CLASSICAL STATISTICS OF PARAMAGNETISM

The most famous types of Magnetic materials are:

(i) *Paramagnetic*: A property exhibit by substances which, when placed in a magnetic field, are magnetized parallel to the field to an extent proportional to the field (except at very low temperatures or in extremely large magnetic fields).
(ii) *Ferromagnetic*: A property, exhibited by certain materials, alloys, and compound of the transition (iron group), rare-earth, and actinide elements, in which the internal magnetic moments spontaneously organized in a common direction; gives rise to a permeability considerably greater than that of vacuum, and to magnetic hysteresis.
(iii) *Diamagnetic*: Having a magnetic permeability less than one; materials with this property are repelled by a magnet and tend to position themselves at right angles to magnetic lines of force.

Type	Example	Susceptibility (χ)	Permeability	Comments
Paramagnetic	Aluminum	positive	>1, (1.001)	Temperature dependant
Ferromagnetic	Iron, nickle	≈ 0	10^4	Magnetic domain, hysteresis
Diamagnetic	bismuth	negative	< 1, (0.999)	

Magnetic susceptibility χ represents the response of a system to the external field.

Hysteresis means the dependence of the polarization of ferromagnetic materials not only on the applied (magnetic) field but also on their previous history.

Magnetic domain, a region of ferromagnetic material within which atomic or molecular magnetic moments are aligned parallel.

Permeability, a factor, characteristic of a material, that is proportional to the magnetic induction produced in a material divided by the magnetic field strength; it is a tensor when these quantities are not parallel.

Consult Phys-102 book for more details discussion.

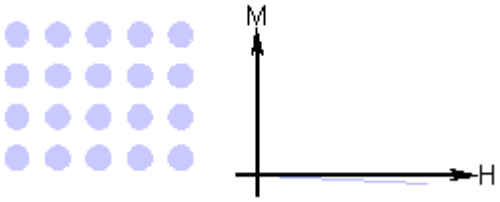
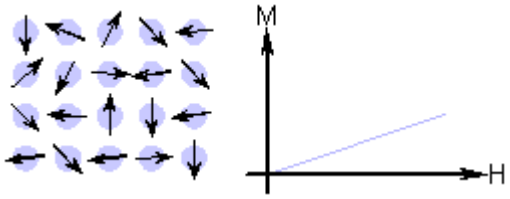
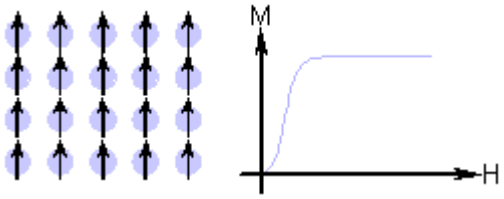
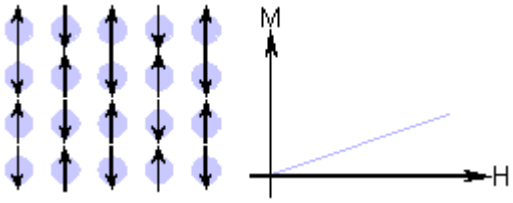
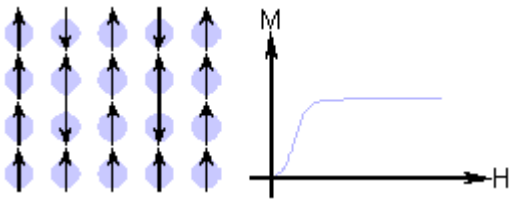
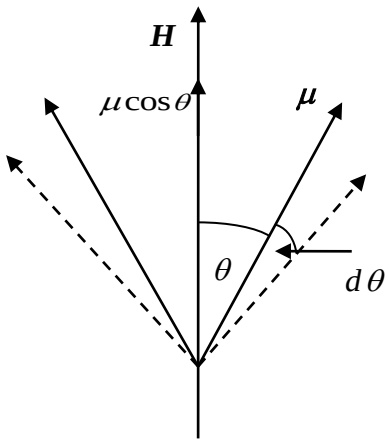
Type of Magnetism	*Susceptibility*	*Atomic / Magnetic Behaviour*	*Example / Susceptibility*
Diamagnetism	Small & negative.	Atoms have no magnetic moment 	Au -2.74x10^{-6} Cu -0.77x10^{-6}
Paramagnetism	Small & positive.	Atoms have randomly oriented magnetic moments 	β-Sn 0.19x10^{-6} Pt 21.04x10^{-6} Mn 66.10x10^{-6}
Ferromagnetism	Large & positive, function of applied field, microstructure dependent.	Atoms have parallel aligned magnetic moments 	Fe ~100,000
Antiferromagnetism	Small & positive.	Atoms have mixed parallel and anti-parallel aligned magnetic moments 	Cr 3.6x10^{-6}
Ferrimagnetism	Large & positive, function of applied field, microstructure dependent	Atoms have anti-parallel aligned magnetic moments 	Ba ferrite ~3

Table 2: Summary of different types of magnetic behaviour.

