

# Chapter 6

- In this chapter we want to continue investigating the concept of entropy. In addition, we will look at
  - A new definition of temperature
  - The Boltzmann Factor and some applications.
- Recall back in Chapter 1, we went through a rather detailed discussion of temperature and how to define it through a standard thermoscope.
- Now we can actually **define** temperature via entropy
  - This is perhaps a much more scientifically satisfying way of defining temperature.
- Consider two objects A and B that are brought into thermal equilibrium
  - They are now in the macropartition with

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- If we consider the case where we hold quantities like V, N, and other macroscopic quantities fix, then the macropartition is completely determined by  $U_A$  and  $U_B$ .

- The condition of maximum  $S_{TOT}$  can be expressed mathematically by  $\frac{dS_{TOT}}{dU_A} = 0$

- Since  $S_{TOT}$  is just the sum of  $S_A$  and  $S_B$  we have

$$\frac{dS_{TOT}}{dU_A} = \frac{d(S_A + S_B)}{dU_A} = \frac{dS_A}{dU_A} + \frac{dS_B}{dU_A} = 0$$

- Since  $U_B = U - U_A$   $\frac{dS_B}{dU_A} = \frac{dS_B}{dU_B} \frac{dU_B}{dU_A} = \frac{dS_B}{dU_B} (-1) = -\frac{dS_B}{dU_B}$

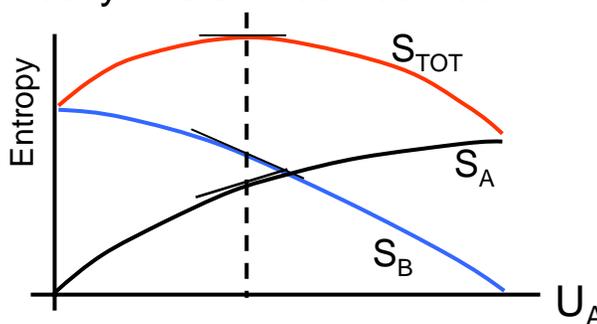
# Definition of Temperature

- Taking the last two expressions and combining them we find

$$\frac{dS_A}{dU_A} = -\frac{dS_B}{dU_A}$$

$$\frac{dS_A}{dU_A} = \frac{dS_B}{dU_B}$$

- Each condition (they are the same...just different forms) is the condition that two objects are in thermal equilibrium.
  - The first form says that the two objects are in thermal equilibrium when the two slopes relative to  $U_A$  (or  $U_B$ ) are equal in magnitude but opposite in sign.
    - Graphically this can be seen as:



- In the second form we are determining the derivative of **each** object's entropy with respect to its own  $U$ ...there is no reference to the other object.
      - The place where these two derivatives are equal we have thermal equilibrium.
- But the **Zeroth Law of Thermodynamics** says when two objects are in thermal equilibrium they are at the same temperature.

# Temperature

- This last reminder of the 0<sup>th</sup> Law of Thermodynamics implies that the derivative should be related to the temperature in some way

$$f(T) = \frac{dS}{dU}$$

- Note that the choice of  $f(T)$  is somewhat arbitrary however, it must have the following characteristic
  - $f(T)$  has a unique value for each  $T$ .
- However, we will choose this functional dependence so that this “new” definition of temperature mostly closely matches our old definition of temperature

$$\frac{1}{T} \equiv \frac{dS}{dU} \text{ (with } V, N \text{ etc held constant)} = \frac{\partial S}{\partial U}$$

- Much of thermodynamics is related to understanding the implications of this expression. But let's start by seeing how this definition seems to be consistent with our old definition.
- Let's use the Einstein Solid as an example. We must differentiate the multiplicity of states with respect to  $q$ .

# Temperature

- Now let's plug that derivative back into our definition
- We see that we get back to the relationship between internal energy and temperature that we stated was empirically observed for a solid!
  - What's really nice is that we have now (in some sense) derived this  $U \rightarrow T$  functional dependence.
- If by some model we determine how the multiplicity depends on  $U$  and  $N$ , we can use our definitions to determine how the internal energy depends on temperature.
- Example: T6S.4:
  - The multiplicity of a substance is given by:

$$\Omega(U, N) = Ne^{\sqrt{NU/\epsilon}}$$

- Determine how  $U$  is related to  $T$ .

# The Boltzmann Factor

- Much of what will do in the remain lectures of this term deals with the equations:

$$\frac{1}{T} \equiv \frac{\partial S}{\partial U} \quad S = k_B \ln \Omega$$

- One special case that is of considerable interest:
  - Small System:
    - ❑ This could be a single atom
    - ❑ It is in thermal equilibrium with a large system
    - ❑ It has discrete energy levels that are it's microstates.
  - Large System:
    - ❑ Very large compared to the small system.
    - ❑ Any change in the energy of the small system results in an **immeasurable** (negligible) change in temperature of the large system.
      - We often call this large system a “reservoir”.
  - Question: “What is the probability of the small system being in a given quantum state (or microstate), if the temperature of the reservoir is T”.
- To answer this question consider a small system that can be in two possible quantum states with  $E_1 > E_0$ .
  - According to the fundamental assumption that we made regarding microstates, the ratio of the probability that the small system is in  $E_1$  versus  $E_0$  is

$$\frac{P(E_1)}{P(E_2)} = \frac{\Omega_{SR,1}}{\Omega_{SR,0}}$$

Corresponds to two different macropartions.

