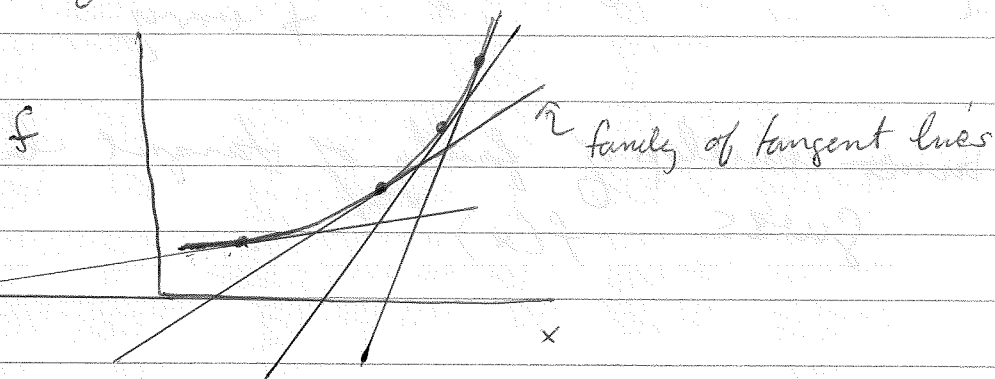hence writing the function as a function of the derivative $p = \frac{df}{dx}$, rather than x, results in the same $g(p)$ in each case.

However an alternate, correct, approach is given by noting that any curve can be described by the envelope of its tangent lines

family of tangent lines

the line tangent to the curve $f(x)$ at point x_0 is given by the equation

$$y = px + b \qquad \text{where} \quad p = \frac{df}{dx}\bigg|_{x = x_0}$$

$$\text{and} \quad f(x_0) = p x_0 + b \implies b = f(x_0) - p x_0$$

b is the y-intercept, ie $y = b$ when $x = 0$.

Define the function

gives the y-intercept of the tangent to the curve at the point where the curve has slope p

$$\boxed{g(p) = f(x) - px} \qquad \text{where} \quad p = \frac{df}{dx}$$

In above one solves $p(x) = \frac{df}{dx}$ to get the inverse function $x(p)$, and substitutes this $x(p)$ in above expression for g to get a

function of only P.

Alternatively, one can define $g(p)$ by

$$g(p) = \underset{x}{\text{extremum}} \left[f(x) - px \right]$$

↰ take the value of x that gives an extremum
of $[f(x) - px]$

In this way, $g(p)$ is $\overset{\text{clearly}}{\text{independent}}$ of x, and the extremum
condition guarentees that

$$\frac{df}{dx} - p = 0 \quad \Rightarrow \quad p = \frac{df}{dx}$$

When $f(x)$ is convex, ie $\frac{d^2f}{dx^2} > 0$, then the extremum
is the _minimum_ of $f - px$.
When $f(x)$ is concave ie $\frac{d^2f}{dx^2} < 0$, then the extremum
is the _maximum_ of $f - px$

Note:

$$\frac{dg}{dp} = \frac{d}{dp} \left[f(x) - px \right] = \frac{df}{dx} \frac{dx}{dp} - x - p \frac{dx}{dp}$$

$$= \left[\frac{df}{dx} - p \right] \frac{dx}{dp} - x \qquad = 0 - x$$

$$= -x \qquad\qquad\qquad \text{since } \frac{df}{dx} = p$$

To summarize

$$f(x) \qquad\qquad p \equiv \frac{df}{dx}$$

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

One says that $g(p)$ is the Legendre transform of $f(x)$
and that x and p are ~~canonic~~ 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 $p = \frac{\partial \mathcal{L}}{\partial \dot{q}}$. The fundamental function to use,

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

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

where $\mathcal{H}$ is the Hamiltonian. Because p 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 Hamilton's dynamic equations

(the other is $\frac{\partial H}{\partial q} = -\dot{p}$)

Legendre transformation and Thermodynamics

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

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, transforming from S to the conjugate variable T.

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

$$A(T, V, N) = E - TS \qquad \underline{\text{Helmholtz Free Energy}}$$

sometimes written as $F(T, V, N)$

From our results for Legendre transforms, we then have

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

To see this more clearly, we proceed as follows:

From $\left(\frac{\partial E}{\partial S}\right)_{V,N} = T(S, V, N)$ we invert this function with respect to S to get

$$S(T, V, N)$$

Then we substitute this $S(T, V, N)$ into the Legendre transform

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

Now by the chain rule

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

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

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

So

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

Similarly we can consider the other first partial derivatives of A

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

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

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

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

Similarly we can show,

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

So now we can write

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

$$= -S\,dT - p\,dV + \mu\,dN$$

Also, since the Euler relation gives

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

and

$$A = E - TS$$

(follows from fact that E is a homogeneous function of first degree)

we have

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

Enthalpy $\quad H(S, p, N)$

use pressure instead of volume

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

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

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

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

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

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

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

use temperature and pressure instead of entropy and volume

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

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

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

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

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

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

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

the chemical potential is the Gibbs free energy per particle

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

Combining with $\quad dG = -SdT + Vdp + \mu dN$

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

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

we regain the Gibbs-Duhem relation

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

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

where $\mu_i = \left(\dfrac{\partial G}{\partial N_i}\right)_{T, P, N_{j \neq i}}$

