

3.23 Lecture 8

Last time the first and second law was joined and there was a statement of variations in internal energy.

$$dU = T dS + \text{Sum}[y_i dX_i]$$

The internal energy is related to the entropy variation and work terms. Intensive variables are partial derivatives and relate to equations of state.

$$T = (\delta U / \delta S)_{X_i}$$
$$Y_i = (\delta U / \delta X_i)_{S, X_{j \neq i}}$$

Forces are derivatives of energy with respect to displacement.

Equilibrium for isolated systems

The expression $dS > 0$ can be turned into an equilibrium condition. Write the variational in terms of internal degrees of freedom. This puts a condition on variables and what you get out is that the extensive variable has to be distributed. The conjugate intensive has to be homogeneous. For example, when charge can move, the potential of the conductor has to be the same everywhere. When the extensive variable flows independently, its conjugate intensive is homogeneous. The mass is extensive and it is the chemical potential that is homogeneous at equilibrium. The chemical potential is a derivative of energy.

$$\mu_i = (\delta U / \delta N_i)$$

When there is a couple of flow of variables, the amount of exchange could be linearly related.

$$dX_i = -dX_{II}$$

This leads to a less restrictive condition. A linear combination of Y_I and Y_{II} is the same everywhere at equilibrium.

A couple of flow of variables is easy to implement practically. Move charged ions across a barrier. The transfer of charge is related to mass flow. It is the conjugates, chemical potential and electrical potential that need to be homogeneous, but not mass or charge.

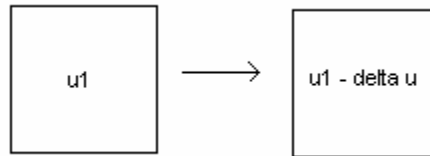
When charge and heat flow are coupled, it is not the temperature that is homogeneous but the combination of temperature and potential. There are thermoelectric effects, and a device can be constructed wherein there is an electric potential under a temperature gradient.

Energy minimum principle

There has been a discussion involving the entropy maximization principle. Find equilibrium by finding the point of maximum entropy. The complement to this is the energy minimum principle. Equilibrium can also be achieved by minimizing energy at constant entropy; this results in the same state as achieved by maximizing entropy. There is a proof in Callen (p. 132 – 35)

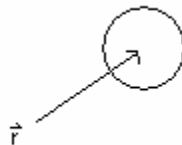
Suppose in a state that S is a maximum for a given value of $U = U_1$. Suppose that U_1 is not minimal for that value of S . What is the implication?

If energy is not a minimum, energy can be extracted while keeping entropy the same. Perform work and expel energy somewhere. That work can be converted into heat and fed into the system, resulting in a state with energy, U . A state with higher entropy was produced, which means that the entropy S was not maximal.



Look at this graphically. There is a handout. Look at the convexity and the derivatives $\delta U / \delta S$

We've derived equilibrium under discrete conditions but this can be generalized to a continuum. Equilibrium conditions can still be applied to inhomogeneous systems.



Define properties and local variables in this region of space.

$$\begin{aligned} S &= S / V \\ U &= U / V \\ X_i &= X_i / V \end{aligned}$$

Find the minimum energy of system and maximum entropy. The total entropy is obtained by integrating

$$S_{tot} = \text{Integrate}[S(r), r]$$

Under the constraint of conserved extensive variables, the integral of extensive variable densities is equal to a constant.

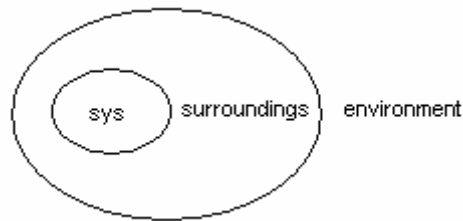
$$X_i = \text{Integrate}[X_i(r), r]$$

Kinetics

Look at how a system gets to its final state by taking the gradient of the expression. Take the gradient of the entropy function. Look at how fast go up or down the path, and go up path of maximum entropy. The study of kinetics helps show that the system follows the steepest path. From the expression of S_{total} , the diffusion equations could be derived. For instance, make the concentration go up the path as fast as possible.

Equilibrium under general conditions

The surroundings are the complement of the system.



How do extensive quantities change during the evolution of a system? Consider a system that is neither closed nor does it satisfy the conditions of energy or entropy. Look at a larger boundary to satisfy conditions of entropy. Distill this to the equilibrium condition.

Make the environment large. If the environment is large, the flow of energy does not modulate the temperature of the surroundings.

