Lecture 21: 11.22.05 Two Postulates of Statistical Mechanics and the Microscopic Definition of Entropy

Today:

**Reading:**   Engel and Reid 31.1-31.4

Supplementary Reading:

Last time

A simple model: the Einstein solid

- Our introduction to the connection of thermodynamic quantities to microscopic behavior begins by considering a simple model of a monoatomic crystalline solid- *models of materials are the starting point for statistical mechanics calculations*.

- **Suppose for definiteness we have a crystalline solid:** As a model for how this material behaves in response to temperature, we propose that the most important degree of freedom available to the atoms to respond to thermal energy is vibration of the atoms about their at-rest positions.

  - The bonding between atoms creates a potential energy well in which the atoms are centered at their at rest position. Oscillations of the atoms about the at rest position can be induced by thermal energy in the material. The potential is called a *harmonic potential* because of its shape- similar to the potential of a spring in classical mechanics. Because the oscillation of the atoms is constrained by bonding to center about their at-rest positions in the crystal lattice, the energy of vibration for each atom is quantized:
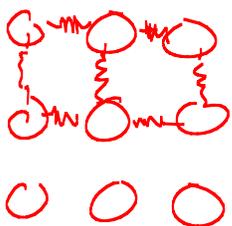
Model for a 3-atom solid as 1D harmonic oscillators

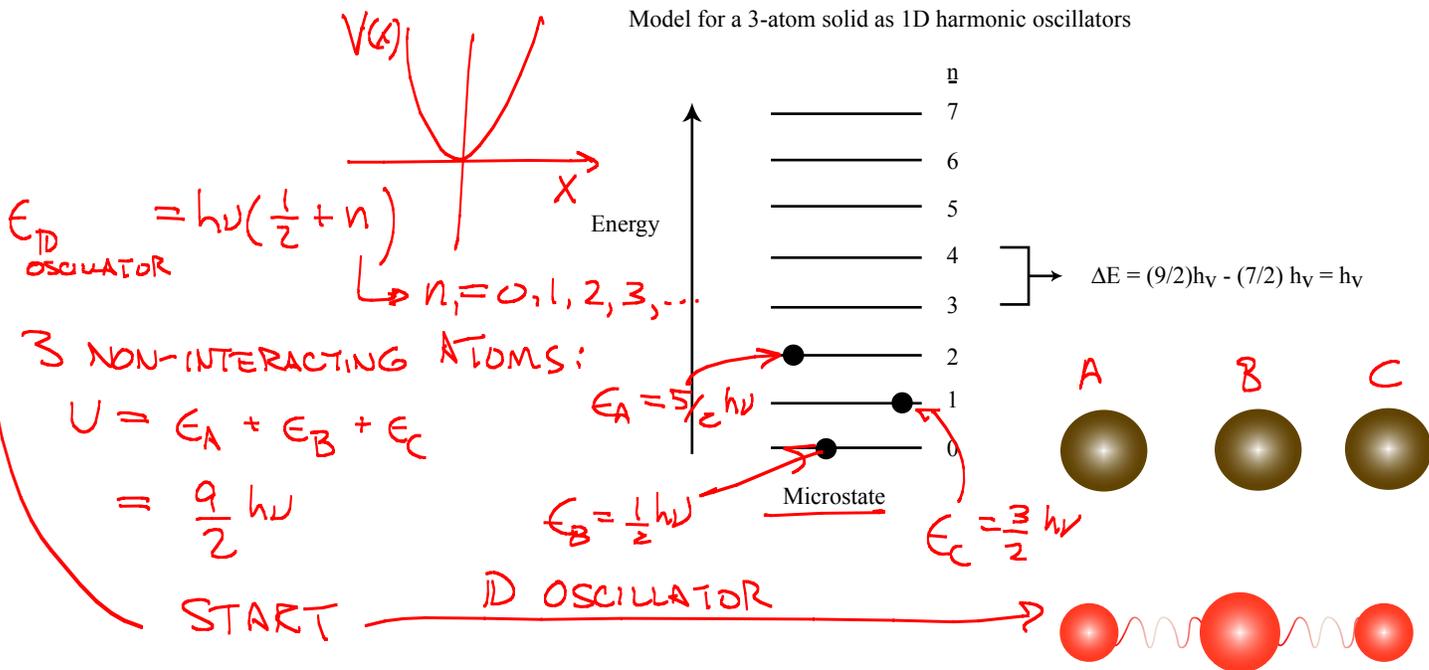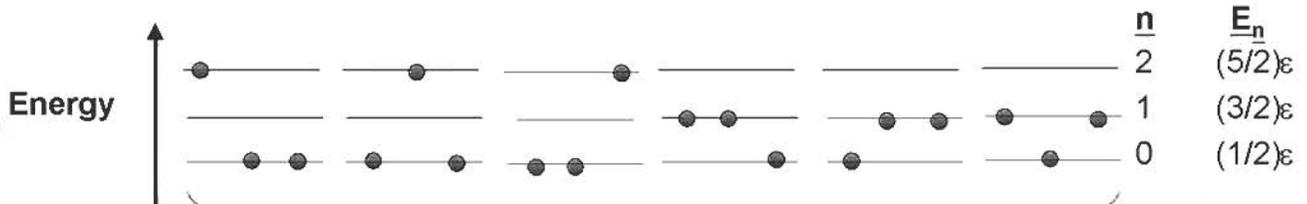Model for a 3-atom solid as 1D harmonic oscillators

