## Physics 141. Lecture 22.



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# Physics 141. Lecture 22.

- Course Information.
- Entropy.
  - Quick review of topics discussed during our last lecture.

  - The Maxwell-Boltzmann velocity distribution of gas molecules.

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# Analysis of experiment # 5. Updated Timeline.

- √11/14: collisions in the May room
- ✓ 11/20: analysis files available.
- https://www.pas.rochester.edu/~tdimino/phy141/lab05/
  ✓ 11/20: each student has determined his/her
- best estimate of the velocities before and after the collisions (analysis during regular lab periods).
- ✓ 11/21: complete discussion and comparison of results with colliding partners and submit final results (velocities and errors).
- ✓ 11/25: results will be compiled, linear momenta and kinetic energies will be determined, and results will be distributed.
- 12/4: office hours by lab TA/TIs to help with analysis and conclusions.

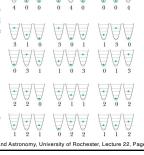


12/6: students submit lab report # 5.
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## Distributing 4 units of energy among three degrees of freedom.

- · Consider an atom with three degrees of freedom; each degree of freedom has a vibrational character with the
- characteristic frequency.
- For this system we find:
  - 3 ways: 4:0:0 configuration.

  - 6 ways: 3:1:0 configuration.
    3 ways: 2:2:0 configuration.
    3 ways: 1:1:2 configuration.
- · What is the probability to see the different configurations?



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## Distributing energy. The fundamental assumption.

• In order to determine the probability to observe a certain configuration, we rely on the fundamental assumption of statistical mechanics to make this determination:

A fundamental assumption in statistical mechanics is that in our state of microscopic ignorance, each microstate (microscopic distribution of energy) corresponding to a given macrostate (total energy) is equally probable.

- For example N = 3:
  15 microstates; probability of each one is 1/15.
  - 3 ways: 4:0:0 configuration (20% probability). 6 ways: 3:1:0 configuration (40% probability).

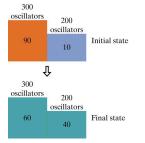
  - 3 ways: 2:2:0 configuration (20% probability).
    3 ways: 1:1:2 configuration (20% probability).

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# Distributing energy. Achieving equilibrium.

- · Consider bringing the two blocks in contact when the first block has 90 quanta of vibrational energy and the second block only 10.
- The process of exchange of energy is a random (statistical) process, the direction of transfer will be in the direction in which the number of possible states increases.
- The exchange of energy will continue



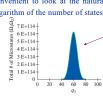
even when the most probable distribution is reached, but at that point there will only be small fluctuation around the most probable

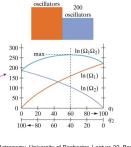
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# Distributing energy. Number of states: different representations.

 Since the number of states of a system is enormous (even for small system with a few hundred oscillators) it is often more convenient to look at the natural logarithm of the number of states.





 $S = S_1 + S_2$ 

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## Entropy.

 $300k_B$ 

 $250k_B$ 

 $200k_{B} = 150k_{B} = 100k_{B} = 100k_{B}$ 

 $50k_B$  $0k_B$ 

80

40 20

- Since the evolution of the system depends on the number of microstates, the concept of entropy is introduced.
- The entropy S of one of the blocks we have been discussing is defined

 $S = k \ln \Omega$ 

where k is the Boltzmann constant (1.4 x  $10^{-24}$  J/K).

• The entropy of the total system is the sum of the entropy of the blocks

that make up the system.

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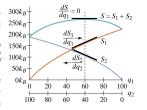
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# Entropy and the Second Law of Thermodynamics.

- To achieve thermal equilibrium, the
- system will maximize its entropy.
- The most likely evolution of the system is the focus of the second law of thermodynamics:  $200k_B$

If a closed system is not in equilibrium, the most probable consequence is that the entropy of the system will increase.

 Note: even when the two blocks are in thermal equilibrium, there may still be exchange of energy between the blocks, but the time averaged energy exchange will be zero.



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# Entropy and the Second Law of Thermodynamics.

 $200k_B$  $150k_B$ 

 $100k_B$  $50k_B$  $0k_B \stackrel{\checkmark}{0}$ 20

• If we know the entropy as function of for example the number of vibrational quanta of block 1, we  $300k_B$ can express the condition for  $250k_B$ . equilibrium as

$$\frac{dS}{dq_{_{1}}} = \frac{dS_{_{1}}}{dq_{_{1}}} + \frac{dS_{_{2}}}{dq_{_{1}}} = 0$$



80

100

60 80

60 40

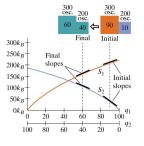
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## Entropy and the temperature.

• Since  $q_1 + q_2 = \text{constant}$  (assuming there is no exchange of energy with the environment surrounding the two blocks), the condition for equilibrium can be rewritten as

$$\frac{dS_1}{dq_1} = \frac{dS_2}{dq_2}$$

· Since thermal equilibrium is achieved when the temperature of the blocks are the same, the slope of the entropy curves must be related to the temperature of the blocks.



