6   THERMODYNAMICS OF PHOTONS & PARAMAGNETS.

The presentation of thermodynamics so far has relied almost completely on the application of this powerful tool to the regime of gases usually ideal but occasionally the notion of the van der Waals gas has been summoned up to give thermodynamics a wider currency (or to make it a little harder). Thermodynamics itself presents us with a powerful and completely general methodology that can be applied over an enormous range of systems. We shall now look at a further two areas of applicability where thermodynamics offers us useful insights; the photon gas and the paramagnet.

a)   Thermodynamics of Cavity Radiation.

In the course so far we have made great inroads into thermodynamics using the paradigm of the "Ideal Gas". The simple idea is that collisions of particles with the wall of a container containing the gas and consequent exchange of momentum lead to a pressure and this was related to the internal energy (kinetic energy) of the gas particles, $U = \frac{3}{2}PV$. Collisions of gas particles with each other (except in as far as they help to establish a mean momentum/kinetic energy) and potential energy interactions were ignored by making the gas dilute. It is the case that many other systems may be treated as gases albeit not ideal gases obeying Boyle's law. Common examples are;

(i)   **The photon gas** applied to the radiation contained within a cavity being treated as a gas of photons and

(ii)   **The conduction electrons in a metal** being approximated as an electron gas.

The former are bosons and as such do not interact with each other. It is those that we shall deal with in order to break away from the ideal gas paradigm and demonstrate the more general applicability of thermodynamics.

As was seen earlier we can find the relation between the total internal energy, U, of a gas of , N, photons and its pressure ie. the equation of state, in the following manner.

A photon's momentum, p, and energy, E, are given by;

$$p = \frac{h}{\lambda} = \hbar k \quad \text{(de Broglie)} \qquad E = h\nu \qquad \text{(Planck)}$$

Using the relation, $c = \nu\lambda$, we can re-arrange to find

$$E = pc \qquad \text{(Einstein)}$$

We also have $\qquad |\vec{v}| = c \qquad$ (Einstein)

Therefore

$$\vec{p} \bullet \vec{v} = \left(\frac{E}{c}\right)c = E$$

We already have for an ideal gas the equation of state written in the form

$$PV = \frac{N}{3}\langle \vec{p} \bullet \vec{v} \rangle$$

Now all photons have the same momentum (if the wavelength is the same) and the average is no longer necessary. Thus for photons this equation of state, using what we have so far derived becomes

$$PV = \frac{N}{3}E = \frac{1}{3}U$$

Or we can define an energy density, $u = U/V$ and have for the pressure,
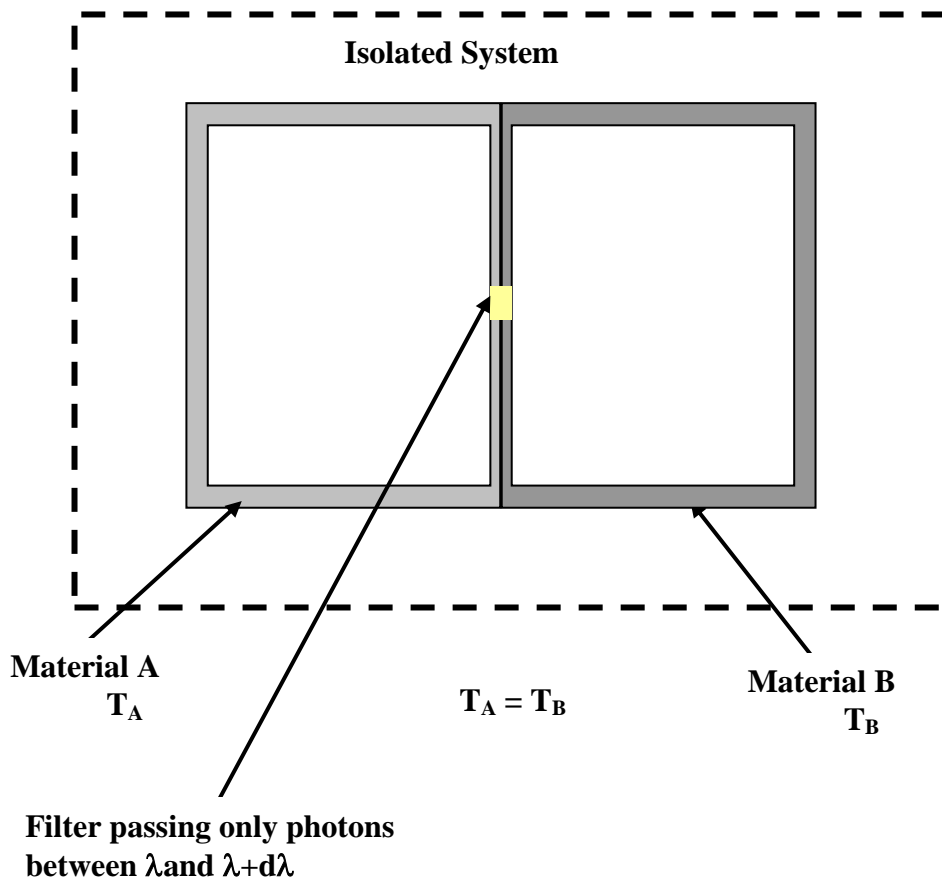
$$P = \frac{1}{3}u$$

We should note that radiation pressure is a real phenomenon and is used for example in attempts to confine thermonuclear reactions in fusion experiments and also to try and achieve laser cooling of atoms.

The photons in the cavity are spread across all wavelengths and so we split U up into its spectral components;

$$u = \int\limits_{0}^{\infty} u_\lambda \, d\lambda$$

Where $u_\lambda d\lambda$ is the internal energy density contained in the wavelength range between λ and $\lambda + d\lambda$.

In **equilibrium** u_λ must be **isotropic** just as in a material gas where the molecules will have an isotropic distribution due to many random collisions with the walls. It is also the case that u_λ must be **independent of the wall material.** We can prove this by considering two cavities of different materials but at same temperature, $T = T_A = T_B$ separated by a wall with a hole fitted with a filter that transmits only photons in the wavelength range between λ and $\lambda + d\lambda$.

Isolated System

Material A
T_A

$T_A = T_B$

Material B
T_B

Filter passing only photons between λ and λ+dλ

145

Suppose that it is the case that $u_\lambda^A > u_\lambda^B$. Then net energy at λ must flow from cavity A to cavity B. This would mean that T_B increases while T_A decreases and then we have $T_B > T_A$. But the walls of A and B are like heat reservoirs and **we have transferred heat from a cooler to a warmer reservoir without doing work and this is illegal according to the Clausius form of the second law!** It must then be the case that $u_\lambda^A = u_\lambda^B$. A little thought tells us that the only property of a cavity that u_λ can depend on is the temperature, T *(it is the energy density, U/V)*.

$$u_\lambda = u_\lambda(T).$$

And therefore from this it follows that

$$u = \int_0^\infty u_\lambda d\lambda = u(T)$$

According to an argument by Boltzmann the cavity radiation can be treated like a *P-V-T* system and therefore **the thermodynamic identity** may be used;

$$dU = TdS - PdV$$

$$U(T) = u(T)V \qquad \Rightarrow \qquad dU = d(u(T)V) = TdS - PdV$$

We can use the equation of state $P = \dfrac{1}{3}u$

$$d(u(T)V) = TdS - \frac{1}{3}u(T)dV$$

Rearranging (and dropping the explicit reminder that u is a function of T only $u(T)$

$$TdS = \left(udV + u'VdT\right) + \frac{1}{3}udV \qquad\qquad \left(u' = \frac{du}{dT}\right)$$