# Boltzmann Factor

- The combined multiplicity  $\Omega_{SR}$  is just the product of the individual multiplicities of the reservoir and the small system. However, in both cases, for the small system we are considering only 1 quantum state so  $\Omega_s=1$ .

$$\frac{P(E_1)}{P(E_0)} = \frac{1 \cdot \Omega_{R1}}{1 \cdot \Omega_{R0}} = \frac{\Omega_{R1}}{\Omega_{R0}}$$

- We can define the multiplicity for the reservoir in terms of its entropy

$$\Omega_R = e^{S_R/k_B}$$

- Putting this in above gives us

$$\frac{P(E_1)}{P(E_0)} = \frac{e^{S_{R1}/k_B}}{e^{S_{R0}/k_B}} = e^{(S_{R1}-S_{R0})/k_B} = e^{\Delta S_R/k_B}$$

- The  $\Delta S_R$  is the change in the **reservoir's** entropy when the small system's energy increases from  $E_0$  to  $E_1$ . However, since the total system is isolated, any small increase in energy of the small system must be accompanied by a small decrease in the energy of the reservoir.

$$\Delta U_R = -(E_1 - E_0)$$

- We need to calculate this  $\Delta U_R$

# The Boltzmann Factor

- Now we can use our definition of temperature to determine the change in internal energy of the reservoir.

$$\frac{1}{T} = \frac{\partial S_R}{\partial U_R}$$

- If the reservoir's temperature does not change significantly, this above equation implies

$$\frac{1}{T} \approx \frac{\Delta S_R}{\Delta U_R} \Rightarrow \Delta S_R \approx \Delta U_R / T$$

- Now we can substitute this back into our original equation and we find:

$$\frac{P(E_1)}{P(E_0)} = e^{\Delta S_R / k_B} = e^{\Delta U_R / k_B T} = e^{-(E_1 - E_0) / k_B T} = \frac{e^{-E_1 / k_B T}}{e^{-E_0 / k_B T}}$$

- This implies that

Called the *Boltzmann Factor*

$$P(E) \propto e^{-E / k_B T} \quad \text{and} \quad P(E) = \frac{1}{Z} e^{-E / k_B T}$$

Constant of proportionality

- The constant of proportionality can be determined by demanding that the sum of probabilities over all states must equal 1.

$$1 = \sum_{\text{all states}} P(E) = \sum_{\text{all states}} \frac{1}{Z} e^{-E_i / k_B T} = \frac{1}{Z} \sum_{\text{all states}} e^{-E_i / k_B T}$$

$$Z = \sum_{\text{all states}} e^{-E_i / k_B T}$$

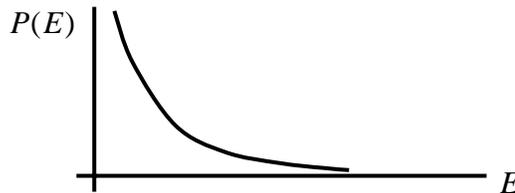
# The Boltzmann Factor

- Collecting what we have learned, we can define the probability that a small system is in quantum state with energy  $E$ , when it is in contact with a reservoir, to be

$$P(E) = \frac{e^{-E/k_B T}}{\sum_{\text{all states}} e^{-E_i/k_B T}}$$

- Features:

- The probability is exponential with Energy



- The probability that the system is in a given state is directly related to the number of microstates available **in the reservoir** when the small system is in that state.
  - ❑ So it makes sense that as the small system's energy goes up, the energy  $U_R$  will go down and so will the number of available microstates for the reservoir.
- This seems like a very simple argument, but there are many interesting applications for this case.
- In Chapter 6 there are two example cases that Moore shows us. Please read through those examples, I will do several different ones.

# Example

- T6S.7: The water molecule can vibrate in many ways. The “flexing” mode is the vibrational mode whose excited energies are the smallest. We can approximate these as a simple harmonic oscillator with  $\omega = 3 \times 10^{14} \text{ s}^{-1}$ . If the water is at room temperature, what is the approximate probability that water is in the ground state and first two excited states of this vibrational mode?
- **Solution:**

First let's calculate the Boltzmann factors for the first few excited states:

# Example

- T6R.1 Cold interstellar molecules often contain CN molecules, whose first excited rotational quantum states all have an energy of  $4.7 \times 10^{-4}$  eV above that of the single ground rotational state. Studies of the absorption lines of starlight traveling through one cloud performed in 1941 implied that for every 10 CN molecules in the ground state, roughly 3 were in the first excited states (degeneracy of 3) (a) Scientists argued at the time the gas was in some thermal equilibrium with a reservoir. What would the temperature of the reservoir be?
- **Solution:**

In the 1960's scientists found the universe was filled with a cosmic microwave background. The temperature of this huge cosmic reservoir was 2.7K. *Aside: Recent measurements of the CMB have allowed scientists to measure the age of the universe to about 1%.*

# Example

- T6S.9 At very high temperatures (early universe), we can model the proton and neutron as being two different quantum states of the same quanton (nucleon). A nucleon can easily be converted from one to the other of its two states by interacting with the energetic electrons and neutrinos that were around. The neutron's rest energy is higher than the proton's by about 1.3 MeV. At the time when the universe had a temperature of about  $10^{11}$  K, what was the approximate ratio of protons to neutrons?

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## **Concluding remarks:**

The “Boltzman Factor” relation can be very powerful.

Note: “small system” can be an atom of the same gas. We can use this in Chapter 7.