example: The ideal monatomic gas

From expt: $PV = Nk_BT \Rightarrow \frac{P}{T} = \frac{N}{V}k_B = \frac{k_B}{v}$

$E = \frac{3}{2}Nk_BT \Rightarrow \frac{1}{T} = \frac{3}{2}k_B\frac{N}{E} = \frac{3}{2}\frac{k_B}{u}$

if we can find μ, then we have entropy S via

$$S = \frac{E}{T} + \frac{P}{T}V - \frac{\mu}{T}N$$

From Gibbs - Duhem relation in entropy representation

$$d\left(\frac{\mu}{T}\right) = u\, d\left(\frac{1}{T}\right) + v\, d\left(\frac{P}{T}\right)$$

$$= u\,\frac{3}{2}k_B\, d\left(\frac{1}{u}\right) + v\, k_B\, d\left(\frac{1}{v}\right)$$

$$d\left(\frac{\mu}{T}\right) = -\frac{3}{2}\frac{k_B}{u}du - \frac{k_B}{v}dv$$

integrate to get

$$\left(\frac{\mu}{T}\right) - \left(\frac{\mu}{T}\right)_0 = -\frac{3}{2}k_B\ln\left(\frac{u}{u_0}\right) - k_B\ln\left(\frac{v}{v_0}\right)$$

where u_0 and v_0 are some reference state, and $\left(\frac{\mu_0}{T}\right)$ is an unknown constant of integration. Then one gets

$$S = \frac{E}{T} + \frac{P}{T}V - \frac{\mu}{T}N = \frac{3}{2}k_B\frac{E}{(E/N)} + \frac{k_B V}{(V/N)}$$

$$+ \frac{3}{2}Nk_B\ln\left(\frac{u}{u_0}\right) + k_BN\ln\left(\frac{v}{v_0}\right) - \left(\frac{\mu}{T}\right)_0 N$$

$$S = \frac{3}{2}k_BN + k_BN - \left(\frac{\mu}{T}\right)_0 N + Nk_B\ln\left[\left(\frac{u}{u_0}\right)^{3/2}\left(\frac{v}{v_0}\right)\right]$$

use $E = uN$, $E_0 \equiv u_0 N_0$, $V = vN$, $V_0 \equiv v_0 N_0$

$$\Rightarrow \boxed{S(E,V,N) = \frac{N}{N_0} S_0 + N k_B \ln\left[\left(\frac{E}{E_0}\right)^{3/2}\left(\frac{V}{V_0}\right)\left(\frac{N}{N_0}\right)^{-5/2}\right]}$$

where $S_0 = \frac{5}{2} k_B N_0 - \left(\frac{\mu}{T}\right)_0 N_0$ is a constant

So from experimental knowledge of two of the equations of state $\frac{1}{T}$ and $\frac{p}{T}$ as functions of E, N, V, we have derived the entropy $S(E,V,N)$. All behaviors of the ideal gas can now be deduced from knowledge of S.

Alternatively, we could derive $s = \frac{S}{N}$ as follows:

$$E = TS - pV + \mu N \Rightarrow S = \frac{E}{T} + \frac{p}{T} V - \frac{\mu}{T} N$$

$$\Rightarrow s = \frac{u}{T} + \frac{p}{T} v - \frac{\mu}{T} \qquad \text{where } u = \frac{E}{N},\ v = \frac{V}{N}$$

$$ds = \frac{1}{T} du + \frac{p}{T} dv + \underbrace{u\, d\left(\frac{1}{T}\right) + v\, d\left(\frac{p}{T}\right) - d\left(\frac{\mu}{T}\right)}_{\text{these cancel due to the Gibbs-Duhem relation as expressed in the entropy formulation}}$$

