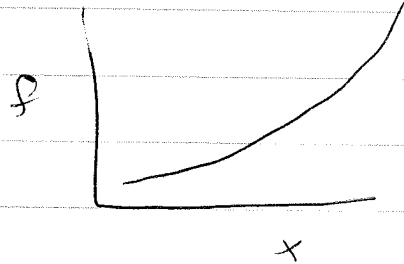# Legendre Transformations

We treat this problem in general.

a general function $f(x)$

define the variable $p \equiv \dfrac{df}{dx}$

How do we find a function that contains all the information in $f(x)$, but depends on p rather than x?

<u>First guess</u> is just to "invert" $p(x) \equiv \dfrac{df}{dx}$ to solve for x as a function of p, ie $x(p)$. Then one could substitute this into $f(x)$ to get

$$g(p) = f(x(p))$$

This does <u>not</u> have the complete information contained in $f(x)$!

For example: $f = ax^2 + bx + c$

$$p = \frac{df}{dx} = 2ax + b \implies x = \frac{p-b}{2a}$$

$$g(p) = f(x(p)) = a\left(\frac{p-b}{2a}\right)^2 + b\left(\frac{p-b}{2a}\right) + c$$

$$= \frac{a}{4a^2}\left(p^2 - 2pb + b^2\right) + \frac{bp}{2a} - \frac{b^2}{2a} + c$$

$$= \frac{p^2}{4a} - \frac{bp}{2a} + \frac{b^2}{4a} + \frac{bp}{2a} - \frac{b^2}{2a} + c$$

$$g(p) = \frac{p^2}{4a} - \frac{b^2}{4a} + c$$

Consider now $f(x) = a(x-x_0)^2 + b(x-x_0) + c$

$$= ax^2 - 2axx_0 + ax_0^2 + bx - bx_0 + c$$

$$= ax^2 + b'x + c'$$

where $b' = b - 2ax_0$

$c' = c + bx_0 + ax_0^2$

$$\Rightarrow g'(p) = \frac{p^2}{4a} - \frac{b'^2}{4a} + c'$$

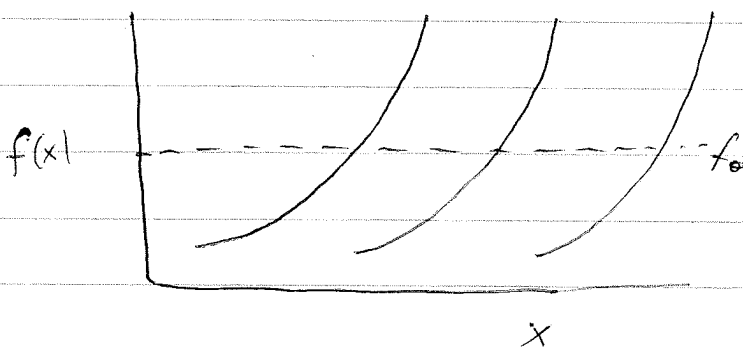$$= \frac{p^2}{4a} - \frac{(b^2 - 4abx_0 + 4a^2x_0^2)}{4a} + c - bx_0 + ax_0^2$$

$$= \frac{p^2}{4a} - \frac{b^2}{4a} + bx_0 - ax_0^2 + c - bx_0 + ax_0^2$$

$$= \frac{p^2}{4a} - \frac{b^2}{4a} + c$$

$$g'(p) = g(p)$$

clearly $g(p)$ has lost some information since we
get the same $g(p)$ for $f(x)$ and $f(x-x_0)$.

<u>In general</u> this is true: the procedure above
cannot distinguish between $f(x)$ and $f(x-x_0)$ for
any function $f(x)$.

← a set of functions
displaced from each
other by fixed amount
along x axis. For each
function, the slope at
constant $f = f_0$ is the same

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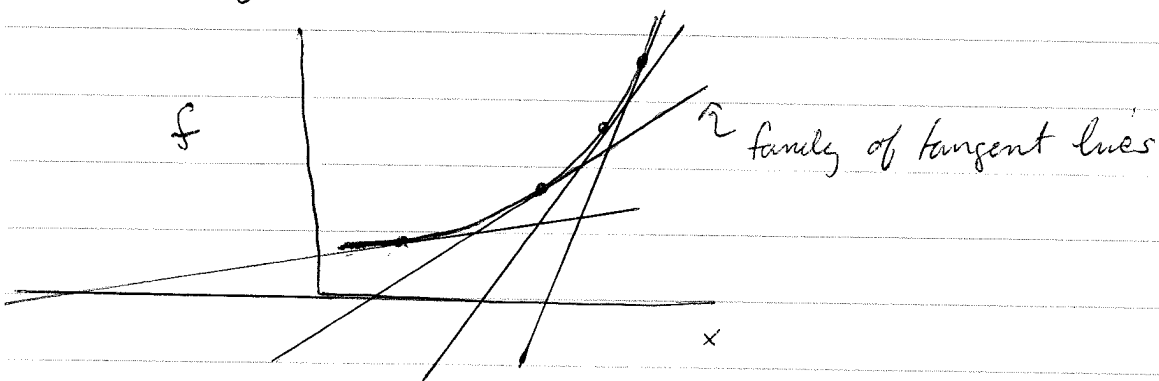
the line tangent to the curve $f(x)$ at point x_0 is
given by the equation

