Legendre Transforms

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In class and during recitation, we have seen how Legendre transforms allow us to change the independent variables that we need to control in any experimental condition that we may encounter in practice:

In practical applications, for example, it is impossible to have the entropy of the system (at constant volume) as the controlled variable, it is much easier and intuitive to measure and control the temperature. To change the independent variable, we then perform the Legendre Transform:

$$\Phi\left(T,V,N\right) \rightarrow U\left(S,V,N\right) - TS$$

From what we have learned, the potential Φ is usually known as the Helmholtz Free Energy, F. Its differential form is:

$$dF = -SdT - PdV + \mu dN$$

To represent the Legendre transformation above in a more general way, we can represent both the Internal Energy and the Helmholtz potential in matrix notation:

$$\begin{array}{cccc} \Phi/Y_iX_i & TS & PV & \mu N \\ U\left(S,V,N\right) & + & - & + \\ F\left(T,V,N\right) & - & - & + \end{array}$$

The matrix can be read in the following manner:

The first column identifies the potential Φ, having a set of independent variables indicated by the set of variables in the parenthesis. The first row of this matrix represents the conjugate pairs Y_iX_i that have to be used to define the system and that establish the nature of the energy interactions between the system and the environment. To write down the differential form of the potentials we can do the following:

1 Identify the independent variables for the potential Φ. In the case of $U\left(S,V,N\right)$, the independent variables are S, V, N

2 The independent variables must appear as differentials in the differential expression of the potential Φ, $d\Phi$. For $U\left(S,V,N\right)$, dS, dV and dN appear in the expression for dU.

3 The differentials of the independent variables must be multiplied by their respective conjugates. For $U\left(S,V,N\right)$, we have TdS, PdV, μdN.

4 The sign of each conjugate pair in the differential expression for the differential of the potential Φ, $d\Phi$, is given by the interception of the row corresponding to the potential, Φ, and the corresponding conjugate pair Y_iX_i. For the internal energy, $U\left(S,V,N\right)$, we finally have:

$$dU = TdS - PdV + \mu dN$$

Note that the work terms other than PV, $\sum_i Y_iX_i$ are always positive in the internal energy representation.

We can use the matrix presented above to Legendre Transform the Internal Energy:

For example, for the transformation $(S, V, N) \rightarrow (T, V, N)$, we easily find the correct transformation, and even its differential, by using the following procedure:

1 Identify the intensive(s) properties that appear in the potential as independent variables. In the case of $F\,(T, V, N)$, T substitutes S as the independent variable.

2 To make this Legendre transformation, just **switch the sign** of the conjugate pair located at the intersection of the row of potential Φ and the column $Y_i X_i$ of the internal energy representation. For the case of $F\,(T, V, N)$ just change the sign of the conjugate pair TS.

3 To obtain the differential form of the potential Φ, use the procedure outlined above.

To illustrate this procedure, we can find the potential $\Phi\,(T, P, \mu)$ using the matrix method:

1 The independent variables are T, P, and μ.

2 The signs corresponding to TS, PV and μN must be switched with respect to those of the row corresponding to the internal energy.

The Matrix, including U, F and Φ will the be:

$\Phi/Y_i X_i$	TS	PV	μN
$U\,(S, V, N)$	$+$	$-$	$+$
$F\,(T, V, N)$	$-$	$-$	$+$
$\Phi\,(T, P, \mu)$	$-$	$+$	$-$

The differential form of Φ would be:

$$d\Phi = -SdT + VdP - Nd\mu$$

It is possible to do the same with the enthalpy: $H\,(S, P, N)$:

$\Phi/Y_i X_i$	TS	PV	μN
$U\,(S, V, N)$	$+$	$-$	$+$
$F\,(T, V, N)$	$-$	$-$	$+$
$\Phi\,(T, P, \mu)$	$-$	$+$	$-$
$H\,(S, P, N)$	$+$	$+$	$+$

and

$$dH = TdS + VdP + \mu dN$$

The table gets a little bit more complicated if one adds more work terms into the internal energy representation, but the procedure is the same:

Φ/Y_iX_i	TS	PV	μN	HM	Y_iX_i
$U\left(S,V,N,M,X_i\right)$	$+$	$-$	$+$	$+$	$+$
$F\left(T,V,N,M,X_i\right)$	$-$	$-$	$+$	$+$	$+$
$\Phi\left(T,P,\mu,M,X_i\right)$	$-$	$+$	$-$	$+$	$+$
$H\left(S,P,N,M,X_i\right)$	$+$	$+$	$+$	$+$	$+$
$G\left(T,P,N,M,X_i\right)$	$-$	$+$	$+$	$+$	$+$
$\Psi\left(T,P,\mu,H,Y_i\right)$	$-$	$+$	$-$	$-$	$-$

Note that Ψ is the complete Legendre Transform of the Internal Energy to all the intensive properties of a system. For $d\Psi$ we have

$$d\Psi = -SdT + VdP - Nd\mu - MdH - X_i dY_i$$

Later, it will be shown how we can use the matrix above to obtain Maxwell Relations.

General Rule for Maxwell Relation

In class, Prof. Ceder gave you a general rule to determine Maxwell Relations:

$$\left.\frac{\partial X}{\partial Y}\right)_{Conj(X)} = \pm \left.\frac{\partial Conj\left(Y\right)}{\partial Conj\left(X\right)}\right)_Y$$

In order to know the sign of the equality, there is a very simple technique:

X and $CONJ(Y)$ should be the dependent variables of the potentials. So, we need to find a potential that has $CONJ(X)$ and Y as their **independent** variables. These independent variables are identified in the Maxwell Relation by the fact that they are held **constant** in the partial derivatives.

$$\Phi\left(Conj\left(X\right), Y\right)$$

To find the proper signs and differential form of this potential, we can use the Matrix of Legendre Transforms. We can assume that $Conj\left(X\right)$ and Y are intensive properties:

Φ/Y_iX_i	$C\left(X\right)\cdot X$	$Y\cdot C\left(Y\right)$
$U\left(X, C\left(Y\right)\right)$	$+$	$+$
$\Phi\left(C\left(X\right), Y\right)$	$-$	$-$

From the row corresponding to the Φ potential, it is evident that the conjugate pairs in

$$\left.\frac{\partial X}{\partial Y}\right)_{Conj(X)} = \pm \left.\frac{\partial Conj\left(Y\right)}{\partial Conj\left(X\right)}\right)_Y$$

have the same sign in the $d\Phi$ expression and therefore:

$$\left.\frac{\partial X}{\partial Y}\right)_{Conj(X)} = + \left.\frac{\partial Conj\left(Y\right)}{\partial Conj\left(X\right)}\right)_Y$$

Example:

Find the Maxwell Relation for:

$$\left.\frac{\partial S}{\partial H}\right)_{T,V,\mu}$$

Solution:

We use the generalized form of the Maxwell Relations:

$$\left.\frac{\partial S}{\partial H}\right)_{T,V,\mu} = \pm \left.\frac{\partial M}{\partial T}\right)_{H,V,\mu}$$

We can find the corresponding potential by examining all the variables that are held constant in the expressions, namely, T, V, H, μ:

$$\Psi\left(T, V, \mu, H\right)$$

We use the matrix formalism (see how the rows corresponding to TS, μN and HM have to switch sign):

$$\begin{array}{ccccc} \Phi/Y_iX_i & TS & PV & \mu N & HM \\ U\left(S, V, N, M\right) & + & - & + & + \\ \Psi\left(T, V, \mu, H\right) & - & - & - & - \end{array}$$

The conjugate pairs TS and HM have the same sign in the differential form of the potential Ψ and therefore:

$$\left.\frac{\partial S}{\partial H}\right)_{T,V,\mu} = + \left.\frac{\partial M}{\partial T}\right)_{H,V,\mu}$$

Example 2:

$$\left.\frac{\partial S}{\partial M}\right)_{T,V,\mu} = \pm \left.\frac{\partial H}{\partial T}\right)_{M,V,\mu}$$

The potential now is:

$$\Psi\left(T, V, \mu, M\right)$$

And the Matrix Formalism is:

$$\begin{array}{ccccc} \Phi/Y_iX_i & TS & PV & \mu N & HM \\ U\left(S, V, N, M\right) & + & - & + & + \\ \Psi\left(T, V, \mu, M\right) & - & - & - & + \end{array}$$

Now, the conjugate pairs TS and HM have **different** signs in the differential form of the potential Ψ and therefore:

$$\left.\frac{\partial S}{\partial M}\right)_{T,V,\mu} = - \left.\frac{\partial M}{\partial T}\right)_{H,V,\mu}$$