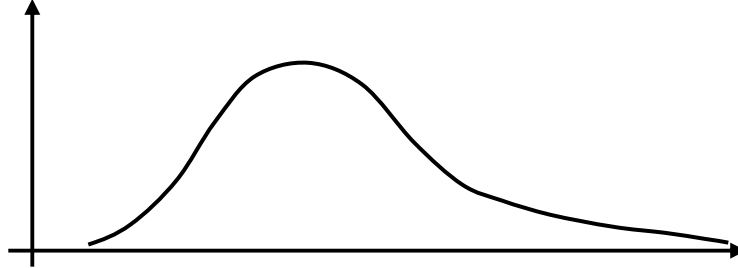


# Chapter 7

- In this chapter we solve some of the interesting mysteries that have popped up along our path through thermodynamics.
  - We will make extensive use of the Boltzmann Factor that we derived in Chapter 6.
  - We want to study the
    - ❑ Maxwell-Boltzmann Distribution
      - Tells how molecular velocities are distributed in a gas with temperature  $T$ .
    - ❑ Count Velocity States.
    - ❑ Average Energy of a Quantum System
    - ❑ Energy storage in a Gas molecule
- In our study of a small system in contact with a large reservoir we never stated that the two substances needed to be different.
  - They don't! In fact, we can think of a large container of gas and treat *one* of the molecules as the small system and the other molecules as the reservoir.
  - We know from our study of an ideal gas that
    - But we would like to know what the **distribution** of velocities looks like
      - ❑
      - ❑
      - ❑

# Maxwell-Boltzmann Distribution

- So we are looking for something like this



- We know from our study in chapter 6 that

$$\Pr(\text{state with speed } v) \propto e^{-E/k_B T} = e^{-\frac{1}{2}mv^2/k_B T}$$

- Note: this is the probability that we are in **a** state with speed  $v$  but it is not the probability that it simply **has** speed  $v$ .
  - If there are many states with speed  $v$ , the probability that the particle will have a speed  $v$  is proportional to the number of states with speed  $v$ .
  - The number of states with speed between  $v-dv/2$  and  $v+dv/2$  is given by  $v^2 dv$ 
    - Rough Justification for this statement

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- 
- 
- 
-

# Maxwell Boltzmann Distribution

- So now the probability that we are in *any* state within  $dv$  centered on  $v$  is

$$\text{Pr}(\text{within } dv \text{ around } v) \propto v^2 dv e^{-mv^2/2k_B T}$$

- We have a term which depends on mass ( $m$ ),  $k_B$ , and  $T$ , which has units of  $m^2/s^2$ . Let's define that as a special parameter  $v_p$ .

- Since  $v_p$  is just a constant, we can put it in our relationship (it just changes the constant of proportionality)

$$\text{Pr}(\text{within } dv \text{ around } v) \propto \left(\frac{v}{v_p}\right)^2 \left(\frac{dv}{v_p}\right) e^{-\left(\frac{v}{v_p}\right)^2}$$

- Notice that this version is unitless...like what we would expect for a probability. That means the constant of proportionality that is left to determine is also unitless. By demanding that the total probability is equal to 1 we can determine this remaining constant of proportionality.

➤ It is  $4/\pi^{1/2}$   $\text{Pr}(\text{within } dv \text{ around } v) = D(v) \left(\frac{dv}{v_p}\right)$

$$D(v) = \frac{4}{\pi^{1/2}} \left(\frac{v}{v_p}\right)^2 e^{-\left(\frac{v}{v_p}\right)^2} \quad v_p = \left(\frac{2k_B T}{m}\right)^{1/2}$$

# Maxwell-Boltzmann Distribution

- Some features of this distribution:

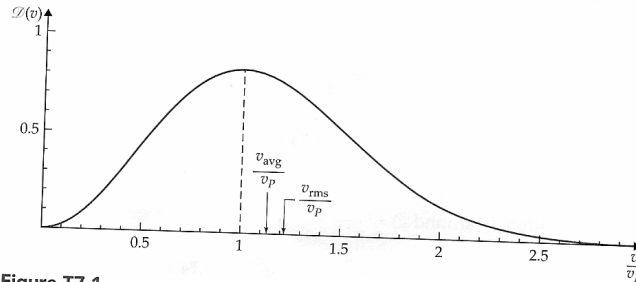
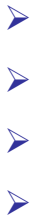


Figure T7.1  
A graph of the Maxwell-Boltzmann distribution function  $\mathcal{D}(v)$  as a function of  $v/v_p$ .

