



**Lecture TOPIC 11** (Finn: 2.9, 8.4, 8.5, 8.6, 8.7, 8.8, 8.9, 8.10)

**Synopsis:** Additional thermodynamic coordinates –

**Additional thermodynamic coordinates for other systems**

So far we generally assumed material properties are restricted to P, V, T and S. But there are other possibilities which can be treated similarly. The table shows different co-ordinates, distinguishing between intensive variables (like pressure  $P$ ) and extensive variables (like volume  $V$ ).

system	intensive variable	extensive variable	infinitesimal work <b>ON</b> system
gas or fluid	$P$	$V$	$-PdV$
wire or rod	$\mathcal{F}$ (tension)	$L$ (length)	$\mathcal{F} dL$
(electric) cell	$\mathcal{E}$ (“emf”)	$Z$ (charge)	$\mathcal{E} dZ$
magnetic material	$B_0$ (applied induction)	$\mathcal{M}$ (magnetic moment)	$B_0 d\mathcal{M}$
dielectric material	$E$ (electric field)	$\mathcal{P}$ (polarisation)	$E d\mathcal{P}$

**Types of Entropy**

Clausius introduced entropy in relation to integrals relating to heat. Boltzmann gives us a little more intuition that entropy is to do with degrees of freedom and how many microscopic arrangements give the same macroscopic phase. Mainly, we considered ways of arranging atomic positions and momenta.

The interpretation of entropy can also be extended if there are additional microscopic degrees of freedom “Ways” beyond atomic positions. For example, the orientation of atomic magnetic moments on long molecules.

If there are two “types” of entropy, then an isentropic process might still allow transfer of entropy from one type to the other.

**The rubber band or “wire”**

The first law (for infinitesimal reversible changes) has to be extended, to include work done **ON** the band,  $\mathcal{F} dL$ , and then simplified, because normally  $-PdV \ll \mathcal{F} dL$ :

$$dU = \delta Q - PdV + \mathcal{F} dL \rightarrow dU = \delta Q + \mathcal{F} dL$$

Where it is sensible to do so, the equations already derived for gases and fluids can be re-used replacing  $V$  with  $L$  and  $P$  with  $-\mathcal{F}$ . Thus

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \rightarrow \left(\frac{\partial S}{\partial L}\right)_T = -\left(\frac{\partial \mathcal{F}}{\partial T}\right)_L$$

Mechanical stability requires that pulling a wire makes it longer, i.e.

$$\left(\frac{\partial \mathcal{L}}{\partial \mathcal{F}}\right)_T > 0$$

For an isothermal increase in length of a rubber band, the chain-like molecules reorient in the direction of the strain, becoming less tangled, i.e. they become more ordered. Having fewer allowed orientations

means the associated entropy will decrease as the band stretches.

$$\left(\frac{\partial S}{\partial L}\right)_T < 0 \rightarrow \left(\frac{\partial \mathcal{F}}{\partial T}\right)_L > 0$$

Putting these together and applying the triple product.

$$0 > -\left(\frac{\partial \mathcal{L}}{\partial \mathcal{F}}\right)_T \left(\frac{\partial \mathcal{F}}{\partial T}\right)_L = \left(\frac{\partial L}{\partial T}\right)_{\mathcal{F}}$$

Thus a rubber band heated at constant tension is expected to shrink: ie rubber is expected to have a negative coefficient of linear expansion  $\alpha_L = \frac{1}{L} \left(\frac{\partial L}{\partial T}\right)_{\mathcal{F}}$ .

### Deducing materials properties from Second Law

Consider an “engine”, where work is done raising a mass  $M$  against gravity by heating a rubber band (length,  $L$ , crosssection  $A$ ). Work is force  $\times$  distance

$$W = MgL\alpha\Delta T; \quad Q = C_p\Delta T.$$

So the efficiency of such an “engine” would be

$$\frac{W}{Q} = \frac{MgL\alpha_L}{C_P} = \frac{Mg\alpha_L}{Ac_P}$$

At first glance, it seems efficiency could be made arbitrarily large by increasing  $M$ , violating the Second Law. In practice, it means that  $\alpha_L$  must depend on the tension.

### Electromagnetic Thermodynamics

An electromagnetic system has internal energy, exerts a pressure and comprises countable photons. So we can treat it using thermodynamics. As the field or voltage is increased, so is the energy, which gives us the magnetic equivalent of “Work”.