Model: Consider *N* identical, localized (i.e. distinguishable), practically static, mutually noninteracting and freely orientable dipoles at absolute temperature *T* and placed in an external magnetic field *H* pointing along *z* direction. Then the torque acting on the dipole is given by: $\bar{\tau} = \bar{\mu} \times \bar{H} = \mu H \sin\theta$, and the (magnetic) potential energy can be written as: $\varepsilon = -\bar{\mu}.\bar{H} = -\mu H \cos\theta$, where θ is the angle between the magnetic field and the dipole and μ is the magnetic dipole moment.



$$\varepsilon = \int_{\pi/2}^{\theta} \tau d\theta = \mu H \int_{\pi/2}^{\theta} \sin\theta d\theta = -\mu H \cos\theta = -\boldsymbol{\mu} \cdot \boldsymbol{H} = \mu_z H,$$

1- Qualitative Description:

A non-interacting atom with magnetic dipole moment μ (μ is positive) could be point either parallel or anti-parallel to an external magnetic field H. At temperature T, we have the question:

Q: What is the mean magnetic moment $\bar{\mu}_H$ (in the direction H) of such an atom?

A: There are two possible states, and they are:

state	condition	Magnetic energy	probability
(+)	$\mu\uparrow H\uparrow$	$\varepsilon_+ = -\mu H$ (lower $\bar{\mu}_H = \mu$)	$P_+ = Ce^{\beta\mu H}$
(-)	$\mu\downarrow H\uparrow$	$\varepsilon_- = \mu H$ (higher $\bar{\mu}_H = \mu$)	$P_- = Ce^{-\beta\mu H}$

ε_+ is lower energy	$\Rightarrow$	atom is more likely to be found
ε_- is higher energy	$\Rightarrow$	atom is less likely to be found

Define

$$\eta = \beta\mu H = \frac{\mu H}{k_B T} = \frac{\text{(magnetic) potential energy}}{\text{(thermal) translational energy}}$$

η is a dimensionless parameter which measure the ratio of the magnetic energy μH, which tends to align the magnetic moment, to the thermal energy $k_B T$, which tends to keep it randomly oriented. Then

Case 1	$\eta << 1$	$T >> 1$	$P_+ = P_-$	$\bar{\mu}_H = 0 \Rightarrow \mu$ is randomly oriented (disorder)
Case 2	$\eta >> 1$	$T << 1$	$P_+ = 1,\ P_- = 0$	$\bar{\mu}_H = \mu \Rightarrow \mu\uparrow H\uparrow$ (ordered)

1- Qualitative Description:

the mean magnetic moment $\bar{\mu}_H$ is given by:

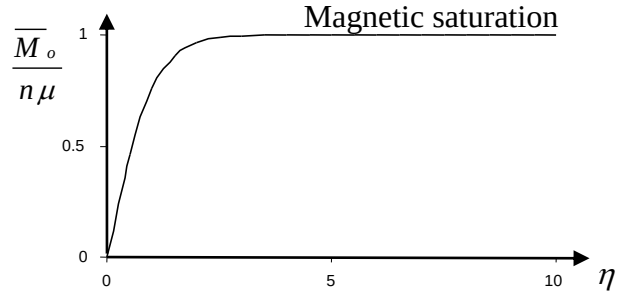
$$\bar{\mu}_H = \frac{\mu P_+ + (-\mu)P_-}{P_+ + P_-} = \mu \frac{e^{\eta} - e^{-\eta}}{e^{\eta} + e^{-\eta}} = \mu \tanh\eta$$

The ''magnetization'' $\bar{M}_o$, or mean magnetic moment per unit volume, is then in the direction of H and reads

$$\bar{M}_o = n\bar{\mu}_H = \begin{cases} n\mu\eta = \chi H & \text{for } \eta << 1 \text{ (high temperature)} \\ n\mu & \text{for } \eta >> 1 \text{ (low temperature)} \end{cases}$$

where *n* is the total number of magnetic atoms per unit volume. The above results agree with the qualitative descriptions. Here, $\chi = \frac{n\mu^2}{k_B T}$ is the "magnetic susceptibility". The result $\chi \propto \frac{1}{T}$ is

known as **Curie's law**. At very low temperature $\overline{M}_o$ becomes independent of *H* and equal to the maximum (or "saturation magnetization") magnetization which the substance can exhibit. Saturation magnetization means complete alignment of the magnetic dipoles in the field direction.



