Unit 1-4: Legendre Transformations

We now have two equivalent representations for our thermodynamic system:

1) Entropy formulation in terms of $S(E, V, N)$ – energy E, volume V, number of particles N held fixed.

2) Energy formulation in terms of $E(S, V, N)$ – entropy S, volume V, number of particles N held fixed.

In certain cases it is more natural to regard the temperature T as held constant, rather than the entropy S (in the lab, you will seldom see an apparatus with a knob to tune S); or to regard the pressure p as held constant, rather than the volume V; or to regard the chemical potential μ as held constant, rather than N.

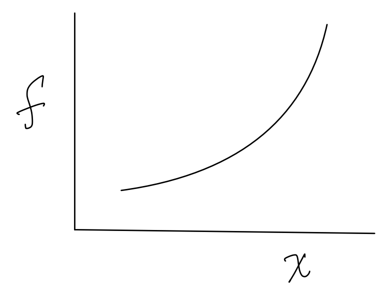
We therefore wish to develop new formulations of thermodynamics that will allow us to regard T, p, or μ as a fundamental variable rather than S, V, or N. These new formulations will lead to the Helmholtz and Gibbs *free energies*, that play the role analogous to energy as the fundamental thermodynamic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

For example, we have $E(S, V, N)$ with $T = (\partial E/\partial S)_{V,N}$. How can we make a thermodynamic potential that contains all the information of $E(S, V, N)$ but that depends on T rather than S? This leads us to a discussion of ...

Legendre Transformations

We will first discuss Legendre transforms in a general mathematical context.

Suppose one has some monotonic function $f(x)$.



We define the variable $p(x) = \dfrac{df}{dx}$.

How do we find a function $g(p)$ that contains all the information that is in $f(x)$, but depends on p rather than x? By "contains all the information that is in $f(x)$," we mean that one should be able to completely reconstruct $f(x)$ from the knowledge of $g(p)$.

First guess: As a first guess one might think the following. Invert $p(x) = df/dx$ to solve for x as a function of p. Then insert this $x(p)$ into $f(x)$ to get,

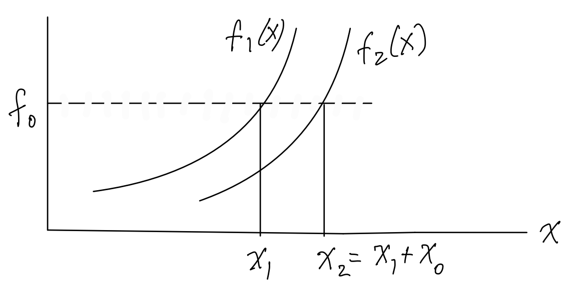
$$g(p) = f(x(p)) \tag{1.4.1}$$

But it turns out that this *does not* have all the complete information that is contained in $f(x)$!

To see this, consider two functions:

$$f_1(x) = h(x) \qquad \text{and} \qquad f_2(x) = h(x - x_0) \tag{1.4.2}$$

f_2 is just a copy of f_1 translated by x_0 along the x-axis, as in the sketch.



Let

$$p_1(x) = \frac{df_1(x)}{dx} = \frac{dh(x)}{dx}, \quad p_2(x) = \frac{df_2(x)}{dx} = \frac{dh(x - x_0)}{dx} \tag{1.4.3}$$

If $f_1 = f_0$ at $x = x_1$, then $f_2 = f_0$ when $x = x_1 + x_0 \equiv x_2$.

It follows that $p_1(x_1) = p_2(x_2) = p_2(x_1 + x_0)$, and so inverting, $x_2(p) = x_1(p) + x_0$.

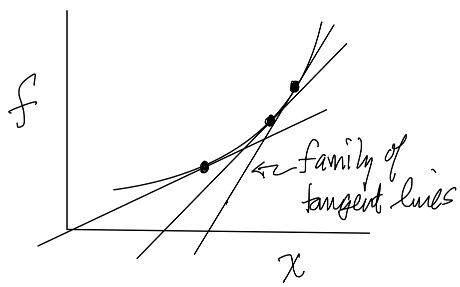
Substituting back into f_1 and f_2 we get,

$$g_1(p) = f_1(x_1(p)) = h(x_1(p)) \tag{1.4.4}$$

$$g_2(p) = f_2(x_2(p)) = f_2(x_1(p) + x_0) = h(x_1(p) + x_0 - x_0) = h(x_1(p)) = g_1(p) \tag{1.4.5}$$

So $g_1(p)$ and $g_2(p)$ are the same even though $f_1(x)$ and $f_2(x)$ are different! Clearly $g(p)$ constructed this way does not contain all the information in $f(x)$, since we cannot uniquely reconstruct $f(x)$ from this $g(p)$.

The correct approach is given by the Legendre transform. The Legendre transform starts with the idea that any curve $f(x)$ can be described by the envelope of its tangent lines, as in the sketch below. For a monotonic convex curve, as in the sketch, draw all the tangent lines and the upper envelop of those tangents gives the curve (for a concave curve, it will be the lower envelop).



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

$$y = px + b \quad \text{where} \quad p = \left.\frac{df}{dx}\right|_{x=x_0} \tag{1.4.6}$$

and b is determined by,

$$f(x_0) = px_0 + b \quad \Rightarrow \quad b = f(x_0) - px_0 \tag{1.4.7}$$

b is the y-intercept of the curve, i.e. $y = b$ when $x = 0$.