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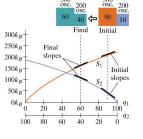
## Entropy and the temperature.

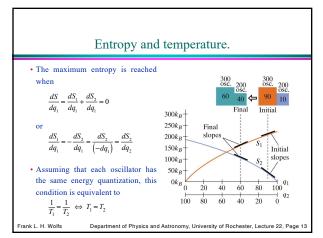
• The temperature of a system is defined as

$$\frac{1}{T} = \frac{dS}{dE_{\rm int}}$$

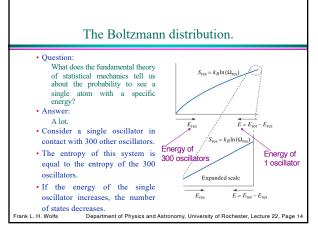
• The temperature defined in this manner is expressed in units of Kelvin (K) since the internal energy is 100k<sub>B</sub>. measured in units of Joules and the entropy is measured in units of J/K.







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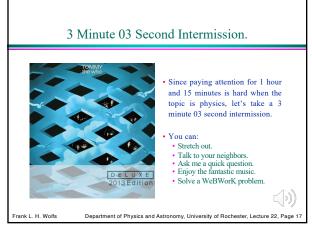


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#### The Boltzmann distribution. • The entropy curve is close to linear at small $\Delta E$ and its slope is $S_{res} = k_B \ln (\Omega_{res})$ equal to $dS/dE_1$ . • We can approximate the dependence of the entropy on $\Delta E$ in the following manner: $E = E_{\text{tot}} - E_{\text{res}}$ $= k_B \ln{(\Omega_{\rm res})}$ Energy of • The number of states of the 300 oscillators Energy of 1 oscillator system, as function of $\Delta E$ , can Expanded scale $\Omega = e^{\ln \Omega} = e^{S/k} = e^{A/k} e^{-\Delta E/kT}$ $E = E_{\text{tot}} - E_{\text{res}}$ Department of Physics and Astronomy, University of Rochester, Lecture 22, Page 15

# The Boltzmann distribution. • Since the probability is proportional to the number of states, we conclude that: the probability of finding a microscopic system to be in a state with energy $\Delta E$ above the ground state of the system is proportional to $e^{\Delta E kT}$ . • This probability distribution is called the **Boltzmann distribution**.

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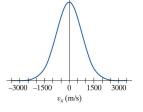
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#### The Boltzmann distribution. • The energy of a gas molecule can have various components: TranslationalVibrationalRotational Gravitational • For each component, Translation probability will show exponential dependence energy. • I will first focus on translational component. Department of Physics and Astronomy, University of Rochester, Lecture 22, Page 18

#### The Boltzmann distribution.

- Consider that the gas molecule is moving with a velocity  $v_x$  along the x axis.
- The energy of the gas molecule, associated with its motion along the x axis, will be  $(1/2)Mv_x^2$ .
- The probability of finding the gas molecule with a velocity between  $v_x$  and  $v_x + dv_x$  is equal to

$$P(v_x)dv_x \propto e^{-\left(\frac{1}{2}Mv_x^2\right)/kT}dv_x$$



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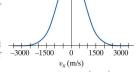
#### The Boltzmann distribution.

• We can do the same calculation for the velocity distribution along the y and z axes:

$$P(v_y)dv_y \propto e^{-\left(\frac{1}{2}Mv_y^2\right)/kT}dv_y$$

$$P(v_z)dv_z \propto e^{-\left(\frac{1}{2}Mv_z^2\right)/kT}dv_z$$

to determine the dependence of



the probability on v:

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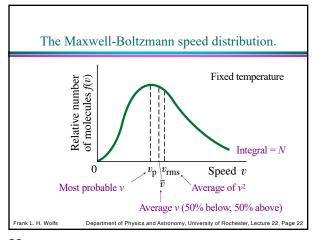
## The Maxwell-Boltzmann speed distribution.

• The probability to find a molecule with a speed between v and v + dv is thus proportional to

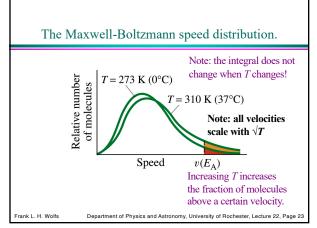
$$P(v)dv \propto 4\pi v^2 e^{-\left(\frac{1}{2}Mv^2\right)/kT} dv$$

• But the probability to find the molecule with a speed between 0 and infinity is equal to 1. Thus:
$$1 = \int_{0}^{\infty} P(v) dv = 4\pi C \int_{0}^{\infty} v^{2} e^{-\left(\frac{1}{2}Mv^{2}\right)^{kT}} dv = C \left(\frac{2\pi kT}{M}\right)^{3/2}$$

• The velocity distribution is thus equal to
$$P(v) = 4\pi \left(\frac{M}{2\pi kT}\right)^{3/2} v^2 e^{-\left(\frac{1}{2}Mv^2\right)/kT}$$



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# The Boltzmann distribution and internal energy.

