Lecture 21

03.04.2019

Paramagnetic systems

Paramagnetic spin model

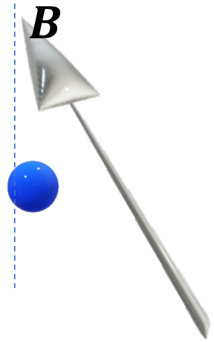
Magnetic materials

- Have a magnetic dipole moment associated with the spin of electrons

- Spins interact with an external magnetic field

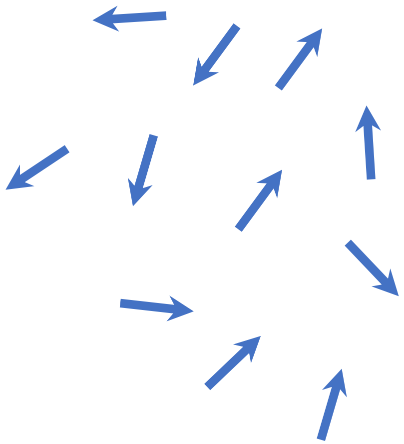
- Susceptible to change their magnetization in the presence of a magnetic field
    - ❑Paramagnetism – retain magnetization only in the presence of a magnetic field

    - ❑Ferromagnetism – have a permanent magnetization even in the absence of an applied magnetic field

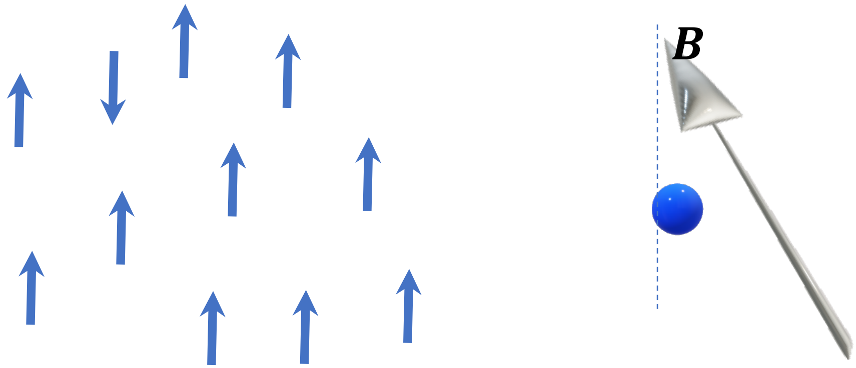


Paramagnetic materials

No applied magnetic field



With applied magnetic field



Example:

Aluminum, copper, gold

Iron bearing minerals at sufficiently big temperatures

Origin of magnetism: electron spin

Orbital magnetic moment

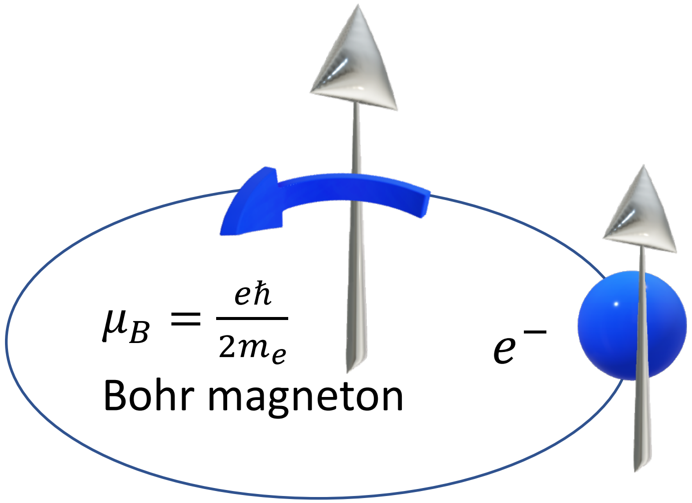
$$\boldsymbol{\mu}_{orbit} = g_l \mu_B \boldsymbol{m}_l,$$

