Homework 2 Solutions

1. Diamagnetic susceptibility of atomic hydrogen:

\[ \psi = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \]

Wave function \( a_0 = 0.529 \text{ Å} \). The appropriate expression for atomic diamagnetic susceptibility is:

\[ \chi_m = \frac{\vec{M}}{\vec{H}} = \frac{n |\langle \vec{m} \rangle |}{| \vec{B} |/ \mu_0} = -\frac{\mu_0 n e^2}{6m_e} < r^2 > \]

where \( n \) is the number of atoms \( N \) per unit volume \( V \).

\[ < r^2 >= < \psi_0^* r^2 \psi_0 > = \frac{1}{\pi a_0^3} \int_0^{2\pi} \int_0^\pi \int_0^\infty e^{-r/a_0} r^2 e^{-r/a_0} r^2 \sin \theta dr d\theta d\phi \]

can immediately integrate over \( r \) and \( f \) to get

\[ < r^2 > = \frac{4}{a_0^3} \int_0^\infty r^4 e^{-2r/a_0} dr \ldots \{ \text{let } u = 2r/a_0, \ du = 2dr/a_0 \} \cdot \]

\[ < r^2 > = \frac{4}{a_0^3} \left( \frac{a_0}{2} \right) \int_0^\infty u^4 e^{-u} du = a_0^2 \frac{4(4!)}{2^5} = 3a_0^2 \]

\[ \chi = -\frac{n\mu_0 \left( 1.6 \times 10^{-19} \right)^2 \cdot 3 \left( 0.53 \times 10^{-10} \right)^2}{6 \left( 9.11 \times 10^{-31} \right)} = -\frac{N}{V} \left( 5.0 \times 10^{-35} \right) = [\text{MKSA}] \]

Let \( N = \text{Avogadro's number} = 6.02 \times 10^{23} \text{ atoms/mole} \).

\[ \Rightarrow \chi = -3.0 \times 10^{-11} / V \text{ where } V \text{ is the volume of the 1-mole sample in m}^3. \]

2. Heat capacity from internal degrees of freedom, energy splitting \( \Delta \cdot k_B \)

(a) By Maxwell Boltzmann Statistics

\[ < U > = \frac{U_1 e^{-U_1/k_B T} + U_2 e^{-U_2/k_B T}}{e^{-U_1/k_B T} + e^{-U_2/k_B T}} \]
Set $U_1$ (arbitrarily) to zero so that $U_2 = k_B \Delta$.

$$\langle U \rangle = \frac{k_B \Delta e^{-k_B \Delta/k_B T}}{1 + e^{-k_B \Delta/k_B T}} = \frac{k_N \Delta e^{-\Delta/T}}{1 + e^{-\Delta/T}}$$

$$C_v = \frac{d < U >}{dT} = \frac{(1 + e^{-\Delta/T}) (\frac{+k_B \Delta}{T^2}) e^{-\Delta/T} - (k_B \Delta e^{-\Delta/T}) (\frac{+\Delta}{T^2}) e^{-\Delta/T}}{(1 + e^{-\Delta/T})^2}$$

$$C_v = \frac{+k_B \Delta^2 e^{-\Delta/T}}{(1 + e^{-\Delta/T})^2} = \frac{k_B (\Delta/T)^2 e^{-\Delta/T}}{(1 + e^{-\Delta/T})^2} = \frac{k_B (\Delta/T)^2 e^{\Delta/T}}{(e^{\Delta/T} + 1)^2}$$

(b) The plot of the heat capacity in (a) is shown below. By graphical means, we determine that the maximum in $C_V$ occurs at a value of $\Delta/T = 2.06$

### 3. Langevin model of Paramagnetism

(a) For the classical magnetic dipole, we have $U_m = -\vec{m}_0 \cdot \vec{B}_{local}$. Without loss of generality we can choose $B_{local}$ (henceforth written as $B_L$) along the z axis in a spherical coordinate system, so that $U_m = -m_B B_L \cos \theta$. The probability phase space is defined simply by the solid angle since the dipole can be
pointed anywhere along a direction $\theta, \phi$. The probability of pointing in a certain direction is dictated by the Boltzmann ansatz,

$$f(\theta, \phi) = \frac{\exp[-U(\theta, \phi)/k_B T]}{\int_0^{2\pi} \int_0^\pi \exp[-U(\theta, \phi)/k_B T] d\Omega}$$

where $d\Omega$ is the differential solid angle, $d\Omega = \sin \theta \, d\theta \, d\phi$. It also allows us to treat the dipole using the inherently random radial unit vector in spherical coordinates,

$$\vec{m} = m_0 \hat{r} = m_0 (\hat{x} \sin \theta \cos \phi + \hat{y} \sin \theta \sin \phi + \hat{z} \cos \theta)$$