Where d(uV) was expanded using the product and the chain rules.

$$dS = \left(\frac{u'}{T} V \right) dT + \left(\frac{4}{3} \frac{u}{T} \right) dV$$

NB. T and V are the natural variables of S as found previously for a gas and the above equation is in the form;

$$dS = a(V,T)dT + b(V,T)dV$$

dS is a perfect differential, therefore, $\dfrac{\partial a}{\partial V} = \dfrac{\partial b}{\partial T}$, $\left\{ \text{ie. } \left(\dfrac{\partial^2 S}{\partial V \partial T} = \dfrac{\partial^2 S}{\partial T \partial V} \right) \right\}$

$$\frac{\partial}{\partial V} \left(\frac{u'}{T} V \right) = \frac{u'}{T} = \frac{\partial}{\partial T} \left(\frac{4}{3} \frac{u}{T} \right) = \frac{4}{3} \left[\frac{u'(T)}{T} - \frac{u}{T^2} \right]$$

$$\frac{u'}{T} = \frac{4}{3} \frac{u'}{T} - \frac{4}{3} \frac{u}{T^2}$$

Re-arranging

$$\frac{1}{3} \frac{u'}{T} = \frac{4}{3} \frac{u}{T^2} \qquad \Rightarrow \qquad u' = 4 \frac{u}{T} = \frac{du}{dT}$$

Re-arranging this

$$\frac{du}{u} = 4 \frac{dT}{T}$$

Integrating

$$\ln u = 4 \ln T + \text{const} = \ln(T^4) + \text{const}$$

$$u(T) = AT^4 = \frac{U}{V}$$

Where A is a constant independent of material.

From what has preceded we may find S by using $u = AT^4$ in our previous expression for dS as follows;

$$dS = \left(\frac{u'(T)}{T} V \right) dT + \left(\frac{4}{3} \frac{u(T)}{T} \right) dV = 4AT^2 V dT + \frac{4}{3} AT^3 dV$$

Because S is a function of T and V we can write the differential of S as follows

$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV$$

By comparing these last two equations we find expressions for the rate of change of S with T at constant volume and with V at constant temperature;

$$\left(\frac{\partial S}{\partial T} \right)_V = 4AT^2 V \quad \textbf{integrate wrt } \boldsymbol{T} \quad \Rightarrow \quad S = \frac{4}{3} AT^3 V + f(V)$$

And

$$\left(\frac{\partial S}{\partial V} \right)_T = \frac{4}{3} AT^3 \quad \textbf{integrate wrt } \boldsymbol{V} \quad \Rightarrow \quad S = \frac{4}{3} AT^3 V + g(T)$$

Where the two deduced differentials of S have been integrated wrt the variable concerned

The only consistent solution to these two forms of S is

$$S = \frac{4}{3} AT^3 V + const$$

If we require that at $T = 0$, $S = 0$ then we require that const $= 0$.

$$\boxed{S = \frac{4}{3} AT^3 V}$$

Or the entropy density, s, is related to temperature by;

$$s = \frac{S}{V} \propto T^3$$

Application;   Adiabatic Expansion of Photon Gas

In an adiabatic expansion $\Delta Q = 0$ and therefore $\Delta S = 0$ or S is constant.

$$S = \text{const} \qquad \Rightarrow \qquad T^3 V = const \qquad \Rightarrow \qquad TV^{1/3} = const$$

For Blackbody Radiation we have $V \propto R^3$ where R is a scale factor

$$TV^{1/3} \propto TR = const$$

We can rewrite this in terms of P and V by using the equations of state $P = \dfrac{u}{3}$ and

$u = AT^4$.

$$P = \frac{AT^4}{3} \qquad \Rightarrow \qquad T = \left(\frac{3P}{A}\right)^{1/4}$$

Substituting

$$P^{1/4} V^{1/3} = const \qquad \Rightarrow \qquad PV^{4/3} = const$$

<u>Blackbody Radiation</u>

Cavity radiation is known in particular circumstances as blackbody radiation. Returning to our cavity and the definition we have for the spectral distribution of the internal energy, u_λ , where $u_\lambda d\lambda$ is the internal energy density contained in the wavelength range between λ and $\lambda + d\lambda$.. Now we turn attention to the walls of the cavity and make the following definitions;

    (i) α_λ is the spectral absorptivity of the surface of the wall at temperature T

    (ii) $\alpha_\lambda d\lambda$ the fraction of incident energy that is absorbed by the surface between
           λ and $\lambda + d\lambda$..

(iii) ε_λ is the spectral emissivity of the surface at temperature T

(iv) $\varepsilon_\lambda d\lambda$ is the energy emitted per unit area per second by the surface between λ and $\lambda + d\lambda$.

It will be shown in later lectures that the number or flux of particles, ϕ , in a gas of **density** n striking unit area of the wall in unit time is given by

$$\phi = \frac{1}{4}n\langle v\rangle$$

where for photons the mean speed $\langle v\rangle = c$ and $\phi = \frac{nc}{4}$.

Consider the surface of the cavity at temperature T. The energy absorbed per unit area per second in the wavelength interval $(\lambda , \lambda + d\lambda)$ is

$$\alpha_\lambda\left(\frac{c}{4}n_\lambda d\lambda E_\lambda\right) \qquad \alpha_\lambda\frac{c}{4}u_\lambda d\lambda$$

Where $n_\lambda d\lambda$ is the photon density in the wavelength interval and $E_\lambda = h\nu = \frac{hc}{\lambda}$ is the photon energy.

Now, we know that in equilibrium the energy absorbed is equal to the energy emitted and thus

$$\alpha_\lambda\frac{c}{4}u_\lambda d\lambda = \varepsilon_\lambda d\lambda$$

And hence

$$\frac{\varepsilon_\lambda}{\alpha_\lambda} = \frac{c}{4}u_\lambda(T)$$

Where the quotient on the left hand side, $\dfrac{\varepsilon_\lambda}{\alpha_\lambda}$ is a universal function of λ and T irrespective of the material of the surface.

This is known as **<u>Kirchoff's Law.</u>**

A black body is one where all of the radiation falling on it is absorbed, $\alpha_\lambda^{Blackbody} = 1$ and it follows from this definition of a blackbody and Kirchoff's law that the emission from a blackbody in the interval range is;

$$\varepsilon_\lambda^{blackbody} = \frac{c}{4}u_\lambda(T)$$

Integrating to find the total energy emitted

$$\int_0^\infty \varepsilon_\lambda^{blackbody}\,d\lambda = \frac{c}{4}\int_0^\infty u_\lambda(T)\,d\lambda = \frac{c}{4}u(T) = \frac{cA}{4}T^4$$

Total energy emitted is

$$\varepsilon_{Tot} = \sigma T^4 \qquad \textbf{The Stefan Boltzmann law}$$

$$\sigma = \frac{cA}{4} = 5.67 \times 10^{-8} Wm^{-2}K^{-4} \qquad \text{is } \textbf{the Stefan constant}$$

It also follows that

$$u(T) = AT^4 = \frac{4\sigma}{c}T^4$$

and

$$S = \frac{4}{3}AT^3V = \frac{16\sigma}{3c}T^3V$$

To find the Planck black body radiation distribution is a little more involved and requires the use of ideas from statistical physics but the result is

$$u_\lambda(T,\lambda) = \frac{8\pi hc}{\lambda^5}\frac{1}{exp\left(\frac{hc}{\lambda k_B T}\right)-1}$$

And noting that the energy of a photon $E = h\upsilon = \frac{hc}{\lambda}$ we may split this expression up into three parts

$$u_\lambda(T,\lambda) = \left(\frac{8\pi}{\lambda^4}\right) \times \left(\frac{1}{\exp\left(\frac{h\nu}{k_BT}\right) - 1}\right) \times (h\nu)$$

The significance of the first two parts of the above expression will become apparent after studying statistical physics but they are;

$$u_\lambda(T,\lambda) = (density\ of\ states) \times (Bose-Einstein\ distribution\ function) \times (photon\ energy)$$

It could be shown using this distribution and the Stefan Boltzmann law that;

$$\sigma = \frac{2\pi^5 k_B^4}{15h^3c^2}$$

We should note at this point that we have not yet used any quantum mechanical formulations explicitly and the closest we have come is the use of E = pc to formulate the equation of state $PV = \frac{1}{3}U$ **.**

Example: Radiative cooling of a satellite.