- **quantization of angular momentum**

orbital number $l = 0, 1, 2 \cdots$

$$m_l = -l, -l+1, \cdots, l-1, l$$

Orbital Lande' factor
$g_l = 1$



Intrinsic spin magnetic moment

$$\boldsymbol{\mu}_s = g_s \mu_B \boldsymbol{s}, \qquad s = \pm\frac{1}{2}$$

$g_s = 2$ Spin Lande' factor

Total magnetic moment

$$\boldsymbol{\mu} = \boldsymbol{\mu}_{orbit} + \boldsymbol{\mu}_{spin} = g_J \mu_B \, \boldsymbol{m}_J$$

$$m_j = m_l + s = -J, -J+1, \cdots, J-1, J$$

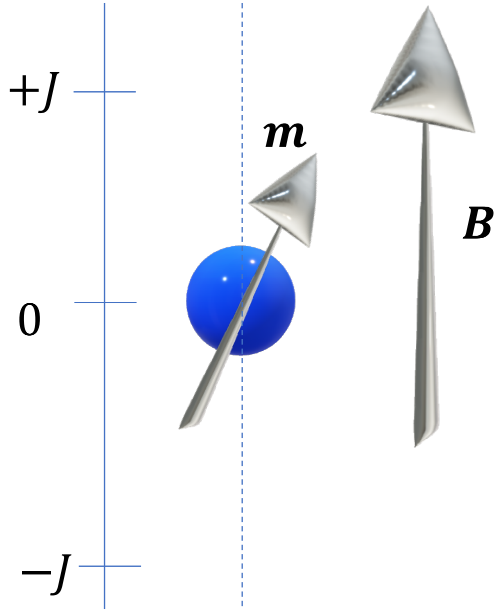
J **total spin number**

Electron spin in a magnetic field

To study paramagnetic properties, it suffices to consider the potential energy of a single electron in a uniform magnetic field

$$\hat{H}_{eff} = -\hat{\mu} \cdot \hat{B}, \qquad \hat{\mu} = g\,\mu_B\,\hat{J}, \qquad \hat{J} = \hat{S} + \hat{L}$$

$\hat{J}$ total spin angular momentum operator (spin+orbital)



- Energy levels for uniform, uniaxial magnetic field $\boldsymbol{B} = (0,0,B)$:

$$\epsilon_m = -g\mu_B m B,$$

where $m = -J, -J+1, \cdots J-1, J$, where J is the spin quantum number determined by the orbital of the electron

Single particle partition function Z_1

Energy levels: $\epsilon_m = -g\mu_B Bm$, where $m = -J, -J+1, \cdots J-1, J$

One particle partition function is descrived by Boltzmann statistics

We mage use of the following substitution: $a = e^{\frac{x}{J}},\ x = \beta g\mu_B BJ$

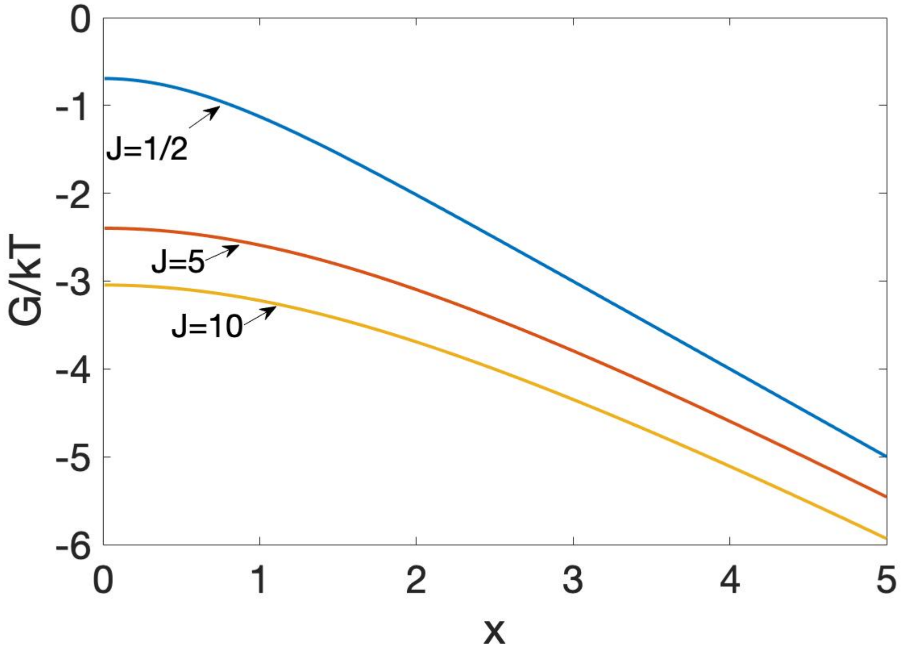
$$Z_1(T,B) = \sum_{m=-J}^{J} e^{\beta g\mu_B Bm} = a^{-J}(1 + a + \cdots + a^{2J-1} + a^{2J}) = \frac{a^{J+1} - a^{-J}}{a-1}$$

$$Z_1(T,B) = \frac{\sinh\left(\frac{2J+1}{2J}x\right)}{\sinh\left(\frac{x}{2J}\right)}$$