So

$$\Rightarrow \boxed{ds = \frac{1}{T} du + \frac{p}{T} dv}$$

$$ds = \frac{1}{T}\,du + \frac{p}{T}\,dv$$

$$= \frac{3}{2}\frac{k_B}{u}\,du + \frac{k_B}{v}\,dv \qquad \text{since} \begin{cases} \frac{1}{T} = \frac{3}{2}\frac{k_B}{u} \\ \frac{p}{T} = \frac{k_B}{v} \end{cases}$$

integrate

$$s - s_0 = \frac{3}{2}k_B \ln(u/u_0) + k_B \ln(v/v_0)$$

$$\boxed{s = s_0 + k_B \ln\left[\left(\frac{u}{u_0}\right)^{3/2}\left(\frac{v}{v_0}\right)\right]}$$

substitute in $S = Ns$, $E = Nu$, $V = Nv$

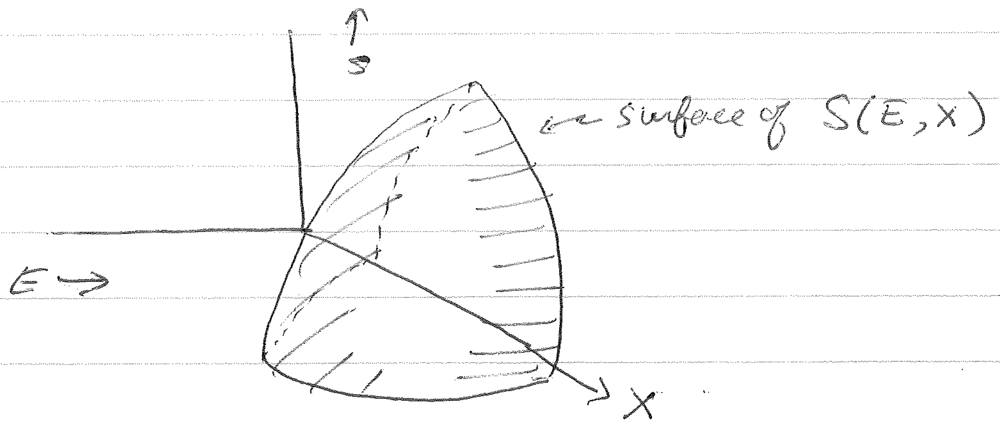
$S_0 = N_0 s_0$, $E_0 = N_0 u_0$, $V_0 = N_0 v_0$

and we recover the earlier result for $S(E, V, N)$

Energy Minimum Principle

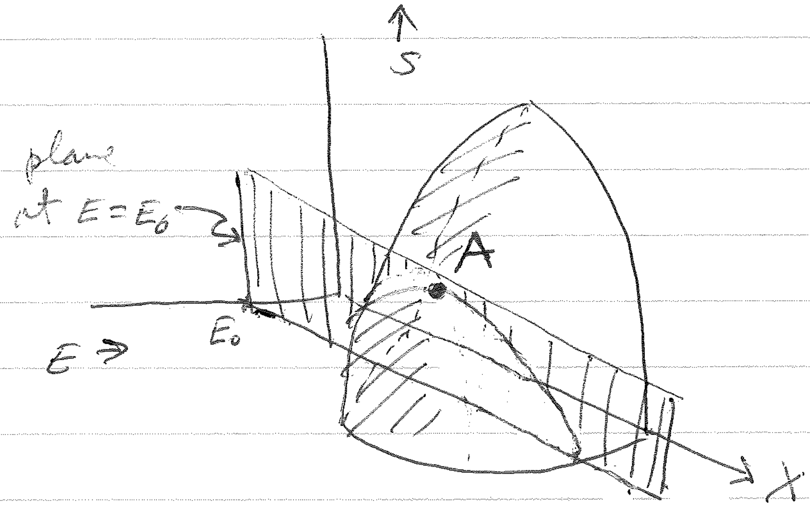
Postulate II stated that when constraints are removed, the equilibrium state will be the one that maximizes the entropy $S(E,V,N,\dots)$

We saw that entropy is a ~~convex~~ concave function of its variables



X = other variables

For a situation where the total E is held fixed, at value E_0, then if X is an unconstrained degree of freedom, it will take in equilib that value X_0 that maximizes S for the given fixed E_0. This is determined by the intersection of the surface $S(E,X)$ with the plane at fixed $E=E_0$