We take for our example a satellite powered by a nuclear heat source supplying 10kW of heat. The satellite is a sphere of radius 1 m and has a black surface (behaves as a black body radiator). We want to find the temperature of the satellite and do this as follows;.

In the steady state we can say that;

Energy produced = Energy radiated away

therefore

$$10\text{kW} = \text{Surface Area} \times \sigma T^4 = 4\pi r^2 \sigma T^4$$

$$T^4 = \frac{10 \times 10^3\,\text{W}}{4 \times 3.14 \times 5.7 \times 10^{-8}\,\text{Wm}^{-2}\text{K}^{-4}} = \frac{10^{12}}{4 \times 3.14 \times 5.7} = \frac{10^{12}}{71.6} = 1.39 \times 10^{10}$$

152

$$T = 343.36K$$

Example: Energy loss from human body.

Assume the human body is an ideal radiator of area $\approx 1.8\text{m} \times 0.3\text{m} \times 2 = 1.08\text{m}^2 \approx 1\text{m}^2$.

The energy loss from radiation is then

$$1\text{m}^2 \times \sigma \times \text{T}^4 = 1 \times 5.7 \times 10^{-8} \times (273 + 37)^4 \, \text{K}^4 = 526\text{W}$$

To maintain a constant body temperature this heat loss will need to be made up by heat absorbed at the body surface plus heat generated within the body by the bodies metabolism.

b)   Thermodynamics of Paramagnetism.

Another system of particles that is susceptible to a thermodynamic analysis is that of a collection of **electron spins** that are able to align in an applied external magnetic field.

A review of magnetic materials and susceptibility.

We need to begin by reviewing the properties of a paramagnetic system in order to find the work done on such a system and to develop the paramagnetic equivalent of the thermodynamic identity. We will also obtain a few simple definitions relating to how we describe the phenomenon of magnetisation.

Consider an external magnetic induction field $\vec{B}_0$, produced for example by a solenoid.

We place a paramagnetic material inside the solenoid and consider that at the molecular level the spins are bar magnets. The electron spins or the entire atom may in fact constitute the "molecular bar magnet". This molecular magnet and its interaction with an applied magnetic field is best described by its magnetic moment.

From electromagnetism we recall that the magnetic dipole moment has the curious units of current × area.
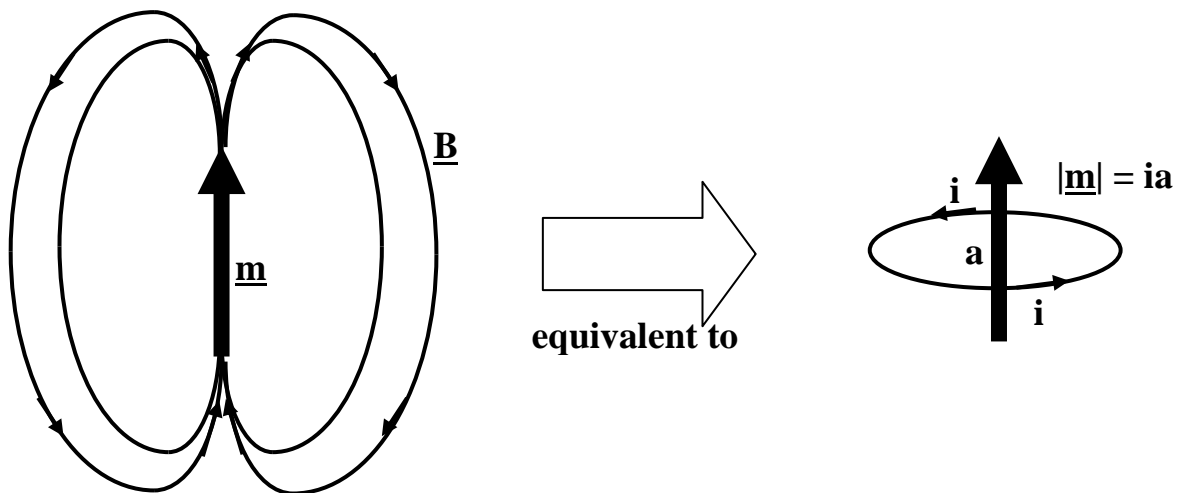
The magnetic moment **_m_** on the left is equivalent to a current loop of area a and current i shown on the right producing the magnetic moment **_m_** = _ia_ directed perpendicular to the area and with an identical magnetic field.

$$\vec{m}_e = \frac{e\hbar}{2m_e} = 9.27 \times 10^{-24}\, Am^2 \qquad \text{is the intrinsic electron dipole moment,}$$

The magnetic moment of a single electron spin is very small and in the paramagnetic material they are aligned randomly and so we observe no macroscopic effect.

However, by putting this material with its collection of magnetic dipoles into an external magnetic field then it is preferable energetically for the spins to align with the magnetic field in order to lower the potential energy of the dipole, $u = -\vec{m}_e \bullet \vec{B}$ and this alignment acts to increase the overall B field in the material, it becomes magnetised. We now see how this is described;

We begin by reminding ourselves of Amperes law relating current to magnetic induction;
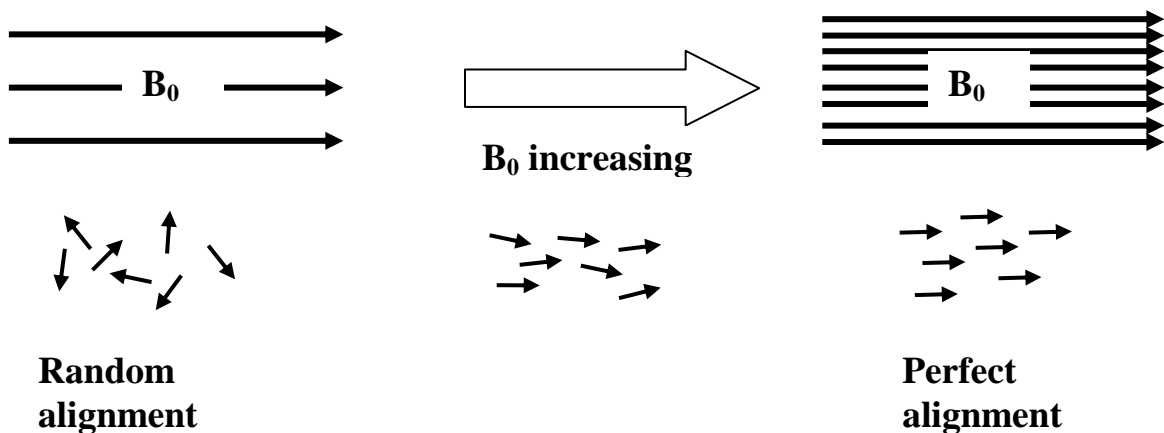
$$\int B \bullet dl = \mu_0 I$$

Where I is the total current enclosed by
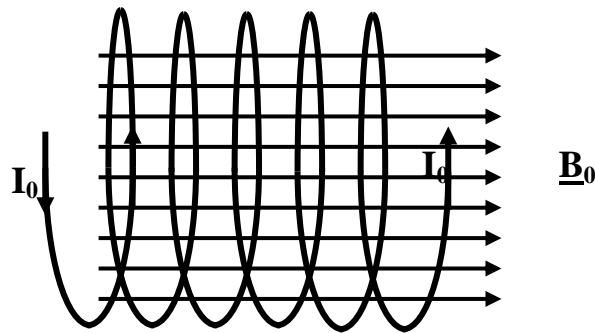
$$B_0 = \mu_0 I_0 n_0$$

Where μ_0 is the permittivity of free space and n_0 is the number of turns per unit length.