Gibbs free energy as a function of T and applied field B

Gibbs free energy follows from the partition function as

$$G(T,B) = -kT\ln Z_1 = -kT\ln\left(\frac{\sinh\left(\frac{2J+1}{2J}x\right)}{\sinh\left(\frac{x}{2J}\right)}\right), \quad x = \beta g\mu_B BJ$$



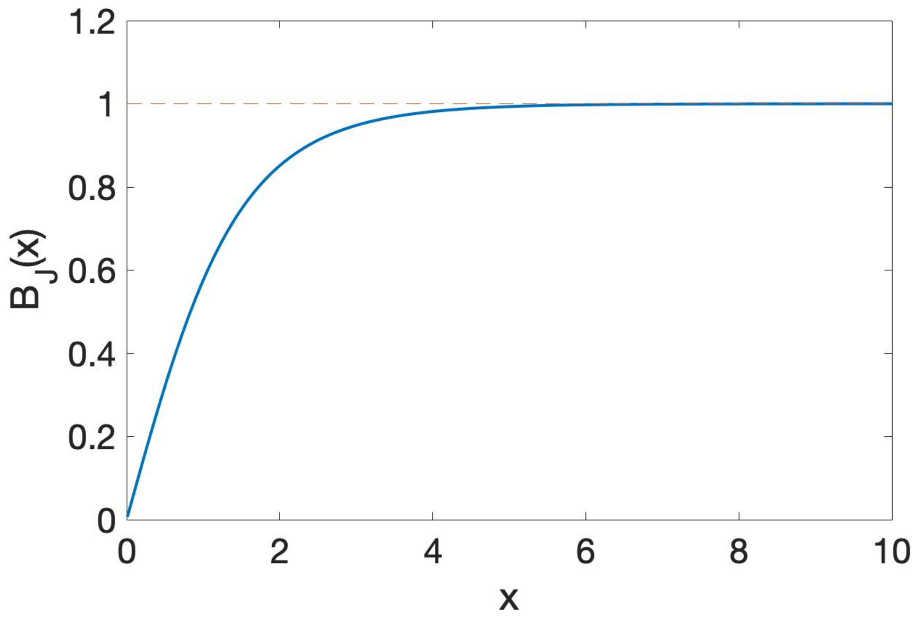
Mean magnetization as a function of T and applied field B

Mean magnetization is the conjugate variable to the applied field

$$\langle m \rangle = -\left(\frac{\partial G}{\partial B}\right)_T = g\mu_B J B_J(x),$$

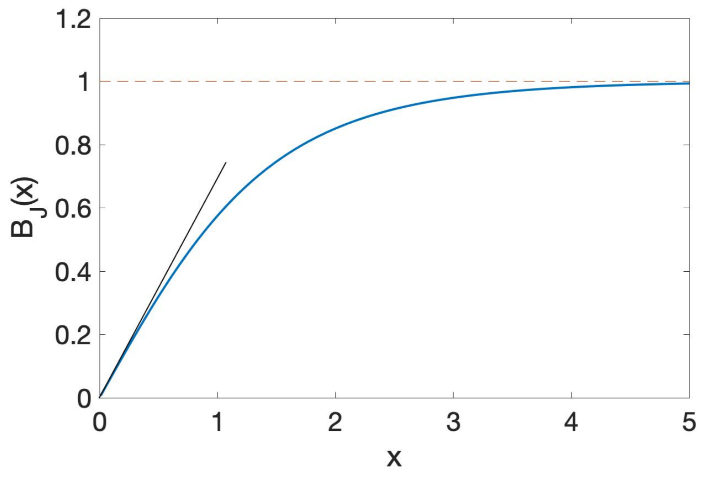
The function $B_J(x)$ is called Brillouin function