$$\epsilon_{1D\ oscillator} = h\nu\left(\frac{1}{2} + n\right)$$

$$n_i = 0, 1, 2, 3, \ldots$$

3 NON-INTERACTING ATOMS:

$$U = \epsilon_A + \epsilon_B + \epsilon_C$$

$$= \frac{9}{2} h\nu$$

$$\epsilon_A = \frac{5}{2} h\nu$$

$$\epsilon_B = \frac{1}{2} h\nu$$

$$\epsilon_C = \frac{3}{2} h\nu$$

START — 1D OSCILLATOR

$$\Delta E = (9/2)h_\nu - (7/2)\,h_\nu = h_\nu$$

Energy

Microstate

Figure by MIT OCW.

- …where *h* is Planck's constant ($h = 6.62 \times 10^{-27}$ gm cm^2 sec^{-2}) and ν is the frequency of the atomic vibrations. The total energy of the solid is the sum of the individual energies of each oscillator:

Microstates in Isolated Systems

CONSIDER AN ISOLATED SYSTEM. WHAT CAN I SAY ABOUT U? <u>FIXED</u>

3 - ATOMS :   Let $E_{total} = (7/2)\varepsilon$. $\hookrightarrow \varepsilon = h\nu$

						$\underline{n}$	$\underline{E_n}$
						2	$(5/2)\varepsilon$
						1	$(3/2)\varepsilon$
						0	$(1/2)\varepsilon$

Energy

PERMUTATIONS ⟶ **6 possible microstates** $= \Omega = $ POSSIBLE # MICROSTATES

- o The total number of allowed microstates is a parameter we will refer to again and again; we give it the symbol Ω. For the system above, $\Omega = 6$. The collection of all Ω microstates for a given system is called its ***ensemble***. (For the case of a system with fixed (E,V,N) it is referred to as the ***microcanonical ensemble***).

Distinguishable vs. indistinguishable atoms/particles

- Two cases arise in modeling real systems: one where we can identify each atom uniquely, and the case of atoms being identical and indistinguishable.