T large, high disorder T small, low disorder
H larger → more ordered

Figure: Total magnetic moment of a spin ½ paramagnet.

Classically, the number of dipoles, *dn*, having axes within the solid angle $d\omega$ lying between two hollow cones on semi-angles θ and $\theta+d\theta$ is given by:

$$dn = Ce^{-\beta\varepsilon}d\omega = Ce^{\beta\mu H\cos\theta}d\omega = Ce^{\beta\mu H\cos\theta}\left(2\pi\sin\theta d\theta\right)$$

Where C is a constant. Each one of these dipoles contributes a component of magnetic moment $\mu\cos\theta$ to the magnetization, where as the components perpendicular to the field direction cancel each other. Hence the average component of the magnetic moment of each atom along the field direction multiplied by the number of atoms per unit volume, *N*, gives the magnetization, i.e.,

$$\bar{M} = N\left\langle\mu\cos\theta\right\rangle = N\frac{\int_0^{\pi}\mu\cos\theta\, dn}{\int_0^{\pi}dn} = N\,\mu\frac{\int_0^{\pi}\cos\theta\sin\theta e^{\beta\mu H\cos\theta}d\theta}{\int_0^{\pi}\sin\theta e^{\beta\mu H\cos\theta}d\theta}$$

Let us define the ratio $\eta = \beta\mu H = \frac{\mu H}{k_B T} = \frac{\text{(magnetic) potential energy}}{\text{(thermal) translational energy}}$, and

$y = \cos\theta \Rightarrow -\sin\theta = dy$, therefore:

$$\bar{M} = N\,\mu\frac{\int_1^{-1} ye^{\eta y}dy}{\int_1^{-1} e^{\eta y}dy} = N\,\mu\left[\frac{e^{\eta}+e^{-\eta}}{e^{\eta}-e^{-\eta}} - \frac{1}{\eta}\right] = N\,\mu\left[\coth\eta - \frac{1}{\eta}\right]$$

$$= N\,\mu L(\eta)$$

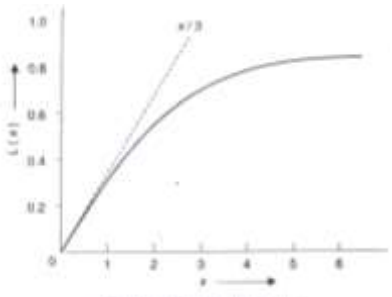
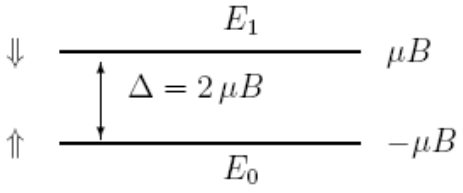


Fig. 8.2. Variation of $L(x)$ with x.

$$\chi = \left(\frac{\partial\bar{M}_o}{\partial H}\right)_{H\to 0} = N\frac{\bar{\mu}_H}{H} = \begin{cases} N\,\mu L(\eta)\big|_{\eta\to 0} = N\,\mu\dfrac{\eta}{3} & \text{for } \eta \ll 1 \text{ (high temperature)} \\ N\,\mu & \text{for } \eta \gg 1 \text{ (low temperature)} \end{cases}$$

Example: A N-monatomic Boltzmann ideal gas of spin ½ atoms in a uniform magnetic field, in addition to its usual kinetic energy, a magnetic energy of $\pm\mu B$ per atom, where is the magnetic



moment. (It is assumed that the gas is so dilute that the interaction of magnetic moments may be neglected.)

a- What is the partition function of the system?

$$Z_{sp} = e^{-\beta\varepsilon_1} + e^{\beta\varepsilon_2} = e^{-\eta} + e^{\eta} = 2\cosh(\eta), \qquad \eta = \beta\varepsilon$$

$$\overline{E} = \frac{1}{Z_{sp}}\left(\varepsilon_1 e^{-\beta\varepsilon_1} + \varepsilon_2 e^{\beta\varepsilon_2}\right) = \frac{\varepsilon e^{-\eta} - \varepsilon e^{\eta}}{2\cosh(\eta)} = -\varepsilon\tanh(\eta)$$

and the total energy $U = N\,\overline{E} = -N\,\varepsilon\tanh(\mu)$. In summary:

Quantity	Formula
Partition function	$Z_{sp} = 2\cosh(\eta) \;\Rightarrow\; Z_N = 2^N \cosh^N(\eta)$
Helmholtz free energy	$F = -Nk_BT\,\ln(Z_N) = -Nk_BT\,\ln\{2\cosh(\eta)\}$
Entropy	$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = Nk_B\,\ln\left[\,2\cosh(\eta) - \eta\tanh(\eta)\right]$
Internal energy	$U = -\left(\frac{\partial \ln Z}{\partial \beta}\right)_{V,N} = -N\,\mu H\,\tanh(\eta)$
Heat capacity	$C_V = \left(\frac{\partial U}{\partial T}\right)_H = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_{V,N} = \frac{Nk_B\eta^2}{\cosh^2\eta}$
Total magnetic moment	$M = -\left(\frac{\partial F}{\partial H}\right)_{V,N} \left(= n\bar{\mu} = \frac{\mu e^{\eta} - \mu e^{-\eta}}{e^{\eta} + e^{-\eta}} = n\mu\tanh(\eta)\right.$

Notice: $U = -M\ \mathrm{H}$

Figure: Heat capacity of spin ½ paramagnet. (Schottky anomaly)

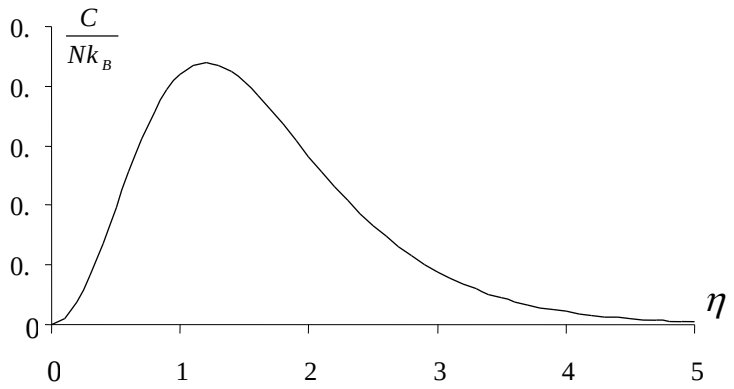
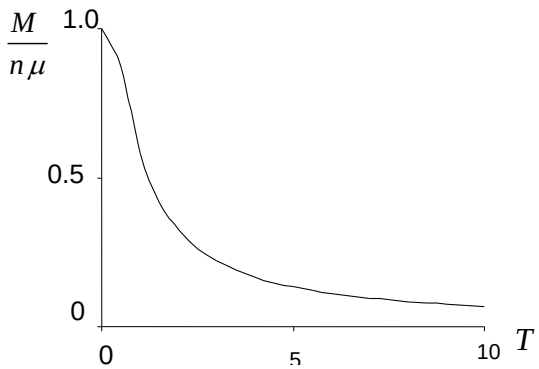


Figure: Total magnetic moment of a spin ½ paramagnet.



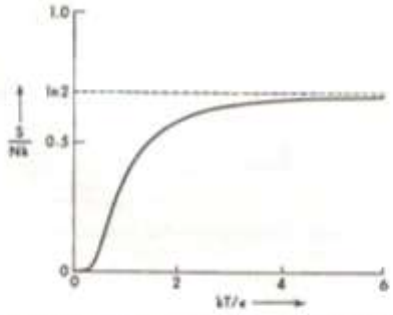


FIG. 3.10. The entropy of a system of magnetic dipoles (with $J = \frac{1}{2}$) as a function of temperature.

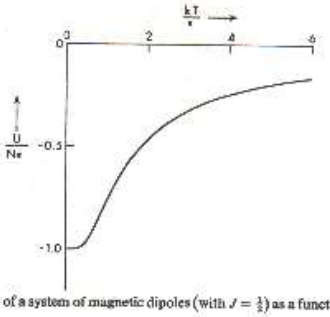


FIG. 3.11. The energy of a system of magnetic dipoles (with $J = \frac{1}{2}$) as a function of temperature.

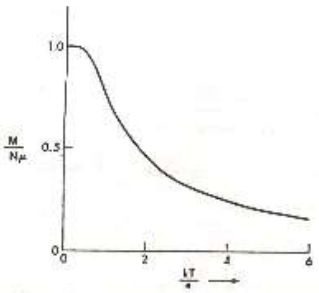


FIG. 3.12. The magnetization of a system of magnetic dipoles (with $J = \frac{1}{2}$) as a function of temperature.

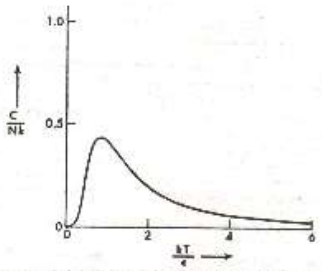


FIG. 3.13. The specific heat of a system of magnetic dipoles (with $J = \frac{1}{2}$) as a function of temperature.