For a magnetic system, we have  $\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M})$  with the magnetisation related to field by the susceptibility. Typically, one can make the simplifying assumption that the induced magnetisation is much weaker than the applied field  $M \ll H$ , and take the field in the magnetic material to be equal to the externally applied field  $B \approx B_0 = \mu_0 H$ . We will also assume that the susceptibility is a *scalar*, so the magnetisation is in the direction of the field. This means we will quickly dispense with vector fields: generalisation to tensorial quantities is straightforward if tedious. We will deal with energy densities, so all quantities are intensive (despite which we retain the electromagnetism convention of using capital letters).

From this, the Magnetic Work done is simply  $dW = BdM$ . The magnetic potential energy density is  $-\mu_0\mathbf{H}\cdot\mathbf{M} \approx -BM$ , and in most cases the change in volume and pressure are negligible, so the Central Equation for magnetic systems becomes:

$$du = Tds + B.dM; \quad \text{with associated Maxwell Relations such as } \left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial M}{\partial T}\right)_B$$

The internal energy  $u$  here does not include the magnetic energy. We could define an intensive quantity which does, say  $e_{tot} = -BM + u$ . From this we obtain.

$$de_{tot} = Tds - MdB$$

and we can associate  $e_{tot}$  as a magnetic analogue of *enthalpy*. Similar equivalents of Gibbs and Helmholtz free energy can be deduced.

The constant magnetism heat capacity is thus  $c_B = T \left(\frac{\partial S}{\partial T}\right)_B$ , and we can then find that

$$\left(\frac{\partial c_B}{\partial B}\right)_T = \frac{\partial}{\partial B_T} \left(T \frac{\partial S}{\partial T_B}\right) = T \left(\frac{\partial^2 S}{\partial T_B \partial B_T}\right) = T \left(\frac{\partial^2 M}{\partial T^2}\right)_B$$

Where we used a magnetic Maxwell Relation  $\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial M}{\partial T}\right)_B$

Exactly analogous arguments leads us to:  $du = Tds + \mathcal{E}dz$  for an electric cell (“EMF times Charge”) and  $du = Tds + \mathcal{E}dP$  for dielectric material (“Electric field times Polarisation”).

## Magnetic Refrigeration

A paramagnet can be used for cooling at very low temperatures. The idea is to remove entropy by aligning the magnetic moments on the atoms in a magnetic field. Then, when the field is removed isentropically, the entropy of the magnetic disorder is restored, and that entropy is lost from thermal fluctuations. To analyse it,<sup>a</sup> we simply replace  $PdV$  work with  $BdM$  and use  $du = Tds + BdM$ .

We also introduce  $\chi_m = \frac{M}{B}$ , the susceptibility which is essentially the same for isothermal and adiabatic processes.

<sup>a</sup>This analysis illustrates the principle, but involves a lot of assumptions, most notably using non-SI units, intensive quantities (including M) and that the magnetic field due to magnetization can be neglected.

The amount of cooling can be deduced from considering a cycle:

- (ab) Isothermal magnetisation: applied field does Work to align the magnetic moments, reducing the magnetic entropy:

$$\Delta Q_T = T \int \left(\frac{\partial s}{\partial B}\right)_T dB = \int T \left(\frac{\partial M}{\partial T}\right)_B dB$$

where we used a magnetic Maxwell relation.

- (bc) Adiabatic/isenthalpic demagnetisation (field is switched off) magnetic entropy increases, so thermal entropy is reduced and temperature drops.

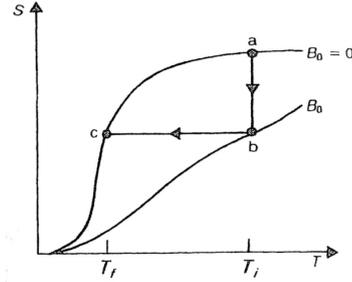
$$\left(\frac{\partial T}{\partial B}\right)_s = -\left(\frac{\partial T}{\partial s}\right)_B \left(\frac{\partial s}{\partial B}\right)_T = -\frac{T}{c_B} \left(\frac{\partial M}{\partial T}\right)_B = -\frac{TB}{c_B} \left(\frac{\partial \chi_m}{\partial T}\right)_B$$

Using Maxwell and product rules, and identifying a heat capacity at constant field  $c_B$ .