 $\bullet$  The root-mean-square velocity associated with one degree of freedom (for example, motion in the x direction) is equal to

$$v_{x,r}^{2} \int_{0}^{\infty} v_{x}^{2} e^{-\left(\frac{1}{2}Mv_{x}^{2}\right)/kT} dv_{x} = \frac{2}{M} \int_{0}^{\infty} \omega^{2} e^{-\omega^{2}/kT} d\omega = \frac{2}{M} \frac{1}{2}kT = \frac{1}{M}kT$$

• The root-mean-square kinetic energy associated with this degree of freedom is thus equal to

$$\overline{K}_{x,rms} = \frac{1}{2} M v_{x,rms}^{2} = \frac{1}{2} kT$$

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# The Boltzmann distribution and internal energy.

• The root-mean-square kinetic energy associated with the three translational degrees of freedom is thus equal to

$$\overline{K}_{rms} = \overline{K}_{x,rms} + \overline{K}_{y,rms} + \overline{K}_{z,rms} = \frac{3}{2}kT$$

- It turns out that the average energy associated with each degree of freedom, including vibrational and rotational degrees of freedom, is (1/2)kT.
- - The internal energy only depends on the temperature; it does **not** depend on the mass of the gas molecules.
- At a given temperature, the rms velocity of heavier molecules will be smaller than the rms velocity of lighter molecules.

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# The Boltzmann distribution and internal energy.

- Up to now we have assumed that the internal energy U of a gas is equal to (3/2)kT.
- · This is correct for a monatomic gas, but is not correct for diatomic or triatomic
- Predictions for a diatomic molecule:
- Linear motion (3 degrees of freedom): U = (3/2)kT.
- U = (3/2)kT. Rotational motion (2 degrees of freedom): U = kT. Vibrational motion (2 degrees of freedom): U = kT.
- The number of degrees of freedom



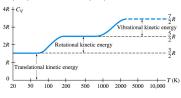
excited depend on the temperature.
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# The Boltzmann distribution and internal energy.

Remember:  $Q = C \Delta T$ 

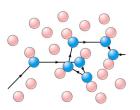
But: K = (1/2)nkT and  $\Delta K = (1/2)nk \Delta T$ 



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# Molecular speed and its consequences. The mean-free path.

- The RMS velocities of individual gas molecules are large. For example, for hydrogen at room temperature, the RMS velocity is 1920 m/s.
- Despite the large RMS velocity, the average diffusion velocity is much smaller and is largely determined by the mean-free path of the molecules.
- We expect that the mean-free path is inversely proportional to the crosssectional area of the molecules and inversely proportional to the density.



Typical values of the mean-free path are between 10<sup>-8</sup> and 10<sup>-7</sup> m

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# Molecular speed and its consequences. The propagation of sound.

- Typical values for  $v_{\rm rms}$ :
  - For H at 300 K:  $v_{\rm rms}$  = 1,920 m/s. • For N at 300 K:  $v_{\rm rms}$  = 517 m/s.
- The speed of sound in these two gases is 1,350 m/s for H and 350 m/s for N.
- Note: The speed of sound in a gas will always be less than  $\nu_{\rm rms}$  since the sound propagates through the gas by disturbing the motion of the molecules. The disturbance is passed on from molecule to molecule by means of collisions; a sound wave can therefore never travel faster than the average speed of the molecules. Since  $\nu_{\rm rms}$  increases with T, we expect vsound to increase with T.

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# Molecular speed and its consequences. The composition of the atmosphere.

- Typical values for  $v_{\rm rms}$ :
- For H at 300 K: ν<sub>rms</sub> = 1,920 m/s.
   For N at 300 K: ν<sub>rms</sub> = 517 m/s.
- A significant fraction of the H molecules in the atmosphere have a velocity that exceeds the escape velocity of the earth. This is one of the reasons that our atmosphere contains virtually no hydrogen and helium.
- Since the escape velocity decreases with decreasing planetary mass, the escape velocity of the moon is so low that it has no atmosphere (even the heavier gas molecules would quickly escape).

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# Molecular speed and its consequences. Evaporation.

- Evaporation: transformation from the liquid to the gas phase.
- the liquid to the gas phase.

  A microscopic view of evaporation:

  Molecules with high velocity moving close to the surface can overcome the strong attractive forces between the molecules and escape from the liquid (evaporation).

  The average velocity of the molecules left behind in the liquid will be lowered.

  Since the average velocity is proportional to the temperature, the temperature of the liquid is lowered when evaporation takes place.



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# Enough physics for this week!



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