

Maxwell Relations

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

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

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

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

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

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 $H \equiv E + PV$

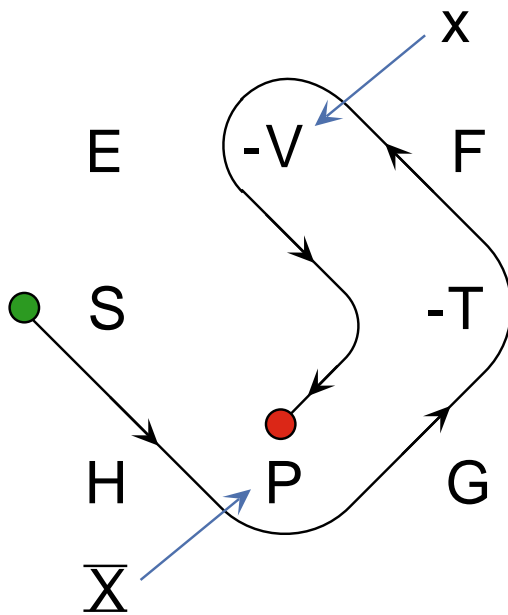
$$dH = TdS + VdP \quad \Rightarrow \quad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

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

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

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

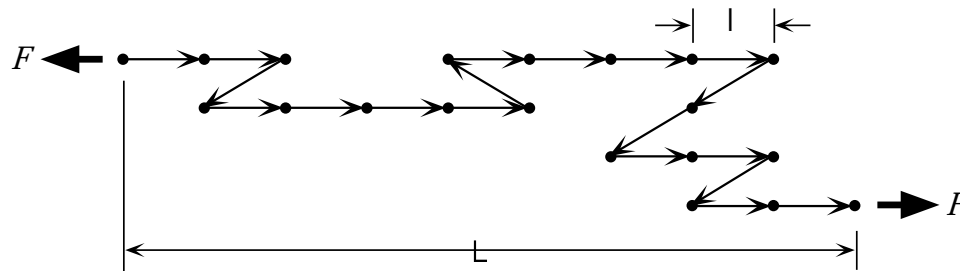
The Magic Square Mnemonic



$$dE = TdS + Xdx$$

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

Homework problem 6-2, A Strange Chain



$$L = Nl \tanh(lF/kT)$$

For small extensions

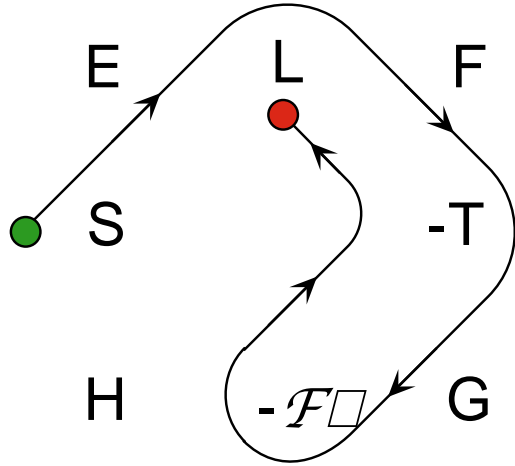
$$\alpha = -\frac{1}{T}$$

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 $S(T, L)$.

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



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

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

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

$$f'(L) = a(L - L_0)$$

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

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

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

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

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

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

A rubber band has a negative thermal expansion coef.

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

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

$$\Rightarrow b > 0$$

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

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

Increase in $L \Rightarrow$ increase in T .