- Features:



- This seems to be a good model for the distribution of velocities in a gas. Experimental results match it.

- **Homework Revisited:**

- Recall the homework problem about the atmosphere of the planet Mercury which has average surface temp of 700K on the sunny side.
- The escape velocity for the planet was 4300 m/s
- When we solved for the **average** velocity of the hydrogen and helium molecules we found:
  -
- But we said these molecules still “boiled off” the planet
- Now we see why
  -

# Homework Revisited

- In fact, we can use these numbers for helium and hydrogen and determine the fraction of molecules with velocity above the escape velocity

$$P_H(v > v_{escape}) = \int_{1.61v_p}^{\infty} D(v) \frac{dv}{v_p} = \frac{4}{\pi^{1/2}} \int_{1.61v_p}^{\infty} \left( \frac{v}{v_p} \right)^2 e^{-\left( \frac{v}{v_p} \right)^2} \frac{dv}{v_p}$$

- We can perform a change of variables on this

$$x \equiv \frac{v}{v_p} \quad dx = \frac{dv}{v_p}$$

$$P_H(v > v_{escape}) = \frac{4}{\pi^{1/2}} \int_{1.61}^{\infty} x^2 e^{-x^2} dx = 0.158$$

- From the *Six Ideas* website there is a program which will perform this integral. (MBoltz). For helium we find

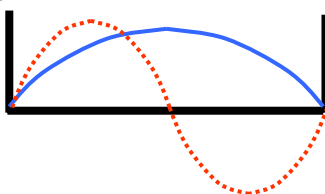
$$P_{He}(v > v_{escape}) =$$

- So the hydrogen will “boil off” faster but over time all those molecules will be lost.

# Velocity States

- In this last discussion we used the fact that the density of states in velocity space was uniform. Let's investigate the validity of this assumption.
- Let's consider a quanton in a 1-D box.

- If we assume the walls have an infinite potential, then we must fit an integer number of  $\frac{1}{2}\lambda$  between the walls of the box.

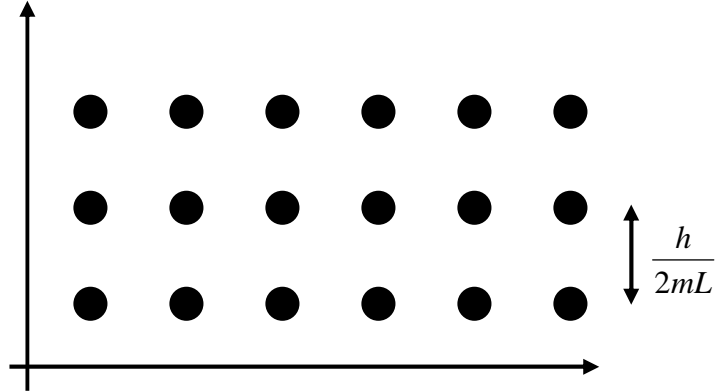


- For this case, (recall the deBroglie relation)
- We see that the velocity is quantized in units of  $h/2mL$ . Which for a macroscopic quantity of gas is very small.
- We can now think about extending this to three dimensions:
  - Each direction could have a different number of half-wavelengths. For this case we have:

$$|v_x| = \frac{n_x h}{2mL} \quad |v_y| = \frac{n_y h}{2mL} \quad |v_z| = \frac{n_z h}{2mL}$$

# Density of Velocity States

- Now we can think of density of states in velocity space



- Because the states are linear with  $n_i$  they are distributed uniformly in this velocity space. This is the result that we were seeking.

