Legenndre 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 a form to insert $p(x) = \frac{df}{dx}$ 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: $f = ax^2 + bx + c$

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

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

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

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

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

$= a(x^2 - 2ax x_0 + ax_0^2) + bx - bx_0 + c$

$= ax^2 + bx + c'$

where $b' = b - 2ax_0$

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

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

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

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

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

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

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 $f(x)$.

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We 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 \( \frac{df}{dx} \), 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

\[
y = px + b \quad \text{where} \quad p = \frac{df}{dx} \bigg|_{x=x_0}
\]

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

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

Define the function \( g(p) = f(x) - px \) where \( p = \frac{df}{dx} \).

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

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

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

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

Note:

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

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

$$= -x \quad \text{since } \frac{df}{dx} = p$$
To summarize

\[ f(x) \quad p = \frac{df}{dx} \]

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

One says that \( g(p) \) is the Legendre transform of \( f(x) \).

and that \( x \) and \( p \) are \textbf{conjugate variables}.

\( g(p) \) contains all the information that \( f(x) \) does, i.e., if one knows \( g(p) \), then one can construct \( f(x) \) from it 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 \( L[\dot{q}, \ddot{q}] \) which depends on the variables \( q \) and \( \dot{q} \). In the Hamilton formulation one wants to replace the variable \( \dot{q} \) by the variable \( p = \frac{\partial L}{\partial \ddot{q}} \). The fundamental function to use is

\[ L[q, \dot{q}] - \dot{q} \ddot{q} = -H[\dot{q}, \ddot{q}] \]

where \( H \) is the Hamiltonian. Because \( p \) and \( \dot{q} \) are conjugate variables, we know that
\[
\frac{\partial (-H)}{\partial \phi} = -\dot{\phi} \quad \text{or} \quad \frac{\partial H}{\partial \phi} = -\dot{\phi}
\]

which is one of the Hamilton dynamic equations (the other is \( \frac{\partial H}{\partial q} = -\dot{q} \)).

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

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

\[
\Rightarrow A(T,V,N) = E - TS
\]

\[
\left( \frac{\partial A}{\partial T} \right)_{V,N} = -S \quad \left( \frac{\partial E}{\partial V} \right)_{S,N} \quad \left( \frac{\partial E}{\partial N} \right)_{S,T}
\]

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

\[
\Rightarrow dA = -SdT -pdV +\mu dN
\]

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 curve

\[ T(S, Y, N) = \left( \frac{\partial S}{\partial T} \right)_{V, N} \]

and invert it to get \( S(T, Y, N) \)

then substitute into the above

\[ A(T, Y, N) = E(S(T, Y, N), Y, N) - TS(T, Y, N) \]

then

\[ \left( \frac{\partial A}{\partial T} \right)_{V, N} = \left( \frac{\partial E}{\partial S} \right)_{V, N} \left( \frac{\partial S}{\partial T} \right)_{V, N} - T \left( \frac{\partial S}{\partial T} \right)_{V, N} - S(T, Y, N) \]

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

\[ \left( \frac{\partial A}{\partial V} \right)_{T, N} = \left( \frac{\partial E}{\partial S} \right)_{T, N} \left( \frac{\partial S}{\partial V} \right)_{T, N} + \left( \frac{\partial E}{\partial V} \right)_{S, N} - T \left( \frac{\partial S}{\partial V} \right)_{T, N} \]

\[ = T \left( \frac{\partial S}{\partial V} \right)_{T, N} + \left( \frac{\partial E}{\partial V} \right)_{S, N} - T \left( \frac{\partial S}{\partial V} \right)_{T, N} \]

\[ = \left( \frac{\partial E}{\partial V} \right)_{S, N} = -\Phi \]

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

\[ E(S, V, N), \quad \phi = -\left(\frac{\partial E}{\partial V}\right)_{S,N} \]

\[ H(S, p, N) = E + pV \]

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

\[ dH = TdS + Vdp + \mu dN \]

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

\[ E(S, V, N), \quad \phi = -\left(\frac{\partial E}{\partial V}\right)_{S,N} \rightarrow T = \left(\frac{\partial E}{\partial S}\right)_{V,N} \]

\[ G(T, p, N) = E - TS + pV \]

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

\[ dG = -SdT + Vdp + \mu dN \]
Since \( E = TS - pV + \mu N \)

\[
G = E - TS + pV = \mu N
\]

or \[
\frac{G}{N} = \rho = \mu
\]

The chemical potential is the Gibbs free energy per particle.

From \( G = \mu N \) we get \( dG = \mu dN + N d\mu \).

Combining with \( dG = -SdT + Vdp + \mu dN \)

\[
\mu dN + N d\mu = -SdT + Vdp + \mu dN
\]

\[
\Rightarrow \quad SdT - Vdp + N d\mu = 0
\]

We regain the Gibbs-Duhem relation.

Note: If we are dealing with a system with more than one species of particles, \( N_1, N_2, \ldots \) then

\[
G(T, p, N_1, N_2, \ldots) = \mu_1 N_1 + \mu_2 N_2 + \mu_3 N_3 + \ldots
\]

where \[
\mu_i = \left( \frac{\partial G}{\partial N_i} \right)_{T, p, N_j}^{N_i}
\]
Grand potential $\Sigma (T, V, N)$

use temperature and chemical potential instead of entropy and particle number

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

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

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

$d\Sigma = -SdT - \mu dN V - N d\mu$

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.