

To summarize

$$f(x) \quad \phi \equiv \frac{df}{dx}$$

$$g(p) = f(x) - px \quad \Rightarrow \quad \frac{dg}{dp} = -x$$

One says that $g(p)$ is the Legendre transform of $f(x)$ and that x and p are conjugate variables.

$g(p)$ contains all the information that $f(x)$ does, i.e. if one knows $g(p)$ then one can construct $f(x)$ from it, by constructing all the tangent lines $y = px + g(p)$. The Legendre transform allows one to switch variables from x to $\frac{df}{dx}$ without losing information.

You may have already seen Legendre transforms in classical mechanics. In the Lagrange formulation, the fundamental function is the Lagrangian $\mathcal{L}[q, \dot{q}]$ which depends on the variables q and \dot{q} . In the Hamilton formulation one wants to replace the variable \dot{q} by the variable $\phi = \frac{\partial \mathcal{L}}{\partial \dot{q}}$. The fundamental function to use,

which is a function of q and ϕ rather than q and \dot{q} , is therefore the Legendre transform of the Lagrangian

$$\mathcal{L}[q, \dot{q}] - \phi \dot{q} = -\mathcal{H}[p, q]$$

where \mathcal{H} is the Hamiltonian. Because ϕ and \dot{q} are conjugate variables, we know that

$$\frac{\partial (-H)}{\partial p} = -\dot{q} \quad \text{or} \quad \frac{\partial H}{\partial p} = \dot{q}$$

which is one of the Hamilton dynamic equations (the other is $\frac{\partial H}{\partial q} = -\dot{p}$)

Legendre transform and Thermodynamics

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

If we want a formulation of thermodynamics in which temperature T rather than entropy S is regarded as an independent variable, we take the Legendre transform of the energy

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

$$\Rightarrow A(T, V, N) \equiv E - TS$$

Helmholtz Free Energy
sometimes written as $F(T, V, N)$

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

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

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

$$dA = \left(\frac{\partial A}{\partial T} \right)_{V, N} dT + \left(\frac{\partial A}{\partial V} \right)_{T, N} dV + \left(\frac{\partial A}{\partial N} \right)_{T, V} dN$$

$$\Rightarrow dA = -SdT - pdV + \mu dN$$

Since $E = TS - pV + \mu N$, $A = E - TS = -pV + \mu N$

$$A = -pV + \mu N$$

checking the derivatives more carefully

$A = E - TS$ to take Legendre transform we use in
principal compute $T(S, V, N) = \left(\frac{\partial E}{\partial S}\right)_{N, V}$
and invert it to get $S(T, V, N)$
then substitute into the above

$$A(T, V, N) = E(S(T, V, N), V, N) - TS(T, V, N)$$

then

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

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

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

Similarly

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

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

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

Similarly

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

Enthalpy $H(S, p, N)$

use pressure instead of volume

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

$$H(S, p, N) \equiv E + pV$$

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

$$dH = TdS + Vdp + \mu dN$$

Since $E = TS - pV + \mu N$

$$H = E + pV = TS + \mu N$$

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

use temperature and pressure instead of entropy and volume

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

$$G(T, p, N) = E - TS + pV$$

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

$$dG = -SdT + Vdp + \mu dN$$

$$\text{Since } E = TS - pV + \mu N$$

$$G = E - TS + pV = \mu N$$

$$\text{or } \boxed{\frac{G}{N} \equiv g = \mu}$$

The chemical potential is the Gibbs free energy per particle

$$\text{From } G = \mu N \text{ we get } dG = \mu dN + N d\mu$$

$$\text{Combining with } dG = -SdT + Vdp + \mu dN$$

$$\cancel{\mu dN} + N d\mu = -SdT + Vdp + \cancel{\mu dN}$$

$$\Rightarrow SdT - Vdp + N d\mu = 0$$

we regain the Gibbs - Duhem relation

Note: If we are dealing with a system with more than one species of particles, N_1, N_2, \dots then

$$G(T, p, N_1, N_2, \dots) = \mu_1 N_1 + \mu_2 N_2 + \mu_3 N_3 + \dots$$

$$\text{where } \mu_i = \left(\frac{\partial G}{\partial N_i} \right)_{T, p, N_j \neq i}$$