Comments:

1- For the internal energy: At low T , all the spins are aligned with the field and the energy per spin is close to $-\mu H$. However as T increases, thermal fluctuations start to flip some of the spins; this is noticeable when $k_B T$ is of the order of μH . As T gets very large, the energy tends to zero as the number of up and down spins become more nearly equal. $\frac{P_-}{P_+} = Ce^{-2\beta\mu H}$, so it never exceeds one. We can say that: at high temperature, the thermal energy is sufficient to disorder the magnetic dipole orientation.

2- The heat capacity tends to zero both at high and low T . At low T the heat capacity is small because $k_B T$ is much smaller than the energy gap $2\mu H$, so thermal fluctuations which flip spins are rare and it is hard for the system to absorb heat. This behavior is universal; quantization means that there is always minimum excitation energy of a system and if the temperature is low enough, the system can no longer absorb heat. The high-T behavior arises because the number of down-spins never exceeds the number of up-spins, and the energy has a maximum of zero. As the temperature gets very high, that limit is close to being reached, and raising the temperature still further makes very little difference. This behavior is *not* universal, but only occurs where there is a finite number of energy levels (here, there are only two). Most systems have an infinite tower of energy levels, there is no maximum energy and the heat capacity does not fall off.

3- It is not easy to attain the maximum of the paramagnetic heat capacity curve as the following calculation shows. The paramagnetic heat capacity becomes important only at very low temperatures. The maximum occurs at $\eta \approx 1$, i.e. $\frac{\mu H}{k_B T} = 1$. Now the magnitude of

$$\frac{\mu}{k_B} = \frac{9.27\times10^{-24}}{1.38\times10^{-23}} \approx 1$$

so to get the maximum we must have $H \approx T$

maximum attainable fields are $H \approx 1$ Tesla

so we need a maximum temperature of $T \approx 1$ K

4- At zero temperature, the magnetization goes to $N\mu$ and all the spins are up. There is an order, and so the entropy is zero. The stronger the field, the higher the temperature has to be before the spins start to be appreciably disordered. At high temperatures the spins are nearly as likely to be up as down; the magnetization falls to zero and the entropy reaches a maximum. The entropy of this state is $Nk_B \ln 2$. Remember that, 2 is the total number of microstates.

5- If it is possible to excite all the particles to the upper energy state so $n_\uparrow = N$ the system would again be completely ordered and in state of zero entropy. According the equation

$$n_\uparrow = \frac{N}{1+e^{\beta\varepsilon}}.$$

This situation could only be achieved if the temperature T approached a value of zero from the negative temperature side, i.e.

$$\frac{N}{1+e^{\varepsilon/(-k_B T)}} \to N \quad \text{at } T \to 0.$$

While a negative temperature of this magnitude is not obtainable in practice, it is possible to obtain finite negative temperatures as defined by the above equation.

Model: Consider *N* identical, localized (i.e. distinguishable), practically static, mutually noninteracting and freely orientable dipoles at absolute temperature *T* and placed in an external magnetic field *H* pointing along *z* direction. Then the torque acting on the dipole is given by: $\bar{\tau} = \bar{\mu} \times \bar{H} = \mu H \sin\theta$, and the (magnetic) potential energy can be written as: $E = -\bar{\mu}.\bar{H} = -\mu H \cos\theta$, where θ is the angle between the magnetic field and the dipole and μ is the magnetic dipole moment. The partition function of the system, *Z*, is given by

$$Z_{\text{sp}} = \sum_{\{\theta_i\}} e^{\beta\mu H \sum_{i=1}^{N} \cos\theta_i},$$

where the first summation for Z_{sp} goes over all sets of orientations of the system. Classically one can have:

$$Z_{\text{sp}} = \sum_{\theta} e^{\beta\mu H\cos\theta} = \int_0^{2\pi} d\varphi \int_0^{\pi} e^{\beta\mu H\cos\theta} \sin\theta d\theta = 4\pi \frac{\sin\eta}{\eta}$$