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



Properties of Brillouin function for small x

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



High temperature /low applied magnetic field limit

$$x \ll 1 \rightarrow \beta g \mu_B B J \ll 1 \rightarrow coth(x) \approx \frac{1}{x} + \frac{x}{3} + O(x^3)$$

$B_J(x)$ *increases linearly near origin:* $\quad B_J(x) \approx \frac{J+1}{3J} x + \cdots$

Magnetic moment:

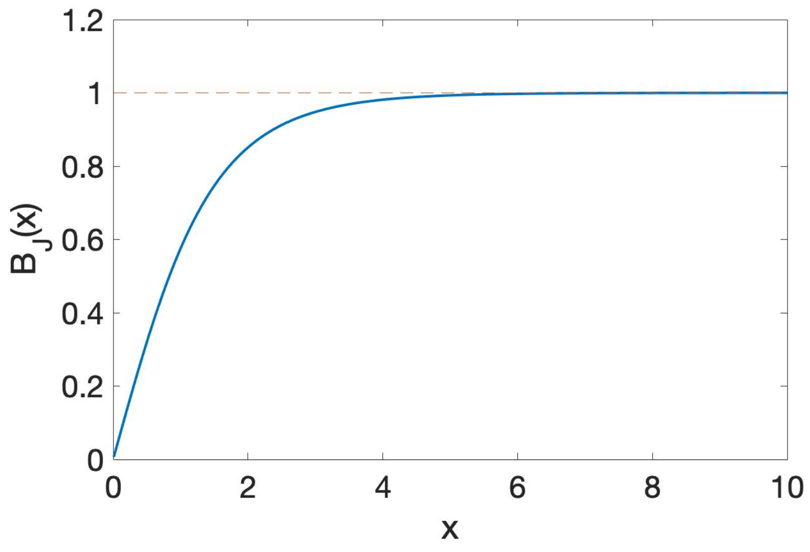
$$\langle m \rangle = g\mu_B J B_J(x) \approx \frac{\mu^2}{3}\beta B, \qquad \mu = g\mu_B\sqrt{J(J+1)}$$

Magnetic susceptibility:

$$\chi(T) = \left(\frac{\partial \langle m \rangle}{\partial B}\right)_T = \frac{\beta}{3}\mu^2 \sim \frac{1}{T} \quad Curie's\ law$$

Properties of Brillouin function for large x

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



Low temperature limit

$x \gg 1 \rightarrow \beta g\mu_B BJ \gg 1 \rightarrow kT \ll g\mu_B BJ$

$B_J(x)$ saturates to a constant $B_J(x) \rightarrow 1$

Magnetic moment $\langle m \rangle = g\mu_B J B_J(x)$ also saturates at $m_0 = g\mu_B J$

Classical magnetism

The magnetic dipole moment μ is a vector that can point in any direction

- Hamiltonian of a classical spin in a uniform magnetic field

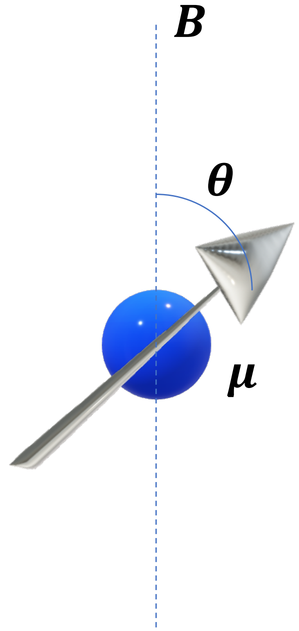
$$\mathrm{H} = -\boldsymbol{\mu} \cdot \boldsymbol{B} = -\mu B \cos\theta$$

- Classical partition function

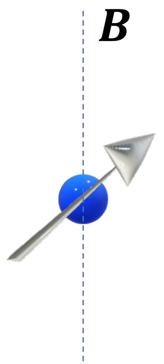
$$Z_1 = \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \; e^{\beta\mu B \cos\theta} = \frac{4\pi \sinh(\beta\mu B)}{\beta\mu B}$$