## Average Energy of Quantum States

- Another quantity that we can determine is the average energy of quantum states.
- First a brief comment about taking an average.
  - This is just math...
  - If we know the probability  $P_i(x_i)$  of having answer  $x_i$ , then we define the average  $x$  in the following manner:

$$x_{avg} = \sum_{\text{all possible } x} x_i P(x_i)$$

- Notice this is not the sum over all  $x$ ...just the *possible*  $x$ .

$$x_{avg} = \frac{1+3+4+2+1+3+4+5+2+3}{10} = \frac{(1+1)+(2+2)+(3+3+3)+(4+4)+(5)}{10}$$

$$= \frac{2}{10}1 + \frac{2}{10}2 + \frac{3}{10}3 + \frac{2}{10}4 + \frac{1}{10}5$$

# Average Quantum Energy

- Since we know the probability of various energy states from the Boltzmann Factor, we can write down the average energy of a quantum state as the following:

$$E_{avg} = \sum_{\text{all states}} E_n P(E_n)$$

- Inserting the probability we get

$$E_{avg} = \sum_{\text{all states}} E_n \left( \frac{e^{-E_n/k_B T}}{Z} \right) = \frac{\sum E_n e^{-E_n/k_B T}}{\sum e^{-E_n/k_B T}}$$

- Notice that if we have a macroscopic object of  $N_{qs}$  *identical* quantum systems at temperature T, we can think about each molecule being the small quantum system. Then the total internal energy can be written as

$$U = N_{qs} E_{avg}$$

- Here we have determined the internal energy without knowing anything about the multiplicities, which we needed to know to determine the internal energy.



# Einstein Solid

- Let's apply the previous analysis to the Einstein Solid.
  - Quantum Mechanically we think of this as a bunch of 1-D simple harmonic oscillators, so the energy is given by

$$E_n = n\varepsilon \quad n = 0,1,2,3,\dots$$

- Remember we removed the “zero-point” energy.
- Now the average energy is given by

$$E_{avg} = \frac{\sum n\varepsilon e^{-n\varepsilon/k_B T}}{\sum e^{-n\varepsilon/k_B T}}$$

- The problem with this is that the sums are infinite. But we know the terms involve exponentials so that eventually for large n, the contribution will be very small and can be ignored.
- Can we think of a systematic way to determine how far out in the sum that we need to go?
  - Let's define a quantity, which we call a **characteristic temperature**  $\varepsilon = k_B T_\varepsilon \Rightarrow T_\varepsilon \equiv \frac{\varepsilon}{k_B}$
  - Note: this is **not** the actual temperature of the solid but represents a *scale* to which we measure the actual temperature. With this definition we can write our equation:

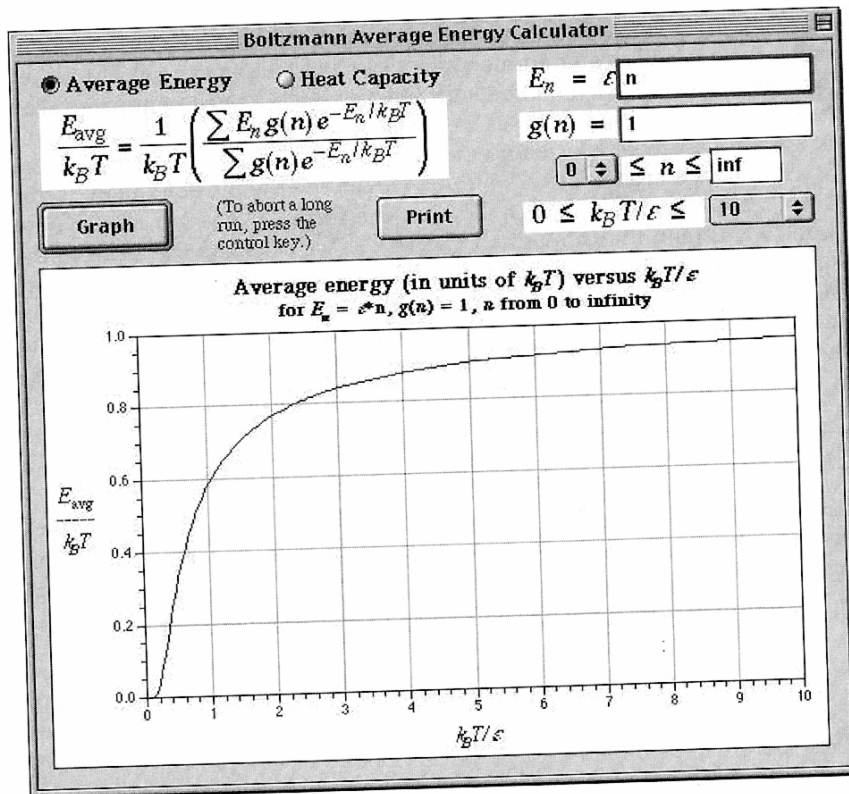
$$E_{avg} = \frac{\sum n(k_B T_\varepsilon) e^{-n(T_\varepsilon/T)}}{\sum e^{-n(T_\varepsilon/T)}} \Rightarrow \frac{E_{avg}}{k_B T} = \frac{\sum n \left( \frac{T_\varepsilon}{T} \right) e^{-n(T_\varepsilon/T)}}{\sum e^{-n(T_\varepsilon/T)}}$$

