

Lecture 8: 10.05.05 Fundamental Equations; Equilibrium and the Second Law

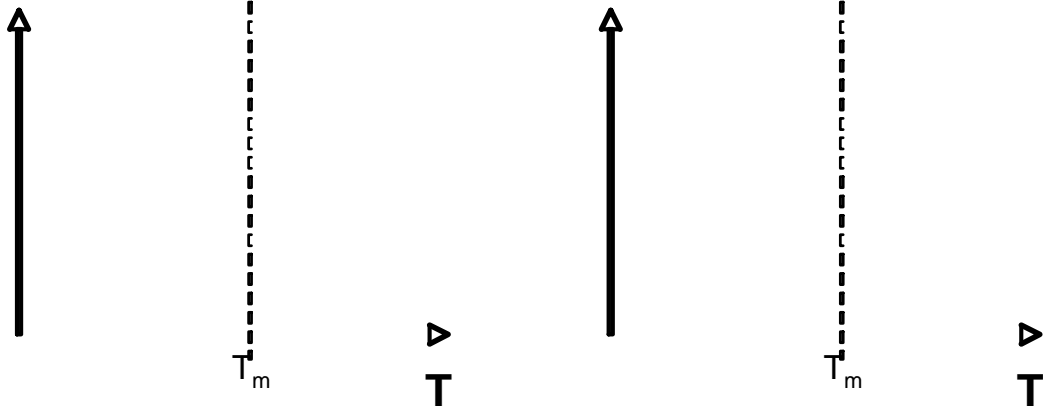
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Reading: Engel and Reid Ch. 5.1-5.8

Supplementary Reading: Dill and Bromberg, Ch. 9 'How to Design a Fundamental Equation,' pp. 153-155

Last time



Thermodynamic driving forces: Writing a fundamental equation

What goes into internal energy?

- When we introduced the concept of work, we stated that every form of work can be thought of as a generalized thermodynamic force acting to create some generalized 'displacement' in the system. In a similar way, we said that temperature can be thought of as a thermodynamic force that causes a 'thermal displacement' which is the change in entropy of the system:

- The internal energy, which sums the contributions from these two terms, can be written as a perfect differential depending on S and V :

The 'natural' variables of state functions

- Why do we write $U = U(S, V)$? Why not $U = U(T, V)$? The answer will unfortunately not be clear until we introduce the second law. The second law dictates that certain thermodynamic functions will reach extrema (maximima or minima) when the system is at equilibrium- e.g. the entropy will be maximized at equilibrium. When U and S are written as function of S, V and U, V respectively, they are said to be written in terms of their **natural variables**. State functions of natural variables have extremum principles at equilibrium (they will be maximized or minimized at equilibrium). In other words, the reason we write U as a function of S and V is that it is the most useful form to write internal energy equations for most problems- we can use this equation for internal energy to calculate equilibrium properties.

Generalized expression for the internal energy: internal energy of open systems

- The first law expression above only applies to very simple thermodynamic systems- which can undergo only hydrostatic work and have no transport or chemical transformation of components. Extending our first law expression is straightforward for any thermodynamic case where other forms of work are important. It is useful to think of the differential as a sum of different forms of internal energy:

The fundamental equation for the entropy

- In a completely analogous manner to the approach described above for identifying driving forces in the internal energy, we can write a differential expression for the entropy in a system with chemical work: One way to obtain the fundamental equation for entropy is to simply rearrange the fundamental equation for internal energy:

$$dS = \left(\frac{\partial S}{\partial U} \right)_{V,n} dU + \left(\frac{\partial S}{\partial V} \right)_{U,n} dV + \sum_{i=1}^C \sum_{j=1}^P \left(\frac{\partial S}{\partial n_i^j} \right)_{U,V,n_{\text{others}}} dn_i^j$$

- The thermodynamic forces **from the point of view of entropy** are:

- This equation and the fundamental equation for internal energy are called 'fundamental' because they completely specify all changes that can occur in a simple thermodynamic system. They will be used as the basis for applying the second law of thermodynamics to identify the equilibrium state of a given system.

