

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

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

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 \mathbf{H} :

$$(2) \quad \mathbf{H} \equiv \frac{1}{\mu_0} \mathbf{B} - \mathbf{M}$$

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

$$(3) \quad \mathcal{H} = nI$$

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 \mathbf{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

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

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

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

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

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

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

$$(8) \quad = AL \mathcal{H} dB$$

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

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

From 2, we have

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

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

The first term can be written as

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

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

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

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

$$(14) \quad E_m = \frac{\mu_0}{2} \mathcal{H}^2$$

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:

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

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

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

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

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

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

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 J K^{-1} . From 2, \mathcal{M} has units of $\text{a(volume)} \times B/\mu_0$ which works out to $\text{m}^3 (\text{Tesla}) (\text{J m}^{-1} \text{Amp}^{-2})^{-1} = \text{m}^3 (\text{J Amp}^{-1} \text{m}^{-2}) (\text{J}^{-1} \text{m Amp}^2) = \text{m}^2 \text{Amp}$. The derivative $\left(\frac{\partial S}{\partial \mathcal{M}} \right)_U$ therefore has units of $\text{J m}^{-2} \text{Amp}^{-1} \text{K}^{-1}$. 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

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

The total entropy change is therefore

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

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

This gives a thermodynamic identity of

$$(22) \quad dU = T dS + \mu_0 \mathcal{H} d\mathcal{M}$$

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

$$(23) \quad H = U - \mu_0 \mathcal{H} \mathcal{M}$$

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

$$(24) \quad dH = dU - \mu_0 \mathcal{H} d\mathcal{M} - \mu_0 \mathcal{M} d\mathcal{H}$$

$$(25) \quad = T dS - \mu_0 \mathcal{M} d\mathcal{H}$$

The Helmholtz free energy is still defined as

$$(26) \quad F = U - TS$$

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

$$(27) \quad dF = dU - T dS - S dT$$

$$(28) \quad = -S dT + \mu_0 \mathcal{H} d\mathcal{M}$$

The Gibbs free energy is thus defined as

$$(29) \quad G = U - TS - \mu_0 \mathcal{H} \mathcal{M}$$

$$(30) \quad = F - TS$$

Its thermodynamic identity is

$$(31) \quad dG = dF - \mu_0 \mathcal{H} d\mathcal{M} - \mu_0 \mathcal{M} d\mathcal{H}$$

$$(32) \quad = -S dT - \mu_0 \mathcal{M} d\mathcal{H}$$