Legendre Transformations

We treat this problem in general.

A general function $f(x)$ defines 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 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: $f = ax^2 + bx + c$.

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

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

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

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

$$g(p) = \frac{p^2}{4a} - \frac{b^2}{4a} + c$$
Consider now \( f(x) = a(x-x_0)^2 + b(x-x_0) + c \)
\[ = ax^2 - 2axx_0 + ax_0^2 + bx - bx_0 + c \]
\[ = ax^2 + bx + c' \]
where \( b' = b - 2ax_0 \)
\[ c' = c - bx_0 + ax_0^2 \]

\[
\Rightarrow g'(p) = \frac{b^2}{4a} - \frac{b'^2}{4a} + c'
\]
\[ = \frac{p^2}{4a} - \frac{(b^2 - 4abx_0 + 4a^2x_0^2)}{4a} + c - bx_0 + ax_0^2
\]
\[ = \frac{p^2}{4a} - \frac{b^2}{4a} + bx_0 - ax_0^2 + c - bx_0 + ax_0^2
\]
\[ = \frac{p^2}{4a} - \frac{b^2}{4a} + c
\]

\[ g'(p) = g'(p) \]

Clearly \( g(p) \) has lost some information since we get the same \( g'(p) \) for \( f(x) \) ad \( f(x-x_0) \).

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

In the 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

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

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
A function of only $p$.

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

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

take the value of $x$ 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

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

When $f(x)$ is convex, 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:

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

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

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

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

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

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,

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 Lagrangian formulation, the fundamental function is the Lagrangian \( L[q, \dot{q}] \) which depends on the variables \( q \) and \( \dot{q} \). In the Hamilton formulation one wants to replace the variable \( \dot{q} \) by the variable \( \phi = \frac{\partial L}{\partial \dot{q}} \).

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

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

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

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

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

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

\[ = A(T, V, N) \equiv E - TS \quad \text{Helmholtz Free Energy} \]

\( \text{Sometimes written as } F(T, V, N) \)

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

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

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

Since \( E = TS - pV + \mu N \), \( A = E - TS = -pV + \mu N \)

\[ A = -pV + \mu N \]
Checking the derivatives one carefully

\[ A = E - TS \]

to take Legendre transform use in principal conjugate

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

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

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

\[ = T \]

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

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

Similarly

\[ \left( \frac{\partial A}{\partial N} \right)_{T, V} = \left( \frac{\partial E}{\partial N} \right)_{S, V} = \mu \]
Enthalpy \( \mathcal{H}(S, p, N) \)

Use pressure instead of volume

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

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

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

\[ d\mathcal{H} = TdS + Vdp + \mu dN \]

Since \( E = TS - pV + \mu N \)

\[ \mathcal{H} = E + pV = TS + \mu N \]

Gibbs Free Energy \( \mathcal{G}(T, p, N) \)

Use temperature and pressure instead of entropy and volume

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

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

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

\[ d\mathcal{G} = -SdT + Vdp + \mu dN \]
Since \( E = TS - pV + \mu N \)

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

or

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

the chemical potential is the Gibbs free energy per particle.

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

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

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

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

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 \( \mu_i = \left( \frac{\partial G}{\partial N_i} \right)_{T, p, N_j \neq i} \)
Grand potential \[ \sum(T,V,N) \]

Use temperature and chemical potential instead of entropy and particle number.

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

\[ \sum(T,V,\mu) = E - TS - \mu N \]

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

\[ d\sum = -SdT - \rho dV - N d\mu \]

Since \[ E = TS - \rho V + \mu N \]

\[ \sum = E - TS - \mu N = -\rho V \]

\[ \frac{-\sum}{V} = \rho \]

The pressure is \((-\) the grand potential per unit volume.)
Extremum Principles for Free Energies

Concept of a thermal reservoir

\[ \left( \frac{\partial E_R}{\partial S_R} \right)_{VN} = T_R \]

- system of interest
  - thermal reservoir \( \gg \) system of interest
  - can exchange only heat between system and reservoir

Suppose we add heat \( dq = T_R ds \) to the reservoir.

