*example*: The ideal monatomic gas

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

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

if we can find $\mu$, 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 $\left(\frac{\mu}{T}\right)_0$ is an unknown constant of integration. Then one gets

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

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

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

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 $S$.

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

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

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

$$ds = \frac{1}{T} du + \frac{p}{T} dv + \underbrace{u\, d\left(\frac{1}{T}\right) + v\, d\left(\frac{p}{T}\right) - d\left(\frac{\mu}{T}\right)}$$

these cancell 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 $S = Ns$, $E = Nu$, $V = Nv$

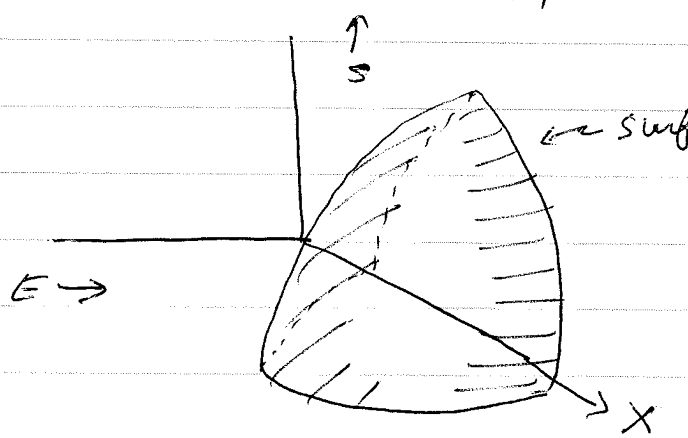
$S_0 = N_0 s_0$, $E_0 = N_0 u_0$, $V_0 = N_0 v_0$

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

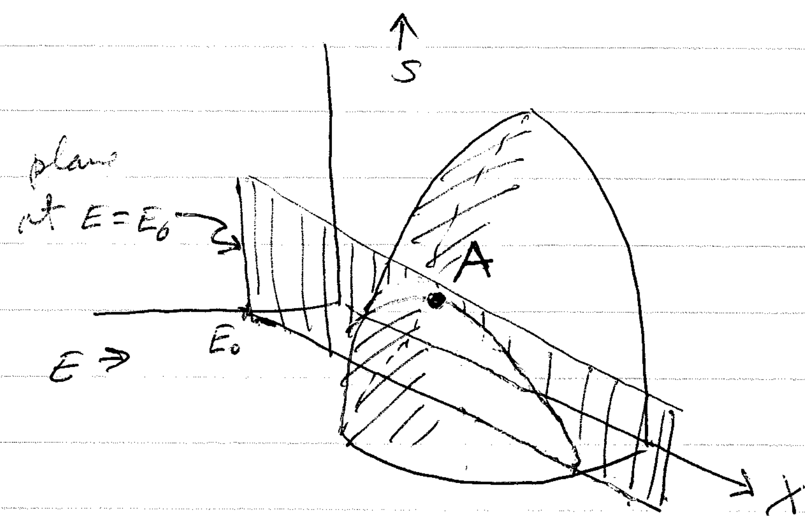
# Energy Minimum Principle

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

We saw that entropy is a ~~convex~~ concave function of its 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 $E = E_0$

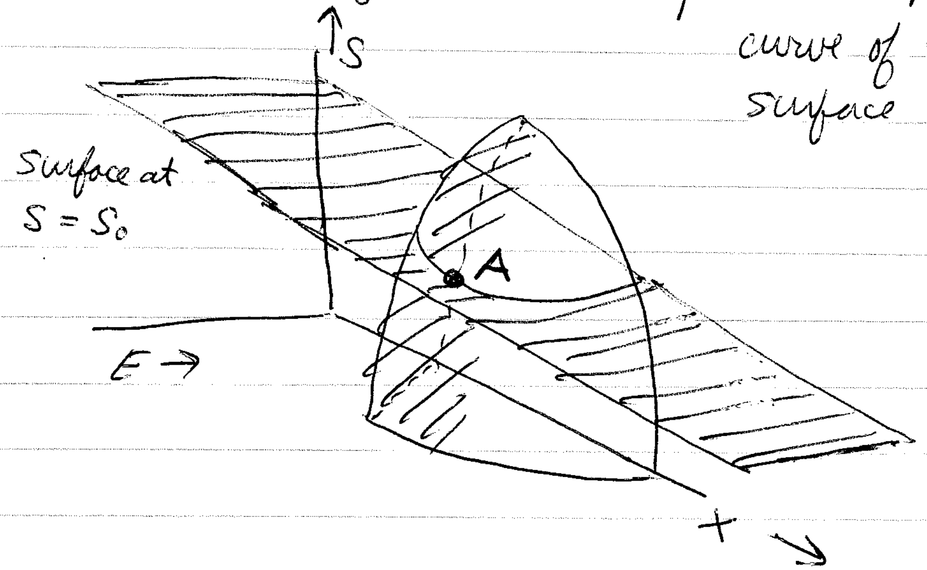



$X_0$ is given by the point A that maximizes $S$ along this curve of intersection

