8.044 Statistical Physics I
Spring 2008

Maxwell Relations

$$dE(S,V) = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV \qquad \text{expansion}$$

$$= TdS - PdV \qquad 1^{st} \text{ and } 2^{nd} \text{ laws}$$

$$\Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$dE(S,L) = TdS + \mathcal{F}dL \Rightarrow \left(\frac{\partial T}{\partial L}\right)_S = \left(\frac{\partial \mathcal{F}}{\partial S}\right)_L$$

$$dE(S,M) = TdS + HdM \Rightarrow \left(\frac{\partial T}{\partial M}\right)_S = \left(\frac{\partial H}{\partial S}\right)_M$$

Observe:

$$d(TS) = TdS + SdT$$

$$d(PV) = PdV + VdP$$

Helmholtz Free Energy $F \equiv E - TS$

$$dF = -SdT - PdV \quad \Rightarrow \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Enthalpy $H \equiv E + PV$

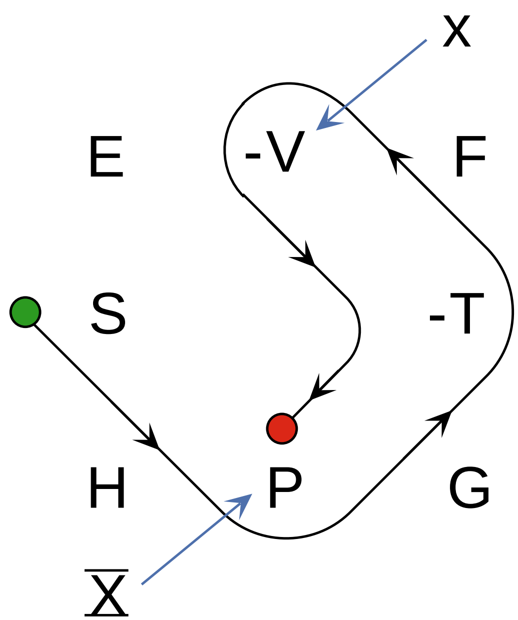
$$dH = TdS + VdP \quad \Rightarrow \quad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

Gibbs Free Energy $G \equiv E + PV - TS$

$$dG = -SdT + VdP \Rightarrow \quad -\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

E, F, H and G are called "thermodynamic potentials".

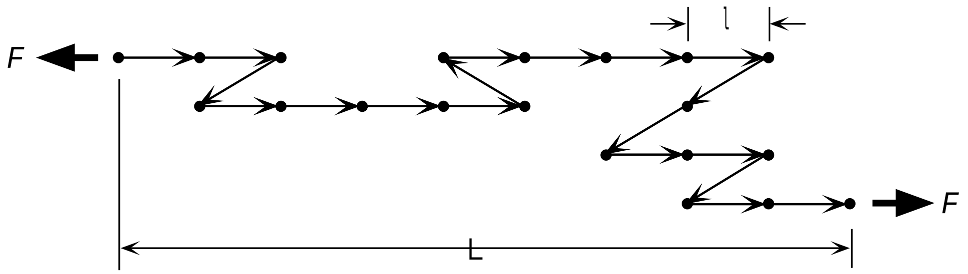
The Magic Square Mnemonic



$$dE = TdS + Xdx$$

$$(-1)\left(\frac{\partial S}{\partial P}\right)_T = \underbrace{(-1)(-1)}_{(+1)}\left(\frac{\partial V}{\partial T}\right)_P$$

Homework problem 6-2, A Strange Chain



$$L = Nl \tanh(l\mathcal{F}/kT)$$

For small extensions

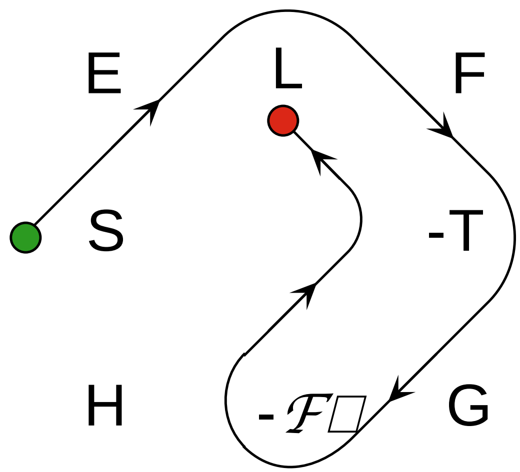
$$\alpha = -\frac{1}{T}$$

Example Elastic Rod

Given $\mathcal{F} = \underbrace{(a + bT)}_{+ \text{ for stability}} (L - L_0)$ and $C_L = \alpha T^3$

Find $E(T, L)$ and $S(T, L)$.

$$dE = \underbrace{T dS}_{đQ} + \mathcal{F} dL = \underbrace{T \left(\frac{\partial S}{\partial T}\right)_L}_{C_L} dT + \left(\underbrace{T \left(\frac{\partial S}{\partial L}\right)_T}_{-bT(L-L_0)} + \mathcal{F} \right) dL$$



$$(-1)\left(\frac{\partial S}{\partial L}\right)_T = \left(\frac{\partial \mathcal{F}}{\partial T}\right)_L = b(L-L_0)$$

$$dE = \alpha T^3 dT + a(L - L_0)dL$$

$$E = \frac{\alpha}{4}T^4 + f(L)$$

$$f'(L) = a(L - L_0) \qquad f(L) = \frac{a}{2}(L - L_0)^2 + c_1$$

$$E(T,L) = \frac{\alpha}{4}T^4 + \frac{a}{2}(L-L_0)^2 + c_1$$

$$dS = \underbrace{\left(\frac{\partial S}{\partial T}\right)_L}_{C_V/T=\alpha T^2} dT + \underbrace{\left(\frac{\partial S}{\partial L}\right)_T}_{-b(L-L_0)} dL$$

$$S = \frac{\alpha}{3}T^3 + g(L)$$

$$g'(L) = -b(L-L_0) \qquad g(L) = -\frac{b}{2}(L-L_0)^2 + c_2$$

$$S(T,L) = \frac{\alpha}{3}T^3 - \frac{b}{2}(L-L_0)^2 + c_2$$

A rubber band has a negative thermal expansion coef.

$$d\mathcal{F} = (a+bT)dL + b(L-L_0)dT \quad \text{set} = 0$$

$$\Rightarrow \left(\frac{\partial L}{\partial T}\right)_{\mathcal{F}} = -\frac{b\overbrace{(L-L_0)}^{+\text{ when extended}}}{\underbrace{(a+bT)}_{+\text{ for stability}}} < 0 \quad \text{for rubber}$$

$$\Rightarrow b > 0$$

$$S(T,L) = \frac{\alpha}{3}T^3 - \frac{b}{2}(L - L_0)^2 + c_2$$

Rapid expansion of rubber band $\Rightarrow \Delta S \sim 0$

Increase in $L \Rightarrow$ increase in T.