - E_{n'}} + \dots$$

$$= \frac{\mu_B \cdot B_z}{\hbar} \langle n | L_z + g_s S_z | n \rangle$$

$$+ \frac{e^2 B_z^2}{8m} \langle n | \sum_i (x_i^2 + y_i^2) | n \rangle$$

$$+ \frac{\mu_B^2 B_z^2}{\hbar^2} \sum_{n \neq n'} \frac{|\langle n | L_z + g_s S_z | n' \rangle|^2}{E_n - E_{n'}}$$

(1) atomic paramagnetism (Langevin)

(2) Larmor diamagnetism (no spin!)

(3) Van-Vleck paramagnetism

(1) $\langle 0 | L_z + g_s S_z | 0 \rangle \approx \hbar \quad \rightarrow \quad \mu_B \cdot B_z \xrightarrow{1T} 10^{-4}\ eV$

(2) $\langle n | \sum_i \underbrace{(x_i^2 + y_i^2)}_{r_i^2} | n \rangle \approx a_B^2 \quad \Rightarrow \quad \frac{e^2 B_z^2}{8m} \cdot a_B^2 \hat{=} \underbrace{\frac{(\mu_B B_z)^2}{E_R}}_{10^{-4} - 10^{-5}} \times$ smaller than (1) $\qquad E_R = \frac{1}{2} \frac{\hbar^2}{m a_B^2} \simeq 13\ eV$

(3) $\frac{\mu_B^2 B_z^2}{\cancel{\hbar^2}} \cdot \frac{\cancel{\hbar^2}}{(E_n - E_{n'}) \sim 1 eV} \quad \Rightarrow \quad 10^{-4} - 10^{-5} \times$ smaller than (1)

2.3 Atomic Paramagnetism

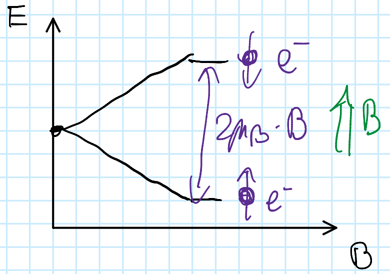
e.g.
- transition metal in an insulator (e.g. NaCl, MgO)
- Magnetic Molecules
- Color centers in Diamond (Nitrogen Vacancy Center)

$\rightarrow$ no conduction electrons

$$E = \mu_B \vec{B} (\vec{L} + g \vec{S}) / \hbar = g_J \mu_B \frac{\vec{J}}{\hbar} \cdot \vec{B}$$

example: Eigenstates for a spin-$\frac{1}{2}$ system

$$J = S = \frac{1}{2} \quad \Rightarrow \quad m_J = \pm \frac{1}{2} \qquad g_J = 2$$



$$E = -\vec{\mu} \cdot \vec{B}$$

What about the Magnetization of the system? $\rightarrow$ state population

- Partition function $Z = \sum_n \exp\left(\frac{-E_n}{k_B T}\right) = \exp\left(\frac{\mu_B B}{k_B T}\right) + \exp\left(\frac{-\mu_B B}{k_B T}\right)$

$$k_B = 1.38 \cdot 10^{-23} \frac{J}{K} = 86 \frac{\mu eV}{K}$$

- Free energy $F = U - T \cdot S = \underset{\text{p. 669}}{\ldots\ldots} = -k_B \cdot T \ln Z$

- Magnetization:

$$M = -\langle m \rangle = -\frac{\partial F}{\partial B} = \frac{m_{\frac{1}{2}} \cdot e^{x} + m_{-\frac{1}{2}} \cdot e^{-x}}{\ldots}$$

$+\mu_B$ $\quad -\mu_B$

Lecture on phase transitions

⚠ the free energy of a finite system is always analytical so non-analyticity can only occur in the thermodynamic limit $N \rightarrow \infty$ $\Rightarrow$ Cooperation of all degrees of freedom in the system.

Statistical physics $F = k_B T \langle e^{-\mathcal{H}/k_B T} \rangle$

average over all possible configurations of the system.

- Magnetization :

$$M := \langle m \rangle = -\frac{\partial F}{\partial B} = \frac{m_{\mu_B} \cdot e^{x} + m_{-\mu_B} \cdot e^{-x}}{e^{x} + e^{-x}} \rightarrow Z$$

$$x = \frac{\mu_B \cdot B}{k_B T} \qquad \frac{e^{x} - e^{-x}}{e^{x} + e^{-x}} = \tanh$$

the system.