This by statistical principles, we can write the mean value of the magnetic dipole moment:

$$<m> = \int_0^{2\pi} \int_0^\pi m_0 (\hat{x} \sin \theta \cos \phi + \hat{y} \sin \theta \sin \phi + \hat{z} \cos \theta) \exp[m_0 B_L \cos \theta / k_B T] \sin \theta \, d\theta \, d\phi$$

Clearly the terms in the numerator that include the $x$ and $y$ unit vectors vanish since they involve integrating $\cos \phi$ or $\sin \phi$ from 0 to $2\pi$. The term containing the $z$ unit vector can be evaluated through the substitution $W = m_0 B_L / k_B T$.

$$<\hat{m}> = \int_0^\pi m_0 (\hat{z} \cos \theta) \exp[W \cos \theta] \sin \theta \, d\theta$$

Evaluation of the denominator leads to

$$\int_0^\pi \exp[W \cos \theta] \sin \theta \, d\theta = -\left. \frac{\exp(W \cos \theta)}{W} \right|_0^\pi = \frac{2}{W} \sinh W$$

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The numerator is a bit more work, requiring integration by parts. We set \( U = \cos \theta \, d\theta \) and \( dV = \sin \theta \exp(W \cos \theta) \), and get \( dU = -\sin \theta \, d\theta \) and \( V = -\exp(W \cos \theta) / W \).

\[
\int_0^\pi m_0 (\hat{z} \cos \theta) \exp[W \cos \theta] \sin \theta \, d\theta \, d\phi = U V|_0^\pi - \int_0^\pi V \, dU
\]

\[
U \cdot V|_0^\pi = \frac{-\cos \theta}{W} \exp(W \cos \theta) \bigg|_0^\pi = \frac{e^{-W}}{W} + \frac{e^W}{W} = 2 \cosh W
\]

and

\[
-\int_0^\pi V \, dU = -\int_0^\pi \sin \theta \exp(W \cos \theta) \, d\theta = \exp(W \cos \theta) \bigg|_0^\pi = \frac{e^{-W}}{W^2} - \frac{e^W}{W^2} = -2 \sinh W
\]

Summing (3) and (4), dividing by (2), and substitution into (1) yields

\[
\langle \vec{m} \rangle = m_0 \hat{z} \left[ (2/W) \cosh W - (2/W^2) \sinh W \right] = m_0 \hat{z} \left[ \coth W - (1/W) \right]
\]

\[
\langle \vec{m} \rangle = m_0 \hat{z} \left[ \coth(m_0 B_L / k_B T) - (k_B T / m_0 B_L) \right]
\]

This is the famous Langevin function

(b) If there are \( n \) such dipoles per unit volume, the mean magnetization becomes

\[
\langle \vec{M} \rangle = n \langle \vec{m} \rangle = n \cdot m_0 \hat{z} \left[ \coth(m_0 B_L / k_B T) - (k_B T / m_0 B_L) \right]
\]

In the limit of high temperature, it is easy to show that the Taylor’s series of \( \coth(x) \) for small \( x \) is

\[
\coth(x) = 1/x + x/3 + \ldots.
\]

The first term of this cancels the last term in (5), so that

\[
\langle \vec{M} \rangle = n \cdot m_0 \left( \frac{m_0 B_L}{k_B T} \right) \hat{z}
\]

The high temperature limit of the paramagnetic susceptibility is

\[
\chi_m = \frac{\langle \vec{M} \rangle}{|B|} = \frac{|\vec{M}|}{|\vec{B}|/\mu_0} = \left( \frac{n m_0^2 \mu_0}{k_B T} \right)
\]

