MAGNETIC SYSTEMS IN THERMODYNAMICS

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References: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problem 5.17;

F. Mandl, *Statistical Physics*, Second Edition, (John Wiley & Sons, 1988) - Section 1.4.

Griffiths, David J. (2007) Introduction to Electrodynamics, 3rd Edition; Prentice Hall - Section 5.3.

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 $\mathbf{M}$. 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

$$\int\left(\frac{1}{\mu_0}\mathbf{B}-\mathbf{M}\right)\cdot d\ell = I_f \tag{1}$$

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 $\mathbf{H}$:

$$\mathbf{H} \equiv \frac{1}{\mu_0}\mathbf{B}-\mathbf{M} \tag{2}$$

Since both $\mathbf{B}$ and $\mathbf{M}$ 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

$$\mathcal{H} = nI \tag{3}$$

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 Φ through a loop causes a back-emf $\mathcal{E}$ to be produced which opposes the change in flux, according to

$$\mathcal{E} = -\frac{d\Phi}{dt} \tag{4}$$

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

$$\frac{d\Phi}{dt} = nAL\frac{dB}{dt} \tag{5}$$

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

$$\begin{aligned} dW &= -\mathcal{E}I\,dt && (6)\\ &= \left(nAL\frac{dB}{dt}\right)\left(\frac{\mathcal{H}}{n}\right)dt && (7)\\ &= AL\mathcal{H}\,dB && (8)\\ &= V\mathcal{H}\,dB && (9) \end{aligned}$$

where $V = AL$ is the volume of the solenoid.
From 2, we have

$$\begin{aligned} dB &= \mu_0\left(d\mathcal{H} + dM\right) && (10)\\ dW_{tot} &= \mu_0 V\left(\mathcal{H}\,d\mathcal{H} + \mathcal{H}\,dM\right) && (11) \end{aligned}$$

The first term can be written as

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

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

$$E_m = \frac{1}{2\mu_0}B^2 \tag{13}$$

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

$$E_m = \frac{\mu_0}{2}\mathcal{H}^2 \tag{14}$$

Thus, 12 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 μ is the permeability of the material, and it is only in a vacuum that $\mu=\mu_0$. Thus, 14 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:

$$dW = \mu_0\mathcal{H}V\,dM \quad (15)$$

$$= \mu_0\mathcal{H}\,d\mathcal{M} \quad (16)$$

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

$$dS_U = \frac{dU}{T} \quad (17)$$

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

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

From 16, we'd like $\left(\frac{\partial S}{\partial\mathcal{M}}\right)$ to be something times $\mathcal{H}$. To find the 'something', we can look at the units. S has units of J K^{-1}. From 2, $\mathcal{M}$ has units of a(volume) $\times B/\mu_0$ which works out to $\mathrm{m}^3\,(\mathrm{Tesla})\left(\mathrm{J\ m^{-1}Amp^{-2}}\right)^{-1} = \mathrm{m}^3\left(\mathrm{J\ Amp^{-1}m^{-2}}\right)\left(\mathrm{J^{-1}m\ Amp^{2}}\right) = \mathrm{m^2Amp}$. The derivative $\left(\frac{\partial S}{\partial\mathcal{M}}\right)$ therefore has units of $\mathrm{J\ m^{-2}Amp^{-1}K^{-1}}$. Multiplying this by T/μ_0 gives a quantity with units of Amp m^{-1} which are the units of $\mathcal{H}$, so we propose

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

The total entropy change is therefore

$$dS = dS_U + dS_{\mathcal{M}} \quad (20)$$

$$= \frac{dU}{T} - \frac{\mu_0\mathcal{H}}{T}d\mathcal{M} \quad (21)$$

This gives a thermodynamic identity of

$$dU = T\,dS + \mu_0 \mathcal{H}\,d\mathcal{M} \tag{22}$$

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

$$H = U - \mu_0 \mathcal{H}\mathcal{M} \tag{23}$$

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

$$\begin{aligned} dH &= dU - \mu_0 \mathcal{H}\,d\mathcal{M} - \mu_0 \mathcal{M}\,d\mathcal{H} && (24) \\ &= T\,dS - \mu_0 \mathcal{M}\,d\mathcal{H} && (25) \end{aligned}$$

The Helmholtz free energy is still defined as

$$F = U - TS \tag{26}$$

since there is no reference to pressure or volume. The thermodynamic potential is

$$\begin{aligned} dF &= dU - T\,dS - S\,dT && (27) \\ &= -S\,dT + \mu_0 \mathcal{H}\,d\mathcal{M} && (28) \end{aligned}$$

The Gibbs free energy is thus defined as

$$\begin{aligned} G &= U - TS - \mu_0 \mathcal{H}\mathcal{M} && (29) \\ &= F - TS && (30) \end{aligned}$$

Its thermodynamic identity is

$$\begin{aligned} dG &= dF - \mu_0 \mathcal{H}\,d\mathcal{M} - \mu_0 \mathcal{M}\,d\mathcal{H} && (31) \\ &= -S\,dT - \mu_0 \mathcal{M}\,d\mathcal{H} && (32) \end{aligned}$$