3.23 Lecture 9

Chapters and sections to read in Callen to date: 2, 3.1 – 5, 5, 7

Legendre transforms

A Legendre transform involves going from an internal energy function to new functions where extensive variables are substituted by intensive variables.

$$U(S, X_i) -- > f(S, Y_j, X_{i \neq j}) = U(S_i, X_i) - Y_i X_j$$

In the switch from extensive variables to intensive variables in the relevant thermodynamic potential for non-isolated systems, there is the same information content as the internal energy function.

Take the Legendre Transform of internal energy, which is historically used as the fundamental equation. One could work with entropy as the fundamental equation.

$$LT(S(U, X_i) \rightarrow Massieu\ functions$$

This transformation is not done in class

Equation of state of *G* is a function of *T* and *P*

$$dG = -S\ dT - V\ dP$$

$$S = -(\delta G / \delta T)_P$$
$$V = -(\delta G / \delta P)_T$$

An equation of state is $S(T, P)$ and a mechanical equation of state is $V(T, P)$

What properties are needed to characterize $S(T, P)$

Look at the differential of *S*

$$dS = (\delta S / \delta T)_P\ dT + (\delta S / \delta P)_T\ dP$$
$$dV = (\delta V / \delta T)_P\ dT + (\delta V / \delta P)_T\ dP$$

The kinds of information in these equations are below

$\delta V / \delta T$	thermal expansion	$\alpha_v = 1 / V\ ((\delta V / \delta T)_P$
$\delta V / \delta P$	compressibility	$-1 / V\ ((\delta V / \delta P)_T$
$\delta S / \delta T$	heat capacity	$C_P = T\ (\delta S / \delta T)_P$
$\delta S / \delta P$		

From these properties, all is known about the system. Since the matrix of partial derivatives is symmetric, $\delta S / \delta P = \delta V / \delta T$.

Thermodynamics can be applied to any situation encountered. It's traditionally used in metallurgy but now used in many different applications, such as thin films and studying a slag in metallurgy. There can be weird boundary conditions.

Example of a bar clamped between two fixed surfaces
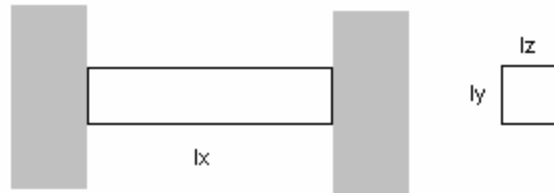
What variables are needed to describe the system? The relevant extensive variables are $S, \varepsilon_{xx}, \varepsilon_{yy}, \varepsilon_{zz}, \varepsilon_{xy}, \varepsilon_{xz}, \varepsilon_{yz}$. This is not an isotropic system. Assume that there are no shear stresses. Three strains define the volume change.

The force is perpendicular to direction and multiplied by stress in the x-direction

$$F_x = l_y\, l_z\, \sigma_{xx}$$

Write the 1st law. This includes all the ways to input energy. There could be internal degrees of freedom, such as change of phase.

$$dU = TdS + l_x\, d\varepsilon_{xx} l_y\, l_z\, \sigma_{xx} + l_x\, d\varepsilon_{yy} l_y\, l_z\, \sigma_{yy}$$

Replace $l_x\, l_y$ and l_z with volume term.

$$dU = TdS + V\, \sigma_{xx}\, d\varepsilon_{xx} + V\, \sigma_{yy}\, d\varepsilon_{yy} + V\, \sigma_{zz}\, d\varepsilon_{zz}$$
$$dU = TdS + V\, \sigma_{xx}\, d\varepsilon_{xx} + \sigma_{yy}\, V\, (d\varepsilon_{yy} + d\varepsilon_{zz})$$

What is the relevant thermodynamic potential? Define the relevant variables, which are control variables. Use G, with contant T, P, which are the variables controlled. What are the variables? Pick a set of independent variables. Volume is not one since length is not constrained in the y and z direction. The bar is constrained in x, but not in y and z. The variable l_x is chosen by choosing the position of the walls. There is no constraint on y and z. Variables that are imposed on the system and control changes of state are below.

