Unit 1-7: The Maxwell Relations

So you thought Maxwell only did E&M? Here we will discuss what are known as the Maxwell relations of thermodynamics. They all follow from taking 2nd derivatives of the various thermodynamic potentials (free energies).

Energy $E(S,V,N)$

Consider the energy, $E(S,V,N)$. We have,

$$\left(\frac{\partial E}{\partial S}\right)_{V,N} = T(S,V,N) \quad \text{so} \quad \left(\frac{\partial^2 E}{\partial V \partial S}\right)_N = \left(\frac{\partial T}{\partial V}\right)_{S,N} \tag{1.7.1}$$

but

$$\left(\frac{\partial E}{\partial V}\right)_{S,N} = -p(S,V,N) \quad \text{so} \quad \left(\frac{\partial^2 E}{\partial S \partial V}\right)_N = -\left(\frac{\partial p}{\partial S}\right)_{V,N} \tag{1.7.2}$$

Since the order in which we take the partials with respect to S and V does not matter we conclude

$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial p}{\partial S}\right)_{V,N} \tag{1.7.3}$$

This equality of 2nd derivatives is known as a Maxwell relation.

We can do the same thing for any thermodynamic potential.

Helmholtz Free Energy $A(T,V,N)$

Consider the Helmholtz free energy, $A(T,V,N)$. We have,

$$-\left(\frac{\partial A}{\partial T}\right)_{V,N} = S(T,V,N) \quad \text{so} \quad -\left(\frac{\partial^2 A}{\partial V \partial T}\right)_N = \left(\frac{\partial S}{\partial V}\right)_{T,N} \tag{1.7.4}$$

but

$$-\left(\frac{\partial A}{\partial V}\right)_{T,N} = p(T,V,N) \quad \text{so} \quad -\left(\frac{\partial^2 A}{\partial T \partial V}\right)_N = \left(\frac{\partial p}{\partial T}\right)_{V,N} \tag{1.7.5}$$

Since the order in which we take the partials with respect to T and V does not matter we conclude

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial p}{\partial T}\right)_{V,N} \tag{1.7.6}$$

Gibbs Free Energy $G(T,p,N)$

Consider the Gibbs free energy, $G(T,p,N)$. We have,

$$\left(\frac{\partial G}{\partial p}\right)_{T,N} = V(T,p,N) \quad \text{so} \quad \left(\frac{\partial^2 G}{\partial N \partial p}\right)_T = \left(\frac{\partial V}{\partial N}\right)_{T,p} \tag{1.7.7}$$

but

$$\left(\frac{\partial G}{\partial N}\right)_{T,p} = \mu(T,p,N) \quad \text{so} \quad \left(\frac{\partial^2 G}{\partial p \partial N}\right)_T = \left(\frac{\partial \mu}{\partial p}\right)_{T,N} \tag{1.7.8}$$

Since the order in which we take the partials with respect to p and N does not matter we conclude

$$\left(\frac{\partial V}{\partial N}\right)_{T,p} = \left(\frac{\partial \mu}{\partial p}\right)_{T,N} \tag{1.7.9}$$

In the same way, by taking any second derivative of any thermodynamic potential, with respect to two different variables, one arrives at a Maxwell relation. See Callen Chapter 7 for a complete list.

If you are given a derivative, say $(\partial V/\partial N)_{T,p}$, and you want to find what is its Maxwell relation pairing, the trick is as follows. Look at what are the dependent variables that are involved. In this example they are N (what we are taking the derivative with respect to) and T and p (the variables held constant). So then we ask, which is the thermodynamic potential that depends on the variables T, p, and N? It is the Gibbs free energy $G(T,p,N)$. Since we are taking the derivative of V, then we should recall that $(\partial G/\partial p)_{T,N} = V$. So the derivate we have can be expressed as the 2nd derivative of G, as $(\partial^2 G/\partial N \partial p)_T$. To find its Maxwell relation pairing, just reverse the order of the derivatives, so $(\partial G/\partial N)_{T,p} = \mu$. Then we have $(\partial^2 G/\partial p \partial N)_T = (\partial \mu/\partial p)_{T,N}$. So we conclude that $(\partial V/\partial N)_{T,p} = (\partial \mu/\partial p)_{T,N}$.