# EBoltz Program

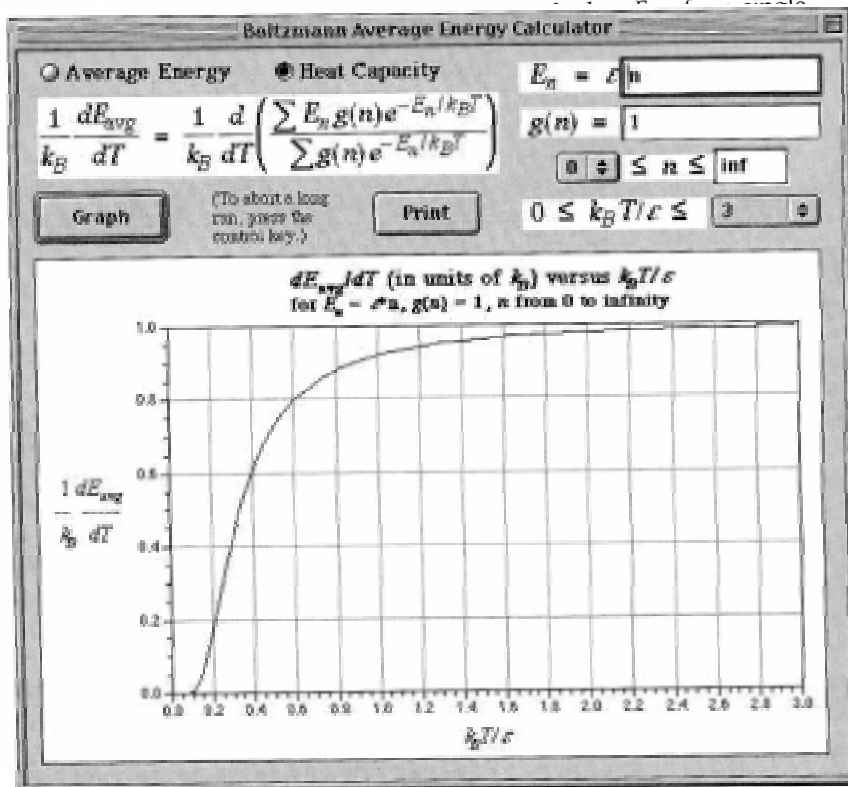
- If we consider this relationship

$$\frac{E_{avg}}{k_B T} = \frac{\sum n \left( \frac{T_\epsilon}{T} \right) e^{-n \left( \frac{T_\epsilon}{T} \right)}}{\sum e^{-n \left( \frac{T_\epsilon}{T} \right)}}$$

- No matter what the value for  $T_\epsilon / T$  we will eventually get to large enough  $n$ , that the terms in the sum will be small enough that we can ignore higher terms.
  - If  $T$  is large,  $T_\epsilon / T$  is small and we will have to go to large  $n$  to make the exponent small enough to ignore the terms.
  - We can use a computer program to do the calculation
    - EBoltz from *Six Ideas* website...only problem is that it does not seem to work on my laptop.
    - Also, there is a way to turn this into an integral and do the integration...that will wait for a future course.



**Figure T7.7**  
A screen shot showing EBoltz set up to calculate the average energy as a function of temperature for an oscillator in an Einstein solid.



**Figure T7.8**  
A screen shot of EBoltz set up to calculate the heat capacity as a function of temperature for an oscillator in an Einstein solid.