- The fundamental equation for entropy contains the **same** information as the fundamental equation for internal energy. We derive the fundamental equation for entropy from the fundamental equation for internal energy, which is in turn derived from the first law. We can theoretically use EITHER form of the fundamental equation to solve problems- we simply CHOOSE the form (internal energy point of view, or entropy point of view) that is easier to solve for a given problem. We will see why one is easier than the other in certain situations next time.

Introduction to the second law

- Thusfar, we have discussed thermodynamic functions that characterize a system, such as the enthalpy, entropy, and heat capacity. We have seen how to make calculations of these quantities from measurable quantities. However, in these calculations we have been limited to analyzing processes whose spontaneous behavior we take as a given - we have not yet made *predictions* of what processes will occur. We have quantified thermodynamic properties at a first-order phase transition, but we have not yet provided the tools to predict where a phase transition will happen in P,T,V space. We will fill this gap with the second law of thermodynamics, which provides the theoretical tools to make predictions and assess the stability of materials- allowing us to predict when materials will undergo spontaneous transformations.

Statements of the second law

- The second law is a rule that governs which way a system will tend to change in order to reach equilibrium, and identifies the criterion for an equilibrium state. **There are numerous ways to formulate a statement of the second law, and we list here several of the simplest, most useful ways of stating it:**
 - **These statements can be shown to be equivalent.** Note the repeated use of the word spontaneous: A spontaneous process is one that will occur under a given set of conditions without any additional external forces acting on the system.
 - The final formulation can also be readily written as a mathematical rule:

- Consider the figure below, a 3D plot of entropy vs. internal energy and volume for some material system. The second law graphically implies that any spontaneous process moves uphill on the entropy surface:

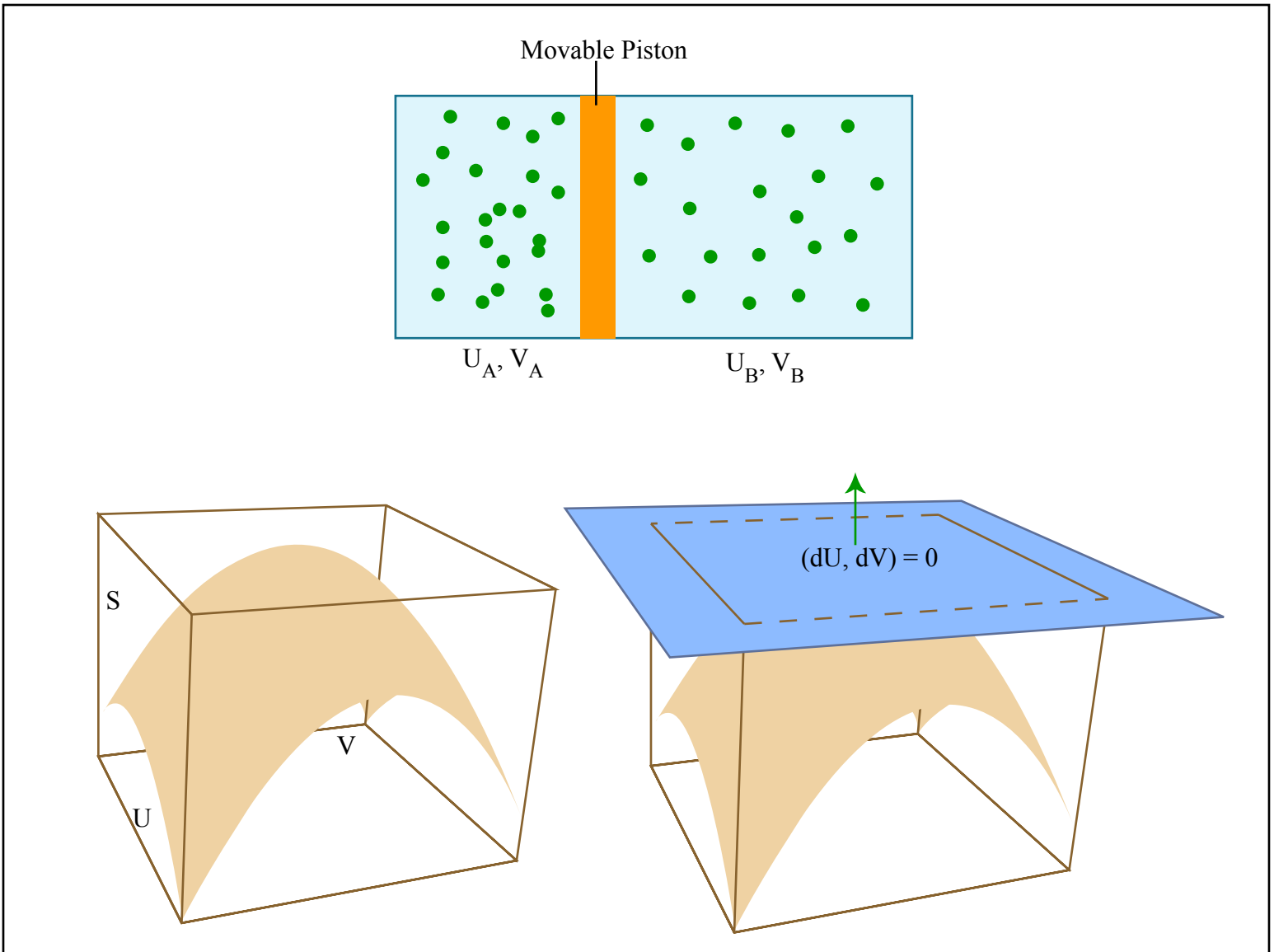


Figure by MIT OCW.

- **The equilibrium point must sit at the apex of maximum entropy.**
- An alternative mathematical criterion that encompasses this graphical description is called the variational statement of the second law:
 - Stated in words, at equilibrium, any small change to the state of the system that induces a small change in the entropy must *lower* the entropy of the system.

Applying the second law

- The second law provides a criterion we can combine with the fundamental equations to identify equilibrium states for isolated systems: the entropy must be maximized for a given internal energy and volume (or equivalently, the internal energy must be minimized for a given total entropy and volume).

Heat flows from hot objects to cold objects

- In lecture 4 we discussed the relationship between heat, temperature and entropy. These three quantities are related by $dS = dq_{\text{rev}}/T$. In our discussion of heat and temperature so far, we have taken one fact of common experience for granted: if we place a hot material in contact with a colder material, heat will pass from the hot object to the cold one and raise its temperature. *The second law is an axiom that says this is what will always happen.* Let's show how the second law predicts that heat always flows from hot to cold:

Thermal equilibrium

- Our example of heat transfer between metal blocks above showed how the second law predicts heat flow. Such spontaneous heat transfer is also a fact of common experience. But a question remains- when will heat transfer stop? In other words- when is the system at equilibrium? What state will blocks A and B be in once equilibrium is reached?
 - Question: Does the zeroth law provide the answer?

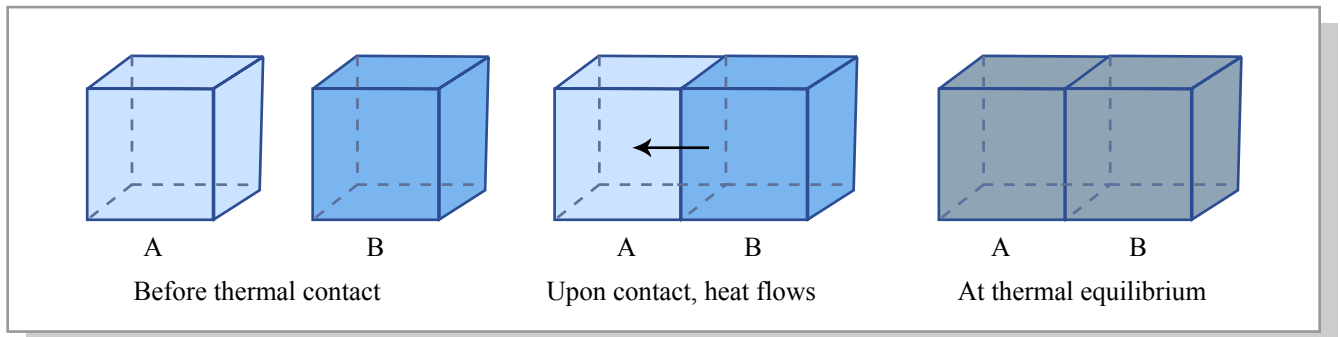


Figure by MIT OCW.