<u>DISTINGUISHABLE</u> MOLECULES :   e.g., CRYSTALLINE SOLID → UNIQUELY EACH ATOM BY ITS POSITION IN LATTICE (x, y, z)

CONSIDER <u>ALL</u> MICROSTATES ⟹ Ω

INDISTINGUISHABLE MOLECULES :   e.g., GAS MOLECULES IN A CONTAINER

<u>ONLY</u> CONSIDER <u>UNIQUE</u> MICROSTATES (STATES) ⟹ W = # STATES   W ≪ Ω

- If we had indistinguishable atoms, then we would only be able to observe the unique microstates, whose number is given the symbol W:

W = 2
Unique states: **j=1**   **j=2**

Energy

$\Omega_1 = 3$ $\Omega_2 = 3$
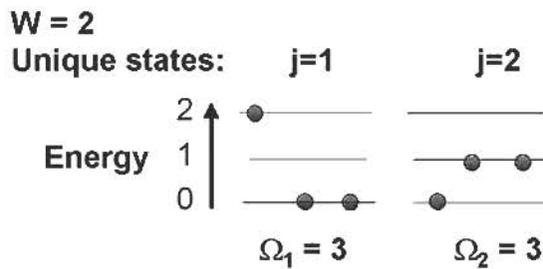
$\Omega = \Omega_1 + \Omega_2 = 6$ total microstates

TYPICAL CASE !

ENSEMBLE = COLLECTION OF POSSIBLE STATES

- o We have collected the individual microstates now into 2 groups characterized by the number of atoms in each energy level (n_0, n_1, and n_2). We will call the set of microstates that has a given set of occupation numbers a **state** (as opposed to microstate). The total number of **distinguishable** states is W.

- For our overly-simplified 3-atom model with a low total energy of $E_{total} = (7/2)\varepsilon$, the number of distinct arrangements is small. However, for a material containing a mole of atoms at room temperature, the number of possible ways to occupy the available energy levels is enormous. Thus, rather than writing diagrams of all the possible microstates, we become concerned with the probability of finding a certain set of microstates *j* in the ensemble that have a given distribution of the atoms among the energy levels.

2 POSTULATES FORM THE BASIS OF STAT. MECH;

The first postulate of statistical mechanics

- The first postulate of statistical mechanics tells us the frequency of each of the possible states or microstates occurring in the ensemble:

$\boxed{I}$ IN AN ENSEMBLE WHERE Ω IS VERY LARGE AT FIXED (U, V, N), EACH ALLOWED MICROSTATE IS EQUALLY PROBABLE.

↳ # MOLECULES

- This postulate is often called the *principle of equal a priori probabilities*. It says that if the microstates have the same energy, volume, and number of particles, then they occur with equal frequency in the ensemble.

- o This postulate tells us what the p_j's for the two states in our 3-atom $E_{total}=7/2\varepsilon$ system are:
  - We have a total of W = 2 states, (3 microstates in each of the two unique states j=1, j=2). Thus the probability for each state is:

SUPPOSE OUR 3 OSCILLATORS ARE INDISTINGUISHABLE:

PROBABILITY OF EACH STATE $= P_j = \dfrac{1}{W}$

W = 2

Unique states: j=1   j=2
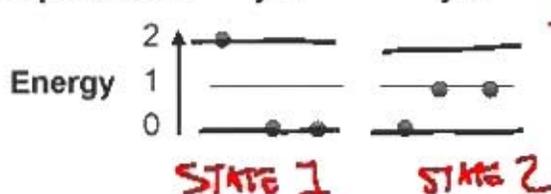
$\rightarrow P_1 = \dfrac{1}{W} = \dfrac{1}{2}$

$P_2 = \dfrac{1}{W} = \dfrac{1}{2}$

STATE 1   STATE 2

  - Each state has a frequency of 50% in the ensemble.

The second fundamental postulate of statistical mechanics[7]

The second postulate connects ensemble averages to measured thermodynamic quantities

- Statistical mechanics makes one postulate that connects the energy-level model of a material to its macroscopic thermodynamic properties:

> **II.** THE ENSEMBLE AVERAGE OF A THERMODYNAMIC PROPERTY IS EQUIVALENT TO THE TIME-AVERAGED MACROSCOPIC VALUE OF THAT PROPERTY FOR THE 'REAL' SYSTEM.