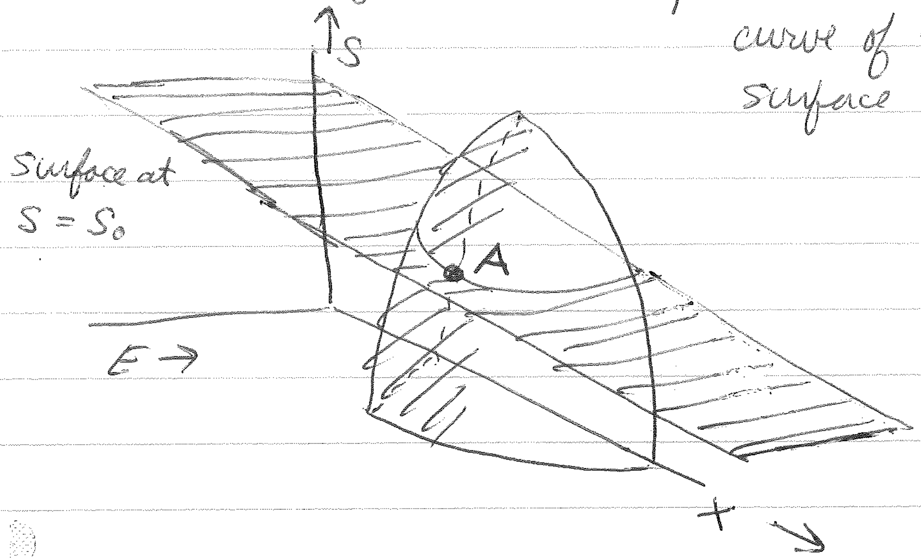


X_0 is given by the point A that maximizes S along this curve of intersection

$$S_0 = \max_{X}\left[S(E_0,X)\right]$$

Callen Fig 5.1

Suppose now an alternative situation in which the total entropy S is held fixed at value S_0. Then if X is an unconstrained degree of freedom we see that the equilibrium state at S_0, E_0 corresponds to minimizing the energy with respect to X, along the curve of intersection between $S(E,X)$ surface and plane of const $S=S_0$



Callen Fig 5.2

$$E_0 = \min_X \left[E(S_0, X) \right]$$

We thus have two contrasting formulations:

<u>entropy formulation</u>: fundamental function is $S(E, X_1, X_2, \ldots)$
if constraint on some X_i is removed, X_i will take the value that maximizes S for the fixed total energy E. In equilib, $d^2S < 0$. S ~~convex~~ concave

<u>energy formulation</u>: fundamental function is $E(S, X_1, X_2, \ldots)$
if constraint on some X_i is removed, X_i will take the value that minimizes E for the fixed total entropy S. In equilib $d^2E > 0$
E ~~concave~~ convex

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 ① doing mechanical work (for example drive a piston) while keeping S constant.

$$\underset{\text{start}}{E_0, S_0} \xrightarrow[\text{work}]{\text{do mechanical ①}} \underset{\text{where } E_1 < E_0}{E_1, S_0} \xrightarrow{\text{add heat ②}} \underset{\text{where } S_1 > S_0}{E_0, S_1}$$

② now return this energy to the system in the form of heat $E_0 - E_1 = dQ = TdS$. 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 maxmin of entropy. ⇒ original E had to have been the minimum.

We have now two equivalent representations

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

2) energy $E(S, V, N)$ entropy S, volume V, nuber 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~~ analogus to energy as the fumamental thermodynamic function of these new formulations.

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

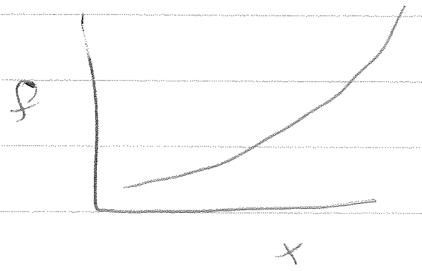
how can we make a thermodynamic "potential" that contains all the information of $E(S, V, N)$ but depends on T rather than S.