The change in the reservoir's temperature \( T_R \) will be

\[ \Delta T_R = \left( \frac{\partial T_R}{\partial S_R} \right) ds = \left( \frac{\partial^2 E_R}{\partial S_R^2} \right) ds \]

Since \( E_R \) and \( S_R \) are both extensive variables, they scale with the number of particles in the reservoir \( N_R \).

So,

\[ \left( \frac{\partial^2 E_R}{\partial S_R^2} \right) \sim \frac{1}{N_R} \rightarrow 0 \quad \text{for infinitely large reservoir} \]

\[ \Rightarrow \Delta T_R \rightarrow 0 \]

Formally, a thermal reservoir is a system so large that its temperature does not change when it exchanges heat with the system of interest.
Consider a system in contact with a thermal reservoir. Only energy can be exchanged between the system and reservoir. The temperature $T_R$ of the reservoir is constant by definition.

If an internal constraint in the system is relaxed, what determines the new equilibrium state?

Use entropy formulation - total energy is conserved $E = E_R + E$

Total entropy is maximized

\[
S^{tot} = S_R(E_R) + S(E)
\]

\[
= S_R(E^{tot} - E) + S(E)
\]

Since $E \ll E^{tot}$ (as $E_R \gg E$ by def of reservoir), we can expand

\[
S^{tot} \approx S_R(E^{tot}) - \left(\frac{\partial S_R}{\partial E_R}\right) E + S(E)
\]

\[
= S_R(E^{tot}) - \frac{E}{T_R} + S(E)
\]

\[
= S_R(E^{tot}) - \frac{E - T_R S}{T_R}
\]

\[
= S_R(E^{tot}) - \frac{A}{T_R}
\]

$T_R = T$

$A$ is a constant - Helmholtz free energy
\[ S^\text{tot} \text{ maximized} \Rightarrow A \text{ minimized} \]

\[ \Rightarrow \text{the equilibrium state of a system in contact with a thermal reservoir will be the one that minimizes the Helmholtz free energy } A(T, V, N) \]

Now consider a system in contact with a thermal and pressure reservoir.

Pressure reservoir always has fixed pressure \( p_R \)

\[ \begin{align*}
  \text{system } E, S, V & \\
  \text{reservoir } E_R, S_R, V_R & \\
  \text{reservoir } \text{ fixed } p_R &
\end{align*} \]

Total energy conserved: \( E^\text{tot} = E_R + E = \text{constant} \)

Total volume conserved: \( V^\text{tot} = V_R + V = \text{constant} \)

System is in equilibrium with reservoir \( \Rightarrow T = T_R, \ p = p_R \)

\[ S^\text{tot} = S_R(E_R, V_R) + S(E, V) \]

\[ = S_R(E^\text{tot} - E, V^\text{tot} - V) + S(E, V) \]

\[ < S_R(E^\text{tot}, V^\text{tot}) - \left( \frac{\partial S_R}{\partial E_R} \right) E - \left( \frac{\partial S_R}{\partial V_R} \right) V + S(E, V) \]

\[ = \text{constant} - \frac{E}{T_R} \rightarrow \frac{p_R}{T_R} V + S \]

\[ = \text{constant} - \frac{(E + p_R V - ST)}{T} = \text{constant} - \frac{G}{T} \]

\[ S^\text{tot} \text{ maximized} \Rightarrow G, \text{ Gibbs Free Energy is minimized} \]
The equilibrium state of a system in contact with a thermal and pressure reservoir will be the one that minimizes the Gibbs free energy $G(T, p, N)$.

Similarly, the equilibrium state of a system in contact with a pressure reservoir will be the one that minimizes the enthalpy $H(S, p, N)$.

And the equilibrium state of a system in contact with a thermal and a particle reservoir (a particle reservoir can exchange particles with the system, but is so large that its chemical potential $\mu$ stays constant) will be the one that minimizes the grand potential $\Sigma(T, V, \mu)$.