- What it means:
  - The postulate tells us that we can calculate the thermodynamic properties of a material if we have a model that provides us with a way to describe the possible microstates of the system. **As we make a measurement on the real system, we might imagine the atoms in the system undergoing thermal fluctuations that allow the system to rapidly fluctuate between the many microstates of our model, making the time average measurement on the real system equivalent to averaging the property in our ensemble of microstates in the model.**

  - Note that though we drew a 'mini-ensemble' for our 3-atom imaginary solid above, the postulate rigorously holds only when the number of microstates possible is very large. Fortunately, this will always be the case in models of real materials containing N_{Av} numbers of atoms!

Taking averages in the ensemble:

  - To take an average over the microstates of the ensemble, we assume we have determined the probabilities of each microstate p_j. Then the average of some quantity X is given by:

$$\text{ENSEMBLE AVERAGE OF } X = \langle X \rangle = \sum_{j=1}^{W} p_j X_j$$

VALUE OF X IN STATE j

PROBABILITY OF STATE j

  - Where X_j is the value of the property X in microstate j. The second postulate further states that the average property over the ensemble is equivalent to the measurable thermodynamic quantity in a real system. Thus, for example, if we want to calculate the thermodynamic pressure:

$$P = \langle P \rangle = \sum_{j=1}^{W} p_j P_j$$

PRESSURE

The second postulate applied to a fixed (E, V, N) system

- We now have what we need to make thermodynamic calculations for our collection of harmonic oscillator atoms at fixed total energy. Suppose we fix the total energy of the 3-atom ($N = 3$) harmonic oscillator solid to a value $E = (7/2)\hbar\omega$. Applying the postulates to the 3-atom harmonic oscillator solid, we can predict the thermodynamic energy:

o The allowed microstates are sketched in the ensemble above. We have a total of $\Omega = 6$ allowed microstates that fit the constraints. First, applying the first postulate, we know the probability of each of the allowed states is $p_1 = p_2 = 1/2$.

o Applying the second postulate, the thermodynamic internal energy is:

W = 2
Unique states: j=1   j=2

Energy 2
        1
        0

$$p_1 = \frac{1}{2} \quad p_2 = \frac{1}{2}$$

$$U = \langle E \rangle = \sum_{j=1}^{W} p_j E_j$$

$$= p_1\left(\frac{7}{2}\epsilon\right) + p_2\left(\frac{7}{2}\epsilon\right)$$

$$= \left(\frac{1}{2}\right)\left(\frac{7}{2}\epsilon\right) + \left(\frac{1}{2}\right)\left(\frac{7}{2}\epsilon\right) = \frac{7}{2}\epsilon$$

• This result is trivial since we fixed the total energy $E_{total} = (7/2)\epsilon$, but it gets interesting when we consider the more practical situation of a system held at fixed temperature instead of fixed energy. We'll tackle this next, after we introduce the microscopic definition of entropy.

KEY CONCEPT: Two postulates that form the basis of statistical mechanics

1. When U, V, and N are fixed, each allowed microstate is equally probable.
2. The ensemble average of a thermodynamic property is equivalent to the time-averaged macroscopic value of the property measured for the real system.

The microscopic definition of entropy

- We have now seen that we can use an ensemble, a collection of all possible microstates accessible to the molecules/atoms of a material, to determine thermodynamic properties of a system. Because the number of microstates is related to the number of degrees of freedom in the material (e.g., how many energy levels can be accessed), we might expect the number of microstates, Ω, to be related to entropy- and in fact, it is directly related to entropy.

- Ludwig Boltzmann sought to connect entropy to the quantum mechanical picture of molecules, and found an answer in the following simple expression that connects the entropy to the probabilities of each state:

$$S = -k_b \sum_{j=1}^{W} p_j \ln p_j$$

$k_b = \text{BOLTZMANN'S CONSTANT}$

$$= \frac{R \text{ (GAS CONSTANT)}}{N_{AV} \text{ (AVOG. \#)}} = \left[\frac{J}{K}\right]$$

- This is equivalent to the famous expression:

$$S = k_b \ln W$$

$$(\text{INDISTINGUISHABLE MOLECULES})$$

$$\left[S = k_b \ln \Omega \quad \text{DISTING. MOLECULES} \right]$$

Image removed for copyright reasons.
Photo of Boltzmann's gravesite. Source: http://www.famegraves.com/graves/Vienna/boltzmann.html

- Here S is the entropy of the system, k_b is Boltzmann's constant ($k_b = R/N_{Av}$ the ideal gas constant/Avogadro's number) and Ω is the number of microstates available to the system.

