<u>Homework 2 Solutions</u>

1. Diamagnetic susceptibility of atomic hydrogen:

Wave function $y = \frac{1}{\sqrt{p\, a_0^3}} e^{-r/a_0}$. $a_0 = 0.529\text{Å}$. The appropriate expression for atomic diamagnetic susceptibility is:

$$c_m \equiv \frac{\vec{M}}{\vec{H}} = \frac{n\,|\langle \vec{m} \rangle|}{|\vec{B}|/m_0} = -\frac{m_0 n e^2}{6 m_e} < r >^2$$

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

$$< r^2 > = < y_0 \left| r^2 \right| y_0 > = \frac{1}{p\, a_0^3} \int_0^{2p} \int_0^{p} \int_0^{\infty} e^{-r/a_0} r^2 e^{-r/a_0} r^2 \sin q \, dr dq \, df$$

can immediately integrate over ? and f to get

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

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

$$c = \frac{-nm_0 \left(1.6\times10^{-19}\right)^2 \cdot 3\left(0.53\times10^{-10}\right)^2}{6\left(9.11\times10^{-31}\right)} = -\frac{N}{V}\left(5.0\times10^{-35}\right) = [MKSA]$$

Let N = Avogadro's number $= 6.02\times10^{23}\ atoms/mole$.

$\Rightarrow c = -3.0\times10^{-11}/V$ where V 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

$$< U > = \frac{U_1 e^{-U_1/kT} + U_2 e^{-U_2/k_B T}}{e^{-U_1/k_B T} + e^{-U_2/k_B T}}$$

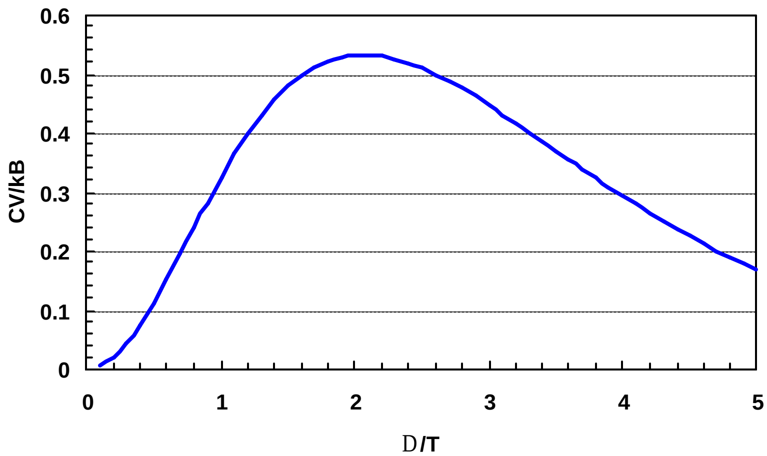

Fig. 1

Set U_1 (arbitrarily) to zero so that $U_2 = k_B\Delta$.

$$<U> = \frac{k_B \Delta e^{-k_B\Delta/k_BT}}{1+e^{-k_B\Delta/k_BT}} = \frac{k_N \Delta e^{-\Delta/T}}{1+e^{-\Delta/T}}$$

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

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

(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 $\boldsymbol{U_m} = -\vec{\boldsymbol{m}}_0 \cdot \vec{\boldsymbol{B}}_{local}$. 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 $U_m = -m_0 B_L \cos\theta$. The probability phase space is defined simply by the solid angle since the dipole can be pointed anywhere along a direction θ,ϕ . The probability of pointing in a certain direction is dictated by the Boltzmann ansatz,

$$\boldsymbol{f}(q,f)=\frac{\exp[-\boldsymbol{U}(q,f)/\boldsymbol{k_B T})]}{\int_0^{4p}\exp[-\boldsymbol{U}(q,f)/\boldsymbol{k_B T}]\boldsymbol{d}\Omega}=\frac{\exp[\boldsymbol{m}_0\boldsymbol{B_L}\cos q/\boldsymbol{k_B T})]}{\int_0^{4p}\exp[\boldsymbol{m}_0\boldsymbol{B_L}\cos q/\boldsymbol{k_B T}]\boldsymbol{d}\Omega}$$

where dΩ is the differential solid angle, dΩ = sinθ dθ dϕ.. It also allows us to treat the dipole using the inherently random radial unit vector in spherical coordinates,

$$\vec{\boldsymbol{m}}=\boldsymbol{m}_0\hat{\boldsymbol{r}}=\boldsymbol{m}_0(\hat{\boldsymbol{x}}\sin q\cos j+\hat{\boldsymbol{y}}\sin q\sin j+\hat{\boldsymbol{z}}\cos q)$$

