

# Paramagnetism [tln58]

Paramagnetic salts contain localized ions with permanent magnetic dipole moments associated with unpaired electron spins. The interaction between the electron spins is negligibly small and there is no kinetic energy associated with their orientational motion. Hence the internal energy vanishes:  $U = 0$ .

The microstate is specified by the instantaneous orientation of the magnetic moments  $\mathbf{m}_i, i = 1, \dots, N$  relative to some coordinate system. The localized moments can be treated as distinguishable particles. They do not need to have a definite permutation symmetry. The macroscopic equilibrium state in the canonical ensemble is characterized by random orientations of the moments  $\mathbf{m}_i$ . It has no magnetisation:  $\mathbf{M} = \sum_i \langle \mathbf{m}_i \rangle = 0$ .

An external magnetic field  $\mathbf{H}$  causes a partial spin alignment. The interaction of the magnetic moments with a field in  $z$ -direction is represented by Hamiltonian (Zeeman energy) of the form:

$$\mathcal{H} = - \sum_{i=1}^N \mathbf{m}_i \cdot \mathbf{H} = -H \sum_{i=1}^N m_i^z.$$

**Classical model:** The permanent atomic magnetic moment is described as a 3-component vector of fixed length:

$$\mathbf{m}_i = (m_i^x, m_i^y, m_i^z) = m(\sin \theta_i \cos \phi_i, \sin \theta_i \sin \phi_i, \cos \theta_i).$$

Each  $\mathbf{m}_i$  represents one degree of freedom described by one pair of canonical coordinates  $q_i = \phi_i$ ,  $p_i = m \cos \theta_i$ . The canonical partition function is calculated in exercise [tex84].

**Quantum model (spin 1/2):** The permanent atomic magnetic moment originates from a single electron spin. This is a two-level system, which also has a host of realizations unrelated to paramagnetism. The magnetic moment in appropriate units is quantized as follows:

$$m_i^z = \pm \frac{1}{2}.$$

The canonical partition function is calculated in exercise [tex85].

**Quantum model (spin  $s$ ):** The permanent atomic magnetic moment originates from an effective spin of quantum number  $s = \frac{1}{2}, 1, \frac{3}{2}, \dots$ . The magnetic moment in appropriate units is quantized as follows:

$$m_i^z = -s, -s + 1, \dots, s - 1, s.$$

The canonical partition function is calculated in exercise [tex86].