- We can show the equivalence of (Eqn 5) and (Eqn 6) easily for the case of the microcanonical ensemble (a system with fixed (E, V, N)): The probabilities $p_i = 1/W$ in the microcanonical ensemble, therefore:

$$S = -k_b \sum_{j=1}^{W} p_j \ln p_j = -k_b \sum_{j=1}^{W} \ln p_j^{p_j} \underset{\underset{\text{ISOLATED}}{\uparrow}}{=} -k_b \sum_{j=1}^{W} \ln\left(\tfrac{1}{W}\right)^{\left(\tfrac{1}{W}\right)}$$

$$= -k_b \left[\ln\left(\tfrac{1}{W}\right)^{\left(\tfrac{1}{W}\right)} + \ln\left(\tfrac{1}{W}\right)^{\left(\tfrac{1}{W}\right)} + \dots \right] = -k_b \, W \ln\left(\tfrac{1}{W}\right)^{\left(\tfrac{1}{W}\right)}$$

$$\underbrace{\qquad\qquad\qquad\qquad}_{W \text{ TERMS}}$$

$$= -k_b \ln\left(\tfrac{1}{W}\right) = \boxed{k_b \ln W = S}$$

- That (Eqn 6) is the correct expression for the entropy in statistical mechanics can be shown rigorously, but we will forgo this more involved derivation here for the sake of time (you can see one derivation, for example, in Chapter 1 of Hill[1].)

Testing the microscopic definition of entropy

- This simple definition is full of physical meaning for the nature of entropy. Let's compare the behavior of $k \ln \Omega$ with the required behavior of the classical thermodynamic quantity S.

Entropy is an extensive quantity

- The statistical mechanical definition of entropy is extensive, just like S. To see this, consider how many states are available to a material formed by combining material A having Ω_A different microscopic states with material B having Ω_B microscopic states:
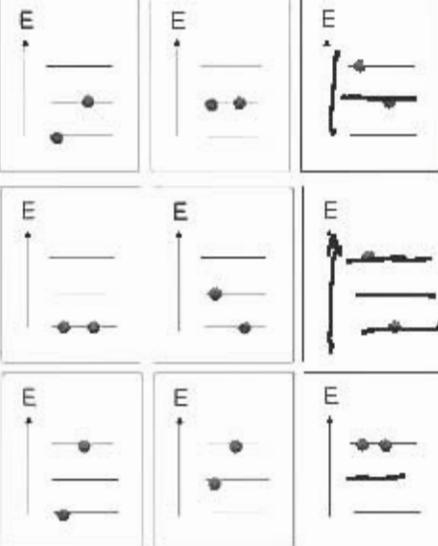
System A   System B   System (A + B)
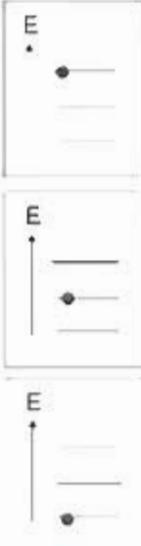
$$S_{A+B} = S_A + S_B$$