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

$$<\vec{\boldsymbol{m}}>=\frac{\int_0^{2p}\int_0^{p}\boldsymbol{m}_0(\hat{\boldsymbol{x}}\sin q\cos j+\hat{\boldsymbol{y}}\sin q\sin j+\hat{\boldsymbol{z}}\cos q)\exp[\boldsymbol{m}_0\boldsymbol{B_L}\cos q)/\boldsymbol{k_B T}]\sin q\,\boldsymbol{d}q\,\boldsymbol{d}f}{\int_0^{2p}\int_0^{p}\exp[\boldsymbol{m}_0\boldsymbol{B_L}\cos q/\boldsymbol{k_B T}]\sin q\,\boldsymbol{d}q\,\boldsymbol{d}f}$$

Clearly the terms in the numerator that include the x and y unit vectors vanish since they involve integrating cosϕ or sinϕ from 0 to 2π. The term containing the z unit vector can be evaluated through the substitution $W = m_0B_L/k_BT$.

$$<\vec{\boldsymbol{m}}>=\frac{\int_0^{p}\boldsymbol{m}_0(\hat{\boldsymbol{z}}\cos q)\exp[\boldsymbol{W}\cos q]\sin q\,\boldsymbol{d}q}{\int_0^{p}\exp[\boldsymbol{W}\cos q]\sin q\,\boldsymbol{d}q} \tag{1}$$

Evaluation of the denominator leads to

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

The numerator is a bit more work, requiring integration by parts. We set U = cosθ dθ and dV = sinθexp(Wcosθ), and get dU = -sinθdθ and V = -exp(Wcosθ)/W

$$\int_0^p \boldsymbol{m}_0(\hat{\boldsymbol{z}}\cos q)\exp[\boldsymbol{W}\cos q]\sin q\,\boldsymbol{d}q\,\boldsymbol{d}f = \boldsymbol{UV}\Big|_0^p - \int_0^p \boldsymbol{VdU}$$

$$\boldsymbol{U}\cdot\boldsymbol{V}\Big|_0^p = \frac{-\cos q}{\boldsymbol{W}}\exp(\boldsymbol{W}\cos q)\Bigg|_0^p = \frac{\boldsymbol{e}^{-\boldsymbol{W}}}{\boldsymbol{W}} + \frac{\boldsymbol{e}^{\boldsymbol{W}}}{\boldsymbol{W}} = \frac{2}{\boldsymbol{W}}\cosh\boldsymbol{W} \qquad (3)$$

and $$-\int_0^p \boldsymbol{VdU} = -\int_0^p \frac{\sin q}{\boldsymbol{W}}\exp(\boldsymbol{W}\cos q)\boldsymbol{d}q = \frac{\exp(\boldsymbol{W}\cos q)}{\boldsymbol{W}^2}\Bigg|_0^p = \frac{\boldsymbol{e}^{-\boldsymbol{W}}}{\boldsymbol{W}^2} - \frac{\boldsymbol{e}^{\boldsymbol{W}}}{\boldsymbol{W}^2} = \frac{-2\sinh\boldsymbol{W}}{\boldsymbol{W}^2} \qquad (4)$$

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

$$<\vec{\boldsymbol{m}}> = \frac{\boldsymbol{m}_0\hat{\boldsymbol{z}}[(2/\boldsymbol{W})\cosh\boldsymbol{W} - (2/\boldsymbol{W}^2)\sinh\boldsymbol{W}}{(2/\boldsymbol{W})\sinh\boldsymbol{W}} = \boldsymbol{m}_0\hat{\boldsymbol{z}}[\coth\boldsymbol{W} - (1/\boldsymbol{W})]$$

$$<\vec{\boldsymbol{m}}> = \boldsymbol{m}_0\hat{\boldsymbol{z}}[\coth(\boldsymbol{m}_0\boldsymbol{B}_{\boldsymbol{L}}/\boldsymbol{k}_{\boldsymbol{B}}\boldsymbol{T}) - (\boldsymbol{k}_{\boldsymbol{B}}\boldsymbol{T}/\boldsymbol{m}_0\boldsymbol{B}_{\boldsymbol{L}})]$$

