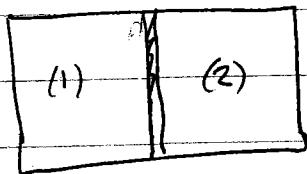


Example

$$dQ = T_1 ds_1 = T_2 ds_2 = 0$$



thermally insulating wall
allowed to slide

Since wall is thermally insulating, no heat flows across 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 for multivar

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

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

$$dE = \left(\frac{\partial E_1}{\partial S_1} \right)_{VN} ds_1 + \left(\frac{\partial E_1}{\partial V_1} \right)_{SN} dV_1 + \left(\frac{\partial E_1}{\partial N_1} \right)_{SV} dN_1 \\ + \left(\frac{\partial E_2}{\partial S_2} \right)_{VN} ds_2 + \left(\frac{\partial E_2}{\partial V_2} \right)_{SN} dV_2 + \left(\frac{\partial E_2}{\partial N_2} \right)_{SV} dN_2$$

$$= T_1 ds_1 - p_1 dV_1 + \mu_1 dN_1 + T_2 ds_2 - p_2 dV_2 + \mu_2 dN_2$$

$$= -p_1 dV_1 - p_2 dV_2 \quad \text{as } ds_1 = ds_2 = dN_1 = dN_2 = 0$$

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

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

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

wall impermeable $\Rightarrow dN_1 = dN_2 = 0$

$$ds_1 = 0 \Rightarrow dE_1 + P_1 dV_1 = 0$$

$$ds_2 = 0 \Rightarrow dE_2 + P_2 dV_2 = 0$$

$$P_1 = - \frac{dE_1}{dV_1}$$

$$P_2 = - \frac{dE_2}{dV_2}$$

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

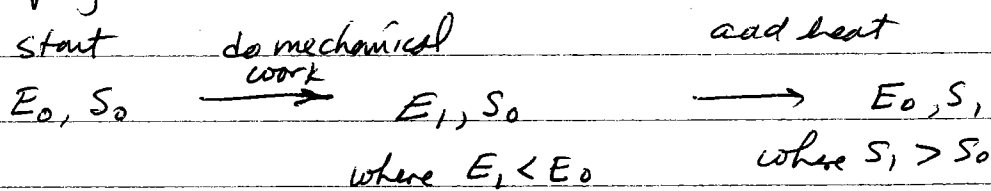
at equilibrium, E is a minimum $\Rightarrow dE = dE_1 + dE_2 = 0$

$$\Rightarrow dE_1 = -dE_2$$

$$\Rightarrow P_1 = P_2 \text{ same as by energy method.}$$

Suppose we had some equilib state for which E was not the minimum possible value for the given S .

Then can withdraw energy from the system by doing mechanical work (for example drive a piston) while keeping S constant.



now return this energy to the system in the form of heat $E_0 - E_1 = dQ = T dS$. The energy is now back to E_0 , but the entropy has increased by $dS = (E_0 - E_1)/T$.

The system is restored to its original energy but with a higher value of entropy. But this contradicts the requirement that the original equilib state was a maximum of entropy. \Rightarrow original E had to have been the minimum.

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~~ ^{energy} analogous to ~~entropy~~ as the fundamental thermodynamic function of these new formulations.

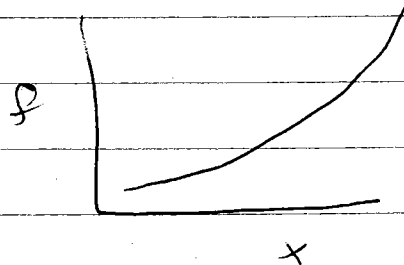
For example, we have $E(S, V, N)$ with $T = \left(\frac{\partial E}{\partial S}\right)_{V, N}$

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 $p(x) \equiv \frac{df}{dx}$ to solve for x as a function of p , i.e. $x(p)$. 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: $f = ax^2 + bx + c$