Random alignment

Perfect alignment

As the external magnetic field is increased the alignment goes from random to perfect at very high magnetic fields where the potential energy reduction is greatest and low temperatures where thermal agitation usually acting to disturb the alignment is reduced.
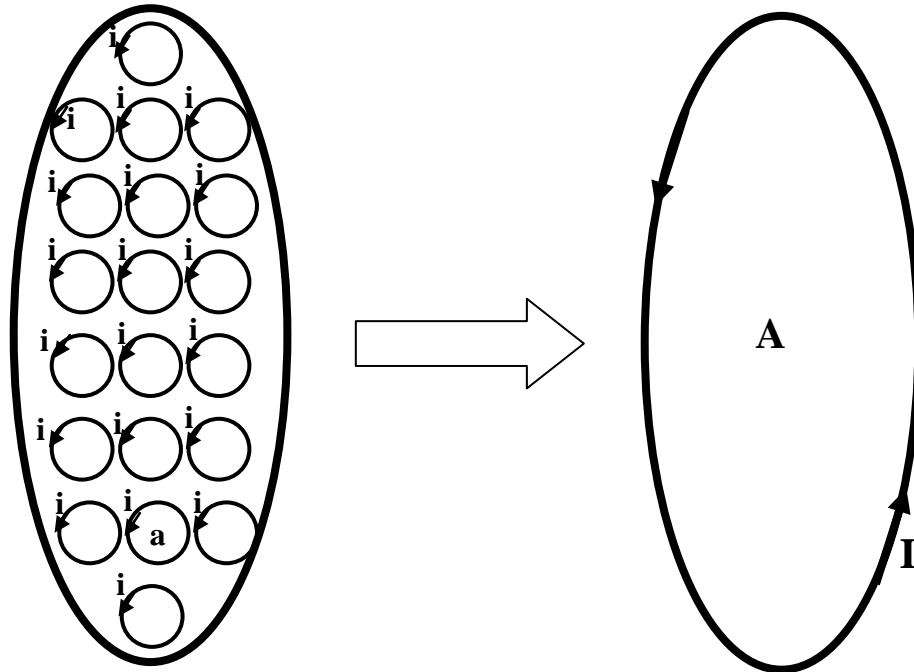
All the aligned dipoles are equivalent to aligned turns of current acting together as a large current loop with magnetisation

$$B_m = \mu_0 i n_m$$ n_m is the number of dipole layers per unit length.

$$B_m = \mu_0 \frac{m}{a} \frac{N^L}{L}$$ N^L is the total number of layers.

$$B_m = \mu_0 \frac{N^A m}{A} \frac{N^L}{L} = \mu_0 \frac{N^V m}{V}$$ N^A is the number of dipoles in area A

$$N^V = N^A N^L$$ is the number of dipoles in volume V

$$B_m = \mu_0 \frac{\mathcal{M}}{V} = \mu_0 M \qquad\qquad \mathcal{M} \text{ is the total magnetic moment in volume}$$

V and M is the magnetisation per unit volume.

The total B field is then

$$B = B_0 + B_m = B_0 + \mu_0 M$$

In reality this is a vector relation but we assume a simple isotropic homogeneous medium in which $\underline{B}_0$ will be in the same direction as $\underline{M}$.

We now have the tools we need in order to find the work done on a paramagnetic system and to thus enable us to use the tools of thermodynamics.

Work done on a paramagnetic system.

We imagine the paramagnetic system of magnetic dipoles to reside within a solenoid which has a current I_0 flowing through it. There will be a total magnetic field, B due to the externally applied magnetic field and the magnetic field created by the aligned dipoles (described by the magnetisation M). If the current is increased from I_0 to $I_0 + dI_0$ the magnetisation is increased as the dipoles are forced further into alignment and this involves the increase in current doing work on the system.

The total field is enclosed by the solenoid wires so that there is a total magnetic flux, Φ, enclosed by the wires;

$$\Phi = total \;\; flux = N \times \phi$$

Where N is the total number of turns and ϕ is the flux enclosed by one turn.

$$\Phi = (Ln_0)(BA) = Bn_0 V$$

L is the length of the solenoid and n_0 the number of turns per unit length. A is the cross sectional area of the coil.

As I_0 changes $\qquad\qquad I_0 \Rightarrow I_0 + dI_0 \qquad\qquad B \Rightarrow B + dB$

This produces a change of flux and by Lenz's law a back emf, ε, is induced of magnitude

$$\varepsilon = \left| \frac{d\Phi}{d\tau} \right| = n_o V \frac{dB}{d\tau}$$

Work is performed in driving charges (current) against this emf. In the interval $d\tau$ an extra charge $dq = I_0 d\tau$ is driven through the circuit against the emf thus doing work

$$dW = dq\varepsilon = \left(n_0 V \frac{dB}{d\tau} \right)(I_0 d\tau) = n_0 I_0 V dB$$

We have already, $\qquad n_0 I_0 = \frac{1}{\mu_0} B_0$

so

$$dW = \frac{VB_0}{\mu_0} dB = \frac{VB_0}{\mu_0} \left(dB_0 + \mu_0 d\mathcal{M} \right)$$

Consider a finite change from B_0^{initial} to B_0^{final} so that we can find the work done, ΔW

$$\Delta W = \int_i^f dW = V \frac{B_0^2}{2\mu_0} \bigg|_i^f + V \int_i^f B_0 dM$$

$$\Delta W = \frac{V}{2\mu_0} \left[B_0^{f\,2} - B_0^{i\,2} \right] + \int_i^f B_0 d(VM)$$

The first term is the change in vacuum field energy and as we are only concerned with the work done on the paramagnetic system we must ignore this and thus

$$dW = B_0 d(VM) = B_0(MdV + VdM) = B_0 d\mathcal{M} \quad (dV = 0)$$

where $\mathcal{M}$, as before, is the total magnetic moment of the system $= VM$.

The work done ON the paramagnetic system is then

$$\boxed{dW = +B_0 d\mathcal{M}}$$

The first law and paramagnetic systems.

Using this we may write down the first law for a paramagnet with a fixed volume

$$\mathrm{d}U = T\mathrm{d}S + B_0\mathrm{d}\mathcal{M}$$

we should compare this first law for a paramagnet with that for a gas

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V$$

There is a clear analogy to be drawn with B_0 playing the role of $-P$ (note the sign) with $\mathcal{M}$ being analogous to V. We know that for the gas the equation of state relates P-V-T and we therefore expect the equation of state for the paramagnetic system to relate B_0, $\mathcal{M}$ and T.

Curie's Law & Equation of State.

The degree of alignment amongst the atomic magnets, as indicated by M, will depend on the magnitude of the applied magnetic field, B_0. It is in fact proportional to the applied field ___at low applied fields___

$$B_\mathrm{m} = \mu_0 M = \chi_\mathrm{m} B_0$$

___At higher applied fields as the alignment tends to saturate___ the magnetisation will vary much more slowly as B_0 is increased.