- Mean magnetization

$$m = \mu\left[\coth\left(\frac{\mu B}{kT}\right) - \frac{kT}{\mu B}\right]$$



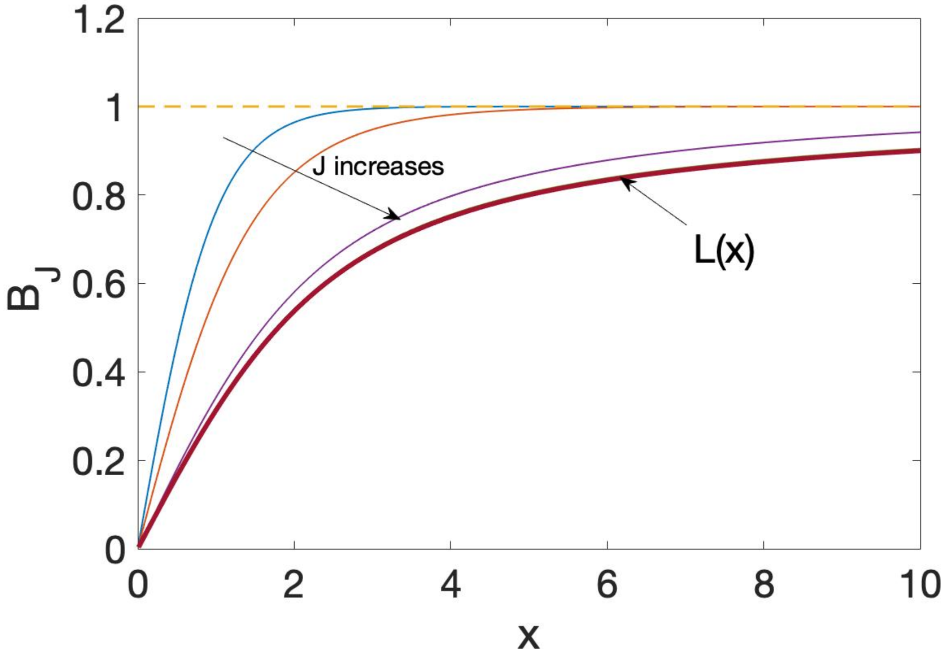
Classical limit of the Brillouin function: at fixed x as $J \gg 1$

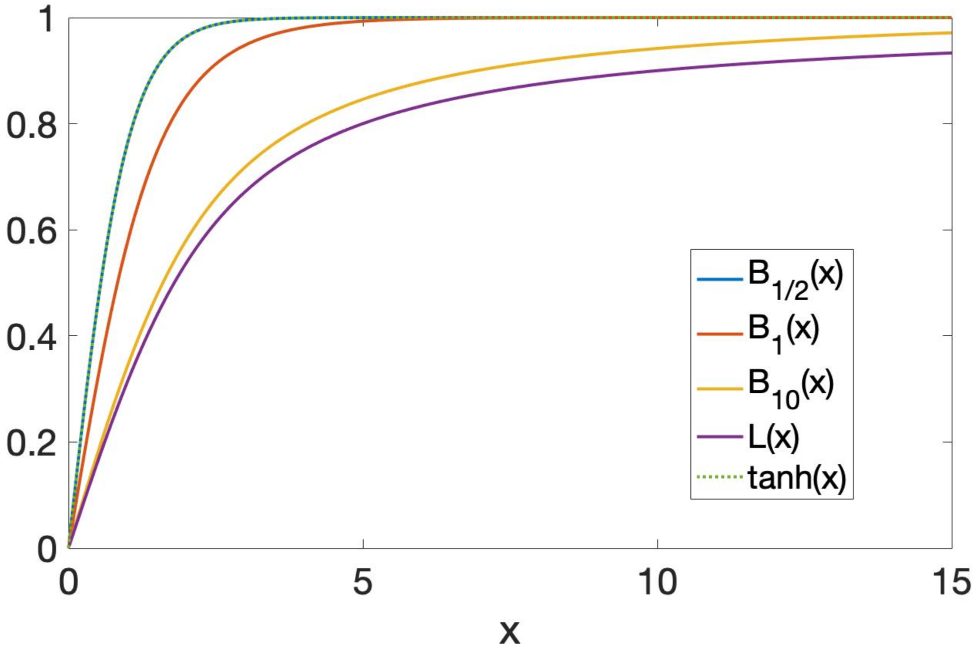


$$B_J(x) = \frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J}\coth\left(\frac{x}{2J}\right)$$