4. Curie-Weiss-Heisenberg Model of Ferromagnetism

(a) If \( \vec{B}_{local} = \vec{B}_{in} + \gamma m_0 \vec{M} \), then by inserting (5) from above, we can write
\[ \vec{B}_{\text{local}} = \vec{B}_L = \vec{B}_{\text{in}} + \gamma \mu_0 n \vec{m} = \vec{B}_{\text{in}} + \gamma \mu_0 n \cdot m_0 \hat{z} \{ \coth(m_0 B_L / k_B T) - (k_B T / m_0 B_L) \} \]  \hspace{1cm} (6)

This can be re-written as

\[ B_L = B_{\text{in}} + \gamma \mu_0 n \cdot m_0 \{ \coth(m_0 B_L / k_B T) - (k_B T / m_0 B_L) \} \]  \hspace{1cm} (7)

since \( B_L \) and \( B_{\text{in}} \) are both along the z axis. Eqn (7) is an *implicit* equation in \( B_L \) since \( B_L \) occurs on both sides and cannot be isolated.

(b) Eqn (7) can be solved uniquely for \( B_L \) in the case of spontaneous magnetization, which means that \( B_L \neq 0 \) even when \( B_{\text{in}} = 0 \). From such a solution, we can get \( M \) through \( M = B_L / (\gamma \mu_0) \). To proceed we re-write (7) using \( \beta = m_0 B_L / k_B T \), under the spontaneous condition:

\[ k_B T \beta / m_0 = \gamma \mu_0 n \cdot m_0 \{ \coth(\beta) - (1 / \beta) \} \]

or

\[ k_B T \beta / (r \gamma \mu_0 m_0^2) \equiv \alpha \cdot \beta = [ \coth(\beta) - (1 / \beta) ] \]  \hspace{1cm} (8)

where \( \alpha \) defines the quantity \( k_B T / [\gamma \mu_0 (m_0)^2] \). This can be solved implicitly using Excel, for example, or some other graphics tool. The solution table is shown on the attached page. The solution for \( \alpha \) as \( \beta \) goes to zero is simply \( \alpha = 0.333 \).

This might look like pure math until we recognize that since \( M = B_L / (\gamma \mu_0) \), and \( \beta = m_0 B_L / k_B T \), we can express \( M \) in the temperature independent form,

\[ M = k_B T \beta / m_0 \gamma \mu_0 = (\gamma \mu_0 m_0^2) \alpha \cdot \beta = n m_0 \alpha \beta \]

In Fig. 2 we plot the quantity \( M / (n m_0) = \alpha \cdot \beta \) vs both \( \beta \) and \( \alpha \). When plotted vs \( \beta \), we see the vanishing of \( M \) as \( \beta \) goes to zero consistent with the first step of Eqn (9). When plotted vs \( \alpha \), we see something even more interesting – the ferromagnetic phase transition curve. The value of \( \alpha \) where \( M \) reaches zero defines the Curie temperature, \( T_C \), as will be quantified in (c) below.
(c) By definition, $T_C$ can be found from the value of $\alpha$ that make $M$ go to zero. Specifically, it is the (maximum) value of $\alpha$ that solves Eqn (8) as $\beta$ goes to 0. From the table below, this is $\alpha = 0.333$. But we also know $\alpha = k_B T/[\gamma \mu_0 (m_0)^2]$. So we can write

$$T_C = \alpha_{\text{max}} \gamma \mu_0 (m_0)^2 / k_B. \quad (10)$$

To estimate $n$, it is good to start with iron, a bcc solid with lattice constant 2.87 Angstrom and, therefore, an atomic concentration of $2/(2.87 \text{ Ang})^3 = 8.5 \times 10^{28} \text{ m}^{-3}$. And we assume there is one magnetic moment per atom. Thus, if $m_0 = \mu_B = 9.27 \times 10^{-24} \text{ [MKSA]}$, and we set $T_C = 300 \text{ K}$, we can solve for $\gamma = 1355$, which is not much higher than expected. Putting in a more realistic value of $m_0$ would decrease this quadratically as seen from (10) above.

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Fig. 2. Top: Magnetization vs $\beta$. Bottom: Normalized magnetization vs $\alpha$, a quantity proportional to temperature. This is the characteristic ferromagnetic phase transition curve. The value of alpha where $M$ reaches zero defines the Curie temperature.