

# Chapter 4

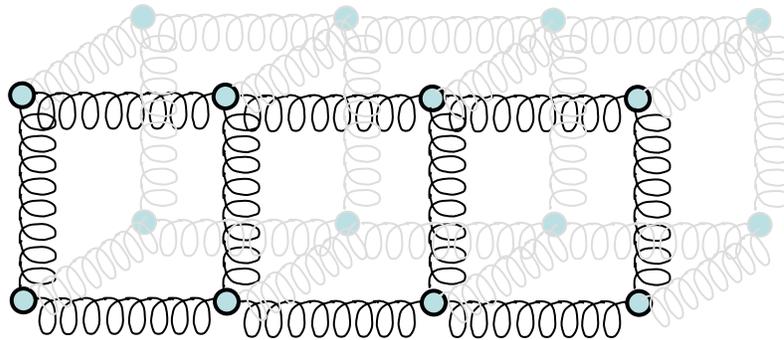
- We have spent some time developing the model of ideal gases and have learned a number of important concepts.
  - However, we still have not learned much regarding why certain processes are irreversible.
  - We are getting closer to that “holy grail”. But we need to define some more terms
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- In this chapter we go through all these points and by the end we will have all the pieces to understand why some processes are irreversible.
- **Macrostate:**
  - We defined this earlier for an ideal gas
    - Most (not all) combinations of three of the following served to describe the macroscopic properties of an ideal gas:
      - U, T, P, V, N, M, along with the composition.
  - For other things like liquid and solids we will have a similar set of variables that define the macroscopic state of the substance.
    - When we define an *Einstein Solid* in a few minutes we will see that we can use the internal energy U and the number of molecules, N to define the state.

# Microstates

- **Microstate:** The microstate of a system (gas, solid, or liquid) is defined as the set of quantities which defines the state of **every** molecule in the system.
  - One option:
  - We could also think about this as being the set of *quantum numbers* that describe each state of each particle. (This is what we will do for the Einstein Solid.)
    - ❑ A quantum in a 1-d box
    - ❑ If we extend this idea to 3-dimensions,
    - ❑ Note that for N molecules we need
  - In practice, it is impossible to determine the microstate of an object.
    - ❑ Think about a gas containing  $10^{23}$  molecules...we cannot possibly determine all the individual states of these particles.
- **Important Point: For any given macrostate there is a HUGE number of microstates.**
  - Think about an ideal gas with U, T, N
    - ❑ The total internal energy U is in the K (monatomic) but this can be shared in many different ways.
- Given a *Microstate* we could get the *Macrostate*.

# Einstein Solid

- We could try develop some of the concepts of microstates, macropartions, etc. in terms of ideal gases but there is a simpler model that we can use.
  - Einstein Solid.
  - Einstein developed a very simple model for solids in order to investigate some of these concepts of statistical mechanics.
- Model:
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  - The oscillations are
  - The picture is a lattice of atoms attached by springs.



- The motion can be viewed independently in each direction.

$$\begin{aligned} E &= \frac{1}{2}mv^2 + \frac{1}{2}k_s r^2 = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2) + \frac{1}{2}k_s(x^2 + y^2 + z^2) \\ &= \underbrace{\left(\frac{1}{2}mv_x^2 + \frac{1}{2}k_s x^2\right)} + \underbrace{\left(\frac{1}{2}mv_y^2 + \frac{1}{2}k_s y^2\right)} + \underbrace{\left(\frac{1}{2}mv_z^2 + \frac{1}{2}k_s z^2\right)} \end{aligned}$$

Each direction looks like a S.H.O.

# Einstein Solid

- We know how to treat a 1-dimensional simple harmonic oscillator in quantum mechanics. The energy levels are quantized and separated fixed  $\Delta E$ .
- For a single atom in a lattice the energy would be given by
  
- Now we can sum over all the  $N$  atoms in the solid to get the total energy:
  
  
- Note: Since the zero point energy would be there even at  $T=0$  (absolute zero), we typically don't include this contribution in the *thermal energy*.

$$U = \sum_{i=1}^{3N} \epsilon n_i$$

- Where  $n_i = 0, 1, 2, \dots$  and  $\epsilon = \hbar\omega = \hbar\left(\frac{k_s}{m}\right)^{1/2}$