# Heat Capacity

- The quantity that is easy to measure is the heat capacity which is

$$\frac{dU}{dT} = \frac{d(U / N_{qs})}{dT} N_{qs} = \frac{dE_{avg}}{dT} N_{qs} = \left( \frac{1}{k_B} \frac{dE_{avg}}{dT} \right) k_B N_{qs} = \left( \frac{1}{k_B} \frac{dE_{avg}}{dT} \right) 3Nk_B$$

- From Figure T7.8 we see that for an Einstein Solid for temperatures,  $T > 3T_\epsilon$ , then

$$\left( \frac{1}{k_B} \frac{dE_{avg}}{dT} \right) \approx 1.0$$

- Examples:

- A) For lead  $\epsilon=0.0057$  eV  $\rightarrow T_\epsilon = 66$  K

- If we consider lead at room temperature  $T=300$  K, we have  $T=4.5T_\epsilon$ , so we expect

$$\frac{dU}{dT} = \left( \frac{1}{k_B} \frac{dE_{avg}}{dT} \right) 3Nk_B = (1.0)3Nk_B$$

- From table T2.2, lead has  $3.18Nk_B$ .

- B) For aluminum  $\epsilon=0.026$  eV  $\rightarrow T_\epsilon = 300$  K

- If we consider lead at room temperature  $T=300$  K, we have  $T=T_\epsilon$ , so we expect

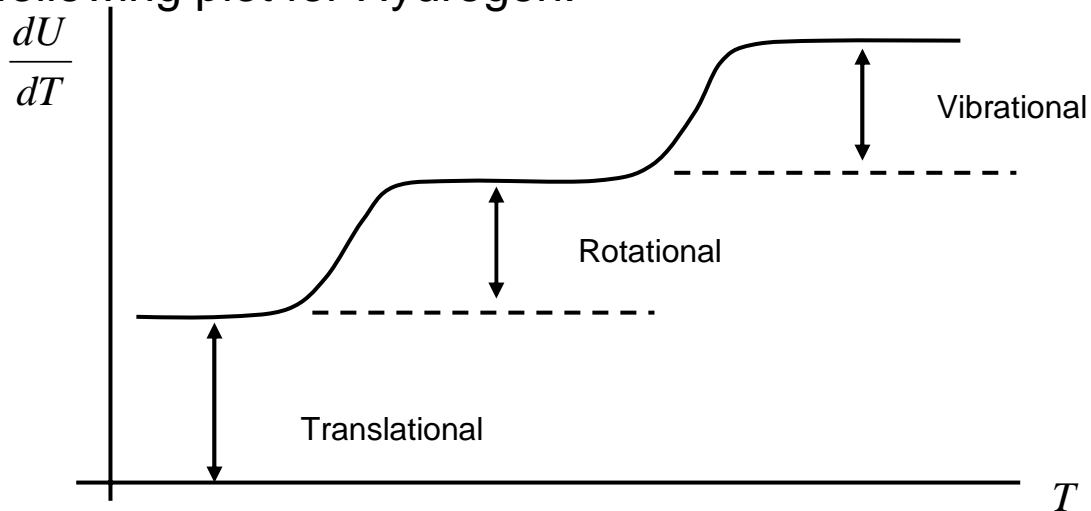
$$\frac{dU}{dT} = \left( \frac{1}{k_B} \frac{dE_{avg}}{dT} \right) 3Nk_B = (0.92)3Nk_B = 2.76Nk_B$$

- From table T2.2, lead has  $2.92Nk_B$ .

- Our results predict the general trends...they are off by a small amount...of the solids.

# Energy Stored in Gas Molecule

- Let's finish this term by returning to a problem that we came across early in our study of unit T. We had the following plot for Hydrogen:



- Let's start by thinking about the *vibrational* mode for  $H_2$ . We can think about these modes being described by a simple harmonic oscillator.
  - The  $\epsilon = 0.44$  eV for the vibrational modes:
    - ❑  $T_\epsilon = \epsilon/k_B = 5100$  K.
    - ❑ At room temperature  $T/T_\epsilon$  is **very** small
    - ❑ From the plot T7.8, this means the amount of energy stored in vibrational modes is nearly zero.
    - ❑ In fact, the amount of energy stored in these modes does not become significant until  $T \sim T_\epsilon$ .
- Although the rotational modes cannot be modeled by a simple harmonic oscillator, there is some characteristic temperature  $T_\epsilon$  where the modes “turn on” for storage.
  - The “ $\epsilon$ ” can be approximated by the  $\Delta E$  to first excited st.
  - Notice this “stepping” is only possible if the energy levels are **quantized**...Newtonian Mechanics doesn't work!