Lecture 5

Objectives:

1. Be able to take any Legendre transform of any arbitrary function.

2. Derive the Gibbsian equations from Legendre transforms.

1. Legendre Transforms. A way to derive the auxiliary energy functions is to use Legendre transforms to change the independent variables. This is a powerful technique, and we don’t have time to discuss it fully here. Please read a math textbook or review Tester & Modell chapter 5.

Consider a function of \( m \) variables:

\[ y^{(0)} = f(x_1, \ldots, x_m) \]

Let \( \xi_i \) be the partial derivative of \( y^{(0)} \)

\[ \xi_i = \left( \frac{\partial y^{(0)}}{\partial x_i} \right)_{x_j \neq i} \]

The first Legendre transform of \( y^{(0)} \) is defined as

\[ y^{(1)} = y^{(0)} - \xi_1 x_1 = y^{(0)} - \left( \frac{\partial y^{(0)}}{\partial x_1} \right)_{x_j \neq 1} x_1 \]

Note that \( x_1 \) could be any variable, because the ordering doesn’t matter. The important thing is that \( y^{(1)} \) is now a function of \( \xi_1 \),

\[ y^{(1)} = f(\xi_1, x_2, \ldots, x_m) \]

So we have traded the dependence on \( x_1 \) for dependence on \( \xi_1 \).

The second Legendre transform is

\[ y^{(2)} = y^{(0)} - \xi_1 x_1 - \xi_2 x_2 \]

and

\[ y^{(2)} = f(\xi_1, \xi_2, x_3, \ldots, x_m) \]

Generalizing, the \( k \)th Legendre transform is

\[ y^{(k)} = y^{(0)} - \sum_{i=1}^{k} \xi_i x_i \]

The total Legendre transform is

\[ y^{(m)} = y^{(0)} - \sum_{i=1}^{m} \xi_i x_i \]
Example: Let \( y^{(0)} = 2x_1^2x_2 - 3x_1x_2^3 \). Then \( \xi_1 = 4x_1x_2 - 3x_2^2 \). Solving for \( x_1 \) we find
\[
x_1 = \frac{\xi_1}{4x_2} + 3/4x_2 \quad \text{and} \quad x_2 = \frac{\xi_1^2}{16x_2^2} + \frac{3}{8}\xi_1 + \frac{9}{16}x_2^2.
\]
Then \( y^{(1)} = -2x_1^2x_2 = -2x_2\left(\frac{\xi_1^2}{16x_2^2} + \frac{3}{8}\xi_1 + \frac{9}{16}x_2^2\right) = -\frac{\xi_1^2}{8x_2} - \frac{3}{4}\xi_1x_2 - \frac{9}{8}x_2^3 = f(\xi_1, x_2), \) Q.E.D.

Say we start with \( U = U(S, V, n_1, \ldots, n_C) \). We want a function \( F = F(T, V, n_1, \ldots, n_C) \). Use Legendre transforms to come up with \( F \).

- Note that we only need to transform one variable \((S \rightarrow T)\) so we only need a first Legendre transform.
- What variable do we want to transform? Recall that \( \frac{\partial U}{\partial S}_{V, n_i} = T \), so we obviously want to transform \( S \).
- Write down the first Legendre transform of \( U \) w.r.t. \( S \), and call this \( F \)

\[
F = U - \left(\frac{\partial U}{\partial S}\right)_{V, n_i} S
\]

\[
F = U - TS
\]

**Question:** What Gibbsian function is \( F \)?

The differential of \( y^{(0)} \) is

\[
dy^{(0)} = \sum_{i=1}^{m} \xi_i dx_i.
\]

The total differential of the \( k \)th transform can be obtained by differentiating \( y^{(k)} \),

\[
dy^{(k)} = \sum_{i=k+1}^{m} \xi_i dx_i - \sum_{i=1}^{k} x_i d\xi_i.
\]

Note that the total differential of the total Legendre transform is

\[
dy^{(m)} = -\sum_{i=1}^{m} x_i d\xi_i.
\]

