example: The ideal monatomic gas

From expt: \( PV = Nk_B T \) \( \Rightarrow \frac{P}{T} = \frac{N}{V} k_B = \frac{k_B}{\mu} \)

\[
E = \frac{3}{2} Nk_B T \Rightarrow \frac{1}{T} = \frac{3}{2} k_B \frac{N}{E} = \frac{3}{2} \frac{k_B}{\mu}
\]

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

\[
d\left(\frac{\mu}{T}\right) = u\ d\left(\frac{1}{T}\right) + \nu \ d\left(\frac{P}{T}\right)
\]

\[
= u \frac{3}{2} k_B \ d\left(\frac{1}{u}\right) + \nu k_B \ d\left(\frac{1}{\nu}\right)
\]

\[
d\left(\frac{\mu}{T}\right) = -\frac{3}{2} k_B \ \frac{d u}{u} - \frac{k_B}{\nu} \ d\nu
\]

Integrate to get

\[
\left(\frac{\mu}{T}\right) - \left(\frac{\mu}{T}\right)_0 = -\frac{3}{2} k_B \ ln\left(\frac{u}{u_0}\right) - k_B \ ln\left(\frac{\nu}{\nu_0}\right)
\]

where \( u_0 \) and \( \nu_0 \) are some reference state, and \( \left(\frac{\mu}{T}\right)_0 \) is an unknown constant of integration. Then one sets

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

\[
+ \frac{3}{2} Nk_B \ ln\left(\frac{u}{u_0}\right) + k_B N \ ln\left(\frac{\nu}{\nu_0}\right) - \left(\frac{\mu}{T}\right)_0
\]

\[
S = \frac{3}{2} k_B N + k_B N \left(\frac{\mu}{T}\right)_0 N + N k_B \ ln\left[\left(\frac{u}{u_0}\right)^{3/2} \left(\frac{\nu}{\nu_0}\right)^{1/2}\right]
\]
\[ E = u N, \quad E_0 = u_0 N_0, \quad V = v N, \quad V_0 = v_0 N_0 \]

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

where \( S_0 = \frac{5}{2} k_B N_0 \) is a constant.

So from experimental knowledge of two of the equations of state \( P = \rho \frac{d}{dV} \) 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 \( \alpha = \frac{S}{N} \) as follows:

\[ E = T S - P V + \mu N \implies S = \frac{E}{T} + \frac{P}{T} V - \frac{\mu}{T} N \]

\[ \implies \alpha = \frac{\mu}{T} + \frac{P}{T} V - \frac{\mu}{T} \quad \text{where} \quad \mu = \frac{E}{N}, \quad v = \frac{V}{N} \]

\[ d\alpha = \frac{1}{T} d\mu + \frac{P}{T} dV + v d\left( \frac{1}{T} \right) + v d\left( \frac{P}{T} \right) - d\left( \frac{\mu}{T} \right) \]

these cancel due to the Gibbs-Duhem relation as expressed in the entropy formulation.

So

\[ d\alpha = \frac{1}{T} d\mu + \frac{P}{T} dV \]
\[ da = \frac{1}{T} du + \frac{P}{T} dv^{-} \]

\[ = \frac{3}{2} \frac{k_b}{u} du + \frac{k_b}{v} dv^{-} \quad \text{since} \quad \left\{ \begin{align*} \frac{1}{T} &= \frac{3}{2} \frac{k_b}{u} \\ \frac{P}{T} &= \frac{k_b}{v} \end{align*} \right. \]

Integrate

\[ a - a_0 = \frac{3}{2} k_b \ln \left( \frac{u}{u_0} \right) + k_b \ln \left( \frac{v}{v_0} \right) \]

\[ a = a_0 + k_b \ln \left[ \left( \frac{u}{u_0} \right)^{3/2} \left( \frac{v}{v_0} \right) \right] \]

Substitute \( S = N \alpha \), \( E = N u \), \( V = N v \)

\[ S_0 = N_0 a_0 \quad E_0 = N_0 u_0 \quad V_0 = N_0 v_0 \]

and we recover the earlier result for \( S(E, V, N) \)
Energy Minima 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 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 equilibrium that value $x_0$ that maximizes $S$ for the given fixed $E_0$. This is determined by the intersection of the surface $S(E_0,X)$ with the plane at fixed $E = E_0$.

$x_0$ is given by the point $A$ that maximizes $S$ along the curve of intersection.

$S_0 = \max_x [S(E_0,X)]$
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 $S = S_0$.

![Diagram of a surface and plane](image)

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

We thus have two contrasting formulations:

**Entropy formulation**: 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, $d^2S < 0 \ldots S$ concave.

**Energy formulation**: 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 $d^2E > 0 \ldots E$ convex.
Suppose we had some equilibrium state for which $E$ was not the minimum possible value for the given $S$.

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

\[
\begin{align*}
E_0, S_0 & \rightarrow E_1, S_0 & \rightarrow E_0, S_1
\end{align*}
\]

where $E_1 < E_0$ and $S_1 > S_0$

Now return the 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 equilibrium 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 $\mu$ 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 energy analogous to 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 \( f(x) \) is

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 that to invert \( p(x) = \frac{df}{dx} \) 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: \( f=ax^2+bx+c \).

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

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

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

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

\[ g(p) = \frac{p^2}{4a} - \frac{b^2}{4a} + c \]
Consider now \( f'(x) = a(x-x_0)^2 + b(x-x_0) + c \)

\[= a(x^2 - 2ax + a^2) + bx - bx_0 + c \]

\[= a x^2 + b' x + c' \]

where \( b' = b - 2a x_0 \)

\( c' = c + b x_0 + a x_0^2 \)

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

\[= \frac{p^2}{4a} - \frac{(b^2 - 4ab x_0 + 4a^2 x_0^2)}{4a} + c - b x_0 + a x_0^2 \]

\[= \frac{p^2}{4a} - \frac{b^2}{4a} + bx_0 + a x_0^2 + c - b x_0 + a x_0^2 \]

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

\( g'(p) = g(p) \)

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 \( f(x) \).
Since 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.

\[ f \]

\[ \text{A family of tangent lines} \]

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

\[ y = px + b \]

where \( p = \frac{df}{dx} \bigg|_{x = x_0} \)

and \( f(x_0) = px_0 + b \Rightarrow b = f(x_0) - px_0 \)

the y-intercept, i.e. \( y = b \) when \( x = 0 \).

Define the function

\[ g(p) = f(x) - px \]

where \( p = \frac{df}{dx} \)

In above one solves \( p(x) = \frac{df}{dx} \) to get the inverse function \( x(p) \), and substitutes the \( x(p) \) in above expression for \( x \) to get a
Function of only $p$.

Alternatively, one can define $g(p)$ by

$$g(p) = \max_x \left[ f(x) - px \right]$$

\[ \text{take the value of } x \text{ that gives an extremum of } \left[ f(x) - px \right] \]

In this way, $g(p)$ is independent of $x$, and the extremum condition guarantees that

$$\frac{d}{dx} f - p = 0 \implies p = \frac{d}{dx} f$$

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

Note:

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

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

$$= -x$$

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