Consider an ion with a partially filled shell of angular momentum $J$, and $Z$ additional electrons in filled shells. Show that the ratio of the Curie paramagnetic susceptibility to the Larmor diamagnetic susceptibility is

$$\frac{\chi_{\text{para}}}{\chi_{\text{dia}}} = -\frac{g_L^2 J(J + 1)}{2Zk_B T} \frac{\hbar^2}{m\langle r^2 \rangle}.$$

where $g_L$ is the Landé $g$-factor. Estimate this ratio at room temperature.

**Solution:**

We have derived the expressions

$$\chi_{\text{dia}} = -\frac{Zne^2}{6mc^2} \langle r^2 \rangle$$

and

$$\chi_{\text{para}} = \frac{1}{3} n (g_L \mu_B)^2 \frac{J(J + 1)}{k_B T},$$

where

$$g_L = \frac{3}{2} + \frac{S(S + 1) - L(L + 1)}{2J(J + 1)},$$

and where $\mu_B = e\hbar/2mc$ is the Bohr magneton. The ratio is thus

$$\frac{\chi_{\text{para}}}{\chi_{\text{dia}}} = -\frac{g_L^2 J(J + 1)}{2Zk_B T} \frac{\hbar^2}{m\langle r^2 \rangle}.$$

If we assume $\langle r^2 \rangle = a_B^2$, so that $\hbar^2/m\langle r^2 \rangle \simeq 27.2 \text{eV}$, then with $T = 300 \text{K}$ (and $k_B T \approx 1/40 \text{ eV}$), $g_L = 2$, $J = 2$, and $Z \approx 30$, the ratio is $\chi_{\text{para}}/\chi_{\text{dia}} \approx -450$.

[2] *Adiabatic demagnetization* – In an ideal paramagnet, the spins are noninteracting and the Hamiltonian is

$$\mathcal{H} = \sum_{i=1}^{N_p} \gamma_i J_i \cdot \mathbf{H}$$

where $\gamma_i = g_i \mu_i/h$ and $J_i$ are the gyromagnetic factor and spin operator for the $i^{\text{th}}$ paramagnetic ion, and $\mathbf{H}$ is the external magnetic field.

(a) Show that the free energy $F(H, T)$ can be written as

$$F(H, T) = T \Phi(H/T).$$

If an ideal paramagnet is held at temperature $T_i$ and field $H_i \hat{z}$, and the field $H_i$ is adiabatically lowered to a value $H_f$, compute the final temperature. This is called “adiabatic demagnetization”.

1
(b) Show that, in an ideal paramagnet, the specific heat at constant field is related to the susceptibility by the equation
\[ c_H = T \left( \frac{\partial S}{\partial T} \right)_H = \frac{H^2 \chi}{T}. \]

Further assuming all the paramagnetic ions to have spin \( J \), and assuming Curie’s law to be valid, this gives
\[ c_H = \frac{1}{3} n_p k_B J (J + 1) \left( \frac{g \mu_B H}{k_B T} \right)^2, \]
where \( n_p \) is the density of paramagnetic ions. You are invited to compute the temperature \( T^* \) below which the specific heat due to lattice vibrations is smaller than the paramagnetic contribution. Recall the Debye result
\[ c_V = \frac{12}{5} \pi^4 n k_B \left( \frac{T}{\Theta_D} \right)^3, \]
where \( n = 1/\Omega \) is the inverse of the unit cell volume (i.e. the density of unit cells) and \( \Theta_D \) is the Debye temperature. Compile a table of a few of your favorite insulating solids, and tabulate \( \Theta_D \) and \( T^* \) when 1% paramagnetic impurities are present, assuming \( J = \frac{5}{2} \).

Solution:

(a) The partition function is a product of single-particle partition functions, and is explicitly a function of the ratio \( H/T \):
\[ Z = \prod_i \sum_{m=-J_i}^{J_i} e^{-m \gamma_i H / k_B T} = Z(H/T). \]

Thus,
\[ F = -k_B T \ln Z = T \Phi(H/T), \]
where
\[ \Phi(x) = -k_B \sum_{i=1}^{N_0} \ln \left[ \frac{\sinh \left( (J_i + \frac{1}{2}) \gamma_i x / k_B \right)}{\sinh \left( \gamma_i x / 2k_B \right)} \right]. \]

The entropy is
\[ S = -\frac{\partial F}{\partial T} = -\Phi(H/T) + \frac{H}{T} \Phi'(H/T), \]
which is itself a function of \( H/T \). Thus, constant \( S \) means constant \( H/T \), and
\[ \frac{H_f}{H_i} = \frac{T_f}{T_i} \Rightarrow T_f = \frac{H_f}{H_i} T_i. \]

(b) The heat capacity is
\[ C_H = T \left( \frac{\partial S}{\partial T} \right)_H = -x \frac{\partial S}{\partial x} = -x^2 \Phi''(x), \]
with $x = H/T$. The (isothermal) magnetic susceptibility is

$$\chi = -\left(\frac{\partial^2 F}{\partial H^2}\right)_T = -\frac{1}{T} \Phi''(x).$$

Thus,

$$C_H = \frac{H^2}{T} \chi.$$ 

Next, write

$$C_H = \frac{1}{3} n_p k_B J(J+1) \left(\frac{g_L \mu_B H}{k_B T}\right)^2,$$

$$C_V = \frac{12}{5} \pi^4 n k_B \left(\frac{T}{\Theta_D}\right)^3,$$

and we set $C_H = C_V$ to find $T^*$. Defining $\Theta_H \equiv g_L \mu_B H/k_B$, we obtain

$$T^* = \frac{1}{\pi} \left[ \frac{5\pi^2}{3} J(J+1) \frac{n_p}{n} \frac{\Theta_H^2 \Theta_D^3}{\Theta_H^3} \right]^{1/5}.$$

Set $J \approx 1$, $g_L \approx 2$, $n_p = 0.01 n$ and $\Theta_D \approx 500$ K. If $H = 1$ kG, then $\Theta_H = 0.134$ K. For general $H$, find

$$T^* \approx 3 K \cdot (H [kG])^{2/5}.$$