- What is the condition of A and B when the point of maximum entropy is reached?
 - To answer this question, we will use the fundamental equation for the entropy and the second law. In the first example, the temperature of the two blocks was assumed to remain unchanged by the transfer of heat. However, we now want to consider the case where the heat transferred does influence the temperature of block A and block B.

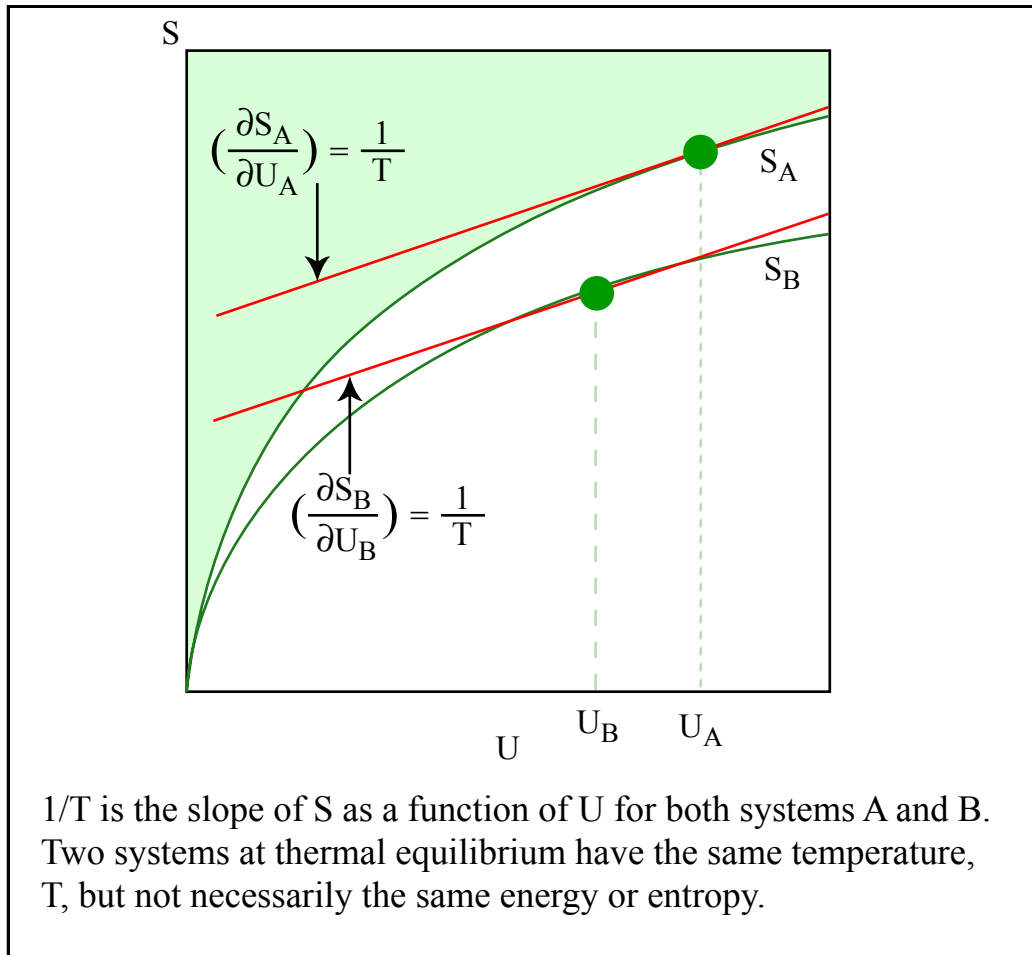


Figure by MIT OCW.

