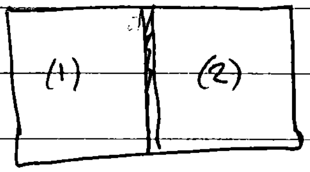
Example



thermally insulating wall
allowed to slide

Since wall is thermally insulating, no heat flows accross it. $\Rightarrow dQ = T\,dS = 0$ So entropy on each side remains constant. S_1, S_2 fixed. or $dS_1 = dS_2 = 0$. What condition determines equilib

Total $S = S_1 + S_2$ is const. Use energy formulation

$$E = E_1(S_1, V_1, N_1) + E_2(S_2, V_2, N_2) \qquad \left.\begin{matrix} N_1, N_2 \\ S_1, S_2 \end{matrix}\right\} \text{fixed}$$

$$V_1 + V_2 = V \text{ fixed} \Rightarrow dV_1 = -dV_2$$

$$dE = \left(\frac{\partial E_1}{\partial S_1}\right)_{VN} dS_1 + \left(\frac{\partial E_1}{\partial V_1}\right)_{SN} dV_1 + \left(\frac{\partial E_1}{\partial N_1}\right)_{SV} dN_1$$

$$+ \left(\frac{\partial E_2}{\partial S_2}\right)_{VN} dS_2 + \left(\frac{\partial E_2}{\partial V_2}\right)_{SN} dV_2 + \left(\frac{\partial E_2}{\partial N_2}\right)_{SV} dN_2$$

$$= T_1 dS_1 - p_1 dV_1 + \mu_1 dN_1 + T_2 dS_2 - p_2 dV_2 + \mu_2 dN_2$$

$$= -p_1 dV_1 - p_2 dV_2 \qquad \text{as } dS_1 = dS_2 = dN_1 = dN_2 = 0$$

$$= (-p_1 + p_2)\, dV_1$$

as expected

at equilib, E is minimum, $dE = 0 \Rightarrow \boxed{p_1 = p_2}$

energy is lowered as system does work by moving wall

We could also do this in the entropy formulation

$$\left.\begin{aligned} ds_1 &= \frac{1}{T_1}dE_1 + \frac{P_1}{T_1}dV_1 - \frac{\mu_1}{T_1}dN_1 = 0 \\ ds_2 &= \frac{1}{T_1}dE_2 + \frac{P_2}{T_2}dV_2 - \frac{\mu_2}{T_2}dN_2 = 0 \end{aligned}\right\} \text{since wall is thermally insulating}$$

wall impermeable $\Rightarrow dN_1 = dN_2 = 0$

$$ds_1 = 0 \quad \Rightarrow \quad dE_1 + p_1 dV_1 = 0$$
$$ds_2 = 0 \quad \Rightarrow \quad dE_2 + p_2 dV_2 = 0$$

$$p_1 = -\frac{dE_1}{dV_1} \qquad p_2 = \frac{-dE_2}{dV_2}$$

$V_1 + V_2 = V$ fixed $\Rightarrow dV_1 = -dV_2$

at equilibrium, E is a minimum $\Rightarrow dE = dE_1 + dE_2 = 0$

$\Rightarrow dE_1 = -dE_2$

$\Rightarrow p_1 = p_2$ same as by energy method.

We have now two equivalent representations

1) entropy $S(E,V,N)$ energy E, volume V, number N held fixed

2) energy $E(S,V,N)$ entropy S, volume V, number N held fixed

In certain cases it is more natural to regard temperature T as held constant, rather than S; or to regard pressure p as held constant, rather than V or to regard chemical potential μ as held constant, rather than N.

We therefore wish to develop new formulations of thermodynamics that will allow us to regard T, p, or μ as a fundamental variable rather than S, V, or N. These new formulations will lead to the Helmholtz ad Gibb free energies that play the role ~~of entropy~~ analogous to ~~entropy~~ energy as the fundamental thermodynamic function of these new formulations.

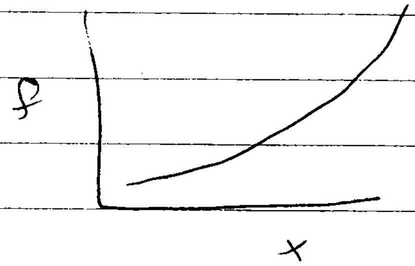
For example, we have $E(S,V,N)$ with $T = \left(\frac{\partial E}{\partial S}\right)_{V,N}$

How can we make a thermodynamic "potential" that contains all the information of $E(S,V,N)$ but depends on T rather than S.