Statistical physics $F = k_B T \langle e^{-\mathcal{H}/k_B T} \rangle$

average over all possible configurations of the system.

it fluctuates – the divergence of the fluctuations yields the transiti

Fluctuations are related to susceptibility.

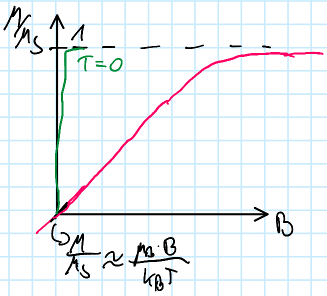
Magnetic case: $\chi = \left(\frac{\partial m}{\partial h}\right)_T$

external field

Effect of the magnetic field ?

$$\frac{M}{M_S} = \tanh\left(\frac{\mu_B \cdot B}{k_B T}\right) \qquad M_S = \max(\langle m \rangle) = \mu_B$$

Saturation

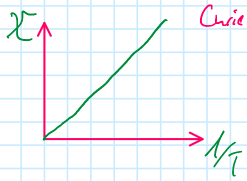


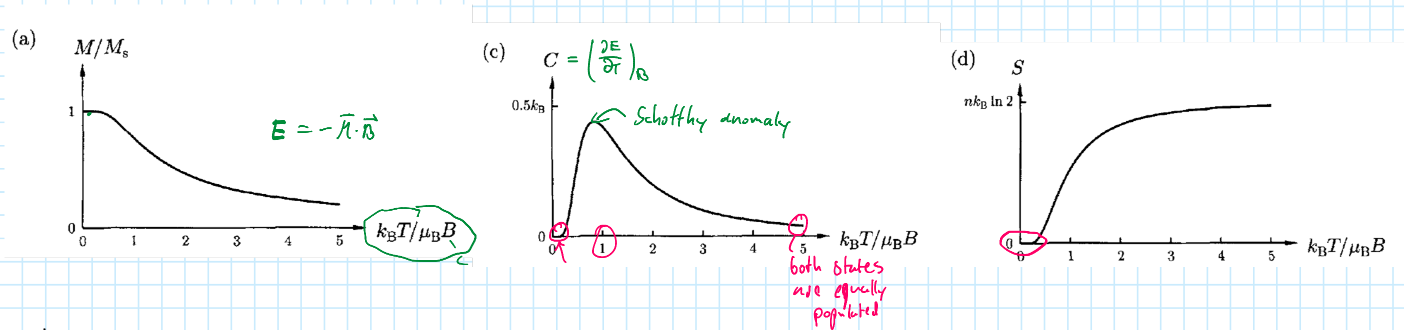
Susceptibility

$$\chi = \mu_0 \left(\frac{\partial M}{\partial B}\right)_{T,V} \underset{\frac{\mu_B \cdot B}{k_B T} \ll 1}{\simeq} \frac{\mu_0 \cdot \mu_B^2}{k_B T} = \frac{C}{T}$$

$$\vec{M} = \chi \cdot \vec{H}$$

Curie-law for Spin 1/2





- Larger Spins

$$\vec{L} = \sum_i \vec{\ell}_i \qquad \vec{S} = \sum_i \vec{s}_i \qquad (\vec{L} + \vec{S}) = \vec{J}$$

⇒ Russel-Saunders coupling (works well for 3d $(L=2)$ and 4f $[L=3]$)

- different magnetic g-factors for S + L

↳ Landé g-factor $g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$

$$\boxed{\text{with } \vec{\mu}_J = -g_J \mu_B \cdot \frac{\vec{J}}{\hbar}} \qquad \boxed{\mu_J = |\vec{\mu}_J| = g_J \sqrt{J(J+1)}\, \mu_B = p \cdot \mu_B}$$

effective number of magnetic moments

Magnetization for larger systems

$$\langle m \rangle = \frac{\sum_{m_J} m_J \cdot \exp(-m_J \cdot x)}{\dots} \qquad x = \frac{g_J \cdot \mu_B \cdot B}{k_B T}$$

$$\langle m \rangle = \frac{\sum_{m_j} m_j \cdot \exp(-m_j \cdot x)}{\underbrace{\sum_{m_j} \exp(-m_j \cdot x)}_{Z}} \qquad x = \frac{g_j \cdot \mu_B \cdot B}{k_B T}$$