Write down the first law for the surroundings

$$\Delta U^* = T^* \Delta S^* + \text{Sum}[Y_i^* \Delta X_i^*]$$

This is a bad start. All the variables are variables of the surroundings. We need evolution laws of the system. Turn this expression into variables of the system

$$\begin{aligned} \Delta U^* &= -\Delta U \\ \Delta U^* + \Delta U &= 0 \end{aligned}$$

The sum of the two entropy changes increases

$$\Delta S^* + \Delta S \geq 0$$

The extensive variables are conserved.

$$\Delta U - T^* \Delta S^* + \text{Sum}[Y_i^* \Delta X_i^*] \leq 0$$

This statement is rarely in textbooks. We want the allowed evolution in terms of changes in extensive variables

The system plus the surroundings has to come to internal equilibrium. Under thermal and force equilibrium, the following statements are true.

$$\begin{aligned} T^* &= T \\ Y_i^* &= Y \end{aligned}$$

There is internal equilibrium while the system as a whole still evolves

$$\Delta U - T \Delta S + \text{Sum}[Y_i \Delta X_i] \leq 0$$

Example of a simple system

$$dU - T dS + p dV = 0$$

Weakness of derivation

The statement that $\Delta X_i^* = -\Delta X_i$ is true for most extensive variables that we know, such as the transfer of mass. In the reaction $A + B \rightarrow AB$, there is still a conserved relation. But the magnetic field is problematic. Electric charge and magnetic field are not independent. One can't change the magnetic field without changing the current. It is not resolved whether the dipole moment is conserved, but the result derived above still works. An idea is to work with vector potential and derive electrical and magnetic behavior, but we are not doing electromagnetism.

Specific conditions

- 1) isolated system

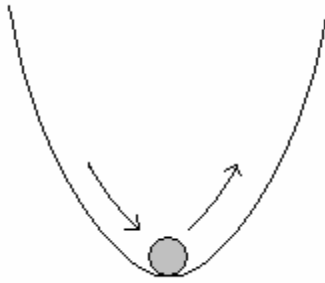
$$dU = dV = 0 \rightarrow dS \geq 0$$

This last expression is related to the second law.

- 2) mechanical system

Entropy doesn't change. There are no work interaction forces and no displacements at equilibrium. Define energy as a potential, and minimize the energy.

$$dU \leq 0$$



3) Isentropic isobaric

Work is exchanged with the environment.

$$dU - pdV \leq 0$$

This is done under constant pressure. Enthalpy is defined as

$$H = U + PV$$

Energy and work terms produce enthalpy.

4) Isothermal and isobaric ($U = \text{constant}$)

There are no work exchanges and no work flows with the environment.

$$dU - TdS \leq 0$$

At constant temperature, the expression below is true.

$$d(U - TS) \leq 0$$

5) Isothermal and isobaric

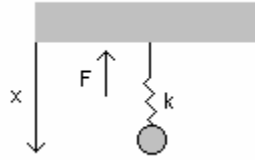
$$dU - TdS + pdV \leq 0$$
$$d(U - TS + pV) \leq 0$$

This is the Gibbs free energy.

What does this mean?

The enthalpy and other functions are thermodynamic potentials. They are functions that are minimized or maximized.

Simple example made more complicated



The ball is in a gravitational field, and there is an upward force on the ball. The force is $-kx$ and the point of zero force is x . We know how to solve equilibrium.

$$U_{sys} = -mgx$$

Write the generalized evolution. We do not need to minimize the energy of the system but rather some other property exchanging with the environment. Write a combination or apply previous equation.

$$dU_{sys} - T^* dS + Y_i^* dX_i \leq 0$$
$$dU_{sys} = -mgdx$$

There are no entropy exchanges, and the force is $-kx$. The displacement is dx . The following expression is true.

$$-mgdx + kxdx \leq 0$$

The variation is kdx

$$(kx - mg)dx \leq 0$$

Equilibrium is achieved when the force of gravity balances the force of the spring.

$$mg = kx$$

Everything should fit in the thermodynamic framework.

Enthalpy

$$H = U + PV$$

The system changes volume. Look for the combination of low energy states and low volume states. At a low volume, the system cannot do much work.

Helmholtz

$$F = U - TS$$

The term TS represents the energy in the thermal environment. It represents the potential to remove energy.

Potentials

U	Under constant
$H = U + PV$	S, V
$F = U - TS$	S, P
$G = U - TS + PV$	T, V
	T, P

The function U is a natural function of extensive variables only.

Differentials

It's important to be comfortable with differentials

$$\begin{aligned}
 H &= U + PV \\
 dH &= dU + PdV + VdP \\
 dU &= TdS - PdV \\
 dH &= TdS + VdP
 \end{aligned}$$

The variation in H is written in terms of variations of S and P .

$$\begin{aligned}
 F &= U - TS \\
 dF &= dU - TdS - SdT \\
 dU &= TdS - pdV \\
 dF &= -SdT - pdV
 \end{aligned}$$

The variations in F is written in terms of variations of T and V .

$$\begin{aligned}
 G &= U + PV - TS \\
 dG &= SdT + PdV \\
 dG &= -SdT + VdP
 \end{aligned}$$

The function G is written in terms of T and P . What about U , S , and V ? In a simple system there is a need for two variables to describe the system. Pressure and temperature are partial derivatives of U . Plug these in to get a function of S and V .