Legendre Transformations

We treat this problem in general.

a general function $f(x)$



define the variable $p = \frac{df}{dx}$

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

First guess is first to invert $p(x) = \frac{df}{dx}$ 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 not have the complete information contained in $f(x)$!

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

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

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

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

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

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

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 $b' = b - 2ax_0$

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

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

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

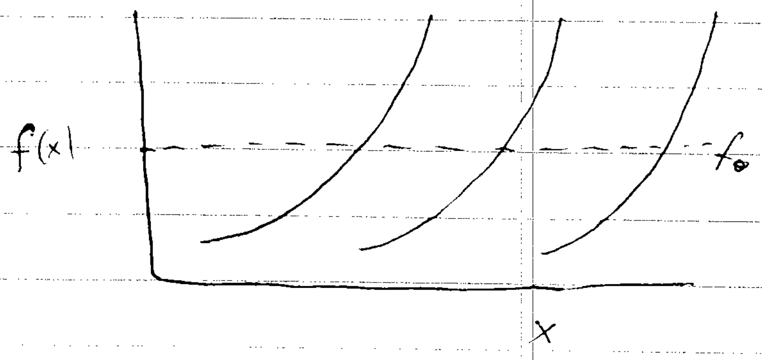
$$= \frac{p^2}{4a} - \frac{b^2}{4a} + bx_0 - ax_0^2 + c - bx_0 + ax_0^2$$

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

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

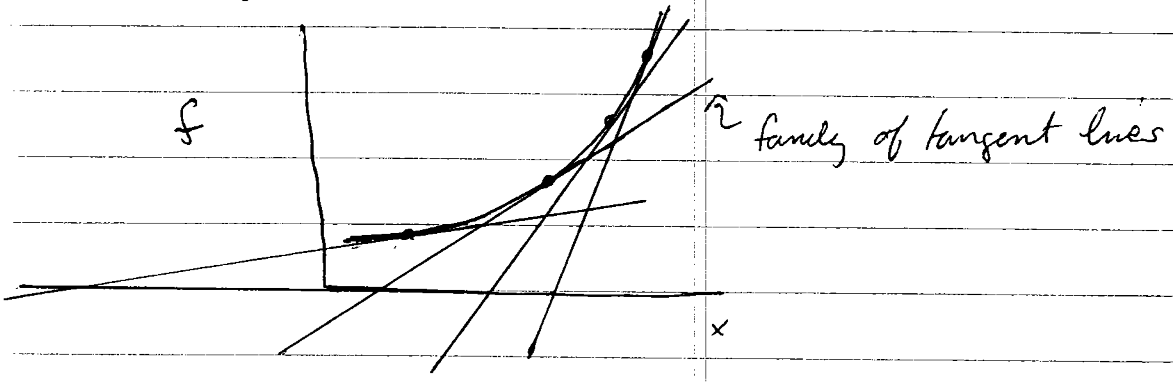
clearly $g(p)$ has lost some information since we get the same $g(p)$ for $f(x)$ and $f(x-x_0)$.

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



← 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



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

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

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

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

Define the function

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

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

Note:

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

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

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

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 <u>Legendre transform</u> of $f(x)$ and that x and p are ~~canno~~ <u>conjugate variables</u>

$g(p)$ contains all the information that $f(x)$ does.

The Legendre transform allows one to swith variables from x to $\frac{df}{dx}$ without loosing 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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\Rightarrow \quad SdT - Vdp + Nd\mu = 0$$

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 $E = TS - pV + \mu N$

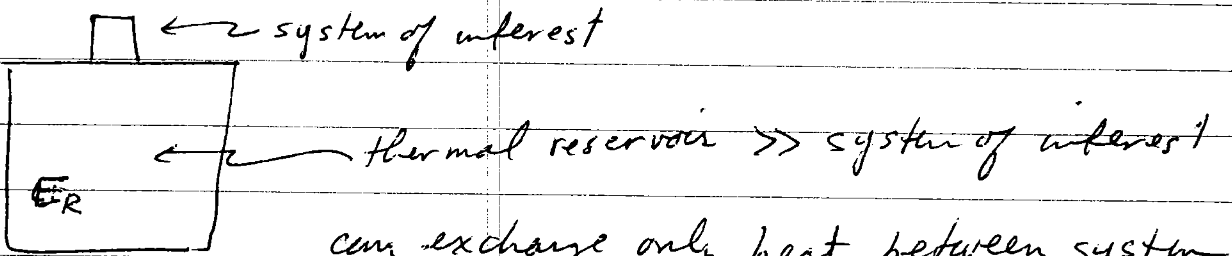
$$\Sigma = E - TS - \mu N = -pV$$

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

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

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

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