Problem Set 6
Paramagnetism of localized magnetic moments

1 Classical treatment

In this first exercise we aim at calculating the contribution of localized magnetic moments to the magnetic susceptibility χ. We consider that the magnetic moments are fixed at the lattice sites of the crystal and take them as distinguishable and independent (*i.e.*, one given magnetic moment does not interact with the others).

(a) To check the validity of the assumption of independence of magnetic moments, one can compare the potential energy (*i.e.*, the Zeeman energy)

$$\begin{aligned} E_\mathrm{Z} &= -\boldsymbol{\mu}\cdot\mathbf{B} \\ &\sim \mu_\mathrm{B} B \end{aligned}$$

of a magnetic moment $\boldsymbol{\mu}$ (which is of the order of the Bohr magneton μ_B) in a magnetic field $\mathbf{B} = B\,\hat{z}$ to the dipole interaction energy. The latter is given by

$$\begin{aligned} E_\mathrm{dip} &= \frac{\mu_0}{4\pi r_{ij}^3}\left[\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_j - 3(\boldsymbol{\mu}_i\cdot\hat{r}_{ij})(\boldsymbol{\mu}_j\cdot\hat{r}_{ij})\right] \\ &\sim \frac{\mu_0\mu_\mathrm{B}^2}{4\pi r_{ij}^3} \end{aligned}$$

where $\boldsymbol{\mu}_i$ and $\boldsymbol{\mu}_j$ correspond to two magnetic moments located at the lattice sites $\mathbf{r}_i$ and $\mathbf{r}_j$, respectively, with $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$.

Estimate the order of magnitude of these two energy scales (in eV) when r_{ij} is of the order of the typical distance between atoms in a solid and for a magnetic field $B = 1\,\mathrm{T}$. Compare also the Zeeman energy to the energy of thermal fluctuations at room temperature.

Values: $\mu_0 = 4\pi\times10^{-7}\,\mathrm{Tm/A}$, $\mu_\mathrm{B} = 9.3\times10^{-24}\,\mathrm{J/T}$, $1\,\mathrm{eV} = 1.6\times10^{-19}\,\mathrm{J}$.

(b) We now treat each (independent) magnetic moment classically and allow for arbitrary orientation of $\boldsymbol{\mu}$ with respect to the magnetic field $\mathbf{B}$. Express the Zeeman energy E_Z in terms of the absolute values of these vectors and the angle θ between them.

(c) The probability density for a given orientation of the magnetic moment $\boldsymbol{\mu}$ in an external magnetic field is determined by its energy through

$$P(\boldsymbol{\mu}) = \frac{1}{Z}\,\mathrm{e}^{-\beta E_\mathrm{Z}(\theta)},$$

with $\beta = 1/k_\mathrm{B}T$ the inverse temperature, and where Z is the (canonical) partition function given by the integral over all orientations

$$Z = \int \mathrm{d}\Omega\,\mathrm{e}^{-\beta E_\mathrm{Z}(\theta)}.$$

Calculate Z.

(d) The mean magnetization $\langle\mathbf{M}\rangle$ of a material that contains a density $n = N/V$ of N magnetic moments (with V the sample volume), under the influence of an external magnetic field, is defined as the total average magnetic moment per unit volume. Show that $\langle\mathbf{M}\rangle = n\langle\boldsymbol{\mu}\rangle$. Calculate explicitely the average magnetization and show that $\langle\mathbf{M}\rangle = \langle M_z\rangle\hat{z}$ with $\langle M_z\rangle = n\mu\mathcal{L}(\beta\mu B)$, where

$$\mathcal{L}(x) = \coth x - \frac{1}{x} \tag{1.1}$$

is the Langevin function.

(e) Discuss the dependence of the magnetization in the limits of low field/high temperature $\mu B/k_\mathrm{B}T \ll 1$ and strong field/low temperature $\mu B/k_\mathrm{B}T \gg 1$. Sketch $\langle M_z\rangle$ as a function of $\mu B/k_\mathrm{B}T$.

(f) The zero-field magnetic susceptibility is defined as

$$\chi = \left.\frac{\partial\langle M_z\rangle}{\partial H}\right|_{H=0},$$

where $\mathbf{H} = \mathbf{B}/\mu_0 - \mathbf{M}$. Argue that

$$\chi \simeq \mu_0 \left.\frac{\partial\langle M_z\rangle}{\partial B}\right|_{B=0}.$$

(g) Calculate the magnetic susceptibility using the low-field limit from Question (e) and show that it is always paramagnetic and follows the Curie law $\chi = C/T$, where C is a constant to be specified.

2 Quantum treatment

In this second exercise, we still consider a system of N independent atoms in a volume V, each of which has a total angular momentum (in units of $\hbar$) $\mathbf{J} = \mathbf{S} + \mathbf{L}$, with $\mathbf{S}$ and $\mathbf{L}$ the spin and orbital angular momentum, respectively. The absolute square value $\mathbf{J}^2 = J(J+1)$, where J is the quantum number of the total angular momentum. The magnetic moment of an atom is $\boldsymbol{\mu} = -g\mu_\mathrm{B}\mathbf{J}$, where g is the Landé factor of the considered atoms.

(a) Write the Hamiltonian describing the Zeeman energy of an atom in an external magnetic field $\mathbf{B}$ parallel to the z axis. Specify the possible values J_z of the projection of the angular momentum $\mathbf{J}$ of an atom on the z axis.

(b) Write the (canonical) partition function Z of each atom. Show that it can be expressed as the ratio of two hyperbolic sines.[1]

(c) The free energy (per atom) is defined as $F = -k_\mathrm{B}T\ln Z$. Show that the mean value of the magnetic moment is given by $\langle\mu_z\rangle = -\partial F/\partial B$.

(d) Show that the average magnetization in z direction $\langle M_z\rangle$ defined as the mean total magnetic moment per unit volume can be expressed as

$$\langle M_z\rangle = M_\mathrm{s} B_J(\beta g\mu_\mathrm{B} J B), \tag{2.1}$$

where

$$B_J(x) = \frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}\,x\right) - \frac{1}{2J}\coth\left(\frac{1}{2J}\,x\right) \tag{2.2}$$

denotes the Brillouin function. What is the expression of the saturation magnetization M_s?

(e) Let us first consider the case of vanishing orbital moment and spin 1/2, *i.e.*, $J = 1/2$. Show that $B_{1/2}(x) = \tanh x$ and discuss then the result of Eq. (2.1).

(f) We now consider the classical limit, in which $\hbar \to 0$, which amounts to consider $J \to \infty$. Demonstrate that $B_\infty(x) = \mathcal{L}(x)$, where $\mathcal{L}(x)$ is the Langevin function from Eq. (1.1).

(g) We finally consider the case of an arbitrary, finite J. Sketch the Brioullin function (2.2) as a function of the parameter x for various values of J.

(h) Still for finite J, deduce the value of the zero-field susceptibility χ. Is the system paramagnetic?

[1] Note that

$$\sum_{k=0}^{n} q^k = \frac{1-q^{n+1}}{1-q}, \qquad (q \neq 1).$$