Chapter 5

- In this chapter we want to review the concept of irreversibility in more detail and see how it comes from the *multiplicity of states*. In addition, we want to introduce the following new topics:
  - Definition for Entropy
  - Second Law of Thermodynamics.
  - Entropy and disorder.
- Let's start by reviewing what we learned last time. Here is the basic line of reasoning for Einstein Solids
  - (1) Define an Einstein Solid
    - Atoms locked in lattice but individual atoms were free to oscillate as simple harmonic oscillators around an equilibrium position.
      - 3-D Problem ➔ 3 x 1-D Problem.
  - (2) Define a Macrostate for a single solid using
    - U : Internal Energy which is related to temperature by

$$U = 3Nk_B T$$

    - N : Number of Atoms
  - (3) The microstate of the solid is given by how much energy is stored in the 3N simple harmonic oscillators
    - 3N integers required.
    - Internal Energy (in terms of microstates)

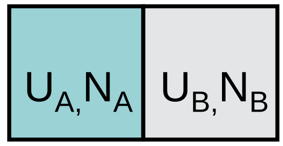
$$U = \sum_{i=1}^{3N} \varepsilon n_i \qquad \varepsilon = \hbar\omega$$

    - There are MANY microstates for each macrostate.

$$\Omega(N,U) = \frac{(q+3N-1)!}{q!(3N-1)!} \qquad q \equiv U/\varepsilon$$

Irreversibility…revisited

- (4) We can bring two Einstein Solids, A & B into thermal contact with one another and define the *macrostate of the* ***system*** by



$U_{sys}=U_A+U_B$

- (5) The two solids can share the total energy in different ways. We call each of the ways a **macropartition.**
  - The number of microstates for the macropartition is given by $$\Omega_{AB}=\Omega_A\Omega_B$$
  - We defined a Macropartition Table to summarize all this information (at least for small N and q)

Macro	U_A	U_B	Ω_A	Ω_B	Ω_{AB}
0:4	0	4	1	15	15
1:3	1	3	3	10	30

↓ More Rows

- (6) **ASSUMPTION:** All microstates are equally likely in the long run (i.e. if we wait a long time)
  - **Consequence:** Since macropartitions have a different number of microstates, macropartitions are NOT equally likely.
    - **The macropartitions with the most microstates are the most likely macropartitions.**
- (7) For large N, most microstates are concentrated in a tight band of macropartitions, near the macropartition which has roughly equal energy per solid.

Implications

- Based on the line of reasoning that we just outlined there are two statements that we would like to show:
  - A) *If the combined system is* ***not*** *in the most probable macropartition to begin with, it will rapidly and inevitably move toward that macropartition*.
  - B) *It will subsequently* ***stay*** *at that macropartition (or near to it), in spite of the random shuffling of energy back and forth between the two solids*.
- These are basically statements of ***irreversibility***.
- Let's be quantitative about seeing how these statements are true:
  - Start with "B"
- Case #1: Two Solids with
  - $N_A = N_B = 4$, $U = 16\varepsilon$
  - Use StatMech to calculate a few quantities:
    - Prob $U_A=U_B=8\varepsilon$ Prob: __________
    - Prob $U_A=16\varepsilon$ and $U_B=0$ Prob: __________
    - Prob $U_A=12\varepsilon$ and $U_B=4\varepsilon$ Prob: __________
  - ~99% of microstates: ____________________________
- Case #2: Two Solids with (2-atoms on a side):
  - $N_A = N_B = 8$, $U = 32\varepsilon$
  - Use StatMech to calculate a few quantities:
    - Prob $U_A=U_B=16\varepsilon$ Prob: __________
    - Prob $U_A=32\varepsilon$ and $U_B=0$ Prob: __________
    - Prob $U_A=24\varepsilon$ and $U_B=8\varepsilon$ Prob: __________
  - ~99% of microstates: ____________

Implications

- Case #3: Two Solids with (5-atoms on a side):
  - $N_A = N_B = 125$, $U = 500\varepsilon$
  - Use StatMech to calculate a few quantities:
    - Prob $U_A=U_B=250\varepsilon$ Prob: __________
    - Prob $U_A=500\varepsilon$ and $U_B=0$ Prob: __________
    - Prob $U_A=375\varepsilon$ and $U_B=125\varepsilon$ Prob: __________
  - ~99% macropartitions _____________
- Case #4: Two Solids with (10-atoms on a side):
  - $N_A = N_B = 1000$, $U = 4000\varepsilon$
  - ~99% macropartitions ______________
- As N gets large (think 10^{23}) the ~99% is going to get extremely narrow!