$$S_0 = \max_X \left[ S(E_0, X) \right]$$

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

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

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 ~~max~~ min 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 $\mu$ as held constant, rather than $N$.

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

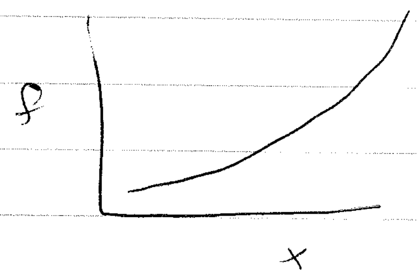
For example, we have $E(S,V,N)$ with $T = \left(\frac{\partial E}{\partial S}\right)_{V,N}$

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 $p \equiv \frac{df}{dx}$

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 $b' = b - 2ax_0$

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

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

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

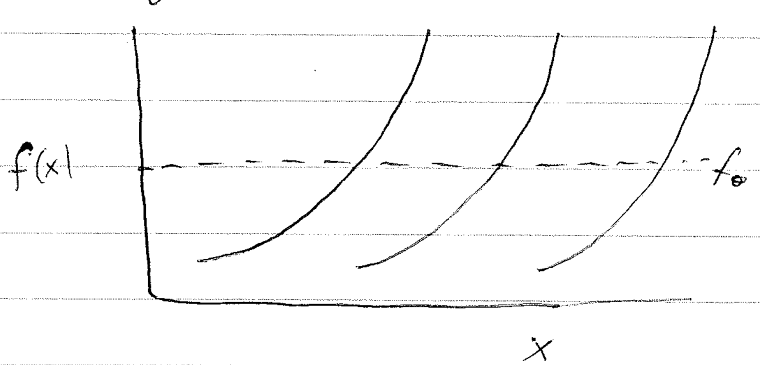
$$= \frac{p^2}{4a} - \frac{b^2}{4a} + bx_0 - ax_0^2 + c - bx_0 + ax_0^2$$

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

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

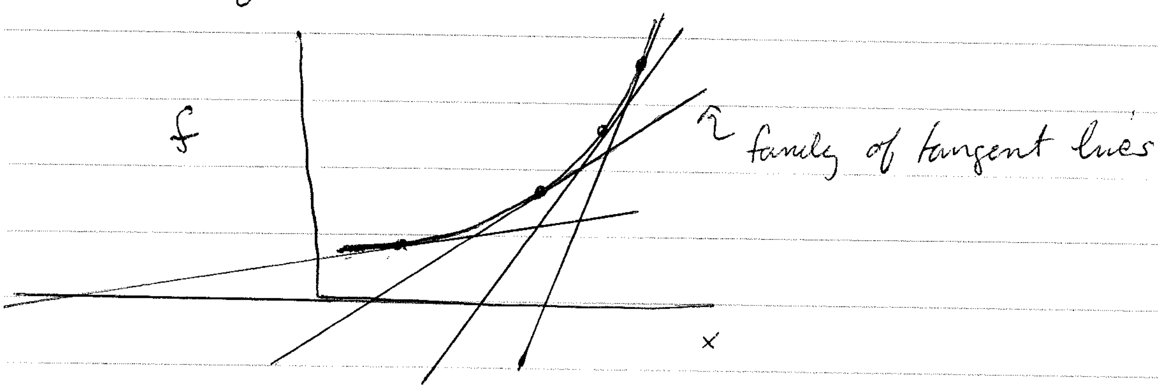
clearly $g(p)$ has lost some information since we get the same $g(p)$ for $f(x)$ and $f(x-x_0)$.

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

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

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

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

Define the function

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

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

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 extremium of $[f(x) - px]$

In this way, $g(p)$ is 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 ~~concave~~ convex, ie $\frac{d^2f}{dx^2} > 0$, then the extremum is the <u>minimum</u> of $f - px$.
When $f(x)$ is concave, ie $\frac{d^2f}{dx^2} < 0$, then the extremum is the <u>maximum</u> of $f - px$

Note:

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

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

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