**Question:** From the above equations, find the following:

\[
\left(\frac{\partial y^{(k)}}{\partial \xi_i}\right) = ? \text{ for } i \leq k
\]

and what is

\[
\left(\frac{\partial y^{(k)}}{\partial x_i}\right) = ? \text{ for } i > k
\]

The above equation is applicable for all cases where \( i > k \), thus, we have the following

\[
\frac{\partial y^{(i-1)}}{\partial x_i} = \frac{\partial y^{(i-2)}}{\partial x_i} = \cdots = \frac{\partial y^{(0)}}{\partial x_i} = \xi_i
\]
2. Three observations from Legendre transforms:

(a) We can show that

\[ \mu_i = \left( \frac{\partial U}{\partial n_i} \right)_{S,V,n_j \neq i} = \left( \frac{\partial A}{\partial n_i} \right)_{T,V,n_j \neq i} = \left( \frac{\partial G}{\partial n_i} \right)_{T,P,n_j \neq i} = \left( \frac{\partial H}{\partial n_i} \right)_{S,P,n_j \neq i} \]

We can see this from the above equation for \( \frac{\partial y^{(i-1)}}{\partial x_i} \), by letting \( x_i \) be \( n_i \). Try it with \( y^{(0)} = U \).

(b) There are at least three pairs of conjugate variables. These are \((S, T)\); \((V, P)\); \((n_i, \mu_i)\). In order to form a functions with complete information we must choose one variable from each of these three pairs. Note that \( U, A, H, G \) are not the only possible complete functions.

The conjugate variables consist of one extensive and one intensive variable in each pair. The pairs of variables are grouped according to specific type of works:

- \((S, T)\) = Heat \\ flow work;
- \((V, P)\) = Pressure-volume work;
- \((n_i, \mu_i)\) = Chemical work;
- \((A, \sigma)\) = Surface tension work, etc.

(c) The Gibbs-Duhem equation can be derived from the total Legendre transform of \( U \),

\[ y^{(C+2)} = U - TS + PV - \sum_{i=1}^{C} \mu_i n_i = 0 \]

hence,

\[ dy^{(C+2)} = 0 = -SdT + VdP - \sum_{i=1}^{C} n_i d\mu_i \]

3. Example of using Legendre transforms.

Consider a system consisting of an emulsion of one liquid in another. The energy of the system depends on the entropy, volume, surface area \((A)\), and number of moles of each component:

\[ dU = TdS - PdV + \sigma dA + \sum_{i=1}^{C} \mu_i d n_i \]

and therefore

\[ U = TS - PV + \sigma A + \sum_{i=1}^{C} \mu_i n_i \]

where \( \sigma \) is the surface tension of the emulsion. The surface tension can be controlled by changing the structure of the surfactant. How does the entropy of the system change in response to the change in surface tension, holding the temperature, volume, surface area, and composition constant? We want to find

\[ \left( \frac{\partial S}{\partial \sigma} \right)_{T,V,n_i} = ? \]
and we would like to be able to measure this experimentally. We need to find some function that has natural (canonical) variables $T, V, \sigma, n_i$. Therefore, we need to transform $S$ to $T$ and $A$ to $\sigma$.

$$y^{(2)} = y^{(0)} - ST - \sigma A = -PV + \sum_{i=1}^{C} \mu_i n_i$$

$$dy^{(2)} = -SdT - PdV - A\sigma + \sum_{i=1}^{C} \mu_i d\mu_i$$

We can therefore write

$$S = -\left(\frac{\partial y^{(2)}}{\partial T}\right)_{V, \sigma, n_i}$$

and therefore,

$$\left(\frac{\partial S}{\partial \sigma}\right)_{T, V, n_i} = -\left(\frac{\partial^2 y^{(2)}}{\partial \sigma \partial T}\right)_{V, n_i} = -\left(\frac{\partial^2 y^{(2)}}{\partial T \partial \sigma}\right)_{V, n_i} = \left(\frac{\partial A}{\partial T}\right)_{\sigma, V, n_i}$$