This is the famous Langevin function

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

$$<\vec{\boldsymbol{M}}> = \boldsymbol{n}<\vec{\boldsymbol{m}}> = \boldsymbol{n}\cdot\boldsymbol{m}_0\hat{\boldsymbol{z}}[\coth(\boldsymbol{m}_0\boldsymbol{B}_{\boldsymbol{L}}/\boldsymbol{k}_{\boldsymbol{B}}\boldsymbol{T}) - (\boldsymbol{k}_{\boldsymbol{B}}\boldsymbol{T}/\boldsymbol{m}_0\boldsymbol{B}_{\boldsymbol{L}})] \qquad (5)$$

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 + ….

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

$$<\vec{\boldsymbol{M}}> \approx \boldsymbol{n}\cdot\boldsymbol{m}_0\left(\frac{\boldsymbol{m}_0\boldsymbol{B}_{\boldsymbol{L}}}{\boldsymbol{k}_{\boldsymbol{B}}\boldsymbol{T}}\right)\hat{\boldsymbol{z}}$$

The high temperature limit of the paramagnetic susceptibility is

$$c_{\boldsymbol{m}} \equiv \frac{|\vec{\boldsymbol{M}}|}{|\vec{\boldsymbol{H}}|} = \frac{|\vec{\boldsymbol{M}}|}{|\vec{\boldsymbol{B}}|/m_0|} = \left(\frac{\boldsymbol{n}\boldsymbol{m}_0^2 m_0}{\boldsymbol{k}_{\boldsymbol{B}}\boldsymbol{T}}\right)$$

4. Curie-Weiss-Heisenberg Model of Ferromagnetism

(a) If $\vec{\boldsymbol{B}}_{\boldsymbol{local}} = \vec{\boldsymbol{B}}_{\boldsymbol{in}} + g m_0\vec{\boldsymbol{M}}$, then by inserting (5) from above, we can write

$$\vec{B}_{local} \equiv \vec{B}_L = \vec{B}_{in} + \gamma\mu_0 n\vec{m} = \vec{B}_{in} + \gamma\mu_0 n \cdot m_0 \hat{z}[\coth(m_0 B_L / k_B T) - (k_B T / m_0 B_L)] \quad (6)$$

This can be re-written as

$$B_L = B_{in} + \gamma\mu_0 n \cdot m_0 [\coth(m_0 B_L / k_B T) - (k_B T / m_0 B_L)] \quad (7)$$

since B_L and B_{in} are both along the z axis. Eqn (7) is an *implicit* equation in B_L since B_L occurs on both sides and can not 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 $B_{in} = 0$. 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

$$k_B T \beta / (n\gamma\mu_0 m_0^2) \equiv \alpha \cdot \beta = [\coth(\beta) - (1/\beta)] \quad (8)$$

where α defines the quantity $k_B T/[n\gamma\mu_0(m_0)^2]$. 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 α as β 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,

$$M = \frac{k_B T \beta}{m_0 \gamma\mu_0} = \frac{n\gamma\mu_0 m_0^2 \alpha \cdot \beta}{m_0 \gamma\mu_0} = n m_0 \alpha\beta \quad (9)$$

In Fig. 2 we plot the quantity $M/(nm_0) = \alpha\cdot\beta$ vs both β and α. When plotted vs β, we see the vanishing of M as β goes to zero consistent with the first step of Eqn (9). When plotted vs α, we see something even more interesting – the ferromagnetic phase transition curve. The value of α 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 α that make M go to zero. Specifically, it is the (maximum) value of α that solves Eqn (8) as β goes to 0. From the table below, this is α = 0.333. But we also know $\alpha = k_B T/[n\gamma\mu_0(m_0)^2]$. So we can write

$$T_C = \alpha_{max}\, n\gamma\mu_0(m_0)^2/k_B. \tag{10}$$

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 $2/(2.87\ \text{Ang})^3 = 8.5\text{x}10^{28}\ \text{m}^{-3}$. And we assume there is one magnetic moment per atom. Thus, if $m_0 = \mu_B = 9.27\text{x}10^{-24}$ [MKSA], and we set T_C = 300 K, we can solve for γ = 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.