$B_J(x)$ approaches the Langevin function

$$B_J(x) \to \mathcal{L}(x) = \coth x - \frac{1}{x}$$





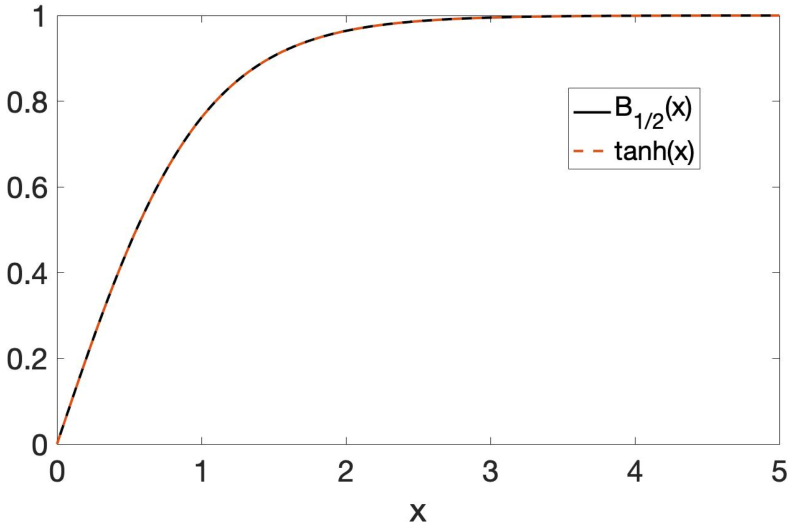
Electron in the first orbital $L = 0,\ g = 2$: Spin ½

The Brilouin function

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

Reduces to

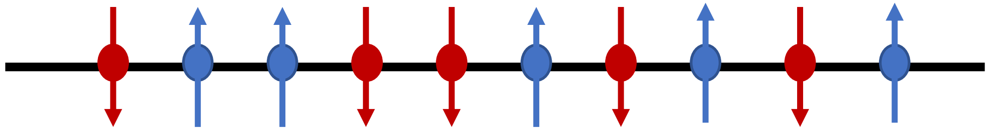
$$B_{\frac{1}{2}}(x) = 2\ \coth 2x - \coth x = \tanh x$$



Mean magnetication

$$\langle m \rangle = \mu_B \tanh(\beta \mu_B B)$$

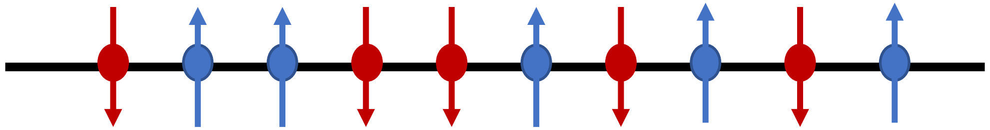
Ising model of paramagnets



- A system of N *independent, localised* particles with spin $s = \pm 1$ at finite temperature
- Spin interact with the applied magnetic field via an interaction potential

$$H_N = -\sum_{i}^{N} \mu_B s_i B$$

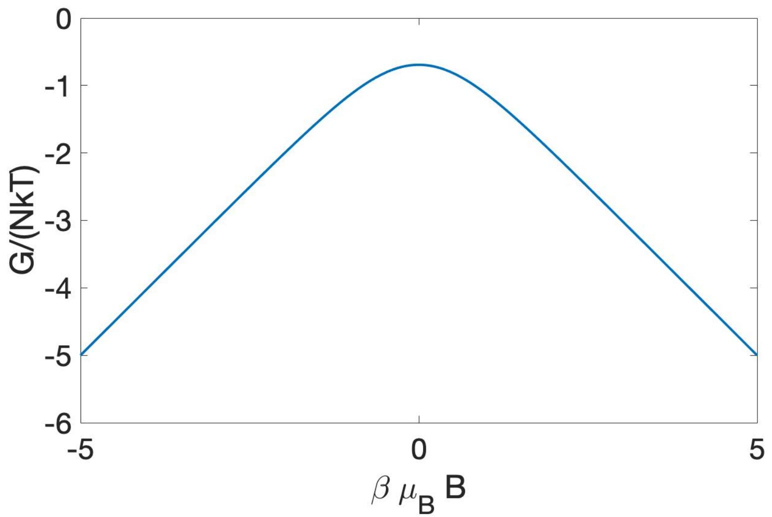
Statistics of paramagnets



- Spin interact with the applied magnetic field via an interaction potential $H_N = -\mu_B S_N \cdot B, \quad S_N = \sum_i^N s_i$
- N particle partition function