Everything can be a function of everything, but unless one sticks with the natural variables, there is a loss of information.

Legendre Transformations

This is a good way to go from functions of extensive variables to conjugate variables. (p. 137 Callen)

$$\begin{aligned} f(\text{extensive}) &\rightarrow f'(\text{intensive}) \\ f(X_i) &\rightarrow f(Y_i) \end{aligned}$$

Write in conjugate intensive in the Legendre transform of U . Legendre transforms involve subtracting a conjugate pair

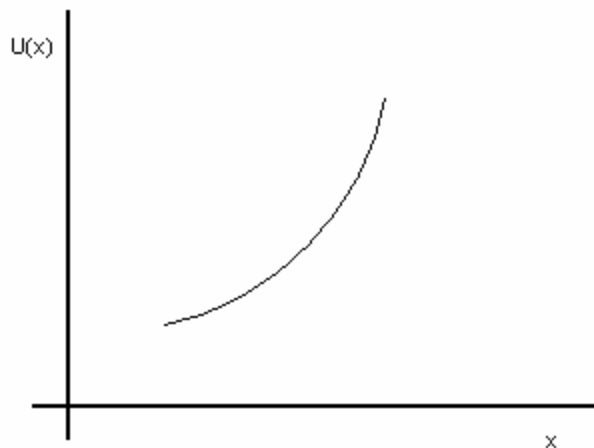
$$U(S, X_i) - Y_i X_i$$

Do this for multiple conjugate pairs and combine Legendre transforms.

$$f(S, X_{j \neq i}, Y_i) \rightarrow f(S, \text{Sum}[X], \text{Sum}[Y])$$

An example of a Legendre transform is to go from a function of S and U to a function of T and V .

If all one wanted were a function of different variables, why not solve the equation of state and plug in? The Legendre transform is the only way to preserve all the information. Consider the graph below of internal energy, a function of extensive variables.

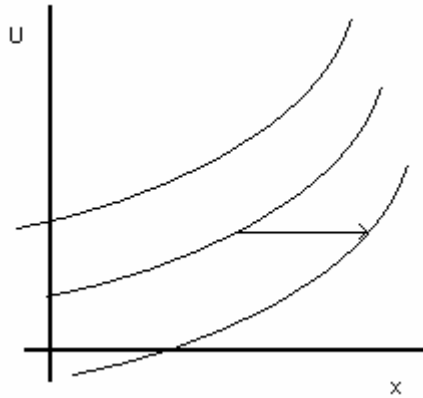


It's easy to go from $U(x)$ to $U'(Y)$, where Y is the conjugate to X , but it is impossible to go from $U'(Y)$ to $U(x)$.

$$Y = \delta U / \delta X$$

Solve $Y(x)$ for X and to create $X(y)$. Plug this expression into the function $U(x)$ to find $U'(Y)$. This is conceptually no problem, but there is a loss of information. When going

from $U'(Y)$ to $U(x)$, there is a need to solve an equation of $\delta U / \delta X$, for $U = U'(\delta U / \delta X)$. When solving the differential equation, there is an unknown integration constant. When working with multivariable equations, there could be an unknown function that results. The difficulty of transforming the function from $U'(Y)$ to $U(x)$ is shown graphically.



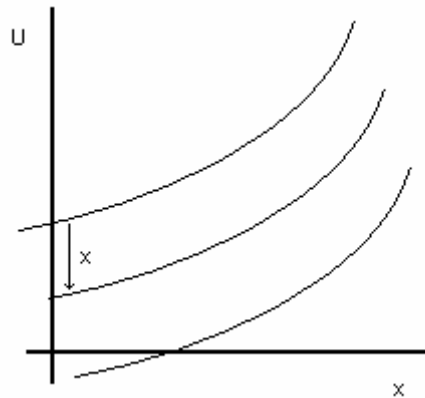
All these curves are translated and show the same relation of slope as a function of x . The relation of the local derivative and U is the same. They are translated by an integration constant.

$$U(Y) = U'(\delta U / \delta X)$$

How do you transform without losing information?

It's possible to transform functions and write anything in terms of anything, but there may be a loss of information. Knowing the value of the intercept of the function preserves information. It specifies the curve. The slope of the curve is $\delta U / \delta X$. Multiply by X to get the Legendre transform.

$$U - (\delta U / \delta X) X = U - Y X$$



Summary

- 1) The Legendre transform gives new function with some extensive variables replaced by intensive variables
- 2) If the energy is known as a function of extensive variables, everything is known. A function that has underwent a Legendre transformation contains the same information as the original function.
- 3) Different potential functions are minimized. The list of constraints is imposed by the environment, and the potential is in terms of natural variables. Internal variations are possible when there is an exchange with the environment. In the case of internal energy, there are variations of S and V . A way to optimize U is to write internal variations of the system that keep the total entropy and volume constant.

$$U(S, V)$$
$$dU = TdS - pdV$$