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

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

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

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

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

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

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 $b' = b - 2ax_0$

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

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

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

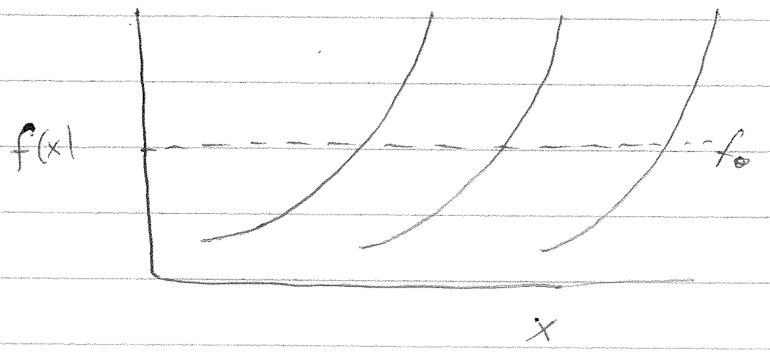
$$= \frac{p^2}{4a} - \frac{b^2}{4a} + bx_0 - ax_0^2 + c - bx_0 + ax_0^2$$

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

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

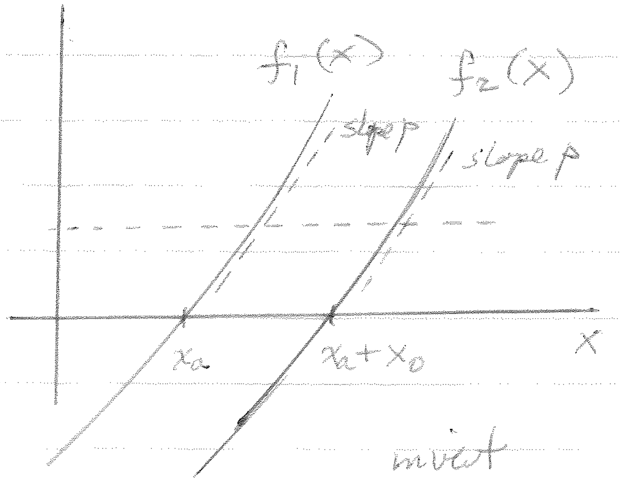
clearly $g(p)$ has lost some information since we get the same $g(p)$ for $f(x)$ and $f(x-x_0)$.

<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 each function, the slope at constant $f = f_0$ is the same

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



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

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

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

$$= \frac{df_1(x-x_0)}{dx} = p_1(x - x_0)$$

$$\Rightarrow x_2(p) = x_1(p) + x_0$$

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

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

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

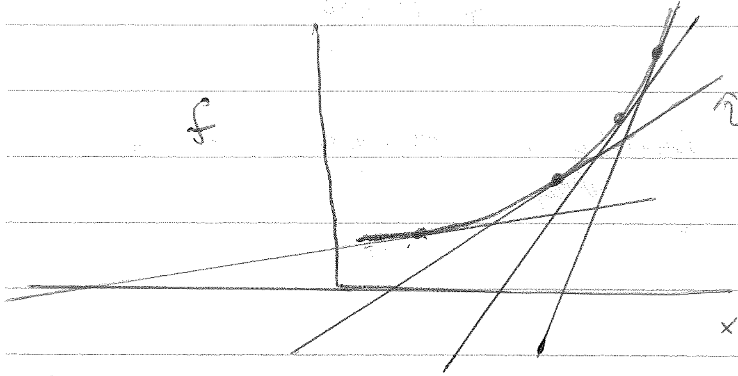
$$= f_1(x_1(p) + x_0 - x_0) = f_1(x_1(p))$$

$$= g_1(p)$$

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 NOT 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



family of tangent lines

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

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

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

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

Define the function

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

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

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

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

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

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

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

Note:

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

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

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

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 ~~[illegible]~~ <u>conjugate variables</u>

$g(p)$ 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 alows one to swith 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 fundemental 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