- Two Important Points:
  - A) Although there is *some* probability of observing the system in the extreme macropartition (all the energy in one of the solids). For all practical purposes it is so unlikely as to be ~impossible.
    - For $N_A = N_B = 50$, $U = 200\varepsilon$ if you "observed" the system 1 billion times per second since the beginning of the universe, the probability you would have every seen it in the extreme macropartition is $\sim 10^{-16}$.
  - B) We have been examining cases with $N_A=N_B$. Consider a case where they are very different. $N_A=5$ and $N_B=20$
    - Most probable partition is near $U_A/N_A = U_B/N_B$…but this makes sense because we want $T_A=T_B$

Moving toward Equilibrium

- So far we calculated the overall probability of various macropartitions and showing that if we are in the region of the most microstates, we stay there. Now let's consider what happens when we start with two objects that are not in thermal equilibrium.
  - There is a steady march toward equilibrium.
- Case Study: $N_A=N_B=250$ and $U=1000\varepsilon$
  - Start a t=0 with $U_A=12\varepsilon$ and $U_B=988\varepsilon$.
  - Now we wait the "characteristic" amount of time four a transfer of a single unit, ε, of energy.
  - As an approximation:
    - The system could be in any microstate of macropartition with $U_A=13\varepsilon$ and $U_B=987\varepsilon$. [A gets hotter]
    - The system could be in any microstate of macropartition with $U_A=12\varepsilon$ and $U_B=988\varepsilon$. [A,B stay same]
    - The system could be in any microstate of macropartition with $U_A=11\varepsilon$ and $U_B=989\varepsilon$. [B gets hotter]
  - Since the system is randomly exploring these possible microstates, the probability of any of these should be the available microstates in each macropartition divided by the total microstates summed over the three.
    - 13:987 Ω_{AB} =____________
    - 12:988 Ω_{AB} =____________
    - 11:989 Ω_{AB} =____________

    } Total States: ___________
  - Prob heat flows from cold to hot ➔ __________
  - Prob. heat does not flow ➔ ___________
  - Prob. heat flows from hot to cold ➔ __________

Moving to Equilibrium

- Notice there are many more microstates in the macropartition that is one step closer to equilibrium than there are in the macropartition one step away from equilibrium or even the macropartition that the system started in.
- As we might expect, the numbers get even more daunting when N gets large. If we increase the study case above by a simple factor of 10, the probability that we “go the wrong way” is about 10^{-30}.
- Once again, think about what happens when we take N to be 10^{23}.
    - **There is a rapid steady progression towards equilibrium simply because the number of microstates increases RAPIDLY in that “direction”.**
- Although I have said it a few times now…we see the source of irreversibility. However, we see this for an Einstein Solid. Can we extend what we learned to other macroscopic systems as well?
    - YES!

General Irreversibility

- What were the critical features of an Einstein Solid that lead us down this path?
  - 1)

    .
  - 2)
  - 3)
- Do most systems share these general features?
  - YES!
- Let's consider each one of these questions:
  - (1) TRUE:
  - (2) "TRUE":
  - (3) TRUE:

Entropy

- Now that we have defined microstates and multiplicity we want to define **Entropy.**
  - Without the microstate background defining entropy can be an obtuse one…most intro text books define the entropy in terms of an integral of temperature.
  - With multiplicity of microstates defined, the definition of entropy,S, is very easy

$$S \equiv k_B \ln \Omega$$

  - Notice this provides a more useful way of talking about multiplicity since taking the "ln" turns very big numbers into small ones.
  - Also, the factor of k_B is not universal but it serves to "reduce the scale" even further.
    - Consider the following example.
      - A mole of a solid has a multiplicity of

$$\Omega \sim 10^{10^{23}}$$

      - With our definition the Entropy is

    - A much easier number to talk about.
  - The other convenience is when we put two systems together (e.g. two Einstein Solids).

  - We just ADD the entropies of the two systems!

Second Law of Thermodynamics

- Now that we have defined microstates and entropy we are ready to state the second law of thermodynamics

The entropy of an isolated system never decreases.

- Given what we have learned we understand why this is true. A system moves from states where there are few microstates (low entropy) to states where there are many microstates (highest entropy).
- For systems with small N the 2nd Law is one of probability. But N does not need to be very large and this statement turns into one of *certainty* for all practical purposes.

- Entropy and Disorder:
  - Many people associate entropy and disorder.
  - **Be very careful about this.** The correct definition is that entropy is high when the multiplicity of microstates is high.
    - Often it is the case that the state of "disorder" is one where there are a lot of microstates.
    - However, "disorder" is a subjective statement and so sometimes this association with entropy is false
    - See Figure T5.7 (page 89) Ice in a glass and water.
      - Entropy of liquid water much higher than ice.
    - Read Section 5.6

Example

- T5S.6: “A certain macropartition of two Einstein Solids has an entropy of 305.2k_B. The next macropartition closer to the most probable one 335.5$k_{B.}$ If the system is initially in the first macropartition and we check it later, how many times more likely is it to have moved to the other than to have stayed in the first?”

- Remember…a small difference in entropy corresponds to a large difference in microstates and the relative probability.