HW #1

Show that the entropy maximum principle
$\Rightarrow$ the energy minimum principle

given $\left(\frac{\partial S}{\partial x}\right)_E = 0$, $\left(\frac{\partial^2 S}{\partial x^2}\right)_E < 0$

show $\left(\frac{\partial E}{\partial x}\right)_S = 0$, $\left(\frac{\partial^2 E}{\partial x^2}\right)_S > 0$

$$(\partial E/\partial x)_S = -\frac{(\partial S/\partial x)_E}{(\partial S/\partial E)_x} = -T\left(\frac{\partial S}{\partial x}\right)_E$$

so $(\partial S/\partial x)_E = 0 \Rightarrow (\partial E/\partial x)_S = 0$

Let $(\partial E/\partial x)_S = y$

$$dy = \left(\frac{\partial y}{\partial x}\right)_E dx + \left(\frac{\partial y}{\partial E}\right)_x dE$$

$$(\partial y/\partial x)_S = \left(\frac{\partial y}{\partial x}\right)_E + \left(\frac{\partial y}{\partial E}\right)_x \left(\frac{\partial E}{\partial x}\right)_S$$

$$\Rightarrow \left(\frac{\partial^2 E}{\partial x^2}\right)_S = -\frac{\partial}{\partial x}\left[T\left(\frac{\partial S}{\partial x}\right)_E\right] = -T\left(\frac{\partial^2 S}{\partial x^2}\right)_E$$

$$\Rightarrow \left(\frac{\partial^2 E}{\partial x^2}\right)_S > 0$$

2. Find the Maxwell relations corresponding to H and G

$$dH = TdS + VdP + \sum \mu_i dn_i$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad \leftarrow$$

I have suppressed the subscript indicating that the n_i are fixed.

$$dG = -SdT + VdP + \sum \mu_i dn_i$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

#3 Using the maxwell relations show that

$$\left(\frac{\partial H}{\partial V}\right)_{T,n} = \frac{T\alpha - 1}{\kappa_T}$$

$$\left(\frac{\partial H}{\partial V}\right)_{T,n} = T\left(\frac{\partial S}{\partial V}\right)_{T,n} + V\left(\frac{\partial P}{\partial V}\right)_{T,n}$$

$$= T\left(\frac{\partial S}{\partial P}\right)_{T,n}\left(\frac{\partial P}{\partial V}\right)_{T,n} + V\left(\frac{\partial P}{\partial V}\right)_{T,n}$$

$$= -T\left(\frac{\partial V}{\partial T}\right)_{P,n}\left(\frac{\partial P}{\partial V}\right)_{T,n} + V\left(\frac{\partial P}{\partial V}\right)_{T,n}$$

$$= (\partial P/\partial V)_{T,n}\left[-T\left(\frac{\partial V}{\partial T}\right)_{P,n} + V\right]$$

$$= \frac{\left[-T\left(\frac{\partial V}{\partial T}\right)_{P,n} + V\right]}{\frac{1}{V}(\partial V/\partial P)_{T,n}} = \frac{\left[-\frac{T}{V}\left(\frac{\partial V}{\partial T}\right)_{P,n} + 1\right]}{1/V\left(\frac{\partial V}{\partial P}\right)_{T,n}}$$

$$= \frac{-T\alpha + 1}{-\kappa_T} = \frac{T\alpha - 1}{\kappa_T}$$

α = coefficient of thermal expansion

κ_T = isothermal compressibility