The quantity χ_m is the magnetic susceptibility of the medium.

Down to very low temperatures, T, the variation of χ_m has been determined to be

$$\chi_m = \frac{\mathcal{C}}{T} \qquad\qquad \textbf{Curie's Law}$$

Where $\mathcal{C}$ is Curie's constant. Curie's constant is a material property depending on the particular material.

Curie's law allows us to write

$$\mu_0 M = \frac{\mathcal{C}}{T} B_0$$

Or equivalently

$$B_0 = \left(\frac{\mu_0 T}{\mathcal{C} V} \right) \mathcal{M}$$

and this is the equation of state of a paramagnetic system at low temperature.

It tells us that if B_0 increases the magnetisation increases proportionately and also that if the temperature increases the magnetisation decreases as thermal agitation destroys any alignment that is producing the magnetisation. At very high fields the molecules tend to complete alignment and Curie's law cannot continue to hold. Similarly at extremely low temperatures where thermal agitation has very little effect on the degree of alignment such that $mB_0 \gg k_B T$, (between 0,01 and 1K) the magnetic alignment tends easily to saturation and Curies law become inapplicable.

We spent a long time at the beginning of the course studying an ideal gas and obtaining things like specific heats at constant pressure and at constant volume. The paramagnetic system has its equivalent with

$$C_{B_0} \equiv \left. \frac{dQ_R}{dT} \right|_{B_0 = const} = \left. T \frac{dS}{dT} \right|_{B_0 = const} = T \left(\frac{\partial S}{\partial T} \right)_{B_0}$$

$$C_M \equiv \left. \frac{dQ_R}{dT} \right|_{\mathcal{M} = const} = \left. T \frac{dS}{dT} \right|_{\mathcal{M} = const} = T \left(\frac{\partial S}{\partial T} \right)_{\mathcal{M}}$$

These heat capacities are measured experimentally to have a simple behaviour in the low temperature range where Curie's law applies. C_{B_0} depends on both T and B_0 but takes a simple form when B_0 is zero described by **Schottky's Law**

$$C_{B_0}(T,B_0)\big|_{B_0=0} = C_{B_0}(T,0) = \frac{Vb}{T^2}$$

b is a material constant.

The Paramagnetic Refrigerator.

At temperatures where the Curie and Schottky laws apply $(0.01 < T < 1K)$ the paramagnetic system is used as a very efficient refrigerator in laboratories where such low temperatures are required. A **_qualitative description_** of the paramagnetic refrigerator now follows before it is formally analysed later on.
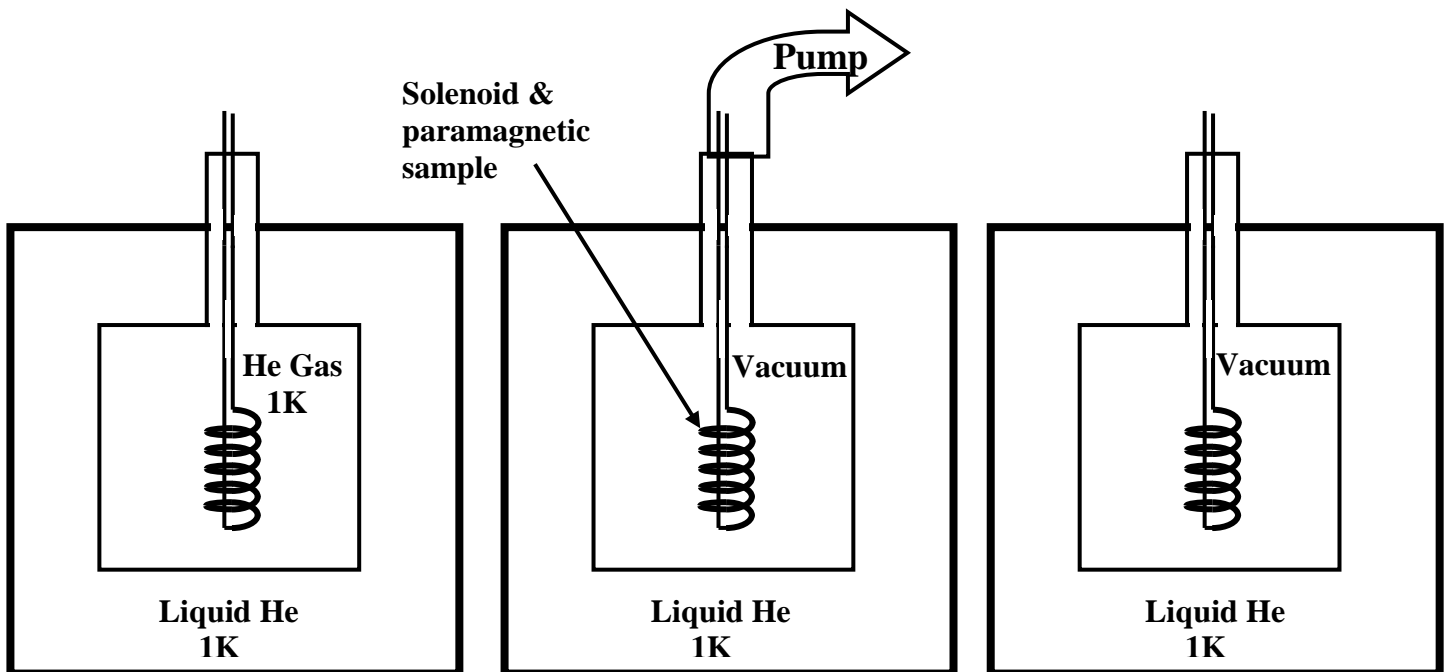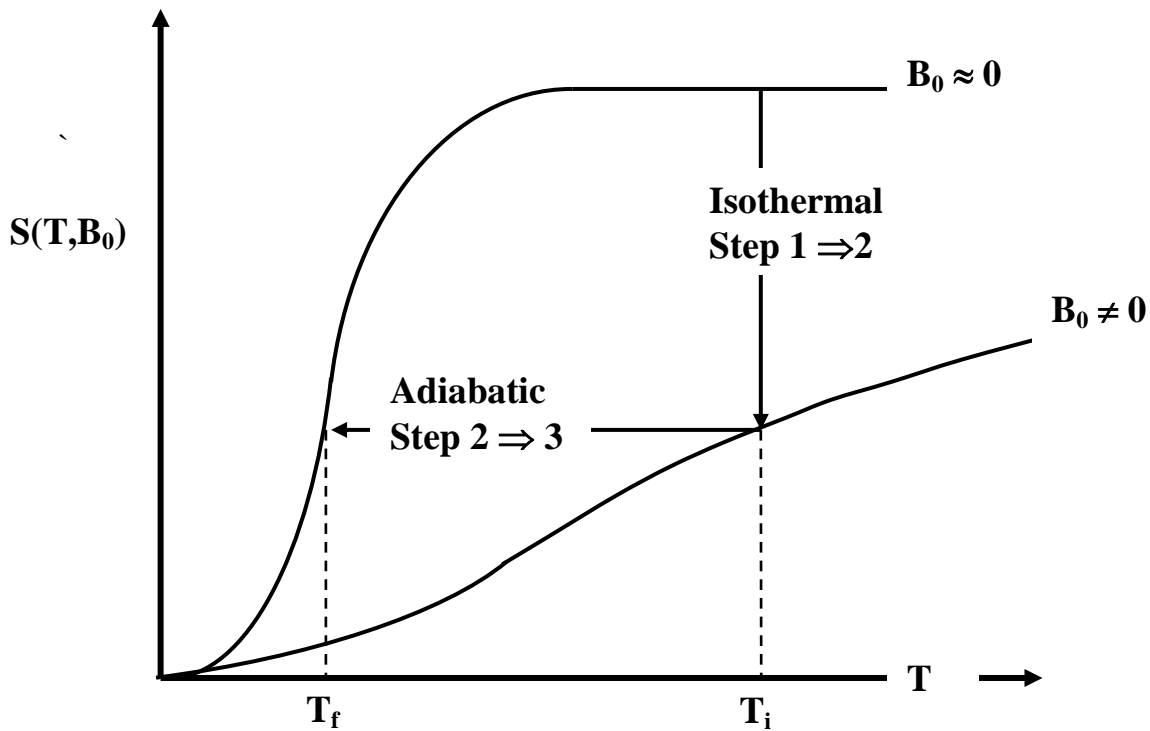

Step 1. Increase B_0 from zero isothermally

Step 2. Pump out the gas maintaining B_0 at a finite fixed value.