Solution table

β	α
0.1	0.333
0.2	0.332
0.3	0.331
0.4	0.33
0.5	0.328
0.6	0.325
0.7	0.323
0.8	0.32
0.9	0.3165
1	0.313
2	0.269
3	0.224
4	0.188
5	0.16
6	0.139
7	0.122
8	0.109
9	0.0987
10	0.09
12	0.076
14	0.066
16	0.059
18	0.052
20	0.0475
30	0.032
40	0.024
50	0.0196
100	0.0099

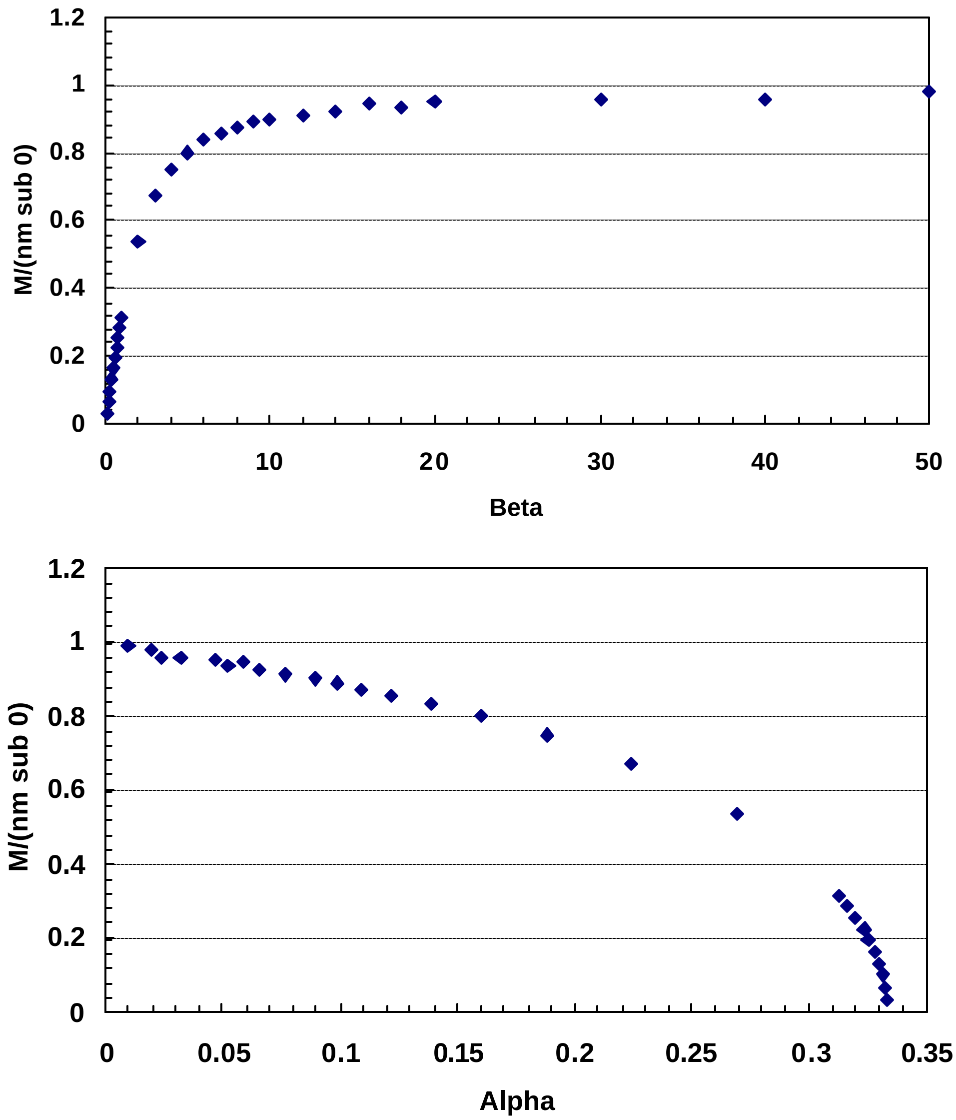

Fig. 2. Top: Magnetization vs β. Bottom: Normalized magnetization vs α, a quantity proportional to temperature. This is the characteristic ferromagnetic phase transition curve. The value of alpha where M reaches zero defines the Curie temperature.