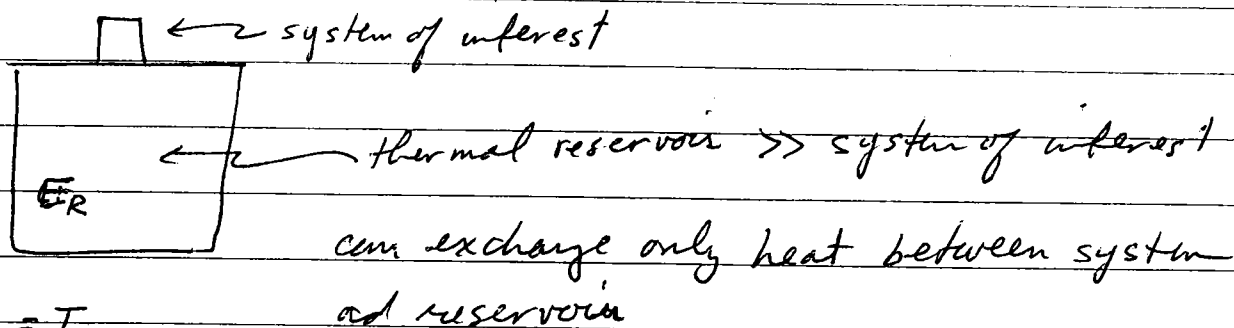


Extremum Principles for Free Energies

Concept of a thermal reservoir



$$\left(\frac{\partial E_R}{\partial S_R}\right)_{V,N} = T_R$$

Suppose we add heat $dQ = TdS$ to the reservoir.

The change in the reservoir's temperature T_R will be

$$\Delta T_R = \left(\frac{\partial T_R}{\partial S_R}\right) dS = \left(\frac{\partial^2 E_R}{\partial S_R^2}\right) dS$$

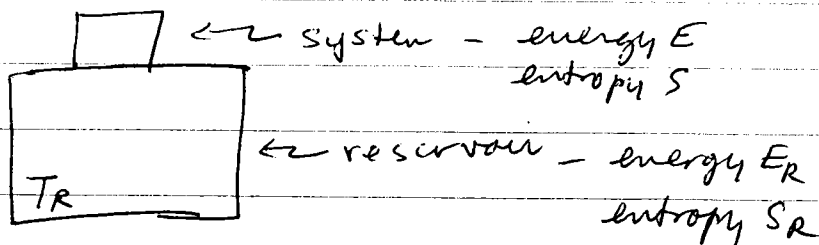
Since E_R and S_R are both extensive variables, they scale with the number of particles in the reservoir N_R .

So

$$\left(\frac{\partial^2 E_R}{\partial S_R^2}\right) \sim \frac{1}{N_R} \rightarrow 0 \quad \left. \begin{array}{l} \text{for infinitely large reservoir} \\ \Rightarrow \Delta T_R \rightarrow 0 \end{array} \right\}$$

Formally, a thermal reservoir is a system so large that its temperature does not change when it exchanges heat with the system of interest.

Consider a system in contact with a thermal reservoir
 Only energy can be exchanged between system + reservoir
 Temperature T_R of reservoir is const by definition



Since system is in equilib with reservoir, the system temp $T = T_R$

If an internal constraint in the system is relaxed, what determines the new equilib state?

Use entropy formulation - total energy is conserved $E = E_R + E$
 total entropy is maximized

$$S^{\text{tot}} = S_R(E_R) + S(E)$$

$$= S_R(E^{\text{tot}} - E) + S(E)$$

Since $E \ll E^{\text{tot}}$ (as $E_R \gg E$ by def of reservoir)
 we can expand

$$S^{\text{tot}} \approx S_R(E^{\text{tot}}) - \left(\frac{\partial S_R}{\partial E_R} \right) E + S(E)$$

$$= S_R(E^{\text{tot}}) - \frac{E}{T_R} + S(E)$$

$$= S_R(E^{\text{tot}}) - (E - T_R S) / T_R$$

$$= \underbrace{S_R(E^{\text{tot}})}_{\text{constant}} - \underbrace{A}_{\text{Helmholtz free energy}} / T_R$$

$T_R = T$
 \uparrow
 system temp

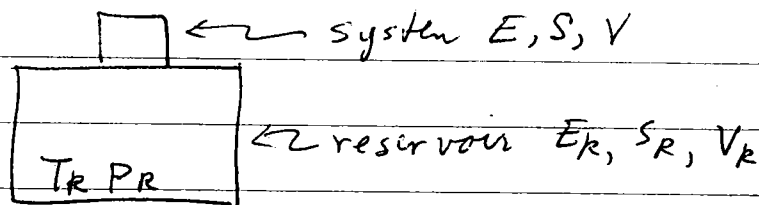
constant Helmholtz free energy

S^{tot} maximized \Rightarrow A minimized

\Rightarrow the equilib-state of a system in contact with a thermal reservoir will be the one that minimizes the Helmholtz free energy $A(T, V, N)$