Step 3. Reduce B_0 to zero adiabatically

Steps 1 to 3 lower the temperature of the paramagnetic system because the entropy of the system depends on B_0 and T in a particular way as shown below.

As B_0 increases at constant temperature S decreases as order (in this case alignment) increases. The initial isothermal process from $B_0 = 0$ to finite B_0 is shown in the above diagram along with the adiabatic reduction of B_0 back to zero. Note the adiabat is the same as $\Delta S = 0$ or isoentropic.

This cooling effect is known as an entropic cooling and is analogous to the cooling of a cup of tea when sugar is added and melts. In that case the sugar goes from an ordered crystalline state (low entropy) to a disordered solution state (high entropy). The increase (positive change) in entropy of the sugar requires that heat is supplied by the tea to the sugar ie positive flow from tea to sugar as $+\Delta S_{Sugar} = {}^{+\Delta Q}/_T$. This is an effect always seen at a phase change (latent heat) and the paramagnetic material is undergoing a phase change in the process of adiabatic demagnetisation from ordered to disordered system.

To obtain a more complete and formal analysis of the process requires that we know more about how S depends on T and B_0 and to find this $S(T,B_0)$ is the next problem.

The Magnetic Gibbs Potential.

To analyse this refrigeration we will want to treat T and B_0 as independent variables of S and find the variation of $S(T, B_0)$. To begin, write the thermodynamic identity (first law)

$$dU = TdS + B_0 d\mathcal{M} = \left(\frac{\partial U}{\partial S}\right)_{\mathcal{M}} dS + \left(\frac{\partial U}{\partial \mathcal{M}}\right)_S d\mathcal{M}$$

This has S and $\mathcal{M}$ as the independent variables, $U = U(S, \mathcal{M})$ and we need to find a way to change variables. In order to do this we take a smart step and change from using U to G^{Mag}, **a new function of state**,

the magnetic Gibbs function defined as follows;

$$G^{Mag} = U - TS - B_0 \mathcal{M}$$

As an aside we will see the general Gibbs function for a *P-V-T* system later and this is defined as

$$G = U - TS + PV = H - TS$$

We can compare this with the current Gibbs magnetic function and note that $+PV$ becomes $-B_0\mathcal{M}$. This brings to mind the infinitesimal work done on a paramagnetic system that we have earlier discovered $dW = +B_0 d\mathcal{M}$ and its comparison with that used for a *P-V-T* system, $dW = -PdV$.

We now return to G^{Mag} and to see how defining this function helps we need initially to find the differential of G^{Mag}. The following process is something used frequently to find a Maxwell Relation between the partial differentials of a state function wrt its natural variables

Step 1. **Identify the natural variables as follows**

$$dG^{Mag} = dU - TdS - SdT - B_0 d\mathcal{M} - \mathcal{M}dB_0$$

By using the thermodynamic identity $dU = TdS + B_0 d\mathcal{M}$ we may tidy this up

$$dG^{Mag} = -SdT - \mathcal{M}dB_0$$

This has identified the natural variables of $G^{Mag} = G^{Mag}(T, B_0)$ and

Step 2 This allows us to write an expression for the infinitesimal dG^{Mag} in terms of its state variables as follows

$$dG^{Mag} = \left(\frac{\partial G^{Mag}}{\partial T}\right)_{B_0} dT + \left(\frac{\partial G^{Mag}}{\partial B_0}\right)_T dB_0$$

Step 3 Comparing the two expressions for dG^{Mag} we may then identified the following relations between the partial differentials of the state function wrt its natural variables and and some other state functions;

$$S = -\left(\frac{\partial G^{Mag}}{\partial T}\right)_{B_0} \qquad\qquad \mathcal{M} = -\left(\frac{\partial G^{Mag}}{\partial B_0}\right)_T$$

We know that G^{Mag} is a state function from its definition

$$\frac{\partial^2 G^{Mag}}{\partial B_0 \partial T} = \frac{\partial^2 G^{Mag}}{\partial T \partial B_0}$$

Step 4. and finally this implies that

$$\frac{\partial^2 G^{Mag}}{\partial B_0 \partial T} = \frac{\partial}{\partial B_0}\left(\frac{\partial G^{Mag}}{\partial T}\right)_{B_0} = -\left(\frac{\partial S}{\partial B_0}\right)_T = \frac{\partial^2 G^{Mag}}{\partial T \partial B_0} = -\left(\frac{\partial \mathcal{M}}{\partial T}\right)_{B_0}$$

In other words the identity

$$\left(\frac{\partial S}{\partial B_0}\right)_T = \left(\frac{\partial \mathcal{M}}{\partial T}\right)_{B_0}$$

must be true. This is an example of what are known as **Maxwell Relations** we will discover others later on.

Since $G^{Mag} = G^{Mag}(T,B_0)$, from the condition $S = -\left(\frac{\partial G^{Mag}}{\partial T}\right)_{B_0}$ we identify the variables of S and know that $S = S(T, B_0)$

To discover $S(T, B_0)$ we begin by finding $\left(\frac{\partial S}{\partial B_0}\right)_T$ and $\left(\frac{\partial S}{\partial T}\right)_{B_0}$ as follows before integrating these derivatives wrt B_0 and T

(i)   To find $\left(\frac{\partial S}{\partial B_0}\right)_T$ we can use **Curie's law**

$$B_0 = \left(\frac{\mu_0 T}{\mathcal{C}V}\right)\mathcal{M} \qquad \Leftrightarrow \qquad \mathcal{M} = \left(\frac{\mathcal{C}V}{\mu_0 T}\right)B_0$$

and the **Maxwell relation** that was just found as follows

$$\left(\frac{\partial S}{\partial B_0}\right)_T = \left(\frac{\partial \mathcal{M}}{\partial T}\right)_{B_0} = \frac{\partial}{\partial T}\left(\frac{\mathcal{C}V}{\mu_0 T}\right)B_0 = -\frac{\mathcal{C}VB_0}{\mu_0}\frac{1}{T^2}$$