$$S_A = k_b \ln \Omega_A$$

$$S_B = k_b \ln \Omega_B$$

$$S_A + S_B = k_b \left(\ln \Omega_A \Omega_B \right)$$

$$= k_b \ln \Omega_{A+B}$$

$$= S_{A+B}$$

$$\Omega_A = 3 \qquad \Omega_B = 3 \qquad \Omega_{A+B} = 9$$

Lecture 22 – Connectiing molecular events t   u

Entropy increases with increasing energy

$\bar{S}$ ↑ $\top$ S ↑ $\left(\dfrac{\partial S}{\partial U}\right) = T$
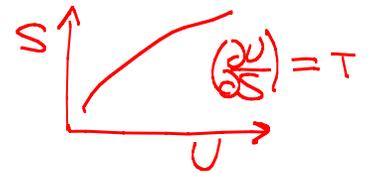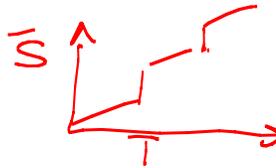
- Entropy increases with E
  - Like the thermodynamic function entropy, $k\ln \square$ and $k\ln \Omega$ increase with increasing energy in a model system. Consider our 3-atom solid once again:

$\underline{n_{TOTAL}} = n_A + n_B + n_C$ (DISTINGUISHABLE)   A   B   C

E_{total}/ε	Ω
3/2	1
5/2	3
7/2	6
9/2	10

0
1
2
3

Energy

E ↑ ε ↑

Figure by MIT OCW.

Ω **S = k$_b$ln Ω**   SLOPE $= \dfrac{1}{T}$

SLOPE → $+\infty$
$(T \to 0)$

n_{total}, E_{total} n_{total}, E_{total}

U
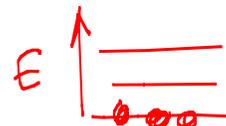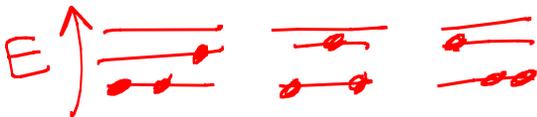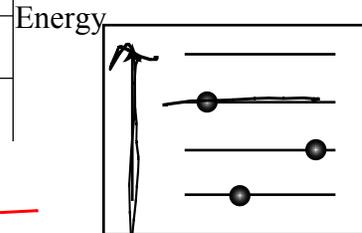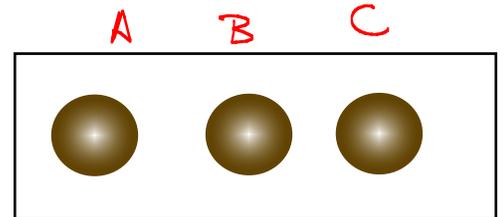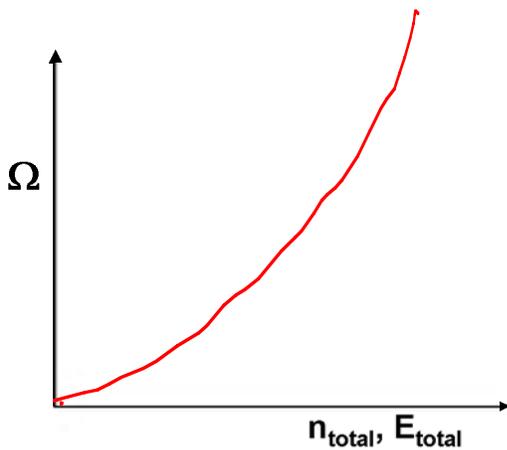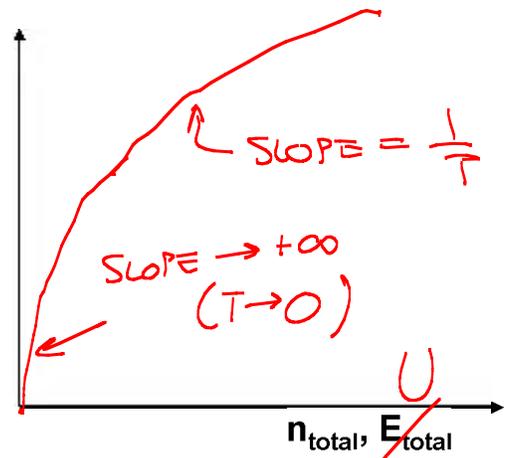
- The derivative is always positive like T