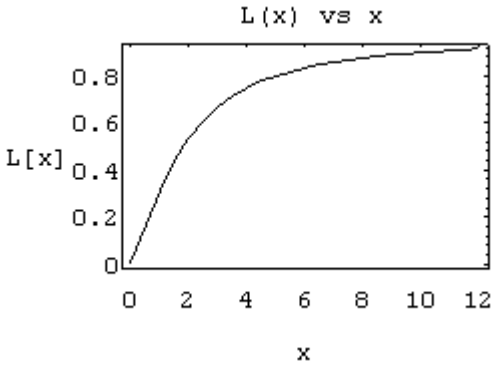
Where $\eta = \beta\mu H = \frac{\mu H}{k_B T}$. The mean magnetic moment ***M*** of the system will indeed be in the direction of the field ***H***; for its magnitude we have:

$$M_z = \left\langle \sum_{i=1}^{N} \mu\cos\theta_i \right\rangle = \frac{1}{\beta} \frac{\partial \ln Z_N}{\partial H} = \frac{N}{\beta} \frac{\partial \ln Z_{\text{sp}}}{\partial H} = N \left\langle \mu\cos\theta \right\rangle.$$

Hence, we obtain the mean magnetic moment per dipole as:

$$\bar{\mu}_z = \frac{M_z}{N} = \mu\left[\coth\eta - 1/\eta\right] = \mu L(\eta),$$

where *L(x)* is the **Langevin's function**, $L(x) = \left[\coth x - 1/x\right]$. The dimensionless parameter $\eta = \beta\mu H$ determines the strength of the (magnetic) potential energy μH against the (thermal) kinetic energy kT. See the plotting of L(x) function.



If we have *n* dipoles per unit volume in the system, then the magnetization of the system, viz. the mean magnetic moment per unit volume, will be given by:

$$M_{zn} = n\bar{\mu}_z = n\mu L(\eta) \ .$$

For $(\eta >> 1,\ L(\eta) = 1)$, i.e. the magnetic fields so strong (or temperature so low), we have the magnetic saturation:

$$\bar{\mu}_z \approx \mu, \quad M_{zn} \approx n\bar{\mu}_z.$$

For η << 1, i.e. the magnetic fields so weak (or temperature so high), we have:

$$M_{zn} \approx n\bar{\mu}_z = n\mu L(\eta << 1) \approx n\mu L(\frac{\eta}{3} - \frac{\eta^3}{45} + \cdots) \approx \frac{n\mu^2}{3kT} H,$$

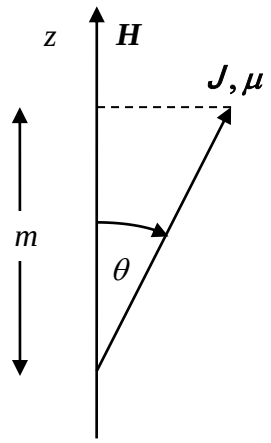
to the lowest order of approximation. So, the high temperature ***susceptibility*** of the system is, therefore, given by:

$$\chi = \lim\left(\frac{\partial M_{zn}}{\partial H}\right)_{H\to 0} \approx \frac{n\mu^2}{3kT} = \frac{C}{T}.$$

The last equation is the **Curie's law** of paramagnetism and the parameter C being the Curie's constant

Appendix (1)
General Calculation of Magnetization

The problem of paramagnetism could be treated classically (Langevin's theory) or quantum-mechanically. Here, we are following the quantum mechanical treatment. Consider a system consisting of N non-interacting dipoles at absolute temperature T and placed in an external magnetic field H pointing along z-direction (Note that: H is the local magnetic field acting on the atom, i.e. it includes both external and field produced by all other atoms). Then the (magnetic) potential energy of a dipole can be written as:



$$\varepsilon = -\boldsymbol{\mu}\cdot\boldsymbol{H} = \mu_g \boldsymbol{J}\cdot\boldsymbol{H} = -\mu_g J_z H$$

Here $\mu_g = g\,\mu_o$, (μ_o is the Bohr magneton = $\frac{e\hbar}{2m_e}$, e and m_e are the charge and the rest mass of the electron, respectively) and is the Lande` g-factor, i.e.

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

S and L being, respectively, the spin and orbital quantum numbers of the dipole and J is the total angular momentum of the atom. In quantum mechanics, the values of J_z are discrete and are given by:

$$J_z = m, \qquad m = -J, -J+1, \cdots\cdots, J-1, J$$

Thus there are $2J+1$ possible values of m corresponding to that many possible projections of the angular momentum vector along the z- axis. The probability P_m that an atom is in a state labeled by m is given by

$$P_m = Ce^{\beta\mu_z H}, \qquad \mu_z = m\,\mu_g$$

The mean $\overline{\mu}_z$ component of the magnetic moment of an atom is therefore:

$$\overline{\mu}_z = \frac{\sum_{m=-J}^{J} \mu_z e^{\beta\mu_z H}}{Z_{\text{sp}}}, \qquad Z_{\text{sp}} = \sum_{m=-J}^{J} e^{\beta\mu_z H}$$

which could be simplified as:

$$\overline{\mu}_z = \frac{1}{\beta}\frac{1}{Z_{\text{sp}}}\frac{\partial Z_{\text{sp}}}{\partial H} = \frac{1}{\beta}\frac{\partial \ln Z_{\text{sp}}}{\partial H}$$