$$Z_1 = \sum_{s=\pm 1} e^{\beta s B} = 2\cosh(\beta \mu_B B),$$

$$\mathrm{Z_N} = Z_1^N = 2^N \cosh^N(\beta \mu_B B)$$

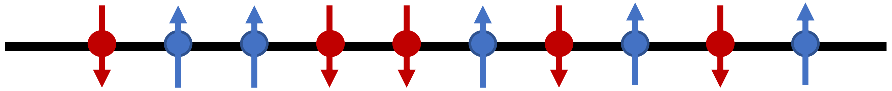


Gibbs free energy

$$G(B,T) = -NkT \ln[2\cosh(\beta \mu_B B)]$$

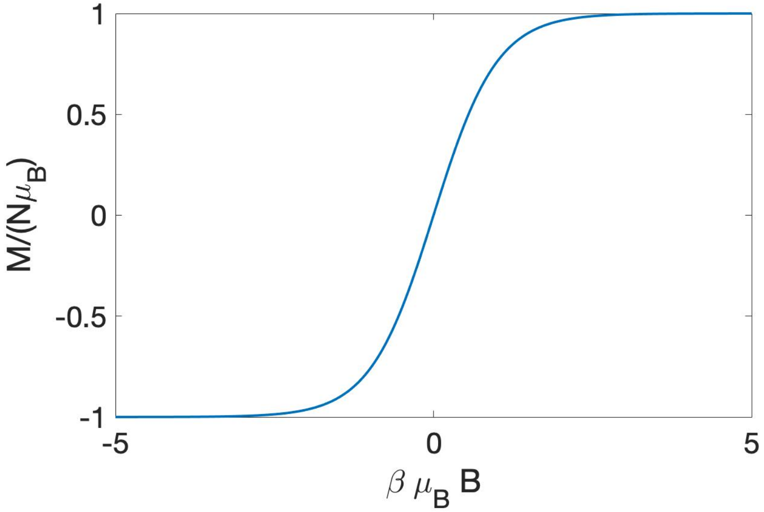
Maximum Gibbs energy at $B = 0$ (disordered spins)

Mean magnetization and susceptibility



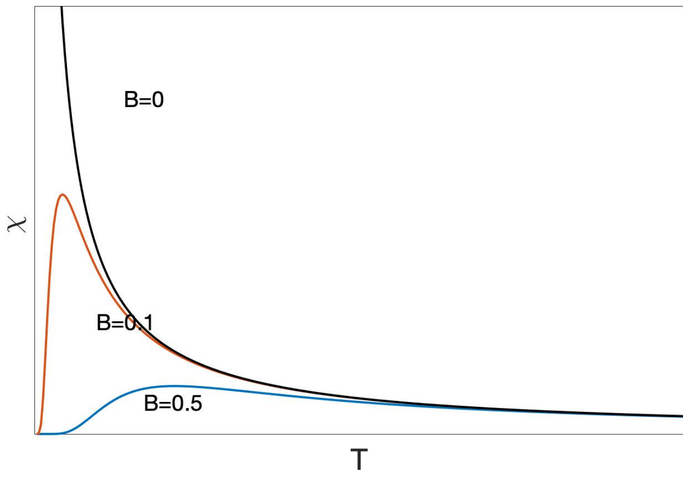
- Mean magnetization

$$M = \mu_B \langle S \rangle = -\frac{\partial}{\partial B} G(T,B) = N\mu_B \tanh(\beta \mu_B B)$$

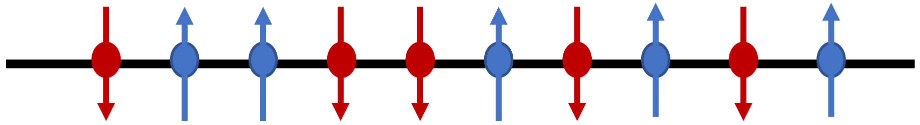


- Susceptibility

$$\chi(B,T) = \left(\frac{\partial M}{\partial B}\right)_T = \frac{1}{kT}\frac{N\mu_B^2}{\cosh^2(\beta \mu_B B)}$$