Grand potential $\Sigma(T, V, \mu)$

use temperature and chemical potential instead of entropy and particle number

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

$$\Sigma(T, V, \mu) = E - TS - \mu N$$

$$\left(\frac{\partial \Sigma}{\partial T}\right)_{V, \mu} = -S, \quad \left(\frac{\partial \Sigma}{\partial \mu}\right)_{T, V} = -N$$

$$d\Sigma = -SdT - pdV - Nd\mu$$

Since $E = TS - pV + \mu N$

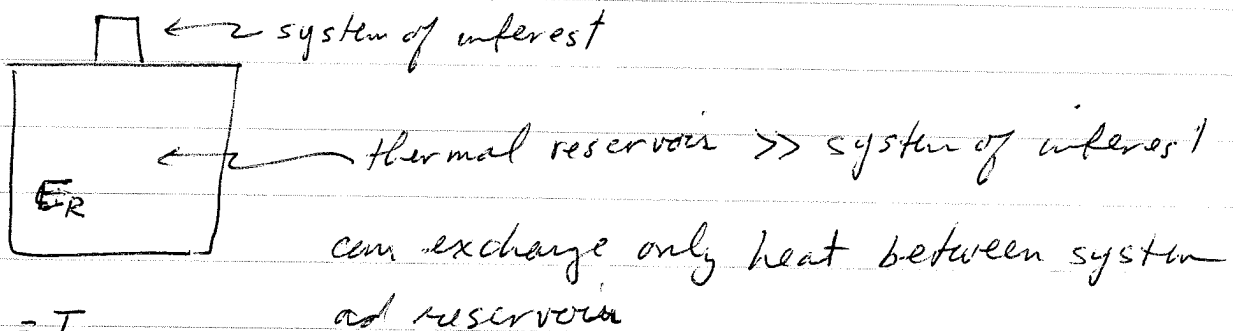
$$\Sigma = E - TS - \mu N = -pV$$

$$-\frac{\Sigma}{V} = p$$

the pressure is (-) the grand potential per unit volume.

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 $dQ = T ds$ to the reservoir.

The change in the reservoir's temperature T_R will be

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

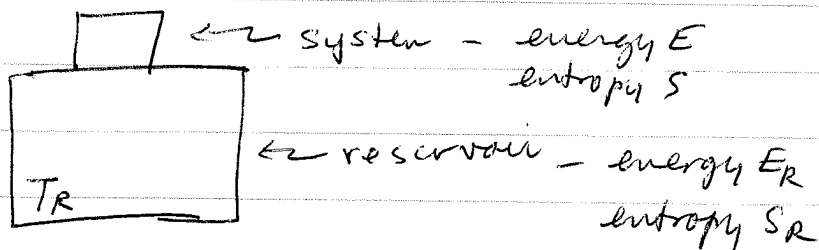
Since E_R and S_R are both extensive variables, they scale with the number of particles in the reservoir N_R .

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

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

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

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

$$T_R = T$$

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

↑
system temp

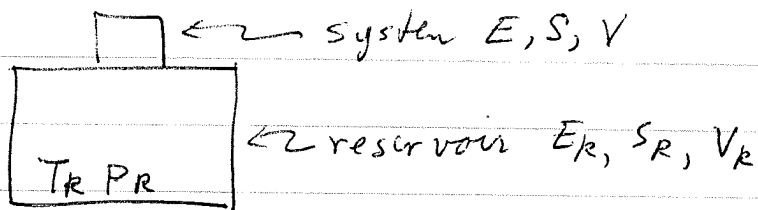
↑
constant Helmholtz free energy

S^{tot} maximized \Rightarrow A minimized

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

and - the equilibrium 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 $\Sigma(T, V, \mu)$