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

$$\text{and} \quad f(x_0) = px_0 + b \implies b = f(x_0) - px_0$$

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

Define the function

$$\boxed{g(p) = f(x) - px}$$

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

where $p = \frac{df}{dx}$

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

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

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

In this way, $g(p)$ is 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 ~~concave~~ convex, ie $\frac{d^2f}{dx^2} > 0$, then the extremum is the minimum of $f - px$.

When $f(x)$ is ~~concave~~ 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

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

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

One says that $g(p)$ is the <u>Legendre transform</u> of $f(x)$
and that x and p are ~~canon~~ <u>conjugate variables</u>

$g(p)$ 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

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

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

Legendre transform 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

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

$$\Rightarrow \quad A(T, V, N) \equiv E - TS \qquad \text{Helmholtz Free Energy}$$

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

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

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

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

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

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

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

checking the derivatives more carefully

$$A = E - TS$$

to take Legendre transform we 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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

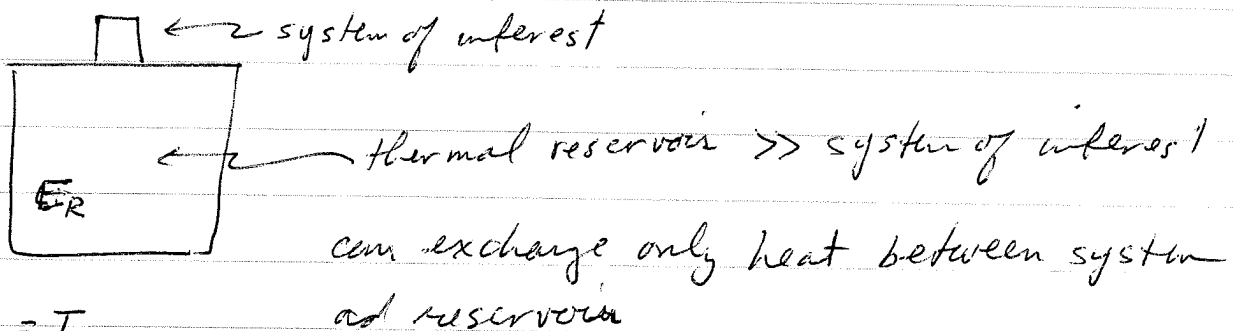Since $\quad E = TS - pV + \mu N$

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

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

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

Extremum Principles for Free Energies

Concept of a thermal reservoir

$\leftarrow$ 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

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

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

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

— system — energy E
entropy S

— reservoir — energy E_R
entropy S_R
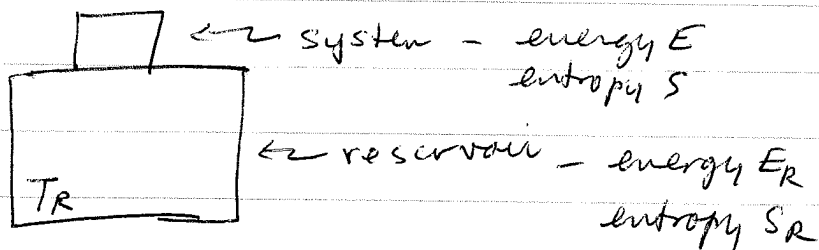
since system is in equilib with reservoir, the system temp $T = T_R$

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

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

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

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

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

$\uparrow$ (under $S_R(E^{tot})$): Constant

$\uparrow$ (under A/T_R): Helmholtz free energy
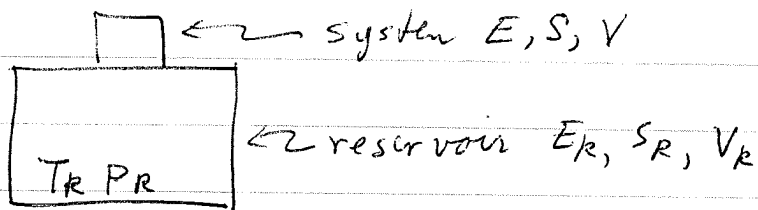
S^{tot} maximized $\Rightarrow$ A minimized

$\Rightarrow$ 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> $A(T,V,N)$

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

pressure reservoir always has fixed pressure p_R

$\leftarrow$ system E, S, V

$\leftarrow$ 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 $\Rightarrow T = T_R, \quad p = p_R$

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

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

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

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

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

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_R stays constant) will be the one that minimizes the grand potential $\Sigma(T, V, \mu)$