# Counting Microstates

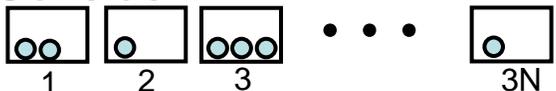
- Now that we have a model to work with, we can investigate an essential point on our path to understanding irreversibility...counting microstates.
- In a Einstein Solid there are two numbers that define the macrostate of the solid
  - U and N
  - Note: P, V are to first order unchanging, if we know U we can determine T since empirically

$$U = 3Nk_B T$$

- To define the microstate we need to define the 3N integers,  $n_i$ , for all the simple harmonic oscillators.
- In general there will be many **microstates** for a given **macrostate**. Each of the individual microstates is not so important, however, the **number** of microstates for a given **macrostate** is important. This is called the multiplicity

$\Omega(N, U) = \text{multiplicity of macrostate } U, N$ $= \text{number of } N\text{-atom microstates that give thermal energy } U.$
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- For an Einstein Solid, calculating this quantity is not hard (maybe time consuming). Consider:

- You have 3N bins (# of SHO) 
- You have energy U which can be divided into  $q=U/\epsilon$  pieces. (Think of these are marbles)
- Multiplicity = number of ways you can divide the marbles into the 3N bins.

# Count Microstates (Example)

- Let's consider an example. But because we want to do this in less than a trillion years let's keep  $N$  small so that we can see the process.
- Simple Cases:
  - Let  $N=1$  so that there are \_\_\_ bins
  - We will denote the number of marbles in each bin by a three digit number "ijk" (e.g. 201) where each integer corresponds to the number of marbles in the first, second, and third bin.
 

Code →

2

1

3

Bin # →

●●

  
1

●

  
2

●●●

  
3
  - Now consider  $U=0$ 
    - $q=U/\epsilon$  implies  $q=$ \_\_\_
    - Possible Microstate(s):
    - So  $\Omega(N=1,U=0)=$ \_\_\_
  - Now consider  $U=1\epsilon$ 
    - $q=U/\epsilon$  implies  $q=$ \_\_\_
    - Possible microstates:
    - So  $\Omega(N=1,U=1\epsilon)=$ \_\_\_
  - Now consider  $U=2\epsilon$ 
    - $q=U/\epsilon$  implies  $q=$ \_\_\_
    - Possible microstates:
    - So  $\Omega(N=1,U=2\epsilon)=$ \_\_\_
  - For  $N=2$   $U=1\epsilon$  ( $3*2 = 6$  bins and  $q=1$ )
    - There are 6 possible states "100000" "010000"  
"001000" "000100" "000010" "000001"
- This looks tedious!

# General Relationship

- Fortunately there is a general relationship for determining the multiplicity of a macrostate of an Einstein solid:

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

where  $n! \equiv n(n-1)(n-2)\dots(2)(1)$  and  $0! \equiv 1$

- Let's see that this works for a couple of the cases that we just did by hand.

➤ N=1 q=1: 
$$\Omega(N, U) = \frac{(1 + 3(1) - 1)!}{1!(3(1) - 1)!} = \frac{3!}{1(2!)} = 3$$

➤ N=1 q=2: 
$$\Omega(N, U) = \frac{(2 + 3(1) - 1)!}{2!(3(1) - 1)!} = \frac{4!}{2!(2!)} = \frac{4 \times 3}{2} = 6$$

➤ N=2 q=1: 
$$\Omega(N, U) = \frac{(1 + 3(2) - 1)!}{1!(3(2) - 1)!} = \frac{6!}{1(5!)} = 6$$

- You can see that the number of microstates gets large very quickly. Consider the case were N=5 and q=5 (still pretty small numbers on the scale of  $10^{23}$ )

$$\Omega(N, U) = \frac{(5 + 3(5) - 1)!}{5!(3(5) - 1)!} = \frac{19!}{5!(14!)} = \frac{19(18)(17)(16)(15)}{5(4)(3)(2)(1)} = 11,628$$

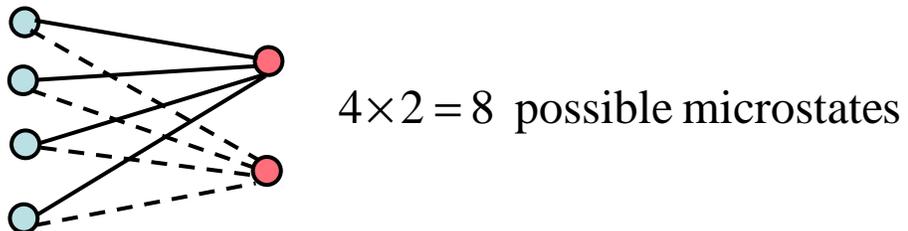
- Fortunately you can put this into a computer program to perform the calculation for you.