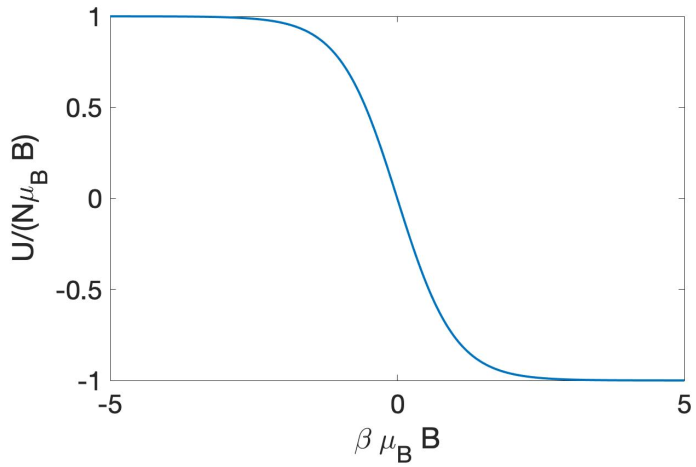


Thermodynamics of paramagnets



- Mean energy

$$U(\mathrm{T},\mathrm{B}) = -\frac{\partial}{\partial\beta}\ln(Z_N) = -N\mu_B B\tanh(\beta\mu_B B)$$

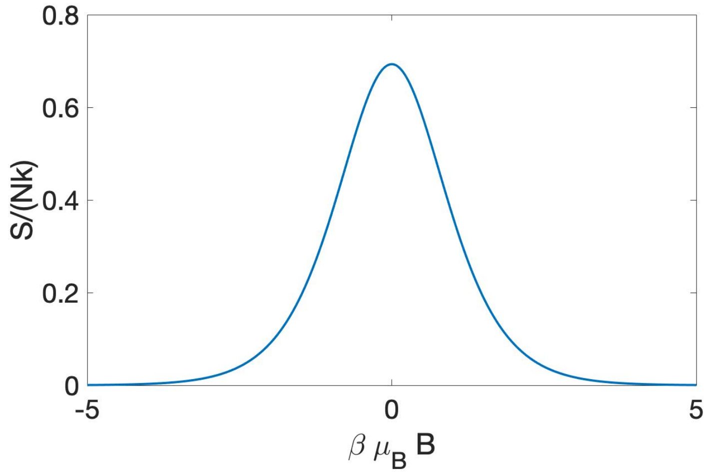


- Entropy

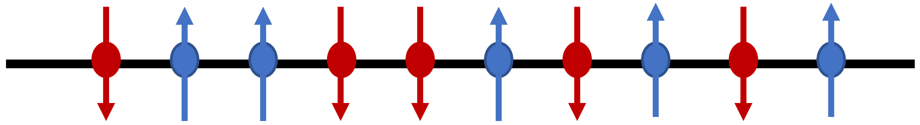
$$S = -\left(\frac{\partial G}{\partial T}\right)_B = \frac{U-G}{T}$$

$$S(T,B) \\ = Nk\left[\ln\left(2\cosh(\beta\mu_B B)\right) - \beta\mu_B B\tanh(\beta\mu_B B)\right]$$

Maximum entropy at $B = 0$ (disordered spins)



Thermodynamics of paramagnets



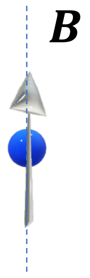
- Mean energy

$$U(T,B) = -N\mu_B B\tanh(\beta\mu_B B)$$

- Entropy

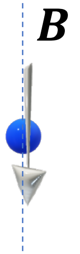
$$S(T,B) = Nk\big[\ln\big(2\cosh(\beta\mu_B B)\big) - \beta\mu_B B\tanh(\beta\mu_B B)\big]$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_B$$



  - $T > 0$: Thermal fluctuations tends to misalign the spins relative to the direction of B. The higher the temperature, the higher the spin disorder and hence the entropy

  - $T = \infty$ Maximum entropy (randomly oriented spins) regardless of B. Equivalent to the entropy of random spins at $B = 0$



  - $T < 0$: Thermal fluctuations are so strong that spins tend to align opposite to the direction of B. The higher the temperature, the smaller the entropy as there are more and more spins pointing downwards