MAGNETIC SYSTEMS IN THERMODYNAMICS

We can derive thermodynamic identities for a magnetic system in which pressure and volume are constant. In such a system, work is done by an external electrical power source such as a battery, with the work resulting in changes to the magnetization and magnetic field present in the system, rather than changes in pressure or volume.

As an example, consider a solenoid with a (very long, so we can approximate the field produced as equivalent to that produced by an infinite solenoid) length \(L\) and \(n\) turns per unit length. Suppose that the interior of the solenoid is filled with a cylinder of magnetic material with a magnetization (magnetic dipole moment per unit volume) of \(M\). By applying Ampère’s law to a loop with one edge inside and the opposite edge outside the solenoid, and using the fact that the magnetic field outside a solenoid is zero (see Griffiths referenced above, example 5.9), we have

\[
\int \left( \frac{1}{\mu_0} B - M \right) \cdot d\ell = I_f
\]

where \(I_f\) is the free current enclosed by the loop. By choosing the loop edge to have a unit length we have \(I_f = nI\), where \(I\) is the current in the wire. The integrand is defined to be the auxiliary field \(H\):

\[
H \equiv \frac{1}{\mu_0} B - M
\]

Since both \(B\) and \(M\) are parallel to the axis of the solenoid, the integrand is non-zero only on the edge of the loop inside the solenoid and we have

\[
\mathcal{H} = nI
\]

I’m using \(\mathcal{H}\) to represent magnetic field to distinguish it from \(H\), which represents enthalpy.
This is true for a steady current, but now suppose we vary the current to change the magnetic field strength $B$. According to Faraday’s law, a change in the magnetic flux $\Phi$ through a loop causes a back-emf $\mathcal{E}$ to be produced which opposes the change in flux, according to

$$\mathcal{E} = -\frac{d\Phi}{dt} \quad (4)$$

The work done by the battery is therefore the work required to overcome this back-emf and thus keep the current flowing at its new value. The total magnetic flux through the solenoid is the flux through a single turn (which is $BA$, where $A$ is the cross-sectional area of the solenoid) multiplied by the total number of turns, which is $nL$. Therefore

$$\frac{d\Phi}{dt} = nAL \frac{dB}{dt} \quad (5)$$

The power (work per unit time) generated by the battery is the voltage times the current, which is $-\mathcal{E}I$, (negative because the battery’s voltage is opposite to the back-emf) so the work done in time $dt$ is

$$dW = -\mathcal{E}I \, dt \quad (6)$$

$$= \left( nAL \frac{dB}{dt} \right) \left( \frac{H}{n} \right) \, dt \quad (7)$$

$$= ALH \, dB \quad (8)$$

$$= V \mathcal{H} \, dB \quad (9)$$

where $V = AL$ is the volume of the solenoid.

From $2$, we have

$$dB = \mu_0 (d\mathcal{H} + dM) \quad (10)$$

$$dW_{tot} = \mu_0 V (\mathcal{H} \, d\mathcal{H} + \mathcal{H} \, dM) \quad (11)$$

The first term can be written as

$$\mu_0 V \mathcal{H} \, d\mathcal{H} = \frac{\mu_0 V}{2} \, d (\mathcal{H}^2) \quad (12)$$

In a vacuum, the energy density in a magnetic field is

$$E_m = \frac{1}{2\mu_0} B^2 \quad (13)$$

and $B = \mu_0 \mathcal{H}$ so

$$E_m = \frac{\mu_0}{2} \mathcal{H}^2 \quad (14)$$
Thus, $\Delta$ is the change in the magnetic field energy in the entire solenoid, assuming there is a vacuum inside the solenoid. [Actually, in a *linear magnetic material* $B = \mu \mathcal{H}$, where $\mu$ is the permeability of the material, and it is only in a vacuum that $\mu = \mu_0$. Thus, $\mu_0 \mathcal{H}$ is the magnetic energy density in a vacuum.]

The second term in 11 is the work required to change the magnetization of the sample inside the solenoid:

$$dW = \mu_0 \mathcal{H} V dM$$ \hspace{1cm} (15)

$$= \mu_0 \mathcal{H} d\mathcal{M}$$ \hspace{1cm} (16)

where $\mathcal{M} \equiv VM$ is the total magnetization of the sample.