Other equilibria

- The second law can be applied to define the conditions for equilibrium for any arbitrary system. Our next step is to introduce the Gibbs free energy, which is a state function useful for determining equilibrium in the most common type of experimental system: one where the pressure and temperature are maintained at a constant value.

The internal energy at equilibrium

- The principle of **maximizing entropy** at equilibrium can be shown to be equivalent to **minimizing the internal energy with the entropy of the system held constant**. Graphically:

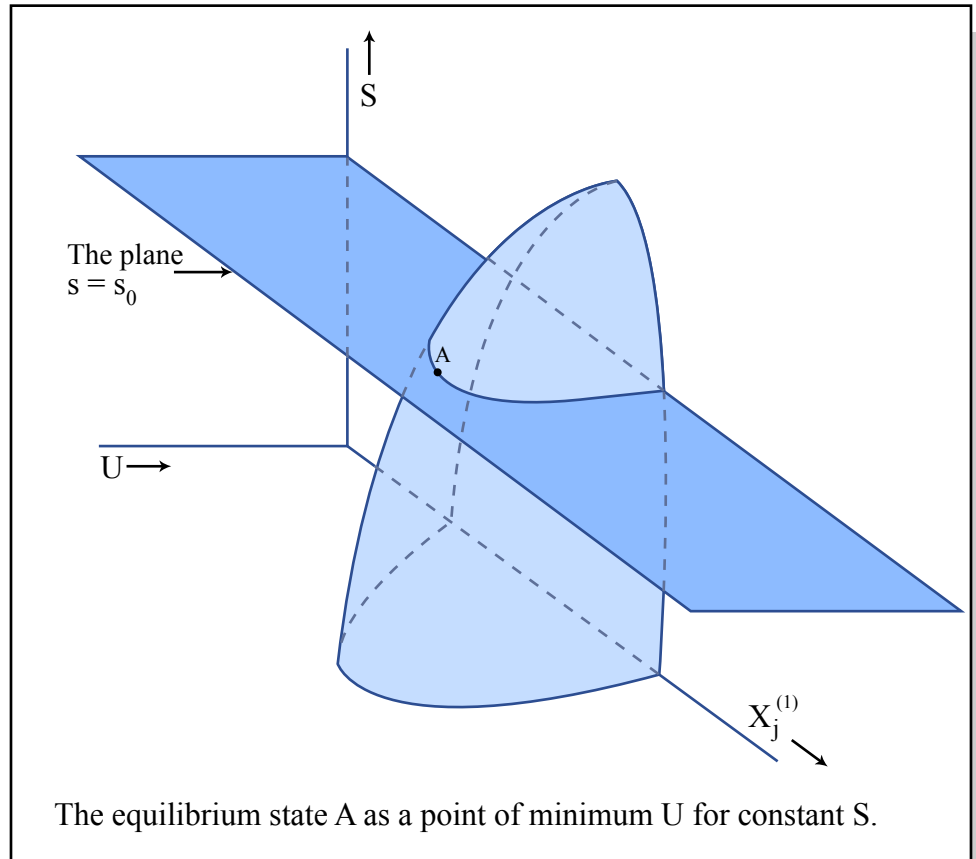


Figure by MIT OCW.

- Minimization of internal energy at constant total entropy is a mathematical consequence of the relationship between internal energy and entropy. We won't go through the proof here, but you can read through a short proof of it in the supplementary reading from Callen.
 - Because the absolute temperature T is always positive, and $\left(\frac{\partial U}{\partial S}\right)_{V,N} = T$, the variational statement of the second law translates to a variational statement for the internal energy at equilibrium:
 - The internal energy reaches a **minimum** at equilibrium.

References

1. Carter, W. C. (2002).
2. Dill, K. & Bromberg, S. *Molecular Driving Forces* (New York, 2003).
3. Callen, H. B. *Thermodynamics* (Wiley & Sons, New York, 1960).