(ii)   To find $\left(\frac{\partial S}{\partial T}\right)_{B_0}$ we **modify the definition of the heat capacity** and obtain

$$\left(\frac{\partial S}{\partial T}\right)_{B_0} = \frac{C_{B_0}(T,B_0)}{T}$$

However, C_{B_0} is only known so far at $B_0 = 0$ from **Schottky Law** so find $C_{B_0}(T, B_0)$

$$C_{B_0} = T\left(\frac{\partial S}{\partial T}\right)_{B_0}$$

$$\left(\frac{\partial C_{B_0}}{\partial B_0}\right)_T = T\frac{\partial^2 S}{\partial B_0 \partial T} = T\frac{\partial^2 S}{\partial T \partial B_0} = T\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial B_0}\right)_T$$

$$\left(\frac{\partial C_{B_0}}{\partial B_0}\right)_T = T\frac{\partial}{\partial T}\left(\frac{-\mathcal{C}VB_0}{\mu_0 T^2}\right) = 2\frac{\mathcal{C}VB_0}{\mu_0 T^2}$$

$$C_{B_0}(T,B_0) - C_{B_0}(T,0) = \int_0^{B_0}\left(\frac{\partial C_{B_0}}{\partial B_0}\right)_T dB_0$$

$$C_{B_0}(T,B_0) = C_{B_0}(T,0) + \int_0^{B_0}\left(\frac{2\mathcal{C}VB_0}{\mu_0 T^2}\right)dB_0 = \frac{Vb}{T^2} + \frac{\mathcal{C}VB_0^2}{\mu_0 T^2}$$

And finally

$$C_{B_0}(T,B_0) = \frac{V}{T^2}\left(b + \frac{\mathcal{C}B_0^2}{\mu_0}\right)$$

So

$$\left(\frac{\partial S}{\partial T}\right)_{B_0} = \frac{C_{B_0}}{T} = \frac{V}{T^3}\left(b + \frac{\mathcal{C}B_0^2}{\mu_0}\right)$$

We now use these two partial differentials from (i) and (ii) to discover the function $S(T, B_0)$ by integration wrt B_0 and wrt T respectively;

(ia)

$$\left(\frac{\partial S}{\partial B_0}\right)_T = -\frac{\mathcal{C}VB_0}{\mu_0}\frac{1}{T^2}$$

Holding T as a constant

$$S = \frac{-\mathcal{C}V}{\mu_0 T^2}\int B_0 dB_0 + f(T)$$

$$S = -\frac{\mathcal{C}V}{2\mu_0}\frac{B_0^2}{T^2} + f(T) = -\frac{V}{2T^2}\frac{CVB_0^2}{\mu_0} + f(T)$$

(iia)

$$\left(\frac{\partial S}{\partial T}\right)_{B_0} = \frac{V}{T^3}\left(b + \frac{\mathcal{C}B_0^2}{\mu_0}\right)$$

Holding B_0 as a constant

$$S = \left(b + \frac{CB_0^2}{\mu_0}\right)V\int T^{-3}dT$$

$$S = -\frac{V}{2T^2}\left(b + \frac{\mathcal{C}B_0^2}{\mu_0}\right) + g(B_0)$$

Taking both of these solutions for S the only consistent solution for S is then

$$S(T,B_0) = const - \frac{V}{2T^2}\left(b + \frac{\mathcal{C}B_0^2}{\mu_0}\right)$$

NB. As $T \to 0$ quantum effects will alter this result and as $T \to 0$ then $S \to 0$ which the above result does not, but it remains good for the range $0.01 \le T \le 1$K.

Now that we have $S(T,B_0)$ the formal analysis of the paramagnetic cooling that was described qualitatively is possible.

ANALYSIS OF PARAMAGNETIC COOLING
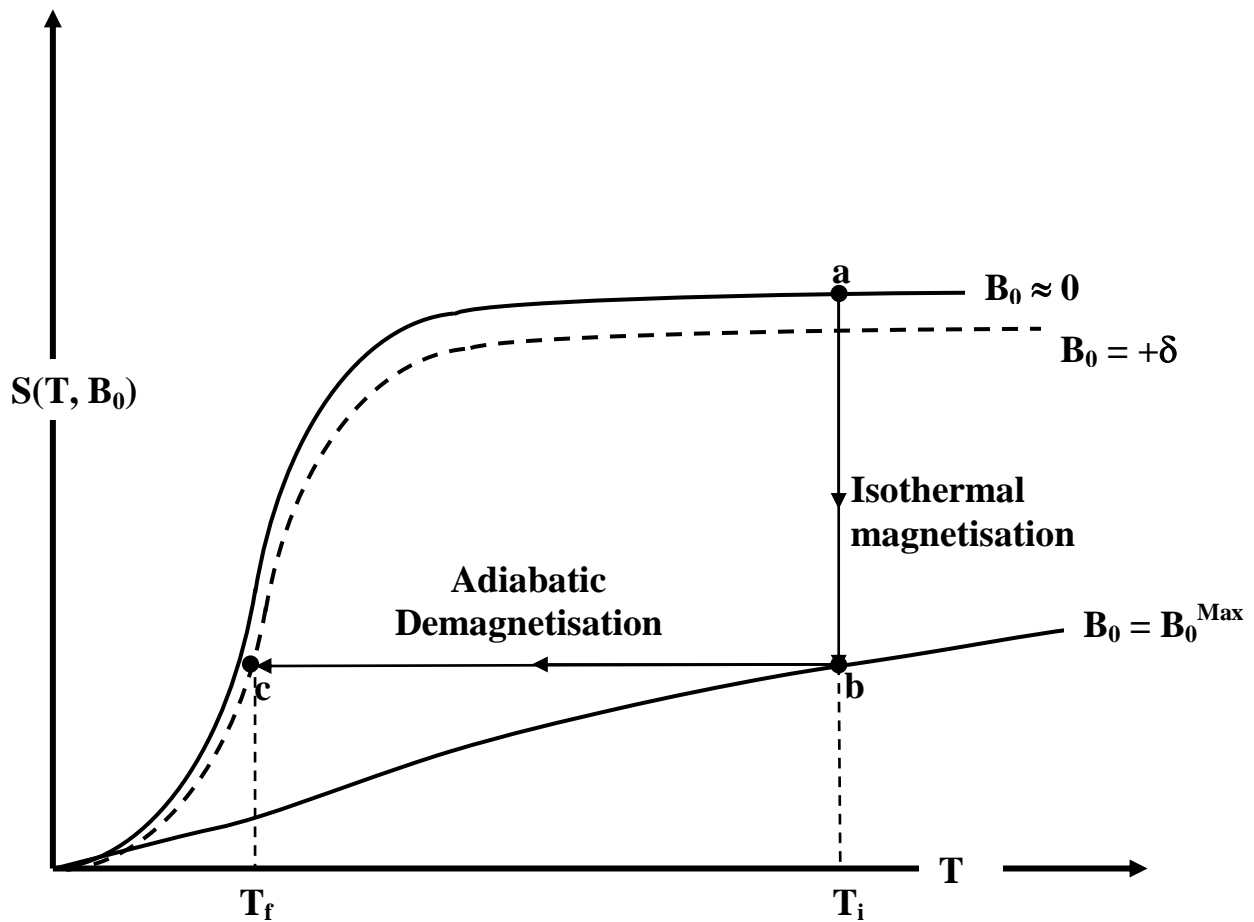
The process of using isothermal magnetisation as a refrigeration process is demonstrated on the diagram above. We begin at some initial temperature T_i (with our system shown previously) and with no applied magnetic field, $B_0 = 0$. A magnetic field is applied isothermally aligning the dipoles and reducing the entropy of the system of paramagnets before reducing the magnetic field to a value, δ, just slightly greater than zero adiabatically (with no heat flow and hence no change in entropy). To analyse this process we calculate the change in entropy

$$\Delta S_{a \to b} = -\frac{V}{2T_i^2}\left(b + \frac{\mathbb{C}B_0^{Max^2}}{\mu_0}\right) + \frac{Vb}{2T_i^2} = -\frac{V\mathbb{C}B_0^{Max^2}}{2\mu_0 T_i^2}$$

All quantities on the RHS of the above equation are positive and therefore the entropy change is negative, the entropy is reduced in a reversible magnetisation and therefore $dQ < 0$ ie. heat has flowed from the paramagnetic system.

