

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

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

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} :

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

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

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

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 \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

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

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

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

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

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

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

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

From 2, we have

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

$$dW_{tot} = \mu_0V(\mathcal{H} d\mathcal{H} + \mathcal{H} dM) \quad (11)$$

The first term can be written as

$$\mu_0V\mathcal{H} d\mathcal{H} = \frac{\mu_0V}{2} d(\mathcal{H}^2) \quad (12)$$

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, 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 $\left(\frac{\partial S}{\partial \mathcal{M}}\right)_U$ 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

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

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

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

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

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

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

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

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

The Helmholtz free energy is still defined as

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

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

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

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

The Gibbs free energy is thus defined as

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

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

Its thermodynamic identity is

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

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