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

use temperature and chemical potential instead of
entropy and particle number

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

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

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

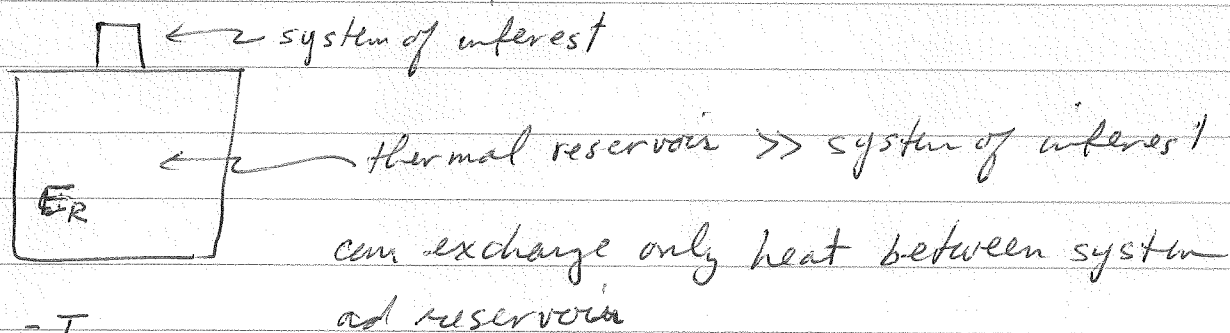$$d\Sigma = -SdT - pdV - Nd\mu$$

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

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

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

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

Extremum Principles for Free Energies

Concept of a thermal reservoir

← system of interest

thermal reservoir $\gg$ system of interest

can exchange only heat between system and 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 reservoirs temperature T_R will be

$$\Delta T_R = \left(\frac{\partial T_R}{\partial S_R}\right) dS = \left(\frac{\partial^2 E_R}{\partial S_R^2}\right) dS$$
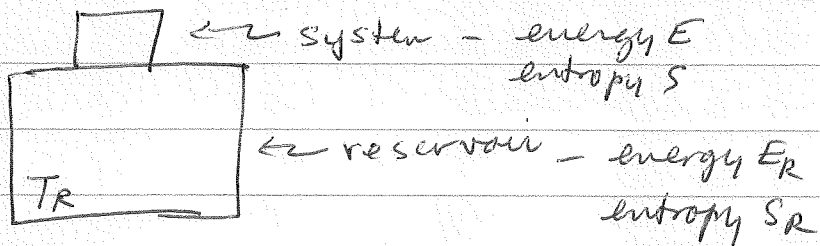
Since E_R and S_R are both extensive variables, they scale with the number of particles in the reservoir N_R.

So

$$\left(\frac{\partial^2 E_R}{\partial S_R^2}\right) \sim \frac{1}{N_R} \to 0 \left.\begin{array}{c} \\ \\ \\ \end{array}\right\} \text{for infinitely large reservoir}$$

$$\Rightarrow \quad \Delta T_R \to 0$$

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 $E^{tot} = E_R + E$
total entropy is maximized

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

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

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

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

$$= S_R(E^{tot}) - (E - T_R S)/T_R \qquad T_R = T$$
$$\underset{\uparrow}{\text{system temp}}$$

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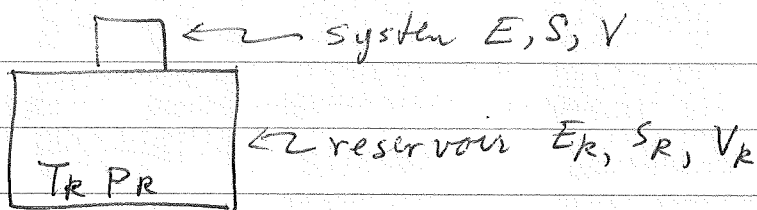$$\quad\underset{\uparrow}{\text{constant}} \quad \underset{\uparrow}{\text{Helmholtz free energy}}$$

S^{tot} maximized $\Rightarrow$ A minimized

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

<u>Now consider a system in contact with a thermal + pressure reservoir</u>

pressure reservoir always has fixed pressure p_R

system E, S, V

reservoir E_R, S_R, V_R

$T_R \; P_R$

total energy conserved $E^{tot} = E_R + E = $ constant
total volume conserved $V^{tot} = V_R + V = $ const

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

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

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

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

$= $ constant $- \dfrac{E}{T_R} + \dfrac{p_R}{T_R} V + S$

$= $ const $- (E + pV - ST)/T = $ const $- G/T$

S^{tot} maximized $\Rightarrow$ <u>G</u>, 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_R stays constant) will
  be the one that minimizes the grand potential
  $\Sigma(T, V, \mu)$