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

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

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

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

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

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 $b' = b - 2ax_0$

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

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

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

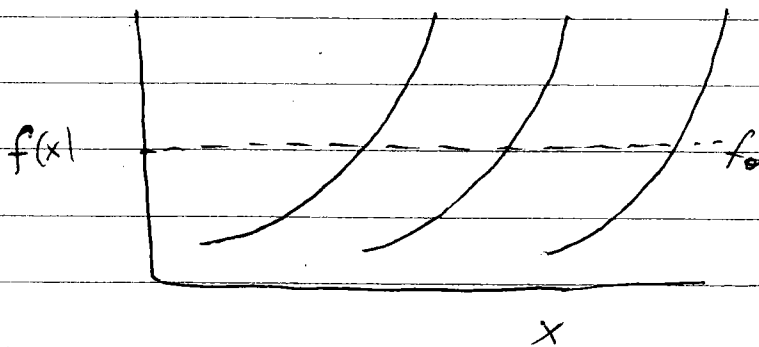
$$= \frac{p^2}{4a} - \frac{b^2}{4a} + bx_0 - ax_0^2 + c - bx_0 + ax_0^2$$

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

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

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

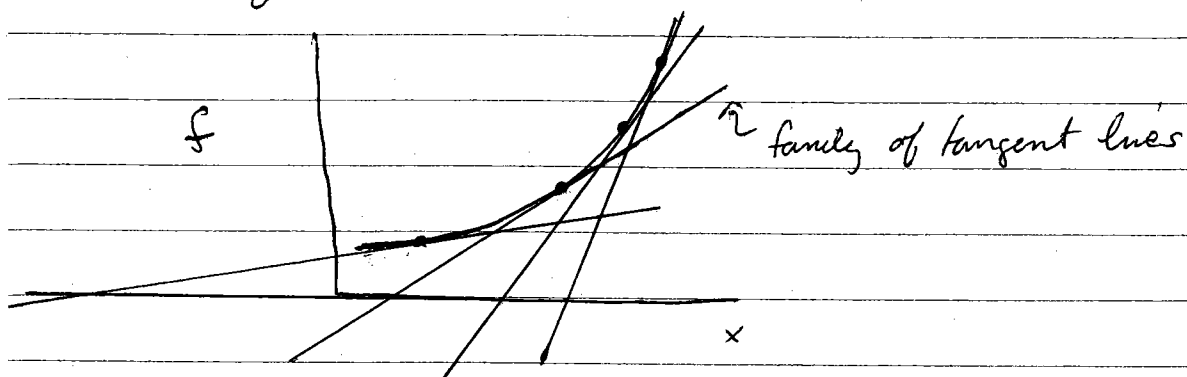
In general this is true: the procedure above cannot distinguish between $f(x)$ and $f(x-x_0)$ for any function $f(x)$.



← 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

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

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

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

Define the function

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

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

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

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

↑ 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

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

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

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

Note:

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

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

$$= -x$$

$$\text{since } \frac{df}{dx} = p$$

To summarize

$$f(x) \quad \phi \equiv \frac{df}{dx}$$

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

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 $\phi \equiv \frac{\partial \mathcal{L}}{\partial \dot{q}}$. 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

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

where \mathcal{H} is the Hamiltonian. Because ϕ and \dot{q} are conjugate variables, we know that

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

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

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

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

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

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

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

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

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

$$\Rightarrow dA = -SdT - pdV + \mu dN$$

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 we use
principal conjugate $T(S, V, N) = \left(\frac{\partial E}{\partial S}\right)_{V, N}$
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 $\left(\frac{\partial E}{\partial S}\right)_{V, N} = T$

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

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

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

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

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

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

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

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

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

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

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

$$\text{Since } E = TS - pV + \mu N$$

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

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

The chemical potential is the Gibbs free energy per particle

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

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

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

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

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, \dots then

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

$$\text{where } \mu_i = \left(\frac{\partial G}{\partial N_i} \right)_{T, p, N_j \neq i}$$

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

use temperature and chemical potential instead of entropy and particle number

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

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

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

$$d\Sigma = -SdT - p dV - N d\mu$$

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.