3.23 Lecture 7

Today is important. The formal structure of thermodynamics and the framework for the mathematical structure is set up. The first and second law is combined, and this leads to a simple structure for all thermodynamics.

The first law states that $dU = \delta W + \delta Q$. The variation of a property of a system is written in process variables, expressed in terms of other variables. Imagine traveling from state 1 to 2, both well-defined states. Pick a reversible path. The variations of dS and dX_i are well-defined and fixed between state variations, or differences in state function.

$$\delta Q = TdS$$
$$\delta W = Sum[y_i \, dX_i]$$

The equation is always true and may be written in terms of S.

$$dS = 1/T \, dU - Sum[y_i / T \, dX_i]$$

The total differential is the same along any path. Keep the general expression and write for a simple system (pdV) work.

$$dU = TdS - pdV$$

The internal energy, U, changes with S and X. Both $U(S, X_i)$ and $S(U, X_i)$ are functions of extensive variables. From these functions all of thermodynamics is known.

Differentials imply something about prefactors. The intensive variables are partial derivatives of fundamental equations.

$$U(S, X_i)$$
$$dU = (\delta U/\delta S)_{X_i} \, dS + Sum[(\delta U/\delta Xi)_{S, \, Xi \neq ?}dX_i$$

This is the differential of a multivariable function

$$dU = T \, dS + Sum[y_i \, dX_i]$$

Each term can be equated

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

The functions of T and Yi are equations of state

$$T = T(S, X_i)$$
$$Y_i = Y_i(S, X_i)$$

The intensive variables are equations of state and are a function of extensive variables. All the material properties are embedded in these equations. The input is a set of constitutive equations.

Temperature is a function of entropy and gives information about heat capacity. The derivative of the extensive property of volume and intensive quantity of pressure yield the material property of compressibility. Knowledge of all the equations of state is equivalent to knowing the fundamental equations.

$$dU = TdS - pdV$$

$$T = (\delta U/\delta S)_V$$
$$-P = (\delta U/\delta V)_S$$

The derivative of extensive quantities yields intensive quantities.

How many equations of state?

There are as many equations of state as there are conjugate pairs, differentials. This is equal to the number of work terms plus (T, S).

Ideal gas

In the equation of state of the ideal gas, there are two conjugate pairs, pdV and TdS. The two equations of state are below.

1) $pV = nRT$
2) $C_x = T (\delta S/\delta T)_x$

The functional behavior of C gives information about S and leads to the equation of state. Below is other equation of state to substitute S.

(3) $P(V, T)$

Euler relation

Following is a proof of the Euler relation

$$U = TS - Sum[y_i \, dX_i]$$

The internal energy is homogeneous of the 1st order in the extensive variables. To be homogeneous of order r means that if the variables of a function are all multiplied by λ, multiplying the function by λ^r yields the same result.

$$f(\lambda x_1, \lambda x_2, \lambda x_3, ..., \lambda x_n) = \lambda^r f(x_1, x_2, x_3, ..., x_n)$$

This is a statement of extensivity; doubling the system size doubles U. This is true in the thermodynamic limit, i.e. take the system size to be infinity. Doubling the size of a nanoparticle, though, is different than doubling the size of bulk materials.

$$U(S, Xi) = (\delta U/\delta \lambda_S)(\delta \lambda_S/\delta \lambda) + Sum[(\delta U/\delta \lambda_{Xi})(\delta \lambda_{Xi}/\delta \lambda)]$$

$$(\delta \lambda_S/\delta \lambda) = S \qquad\qquad (\delta \lambda_{Xi}/\delta \lambda) = X_i$$

Evaluate the special case where $\lambda = 1$.

$$U(S, Xi) = (\delta U/\delta S) S + Sum[(\delta U/\delta \lambda_{Xi})X_i]$$

This proves the Euler relation

$$U(S, X_i) = TS - Sum[y_i \, dX_i]$$

Simple proof of Euler Relation

The equation of internal energy is a first order homogeneous equation.

$$U(\lambda S, \lambda X_i) = \lambda U(S, X_i)$$

Start from differential and integrate. Integrate from nothing to the end state. Grow system along a path, and the intensive variables stay constant along the integration path.

$$dX_i = X_i \, d\lambda$$
$$dS = S \, d\lambda$$

$$Integration[dU] = Integrate[T \, dS] + Integrate[Sum[y_i \, dX_i]]$$

dS integrated from 0 to S
dX integrated from 0 to Y

$$U = TS - Sum[y_i \, dX_i]$$

How many independent variables are needed to characterize a thermodynamic system?