Assuming that only the energy and magnetization change, we can work out a thermodynamic identity for magnetic matter. By analogy with the earlier derivation, we can imagine a system in which the entropy changes by either the energy $U$ changing or the magnetization $\mathcal{M}$ changing. The entropy change due to an increase in energy at temperature $T$ is

$$dS_U = \frac{dU}{T}$$ \hspace{1cm} (17)

How does the entropy change when the magnetization $\mathcal{M}$ increases? A larger magnetization usually means that the dipoles in the sample are more ordered, so we’d expect an increase in $\mathcal{M}$ to cause a *decrease* in $S$. Thus we’d expect

$$\left( \frac{\partial S}{\partial \mathcal{M}} \right)_U < 0$$ \hspace{1cm} (18)

From 16 we’d like $\left( \frac{\partial S}{\partial \mathcal{M}} \right)_U$ to be something times $\mathcal{H}$. To find the ’something’, we can look at the units. $S$ has units of $\text{J K}^{-1}$. From 2 $\mathcal{M}$ has units of $\text{a(volume)} \times B/\mu_0$ which works out to $\text{m}^3 \text{(Tesla)} \left( \text{J m}^{-1} \text{Amp}^{-2} \right)^{-1} = \text{m}^3 \left( \text{J Amp}^{-1} \text{m}^{-2} \right) \left( \text{J}^{-1} \text{m Amp}^2 \right) = \text{m}^2 \text{Amp}$. The derivative $\left( \frac{\partial S}{\partial \mathcal{M}} \right)$ therefore has units of $\text{J m}^{-2} \text{Amp}^{-1} \text{K}^{-1}$. Multiplying this by $T/\mu_0$ gives a quantity with units of $\text{Amp m}^{-1}$ which are the units of $\mathcal{H}$, so we propose

$$\frac{T}{\mu_0} \left( \frac{\partial S}{\partial \mathcal{M}} \right)_U = -\mathcal{H}$$ \hspace{1cm} (19)

The total entropy change is therefore

$$dS = dS_U + dS_M$$ \hspace{1cm} (20)

$$= \frac{dU}{T} - \frac{\mu_0 \mathcal{H}}{T} d\mathcal{M}$$ \hspace{1cm} (21)
This gives a thermodynamic identity of
\[ dU = T \, dS + \mu_0 \mathcal{H} \, d\mathcal{M} \]  
(22)

As we might expect, the last term is just the work done on the system as given by [16].

By analogy with the definition of enthalpy for a pressure-volume system, the enthalpy here is
\[ H = U - \mu_0 \mathcal{H} \mathcal{M} \]  
(23)

This is the energy required to create a magnetic system from scratch, with an internal energy \( U \) and magnetization \( \mathcal{M} \) in a field \( \mathcal{H} \). Presumably the second term is negative, since aligning the dipoles with the external field reduces the energy of the system.

The corresponding thermodynamic identity is
\[ dH = dU - \mu_0 \mathcal{H} \, d\mathcal{M} - \mu_0 \mathcal{M} \, d\mathcal{H} \]  
(24)
\[ = T \, dS - \mu_0 \mathcal{M} \, d\mathcal{H} \]  
(25)

The Helmholtz free energy is still defined as
\[ F = U - TS \]  
(26)

since there is no reference to pressure or volume. The thermodynamic potential is
\[ dF = dU - T \, dS - S \, dT \]  
(27)
\[ = -S \, dT + \mu_0 \mathcal{H} \, d\mathcal{M} \]  
(28)

The Gibbs free energy is thus defined as
\[ G = U - TS - \mu_0 \mathcal{H} \mathcal{M} \]  
(29)
\[ = F - TS \]  
(30)

Its thermodynamic identity is
\[ dG = dF - \mu_0 \mathcal{H} \, d\mathcal{M} - \mu_0 \mathcal{M} \, d\mathcal{H} \]  
(31)
\[ = -S \, dT - \mu_0 \mathcal{M} \, d\mathcal{H} \]  
(32)