$$T, \varepsilon_{xx,}, \sigma_{yy}, \sigma_{zz}$$

In order to obtain the relevant potential, one needs to obtain a function of the variables. Use the Legendre transform and go to the conjugate intensive variables.

$$\Phi = \Phi(T, \varepsilon_{xx}, \, \sigma_{yy}, \sigma_{zz})$$
$$\Phi = U - TS - V\,\sigma_{yy}\,d\varepsilon_{yy} - V\,\sigma_{zz}\,d\varepsilon_{zz}$$
$$d\Phi = -\,SdT + V\,\sigma_{xx}\,d\varepsilon_{xx} + V\,(\varepsilon_{yy} + \varepsilon_{zz})dP$$

Heat Capacity

The heat capacity of a system is defined in terms of thermodynamic quantities and depends on the constraints of the system. There is C_P and C_V. What is the relevant C? Say there is constant x and variable y and z.

$$C_{\,\varepsilon xx, \sigma yy\,\sigma zz} = T\,(\delta S\,/\,\delta T)_{\,\varepsilon xx, \sigma yy\,\sigma zz}$$

When using C_P, there is constant stress from the environment. The above expression can be related to C_P and C_V. If you know one set of heat capacity, all the others can be derived. This is very useful, for you can know many properties from a few measurements.

Mathematical structure

The results from the mathematical structure are practical. Systematically work through this. There is a need to be fluent. This is a most powerful instrument to relate many things. For instance, $(\delta S\,/\,\delta P)_T = -(\delta V\,/\,\delta T)_P$.

This is an amazing relation. Things are equal that are seemingly unrelated. One can form relations with many complicated things.

Maxwell relations

$$F(x, y) \;\rightarrow\; dF = M(x, y)dx + N(x, y)dy$$

The functions $M(x,y)$ and $N(x,y)$ are not arbitrary functions. They are prefactors of the partial derivative of the same function. It is usually not a problem to change the order of differentiation.

$$(\delta M\,/\,\delta Y)_x = -(\delta N\,/\,\delta X)_Y$$
$$\delta\,/\,\delta y\,(\delta F\,/\,\delta x) = \delta\,/\,\delta x\,(\delta F\,/\,\delta y) = (\delta^2 F\,/\,\delta y\,\delta x)$$

Why is this practical? Below is an expression that can be derived based on the expression involving dU

$$dU = TdS - pdV$$
$$(\delta T\,/\,\delta V)_S = -(\delta P\,/\,\delta S)_V$$

It is more practical and interesting to apply Maxwell to thermodynamic relations that are a function of control variables.

$$T, P \rightarrow G(T, P)$$
$$dG = -SdT + VdP$$
$$(\delta S / \delta P)_T = -(\delta V / \delta T)_P$$

The left-hand side is not measurable; there is no entropy meter, and the right-hand side is the thermal expansion term. This shows that the matrix is diagonal.

There are three properties needed to know everything about the system: compressibility, thermal expansion, and heat capacity.

Write down the differential and look for the relevant Maxwell relation. From thermodynamics, many equations can be derived. Most equations need to be derived within a minute. There is a system of derivation and a general structure of Maxwell relations. All Maxwell relations are of this form. There is a cross conjugate relation.

$$(\delta X / \delta Y)_{conj(x)} = +/-(\delta conj(y) / \delta conj(x))_y$$

$$(\delta S / \delta V)_T = +/-(\delta P / \delta T)_V$$

The sign is usually undetermined, but the final result is checked to ensure it makes physical sense. In the above example, we know that the potential is of the form of the Hemholtz free energy. It comes from $U - TS$. Legendre transform to get in terms of V. In differential form:

$$dF = -SdT - pdV$$

The result of two minus signs is a plus sign.

$$(\delta S / \delta V)_T = (\delta P / \delta T)_V$$

Next time we figure out with multiplication work terms