Remember that there is a distinction between variables and parameters.

How many variables are independent? The equations of state couple variables. Two variables are needed in the case of an ideal gas to characterize a thermodynamic system. There are two equations of state, and below are variables

T, P, V, S or U

The number of conjugate pairs, or the number of work terms plus one, is needed to characterize the system. There are n equations of state and $2n - n$ conjugate pairs.

S as fundamental scheme

$$dS = 1/T \; dU - Sum[y_i / T \; dX_i]$$

There are two conjugate pairs (the term Y_i/T is one variable)

$$(1/T, \; U) \quad (Y_i/T, \; X_i)$$

Define the equations of state

$$1 / T = (\delta U/\delta S)_{Xi}$$
$$Y_i / T = (\delta S/\delta X_i)_{Xi \neq ?}$$

The entropy scheme is useful in statistical mechanics. There is a cleaner parallel between statistical mechanics and thermodynamics. The Boltzman factor is from the entropy scheme.

The Euler equation leads to all equations of state. Knowledge of one equation of state does not lead to the fundamental equation. The result of integrating a partial differential equation with a given expression of T is known up to an unknown function of volume.

$$T(S, \; U) = (\delta U/\delta S)_{Xi}$$
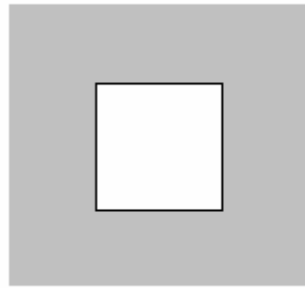$$U = Integrate[T(S,U)dS] + constant \; (or \; function)$$

Both partial derivatives are needed

$$-P = (\delta U/\delta V)_S$$

The function $-P(S, \; V)$ is obtained after differentiating the integral and plugged into the expression $-P = (\delta U/\delta V)_S$.

How are conditions of equilibrium defined?

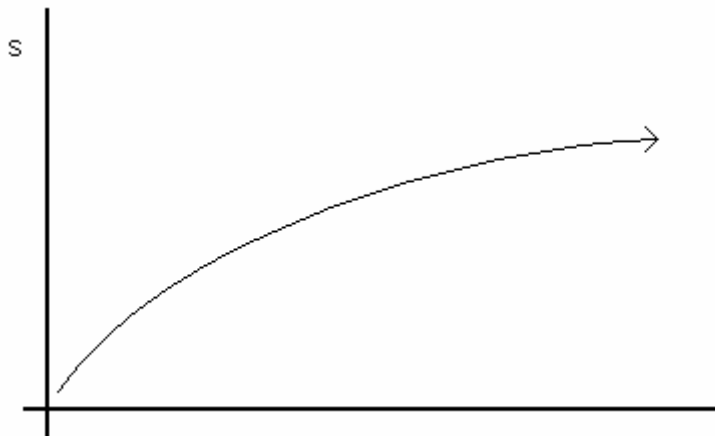An isolated system is isolated from the environment and the extensive variables are constant.

simple system, rigid box, insulated
Xi -- > constant

The evolution law for the system defines equilibrium

$$dS \geq 0$$

Plot entropy as a function in variable space. The max of entropy is the equilibrium point.

To find equilibrium, look for the maximum of S. A source of confusion is related to what is being maximized over. All state variables are constant.

The distribution is minimized or maximized. There are many internal states within 1 m^3. There are many thermodynamic states with given boundary conditions. There are many ways to realize the thermodynamic states; for instance, there could be a constraint of ten moles, and ten moles could be distributed many different ways. The one with maximum entropy is the equilibrium state. In summary, the set of thermodynamic states consistent with the boundary conditions and external constraints on the system are maximized over.

What is a thermodynamic state?

A thermodynamic state is an equilibrium state that can be achieved for some value of constrained extensive variables. The states that are allowed to be passed through are those states that can be equilibrium states under some constraint.

An object held in the hand is not an equilibrium state, but it is an allowed thermodynamic state. Change the state and it would be an equilibrium state.

In a discontinuous process, the system does not go through equilibrium states. A quasi-static process involves passing through a series of equilibrium states.