To calculate Z_{sp}, let us introduce the ratio $\eta = \beta\mu H = \frac{\mu H}{k_B T}$, thus

$$Z_{\text{sp}} = \sum_{m=-J}^{J} e^{m\eta} = \frac{e^{-\eta J} - e^{-\eta(J+1)}}{1 - e^{-\eta J}} = \frac{\sinh(J+\frac{1}{2})\eta}{\sinh(\frac{\eta}{2})}$$

Then

$$\bar{\mu}_z = \frac{1}{\beta}\frac{\partial \ln Z_{sp}}{\partial \eta}\frac{\partial \eta}{\partial H} = \mu_g\, J\, B_J(\eta)$$

Where $B_J(\eta)$ is the Brillouin function and is given by

$$B_J(\eta) \equiv \frac{1}{J}\left[(J+\tfrac{1}{2})\sinh(J+\tfrac{1}{2})\eta - \tfrac{1}{2}\coth(\tfrac{\eta}{2})\right] = \begin{cases} \frac{1}{J}\left[(J+\frac{1}{2})-\frac{1}{2}\right]=1 & ,\eta >> 1 \\ \frac{J+1}{3}\eta & ,\eta << 1 \end{cases}$$

If there are *n* atoms per unit volume, the mean magnetic moment per unit volume (or magnetization) becomes

$$M_{zn} = n\,\bar{\mu}_z = n\mu_g J\, B_J(\eta) = \begin{cases} n\mu_g J & ,\eta >> 1 \\ n\mu_g J\left(\frac{J+1}{3}\right)\eta = \chi H & ,\eta << 1 \end{cases}$$

and $\chi = n\mu_g^2 \frac{J(J+1)}{3k_B T}$ is the "magnetic susceptibility". The result $\chi \propto \frac{1}{T}$ is known as **Curie's law**. In the case $J \to \infty$ and $g \to 0$ but gJ and μ_g stay constants, $B_J(\eta)$ tends to become independent of J and identical with Langevin's function $L(\eta)$.

Appendix (2)
Statistics of various ensembles

1- The microcanonical ensemble:- Systems with fixed N and V , and an energy lying within the interval $(E-\frac{1}{2}\Delta, E+\frac{1}{2}\Delta)$, where $\Delta << E$. The total number of distinct microstates accessible to a system is $\Gamma(E, V, N; \Delta)$. From the equal a priori probabilities

$$p_k = \frac{1}{\Gamma(E, V, N; \Delta)}$$

Thus all the states in the microcanonical ensemble appear with the same weight which implies that

$$\hat{\rho} = \sum_i p_i |\psi_i\rangle\langle\psi_i|$$

with the discrete eigenvalues (E_i) lying within the range $E-\frac{1}{2}\Delta < E_i < E+\frac{1}{2}\Delta$.

$$(\hat{\rho})_{mn} = \sum_i \langle\psi_m|\psi_i\rangle p_i \langle\psi_i|\psi_n\rangle = \sum_i \frac{1}{\Gamma(E)}\delta_{mi}\delta_{in} = p_n\delta_{mn}$$

with

$$p_n = \begin{cases} \frac{1}{\Gamma(E)}, & \text{for each of the accessible states} \\ 0 & \text{for all other states} \end{cases}$$

The entropy

$$S = k_B \ln\Gamma(E)$$

where $\Gamma(E)$ is now calculated quantum mechanically, taking into account the indistinguishability of the particles, which implies no paradox, such as Gibbs' paradox. Also, as $T \to 0$, system goes to the ground state which gives $\Gamma(E) = 1$ i.e. $S = 0$ (third law of thermodynamics)

$$\Gamma(E) = \begin{cases} 1 & \text{pure case, } p = p^2 \\ >1 & \text{mixed case (degenrate), } p \neq p^2, S \neq 0 \end{cases}$$

