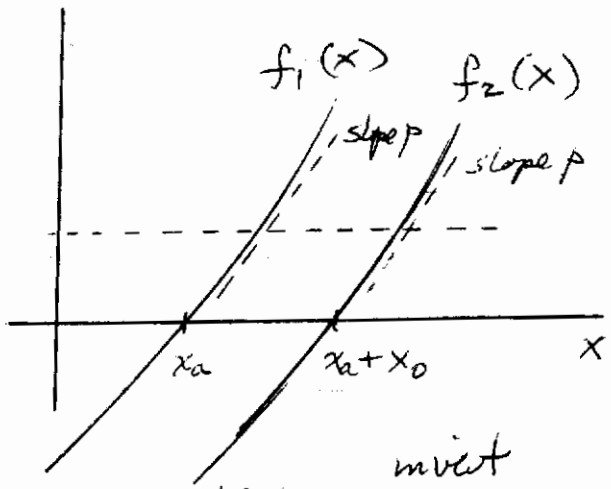
Consider $f_1(x)$ and $f_2(x)$ defined as follows,



$$f_2(x) = f_1(x - x_0)$$

Define $p_1(x) = \dfrac{df_1(x)}{dx} \xrightarrow{\text{invert}} x_1(p)$

$$p_2(x) = \frac{df_2(x)}{dx} \xrightarrow{\text{invert}} x_2(p)$$

$$\frac{df_1(x - x_0)}{dx} \Longrightarrow x_2(p) = x_1(p) + x_0$$

ie If $f_1(x)$ has slope p at x_1, then $f_2(x)$ has slope p at $x_2 = x_1 + x_0$

$$g_1(p) = f_1(x_1(p))$$

$$g_2(p) = f_2(x_2(p)) = f_1(x_2(p) - x_0)$$

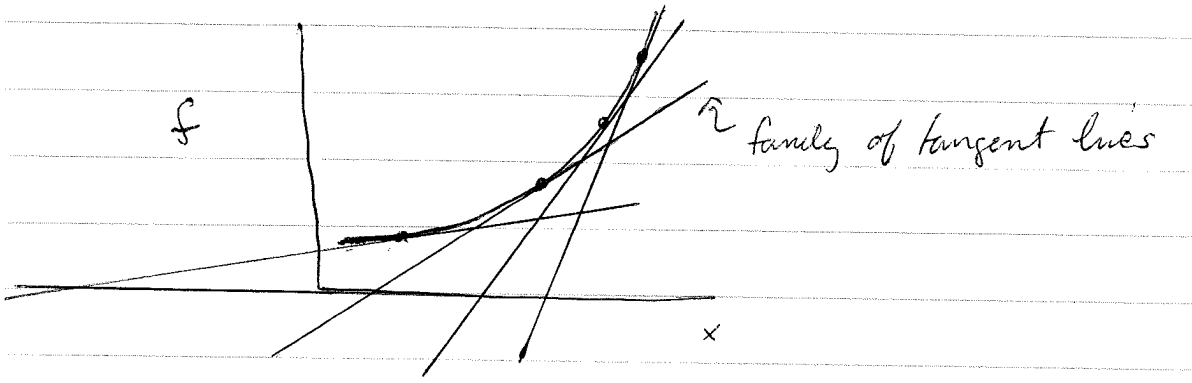
$$= f_1(x_1(p) + x_0 - x_0) = f_1(x_1(p))$$

$$= g_1(p)$$

So given $g(p) = g_1 = g_2$, we cannot tell if the original function was f_1 or f_2! So $g(p)$ does <u>NOT</u> have all the same information as the function $f(x)$.

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



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

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

and $f(x_0) = px_0 + b \Rightarrow b = f(x_0) - px_0$

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

Define the function

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

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

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

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 independent of x, and the extremum condition guarantees that

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

When $f(x)$ is ~~concave~~ convex, i.e. $\frac{d^2f}{dx^2} > 0$, then the extremum is the minimum of $f - px$.

When $f(x)$ is concave, i.e. $\frac{d^2f}{dx^2} < 0$, then the extremum is the maximum of $f - px$

Note:

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

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

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

To summarize

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

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

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, ie. 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 $A(T, V, N)$

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

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

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

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

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

Checking the derivatives more carefully

$A = E - TS$ to take Legendre transform 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

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

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

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

$dH = TdS + Vdp + \mu dN$

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

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

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

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

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

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

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

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

the chemical potential is the Gibbs free energy per particle

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

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

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

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

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

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

use temperature and chemical potential instead of entropy and particle number

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

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

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

$$d\Sigma = -S\,dT - p\,dV - N\,d\mu$$

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

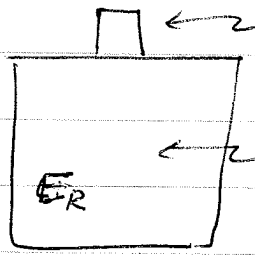
$$\Sigma = E - TS - \mu N = -pV$$

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

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

Extremum Principles for Free Energies

Concept of a thermal reservoir



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

$$\left(\frac{\partial^2 E_R}{\partial S_R^2}\right) \sim \frac{1}{N_R} \to 0$$

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

for infinitely large reservoir

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