What to maximize over

Imagine a system with an adiabatic partition. There are A atoms on one side and B atoms on the other. The partition can slide to the left or to the right, and the goal is to find the equilibrium state, the state where there is maximum entropy.
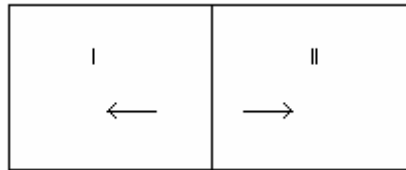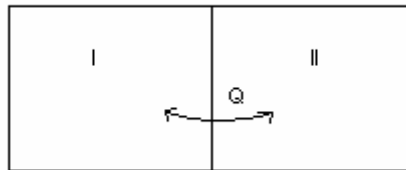

The total entropy is a sum of the entropy in the two compartments

$$S_{tot} = S_I(U_I, V_I) + S_{II}(U_{II}, V_{II})$$

Mathematically optimize where $V_I + V_{II} = V_{Tot}$.

Imagine another scenario, where a partition is fixed and through which heat can flow. Find where there is maximum entropy.

A system can pass through phases. With a constraints of U and V, look at the entropy of both phases. The highest entropy is associated with the equilibrium state.

There can be flow of any extensive variable. Look at the distribution of A. Maximize under the condition of constrained extensive variables.
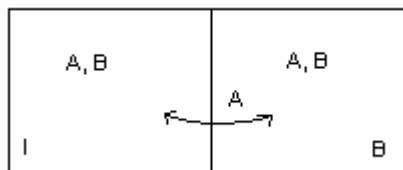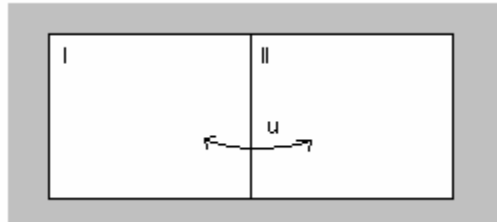
Equilibrium is given by the maximization of the entropy function.

$$S(U_i, X_i) \rightarrow \max S(U, X_i, \text{internal distribution})$$

It's not easy to constrain energy, and the condition of constant entropy is tough.

Thermo equilibrium

Imagine a fixed divider that allows energy through. Maximize the entropy of the system

$$dS_{tot} = dS_I + dS_{II}$$
$$dS = 1 / T \, dU + P/T \, dV$$

Write the variation in terms of allowed flows. In each subsystem there is no dV.

$$dS_{tot} = dU_I / T_I + dU_{II} / T_{II}$$

$$dU_I = - dU_{II}$$

$$dS_{tot} = dU_I (1 / T_I - 1 / T_{II})$$

Unless the factor is zero, the entropy can increase, and the system is not in equilibrium. It would be possible to do an internal variation of the system and make the entropy increase, and the system would evolve to that state. Only when $1 / T_I = 1 / T_{II}$ is $dS = 0$. This proves that if there is a wall that lets heat through the temperature will become the same.

Mechanical equilibrium

Imagine a partition that can move and is diathermal
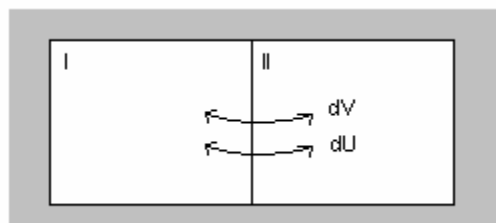
$$dS_{tot} = dS_I + dS_{II}$$

Write dS as a change in dU and dV.

$$dS = dU / T + P / T \, dV$$
$$dS_{tot} = (1 / T_I - 1 / T_{II}) \, dU_I + (P_I / T_I - P_{II} / T_{II}) \, dV_I$$

The variations of temperature and pressure are independent.

$$T_I = T_{II} \qquad\qquad P_I / T_I = P_{II} / T_{II}$$
$$P_I = P_{II}$$

If the wall can move, the pressures must be the same. What if the partition allows only dV? This is the case of distributing the volume without modifying the internal energy. This is mathematically possible but perhaps not meaningful.

In any allowed flow, such as the distribution of mass, look for maximum entropy.

Systematic method of finding equilibrium

Write dS_{sys} in terms of variations of free internal conditions and set $dS_{sys} = 0$. The consequences are simple. It is found that the external quantity flows and that the intensive variable must be homogeneous. If U can flow, the temperature must be homogeneous. If U and V can flow, T and P are homogeneous. If the charge can flow, the potential is homogeneous. If mass can flow, the chemical potential $\mu_i = (\delta U / \delta N_i)$ becomes homogeneous. Wherever there is an extensive flow, the intensive variable is homogeneous at all parts.

Consider what happens when flows are coupled and not free to flow independently, such as the flow of mass and volume or charge and mass.