Now consider a system in contact with a thermal + pressure reservoir

pressure reservoir always has fixed pressure p_R



total energy conserved $E^{\text{tot}} = E_R + E = \text{constant}$

total volume conserved $V^{\text{tot}} = V_R + V = \text{const}$

system in equilib with reservoir $\Rightarrow T = T_R, p = p_R$

$$S^{\text{tot}} = S_R(E_R, V_R) + S(E, V)$$

$$= S_R(E^{\text{tot}} - E, V^{\text{tot}} - V) + S(E, V)$$

$$\approx S_R(E^{\text{tot}}, V^{\text{tot}}) - \left(\frac{\partial S_R}{\partial E_R}\right) E - \left(\frac{\partial S_R}{\partial V_R}\right) V + S(E, V)$$

$$= \text{constant} - \frac{E}{T_R} + \frac{P_R}{T_R} V + S$$

$$= \text{const} - (E + PV - ST)/T = \text{const} - G/T$$

S^{tot} maximized $\Rightarrow G$, Gibbs Free energy, is minimized

⇒ the equilib state of a system in contact with a thermal + pressure reservoir will be the one that minimizes the Gibbs free energy $G(T, p, N)$

Similarly - the equilib state of a system in contact with a pressure reservoir will be the one that minimizes the enthalpy $H(S, p, N)$

and - the equilib state of a system in contact with a thermal and a particle reservoir (a particle reservoir can exchange particles with the system, but is so large that its chemical potential μ_p stays constant) will be the one that minimizes the grand potential $\Sigma(T, V, \mu)$

Maxwell Relations

Follow from 2nd derivatives of the thermodynamic potential
Energy:

$$E(S, V, N) \Rightarrow \left(\frac{\partial E}{\partial S}\right)_{V, N} = T(S, V, N)$$

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

$$\text{but } \left(\frac{\partial E}{\partial V}\right)_{S, N} = -p(S, V, N)$$

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

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

Can do the same for any thermodynamic potential
Helmholtz free energy

$$A(T, V, N) \Rightarrow -\left(\frac{\partial A}{\partial T}\right)_{V, N} = S(T, V, N)$$

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

$$\text{but: } -\left(\frac{\partial A}{\partial V}\right)_{T, N} = p(T, V, N)$$

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

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

Or Gibbs free energy

$$G(T, p, N) \Rightarrow \left(\frac{\partial G}{\partial p} \right)_{T, N} = V(T, p, N)$$

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

$$\text{but } \left(\frac{\partial G}{\partial N} \right)_{T, p} = \mu(T, p, N)$$

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

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

These equivalences, which follow from the independence of the order of taking 2nd derivatives, are called the Maxwell Relations

See Callen Chpt 7 for a complete list

Response functions

specific heat at const volume $C_V = \left(\frac{dQ}{dT}\right)_{V,N} = T \left(\frac{dS}{dT}\right)_{V,N}$

specific heat at const pressure $C_P = \left(\frac{dQ}{dT}\right)_{P,N} = T \left(\frac{dS}{dT}\right)_{P,N}$

isothermal compressibility $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_{T,N}$

adiabatic compressibility $\kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_{S,N}$

coefficient of thermal expansion $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_{P,N}$

All the above may be viewed as a second derivative of an appropriate thermodynamic potential

$$C_V = T \left(\frac{dS}{dT}\right)_V = -T \left(\frac{\partial^2 A}{\partial T^2}\right)_{V,N} \quad \text{since } \left(\frac{\partial A}{\partial T}\right)_{V,N} = -S(T, V, N)$$

$$C_P = T \left(\frac{dS}{dT}\right)_P = -T \left(\frac{\partial^2 G}{\partial T^2}\right)_{P,N} \quad \text{since } \left(\frac{\partial G}{\partial T}\right)_{P,N} = -S(T, P, N)$$

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V} \left(\frac{\partial^2 G}{\partial P^2}\right)_{T,N} \quad \text{since } \left(\frac{\partial G}{\partial P}\right)_{T,N} = V(T, P, N)$$

$$\kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_S = -\frac{1}{V} \left(\frac{\partial^2 H}{\partial P^2}\right)_{S,N} \quad \text{since } \left(\frac{\partial H}{\partial P}\right)_{S,N} = V(S, P, N)$$

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V} \left(\frac{\partial^2 G}{\partial T \partial P}\right)_{N} \quad \text{since } \left(\frac{\partial G}{\partial P}\right)_{T,N} = V(T, P, N)$$

Since all the various thermodynamic potentials can all be derived from one another, the various second derivatives must ~~all~~ be related. If we consider