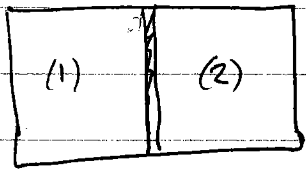
no heat can flow from (1) to (2)

Example

$$dQ = T_1 dS_1 = T_2 dS_2 = 0$$



thermally insulating wall
allowed to slide

Since wall is thermally insulating, no heat flows accross it. $\Rightarrow dQ = TdS = 0$ 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

$$dS_1 = \frac{1}{T_1} dE_1 + \frac{p_1}{T_1} dV_1 - \frac{\mu_1}{T_1} dN_1 = 0$$

$$dS_2 = \frac{1}{T_1} dE_2 + \frac{p_2}{T_2} dV_2 - \frac{\mu_2}{T_2} dN_2 = 0$$

since wall is thermally insulating

wall impermeable $\Rightarrow dN_1 = dN_2 = 0$

$dS_1 = 0 \Rightarrow dE_1 + p_1 dV_1 = 0$
$dS_2 = 0 \Rightarrow dE_2 + p_2 dV_2 = 0$

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

$V_1 + V_2 = V$ 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 and Gibbs free energies that play the role ~~of entropy~~ analogous to ~~entropy~~ energy as the fundamental thermodynamic function of these new formulations.

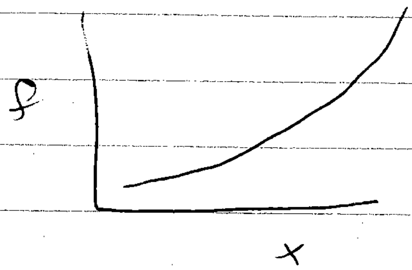
For example, we have $E(S,V,N)$ with $T = \left(\frac{\partial E}{\partial S}\right)_{V,N}$

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 just 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: $f = ax^2 + bx + c$

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

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

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

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

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

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 $b' = b - 2ax_0$

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

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

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

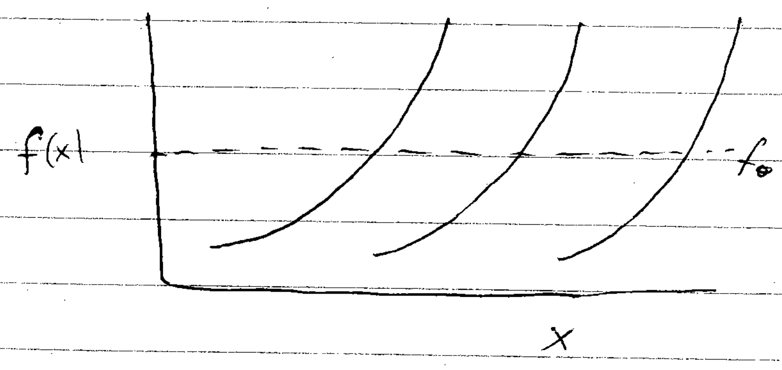
$$= \frac{p^2}{4a} - \frac{b^2}{4a} + bx_0 - ax_0^2 + c - bx_0 + ax_0^2$$

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

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

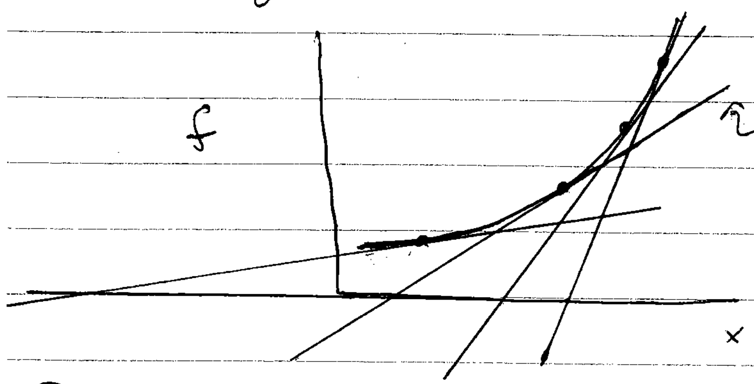
clearly $g(p)$ has lost some information since we get the same $g(p)$ for $f(x)$ and $f(x-x_0)$.

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



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

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

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

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

Define the function

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

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

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

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

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

Note:

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

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

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

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 <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.

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 $\frac{\partial \mathcal{H}}{\partial q} = -\dot{p}$)