The first postulate satisfies the second law

- Just as the second law dictates the equilibrium *macrostate* in classical thermodynamics, the second law dictates what *microstates* the system will reside in at equilibrium:
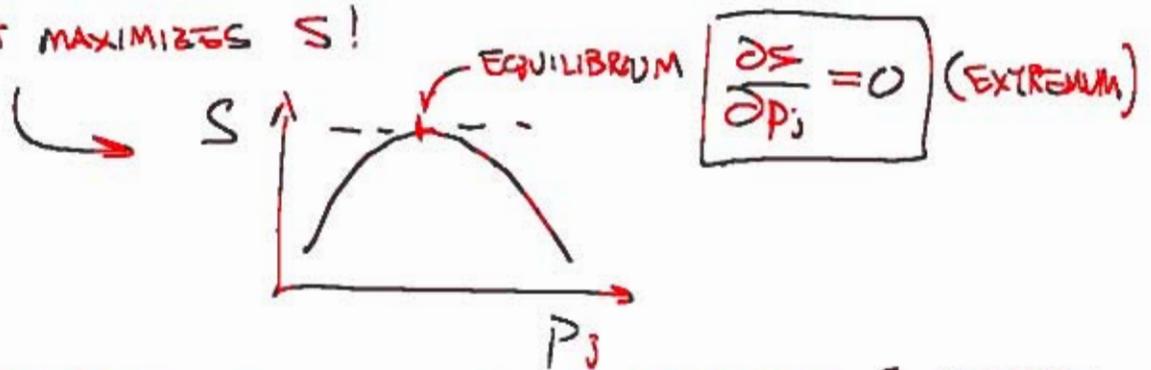
SECOND LAW! S MAXIMIZED AT EQUILIBRIUM!

TO DEFINE EQUILIBRIUM,

WHAT ARE p_j'S?

THE EQUILIBRIUM STATE OF SYSTEM WILL HAVE A SET OF p_j'S

THAT MAXIMIZES S!

EQUILIBRIUM $\boxed{\dfrac{\partial S}{\partial p_j} = 0}$ (EXTREMUM)

TO FIND EQUILIBRIUM: CHOOSE $[p_j]$ THAT MAXIMIZE S, SUBJECT
TO THE CONSTRAINT THAT $\sum\limits_{j=1}^{W} p_j = 1$.

METHOD OF LAGRANGE MULTIPLIERS

$$\frac{\partial}{\partial p_j}\left(S - \alpha\left(\sum_{j=1}^{W} p_j\right)\right) = 0 \qquad \text{FOR EVERY STATE } j \\ (W \text{ EQUATIONS})$$

LAGRANGE MULTIPLIER
(CONSTANT)

The Boltzmann factor and Partition function

- Last time, we began the process of determining the probabilities of microstate occupation for the experimentally interesting case of fixed temperature/volume systems: The ensemble for fixed (T, V, and N) includes all possible microstates for the solid that have the same temperature; it is called the **canonical ensemble** ('canonical' because it is used so often to model real systems).

- *Recall that for systems with constant (T,V,N), the second law is satisfied when the Helmholtz free energy (F = U - TS) is a minimum.*

  - To determine the equilibrium probability p_j for each individual state j, we simply calculate what values of p_j (for each possible state j) minimize the Helmholtz free energy F, subject to the constraint that the p_j's act like a probability and sum to 1:

- We want to calculate the minimum in F with respect to p_j for all possible states j:

- To satisfy the constraint that the p_j sum to 1, we use the method of Lagrange multipliers. We minimize F with the constraint included:

- We can fill in U and S in terms of the probabilities of each state:

References

1.   Hill, T. L. *An Introduction to Statistical Thermodynamics* (Dover Publications, Inc., New York, 1986).
2.   Dill, K. & Bromberg, S. *Molecular Driving Forces* (New York, 2003).
3.   Cima, M. (2002).
4.   Chabay, R. & Sherwood, B. *Matter & Interactions*.