The next step is an adiabatic reduction of the magnetic field to its final value and there is no change of entropy or heat flow.

$$\Delta S_{b\to c} = 0 = -\frac{V}{2T_f^2}\left(b + \frac{\mathfrak{C}B_0^{f\,2}}{\mu_0}\right) + \frac{V}{2T_i^2}\left(b + \frac{\mathfrak{C}B_0^{Max\,2}}{\mu_0}\right)$$

Re arrangement gives

$$\left(\frac{T_i}{T_f}\right)^2 = \frac{b + \dfrac{\mathfrak{C}B_0^{Max\,2}}{\mu_0}}{b + \dfrac{\mathfrak{C}B_0^{f\,2}}{\mu_0}}$$

If the adiabatic reduction of the magnetic field had taken B_0 to zero then

$$\left(\frac{T_i}{T_f}\right)^2 = 1 + \frac{\mathfrak{C}B_0^{Max\,2}}{b\mu_0}$$

This result (for $B_f = 0$) has been well confirmed experimentally with paramagnetic salts including Gadolinium Sulphate and Caesium Magnesium Nitride.

On the other hand, if the final magnetic field is slightly above zero, $B_0 = \delta$, an interesting result follows from the analysis when $\dfrac{\mathfrak{C}B_0^{f\,2}}{\mu_0} \gg b$. Our analysis now simplifies to

$$\left(\frac{T_i}{T_f}\right)^2 = \frac{b + \dfrac{\mathfrak{C}B_0^{Max\,2}}{\mu_0}}{b + \dfrac{\mathfrak{C}B_0^{f\,2}}{\mu_0}} = \left(\frac{B_0^{Max}}{B_0^f}\right)^2$$

Or

$$\frac{T_i}{T_f} = \frac{B_0^{Max}}{B_0^f}$$

$$\frac{B_0^f}{T_f} = \frac{B_0^{Max}}{T_i}$$

But we have Curie's law which gives $\qquad \mathcal{M} = \frac{\mathcal{C}V}{\mu_0} \frac{B_0}{T}$ and so

$$\mathcal{M} = \mathcal{M}^{Max}$$

Telling us that as we reduced the applied field B_0 adiabatically the magnetisation remained the same, the dipoles remain aligned. We knew this anyway as S didn't change on the final step implying no loss (or increase) of order. We can maintain an appreciable magnetisation with a very weak applied field.

This has an interesting experimental application in the hunt for parity violation. A sample of Cobalt 60 was treated in this way being subjected to a high maximum field at $T = 0.01$K before that field was reduced to one just slightly above zero. The aligned electron moments imply aligned nuclear magnetic moments and the experiment observed anisotropic electron, β, emission from the Co_{60} (Ambler, Hudson and Wu) demonstrating that parity is not a symmetry of nature.

A microscopic/statistical viewpoint of paramagnetic cooling.

For a picture of what is occurring microscopically we need to deal with quantum spins which exist in a finite number of states depending on the total spin

Total Spin	Available states
$\frac{1}{2}$	$-\frac{1}{2}$, $+\frac{1}{2}$
1	-1, 0, +1

The energy of the spin states will be slightly different in applied magnetic fields (they prefer to line up) but in zero field they are degenerate (have the same energy). At $T \approx 0$ and $B \approx 0$ there will be equal numbers of electrons (or whatever the spin is) in each of the states. The diagram below illustrates the splitting of spin levels for a spin $\frac{1}{2}$ particle such as an electron.
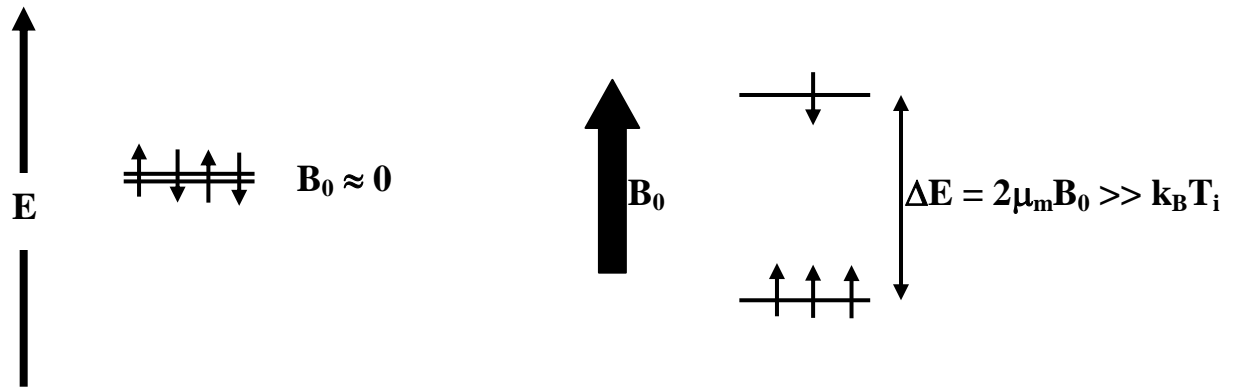
Once a magnetic field is applied there will be many more electrons in the lower of the split states provided the energy of splitting (proportional to the field) is much greater than k_BT. With the paramagnetic cooling this situation remains the case as the magnetic field is taken back to zero and the energy splitting is also removed.

The ratio of electrons in either state is given by the Boltzmann factor which you will see in much greater detail in the Statistical Physics course but simply stated

$$\frac{n(E_\uparrow)}{n(E_\downarrow)} = exp\left(\frac{E_\downarrow - E_\uparrow}{k_BT}\right)$$

Where $E_\uparrow$ and $E_\downarrow$ are the energies of the spin up and spin down electrons respectively. Looking at the Boltzmann distribution given in the above equation. If there is no magnetic field and $E_\uparrow = E_\downarrow$ then the exponential is unity and there are equal numbers in the up and down state. While the field is on and $E_\uparrow$ - $E_\downarrow$ is negative there will be greater numbers in the up state. But once we have reduced the field, B_0, and $2\mu_m B_0^f << k_BT_i$ this situation remains and the Boltzmann distribution is not a good description of the situation any longer unless the temperature has in fact dropped drastically and $2\mu_m B_0^f >> k_BT_f$. This must be the case and it is what we have seen by other analysis.

The temperature as defined by the Boltzmann distribution is known as the **STATISTICAL TEMPERATURE** which may or may not be the same as the kinetic, thermodynamic and empirical temperatures. This is only the case in non-equilibrium circumstances. For example, **far from equilibrium** in a laser **the statistical temperature will be negative!**

$$dW = +B_0 d\mathcal{M}$$

$$dU = TdS + B_0 d\mathcal{M} \qquad \textbf{Thermodynamic Identity}$$

$$B_m = \mu_0 \frac{\mathcal{M}}{V} = \mu_0 M = \chi_M B_0$$

$$B = B_0 + B_m = B_0 + \mu_0 M$$

$$\chi_m = \frac{\mathcal{C}}{T} \qquad \textbf{Curie's Law}$$

$$\mu_0 M = \frac{\mathcal{C}}{T} B_0 \qquad\qquad B_0 = \left(\frac{\mu_0 T}{\mathcal{C}V} \right)\mathcal{M} \qquad \textbf{Equation of State}$$

$$C_{B_0}(T, B_0)\big|_{B_0=0} = C_{B_0}(T,0) = \frac{Vb}{T^2} \qquad \textbf{Schottky's Law}$$

$$G = U - TS + PV = H - TS \qquad \textbf{Gibbs Function}$$

$$\left(\frac{\partial S}{\partial B_0} \right)_T = \left(\frac{\partial \mathcal{M}}{\partial T} \right)_{B_0} \qquad \textbf{Maxwell Relation}$$