2- The microcanonical ensemble:- Systems with fixed N , V and T and different energy E . The probability that a system, chosen at random from the ensemble, possesses an energy E_n is determined by Boltzmaan factor $e^{-\beta E_n}$, and the density matrix in the energy representation is therefore taken as

$$(\hat{\rho})_{mn} = p_n\delta_{mn}$$

with

$$p_n = \frac{e^{-\beta E_n}}{Z}, \qquad n = 0,1,2,\cdots$$

Thus density operator in the canonical ensemble could be written as:

$$\hat{\rho} = \sum_i |\psi_i\rangle p_i \langle\psi_i| = \sum_i |\psi_i\rangle \frac{e^{-\beta E_i}}{Z}\langle\psi_i| = \frac{e^{-\beta\hat{H}}}{Z}\sum_i |\psi_i\rangle\langle\psi_i|$$

$$= \frac{e^{-\beta\hat{H}}}{\mathrm{Tr}\left(e^{-\beta\hat{H}}\right)}$$

The expectation value $\langle\hat{A}\rangle_N$ of a physical quantity A is now given by

$$\left\langle \hat{A} \right\rangle_N = \mathrm{Tr}\left(\hat{A}\hat{\rho}\right) = \frac{\mathrm{Tr}\left(\hat{A}e^{-\beta\hat{H}}\right)}{\mathrm{Tr}\left(e^{-\beta\hat{H}}\right)}$$

the suffix N here emphasizes he fact that the averaging has been done over an ensemble with N fixed.

Example: If $\hat{H} = -\boldsymbol{\mu}\cdot\boldsymbol{B} = -\mu B\hat{\sigma}_z = -\mu B\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$ find $\langle\hat{\sigma}_z\rangle$.

Answer:

$$\begin{aligned}
e^{-\beta\hat{H}} = e^{-\mu B\hat{\sigma}_z} &= \hat{1} + (\beta\mu B)\hat{\sigma}_z + \frac{1}{2!}(\beta\mu B)^2\hat{\sigma}_z^2 + \frac{1}{3!}(\beta\mu B)^3\hat{\sigma}_z^3 + \cdots\\
&= \hat{1}\left(1 + \frac{1}{2!}(\beta\mu B)^2 + \cdots\right) + \hat{\sigma}_z\left((\beta\mu B) + \frac{1}{3!}(\beta\mu B)^3 + \cdots\right)\\
&= \hat{1}\cosh(\beta\mu B) + \hat{\sigma}_z\sinh(\beta\mu B)\\
&= \begin{pmatrix}\cosh(\beta\mu B) & 0\\ 0 & \cosh(\beta\mu B)\end{pmatrix} + \begin{pmatrix}\sinh(\beta\mu B) & 0\\ 0 & -\sinh(\beta\mu B)\end{pmatrix}\\
&= \begin{pmatrix}e^{\beta\mu B} & 0\\ 0 & e^{-\beta\mu B}\end{pmatrix}
\end{aligned}$$

Note that: With the definition $\hat{\sigma}_z = \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$, one finds

$$\hat{\sigma}_z^2 = \hat{\sigma}_z^4 = \hat{\sigma}_z^6 = \cdots = \begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} = \hat{1},$$

$$\hat{\sigma}_z^3 = \hat{\sigma}_z^5 = \hat{\sigma}_z^7 = \cdots = \hat{\sigma}_z,$$

then

$$\mathrm{Tr}(e^{-\beta\hat{H}}) = e^{\beta\mu B} + e^{-\beta\mu B} = 2\cosh(\beta\mu B)$$

$$\Rightarrow \hat{\rho} = \frac{e^{-\beta\hat{H}}}{\mathrm{Tr}(e^{-\beta\hat{H}})} = \frac{1}{2\cosh(\beta\mu B)}\begin{pmatrix}e^{\beta\mu B} & 0\\ 0 & e^{-\beta\mu B}\end{pmatrix}$$

$$\left\langle\hat{\sigma}_z\right\rangle = \mathrm{Tr}\left(\hat{\rho}\hat{\sigma}_z\right) = \frac{1}{2\cosh(\beta\mu B)}\mathrm{Tr}\left(\begin{pmatrix}e^{\beta\mu B} & 0\\ 0 & e^{-\beta\mu B}\end{pmatrix}\times\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\right)$$

$$= \frac{1}{2\cosh(\beta\mu B)}\mathrm{Tr}\begin{pmatrix}e^{\beta\mu B} & 0\\ 0 & -e^{-\beta\mu B}\end{pmatrix}$$

$$= \frac{e^{\beta\mu B} - e^{-\beta\mu B}}{2\cosh(\beta\mu B)} = \frac{2\sinh(\beta\mu B)}{2\cosh(\beta\mu B)} = \tanh(\beta\mu B)$$

$$Z_{\mathrm{sp}} = \sum_{n=0}^{\infty} e^{-\beta E_n} = e^{-a}\sum_{n=0}^{\infty} e^{-2na} = \frac{e^{-a}}{1-e^{-2a}} = \frac{1}{e^{a}-e^{-a}} = (2\sinh a)^{-1}$$