We now define the function

$$\boxed{g(p) = f(x) - px} \qquad \text{where} \quad p = \frac{df}{dx} \tag{1.4.8}$$

$g(p)$ is the y-intercept of the tangent line to the curve $f(x)$ at position x, where $p = df/dx$. Knowing this y-intercept, and the slope p, one can construct the tangent lines at all x and then find the curve $f(x)$ from the envelop of the tangent lines.

To define $g(p)$ as a function of the slope p only, one solves $p(x) = \dfrac{df}{dx}$ to get the inverse function $x(p)$, and then substitutes this $x(p)$ into the above expression for $g(p)$ to get,

$$g(p) = f(x(p)) - px(p) \tag{1.4.9}$$

In this way one can plot all the tangent lines $y = px + g(p)$ as p varies, and so construct the family of tangent lines, and from the envelop of the tangent lines get $f(x)$. Since we can uniquely reconstruct $f(x)$ from knowledge of $g(p)$, then $g(p)$ contains all the information that was originally contained in $f(x)$.

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

Another useful, equivalent, way to define $g(p)$ is by the expression,

$$\boxed{g(p) = \underset{x}{\text{extremum}}\,[f(x) - px]} \tag{1.4.10}$$

where the expression in the brackets is to be evaluated at the value of x that gives its extremal value. When $f(x)$ is convex, i.e. $d^2f/dx^2 > 0$, then the extremum is the *minimum* of $f - px$. When $f(x)$ is concave, i.e. $d^2f/dx^2 < 0$, then the extermum is the *maximum* of $f - px$.

To see that this definition is equivalent, note that the condition for locating the extremum x is,

$$\frac{d}{dx}\left[f(x) - px\right] = 0 \quad \Rightarrow \quad \frac{df}{dx} - p = 0 \quad \Rightarrow \quad \frac{df}{dx} = p \tag{1.4.11}$$

So one solves $df/dx = p$ for $x(p)$ and substitutes it into $[f(x) - xp]$ to get $g(p) = f(x(p)) - px(p)$, and one arrives again at Eq. (1.4.9).

Having defined the Legendre transform $g(p)$, we now note one of its important properties,

$$\frac{dg}{dp} \;=\; \frac{d}{dp}\left[f(x(p)) - px(p)\right] = \frac{df}{dx}\frac{dx}{dp} - x - p\frac{dx}{dp} \;=\; \frac{dx}{dp}\left[\frac{df}{dx} - p\right] - x \;=\; -x \quad \text{since} \quad \frac{df}{dx} = p \tag{1.4.12}$$

For $g(p)$ the Legendre transform of $f(x)$ we thus have,

$$p = \frac{df}{dx} \qquad \text{and} \qquad x = -\frac{dg}{dp} \tag{1.4.13}$$

One says that x and p are *conjugate variables.*

The Legendre transform allows one to take a function $f(x)$, which is described by the variable x, and find an equivalent reformulation $g(p)$ that is described by the conjugate variable $p = df/dx$.

You may have already encountered Legendre transforms in classical mechanics. In the Lagrangian formulation of classical mechanics the fundamental function is the Lagrangian $\mathcal{L}[q, \dot{q}]$, where q is a generalized coordinate and $\dot{q} = dq/dt$ is the corresponding velocity. In the Hamiltonian formulation of classical mechanics one wants to replace the variable $\dot{q}$ by the variable $p = \partial\mathcal{L}/\partial\dot{q}$. This p is called the canonically conjugate momentum to the coordinate q. The fundamental function to use in the Hamiltonian formulation is therefore the Legendre transform of $\mathcal{L}[q, \dot{q}]$ from $\dot{q}$ to p,

$$\mathcal{L}[q, \dot{q}] - p\dot{q} \equiv -\mathcal{H}[p, q] \tag{1.4.14}$$

where $\mathcal{H}[p, q]$ is the Hamiltonian, that depends on the coordinates q and their conjugate momenta p. Because p and $\dot{q}$ are Legendre conjugate variables, we then know that,

$$\frac{\partial\mathcal{L}}{\partial\dot{q}} = p \qquad \text{and} \qquad \frac{\partial(-\mathcal{H})}{\partial p} = -\dot{q} \quad \Rightarrow \quad \boxed{\frac{\partial\mathcal{H}}{\partial p} = \dot{q}} \tag{1.4.15}$$

which gives one of Hamiltonian dynamical equations.

The second of Hamilton's equations of motion follows from Lagrange's equation of motion,

$$\frac{\partial\mathcal{L}}{\partial q} - \frac{d}{dt}\left(\frac{\partial\mathcal{L}}{\partial\dot{q}}\right) = 0 \quad \Rightarrow \quad \frac{\partial\mathcal{L}}{\partial q} = \dot{p} \tag{1.4.16}$$

Then with

$$\frac{\partial\mathcal{H}}{\partial q} = \frac{\partial}{\partial q}\left[p\dot{q} - \mathcal{L}\right] = -\frac{\partial\mathcal{L}}{\partial q} = -\dot{p} \qquad \Rightarrow \qquad \boxed{\frac{\partial\mathcal{H}}{\partial q} = -\dot{p}} \tag{1.4.17}$$