- (ca) Isomagnetizational: heat exchanger extracts heat from cold box into the paramagnet, which warms up and the cycle can be repeated.

The cooling step (bc) is most effective if  $\frac{\partial M}{\partial T}_B$  is large, i.e. a small change of temperature induces a large change in magnetisation. This is the case at a *Magnetic Phase Transition*, so the ideal material for depends on the temperature you want to cool to. Paramagnetic cooling can reach lower temperatures than Joule-Kelvin expansion, the latter being limited by the gas condensing. Like He refrigeration, it requires pre-cooling.

Alternately, if the intention is to cool the paramagnet itself, we can omit step (ca), remagnetise the sample and repeat the isothermal/adiabat processes to reach still lower T.



Entropy/Temperature relation for constant external field. The sharp drop in entropy corresponds to a magnetic ordering phase transition.

## Magnetic Equation of State and Heat Capacity

To go further, we need to use materials properties whose derivation is beyond this course. For the magnetic equation of state, the simplest is the Curie Law:  $M = aB/T$  or equivalently  $\chi_m = a/T$ . From this, we see that

$$\int T \left( \frac{\partial M}{\partial T} \right)_B dB = \int (-aB/T) dB$$

For the non-magnetic contribution heat capacity  $c(T, B)$  we adopt the *Schottky* form which describes the heat capacity close to a  $T=0$  phase transition  $c(T, B=0) = b/T^2$  with  $b$  a constant.

$$c(T, B) = b/T^2 + \int \left( \frac{\partial c_B}{\partial B} \right)_T dB = b/T^2 + \int T \left( \frac{\partial^2 M}{\partial T^2} \right)_B dB = b/T^2 + \int T \cdot \frac{2aB}{T^3} dB = (b + aB^2)/T^2$$

Where we used the general result  $\left( \frac{\partial c_B}{\partial B} \right)_T = \left( \frac{\partial^2 M}{\partial T^2} \right)_B$  from above and the Curie Law.

There are two contributions to the heat capacity: the first is from the entropy of thermal motions, as usual, the second is from the entropy of rotating magnetic moments. There are two types of entropy.

Now we can plug the heat capacity and Curie Law into the expression for process (bc)

$$dT = -BT \cdot \frac{T^2}{(b + aB^2)} \cdot \frac{-a}{T^2} dB$$

and rearrange to get integrals:

$$\int \frac{dT}{T} = \int \frac{aB}{(b + aB^2)} dB$$

$$[\ln T]_i^f = \left[ \frac{1}{2} \ln(b + aB^2) \right]_i^f$$

Plugging in the initial and final data,

$$T_f = T_i \sqrt{\frac{b + aB_f^2}{(b + aB_i^2)}}$$

We see that if the magnetisation/demagnetisation process is repeated over and over, the temperature is reduced by a fixed fraction each time. Even with infinite cycles, it can never reach zero.

## Curie-Weiss Law

Curie's Law looks like another example of properties diverging at  $T=0K$ . But careful measurements showed that the divergence was not happening at the same "zero temperature" from ideal gas/Carnot efficiency etc.

In fact, Curie's "zero temperature" varied from material to material. A better magnetic equation of state is given by the Curie-Weiss Law  $M = aB/(T - T_c)$ , with  $a$  the Curie constant and  $T_c$  the Curie Temperature, below which the paramagnet acquires a permanent magnetisation. The divergent Schottky heat capacity is then  $c(T, B=0) = b/(T - T_c)^2$ . Repeating the derivation above using the Curie-Weiss Law is tedious, so we shortcut by using the observation that we are still free to choose the zero of temperature. If we redefine  $T \rightarrow (T - T_c)$  then we immediately obtain:

$$T_f = T_c + (T_i - T_c) \sqrt{\frac{b + aB_f^2}{(b + aB_i^2)}}$$

Now, repeated cooling cycles can only bring the temperature down to  $T_c$ .

Two reasonable approximations are to ignore the magnetic part of the heat capacity ( $b = 0$ ) or assume the final state is fully demagnetised  $B_f = 0$ . Neither of these change the overall picture, though if *both* are assumed then a single cycle will reduce directly to  $T_c$ .

The impossibility of reaching  $T=0$  is connected with the Third Law of Thermodynamics.