# Two Einstein Solids in Contact

- Now consider two Einstein solids that are in thermal contact.
  - We want to describe the state of the system (the two solids together)
  - We can do this by defining the combine macrostates.
  - Consider two solids with internal energy  $U_A$  and  $U_B$ , the combined internal energy is  $U = U_A + U_B$ .
  - This total energy can be shared between the two solids in many different ways.
    - For example if  $U = 6\varepsilon$ 
      - $U_A = \underline{\quad}$  and  $U_B = \underline{\quad}$
      - $U_A = \underline{\quad}$  and  $U_B = \underline{\quad}$
- Note that this is not saying anything about the microstates since it is not conveying any information about the individual atoms in the two solids.
  - However, this is saying for an overall thermal energy  $U$  of the combined system, there are multiple ways to share that energy between the two objects (in the case above there were 7 ways).

# Macropartition Table

- We can begin to see some interesting structure if we form the information about all the **macropartitions** into a table (**macropartition table**). We want this table to contain the following information:
  - Macropartition
  - Macrostate for each solid
  - Multiplicity of microstates for A and B
  - Multiplicity of microstates for the combined system.
- We know how to calculate everything but this last quantity. However, the last quantity is just the product of the multiplicities of the individual solids.
  - This can be seen by realizing that for each microstate that A can be in, B can be in all of its states:



- Let's make an example table with  $N_A=N_B=1$  and  $U=4\epsilon$

Macro	$U_A$	$U_B$	$\Omega_A$	$\Omega_B$	$\Omega_{AB}$
0:4					
1:3					
2:2					
3:1					
4:0					

# Fundamental Assumption

- When you think about what happens to an ideal gas, as molecules collide with each other and with the container, we will have random changes to the microstate. It should always go into another microstate of the macrostate.
- The same thing happens with the Einstein solids. The atoms are loosely coupled such that energy can be transferred around that lattice and across the boundary between the two solids.
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  - 
  - e.g.
- Here is the fundamental assumption that leads to many concepts in statistical mechanics and thermodynamics.

**All of a system's possible microstates are equally likely in the long run.**

- This seems very simple, but it has amazing consequences...including irreversible processes.

# Consequences

- One of the major consequences of the *fundamental assumption*. Is that the probability for the system to be in a given **macropartition** is directly proportional to the multiplicity  $\Omega_{AB}$  for that macropartition.
- Consider the case for which we made a table
  - There are a total of 126 microstates.
  - So we can determine the probability of being in each macropartition:

Macropartition	$\Omega_{AB}$	Prob
0:4	15	12%
1:3	30	23.8%
2:2	36	28.6%
3:1	30	23.8%
4:1	15	12%

**Important Note: These correspond to the same Macrostate.**

- This means that if we look at these solids in the future, there is a 28% chance we will find them in the macropartition 2:2 where the thermal energy is balanced. (Note:...if  $N_A$  is not equal to  $N_B$  the balance occurs at a different macropartition)
- Now the interesting things start to occur when we go to larger  $N$  and  $U$ . There is a program that we can download from the *Six Ideas* website which calculates these table for us.
  - Let's look at several specific examples.

# StatMech

- Run the case for  $N_A=N_B=1$  and  $U=4\epsilon$  :
- Run the case for  $N_A=N_B=10$  and  $U=40\epsilon$  :
- Run the case for  $N_A=N_B=100$  and  $U=400\epsilon$  :
- Run the case for  $N_A=N_B=1000$  and  $U=4000\epsilon$  :
- Run the case for  $N_A=N_B=10000$  and  $U=40000\epsilon$  :
- What's happening?
  - 
  -
- Do you see irreversibility in all this?
  - Consider starting in macropartition 0:40000
    - After a long time where will the macropartition be?
  - If you some how get to macropartition 20000:20000 what is the probability that you get back to 0:40000?
- **IRREVERSIBILITY!**
  - It is a macroscopic phenomena that is a feature of having a large number of microscopic objects.
  - And it arises even if the microscopic objects only undergo reversible processes!