$$= -\frac{1}{Z} \frac{\partial Z}{\partial x}$$

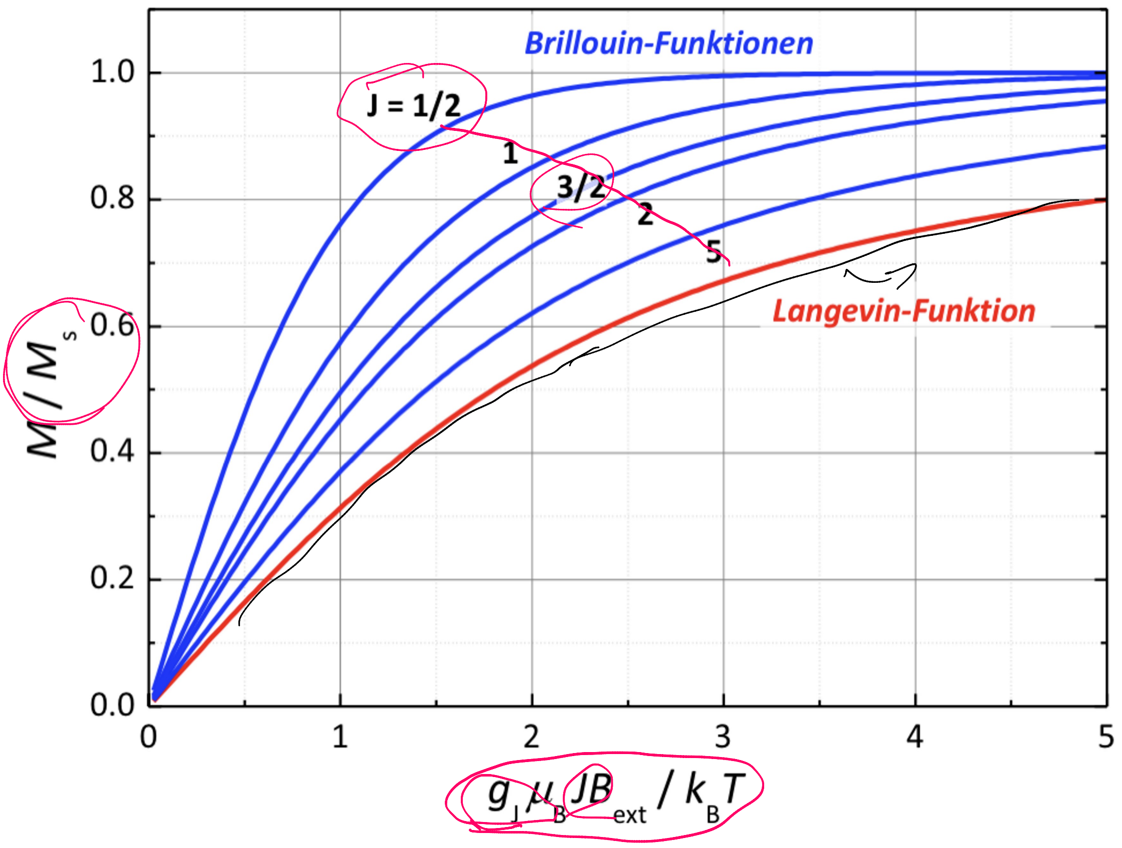
Magnetization

$$M = -\frac{N}{V} \cdot g_j \cdot \mu_B \cdot \langle m \rangle = n \cdot k_B T \cdot \frac{\partial \ln Z}{\partial B} \qquad Z = \frac{\sinh\left[(2J+1)\frac{x}{2}\right]}{\sinh\left(\frac{x}{2}\right)}$$

Brillouin-functions

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

$$y = J \cdot x \qquad M_S = n \cdot g_J \cdot J \cdot \mu_B$$



Susceptibility

$$\chi = \frac{C}{T} \qquad C = \frac{\mu_0 \cdot \mu_B^2 \cdot n \cdot J(J+1) \cdot g_J^2}{3 k_B}$$

$$:= \frac{\mu_{eff}^2 \cdot n \cdot \mu_0}{3 k_B} \qquad \mu_{eff} = p \cdot \mu_B$$

$$:= \frac{\mu_{eff}^2 \cdot n \cdot \mu_0}{3 k_B}$$

$\mu_{eff} = p \cdot \mu_B$