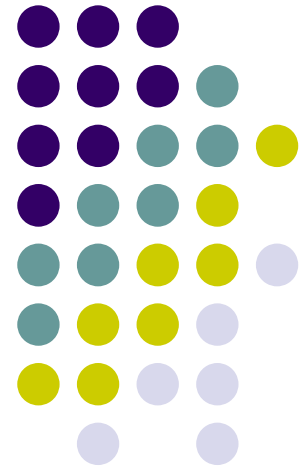


# Chapter 21

## The Kinetic Theory of Gases





# Molecular Model of an Ideal Gas

- Macroscopic properties of a gas were pressure, volume and temperature
- Can be related to microscopic description
  - Matter is treated as a collection of molecules
  - Newton's Laws of Motion can be applied statistically
- The microscopic description is consistent with the macroscopic description developed earlier



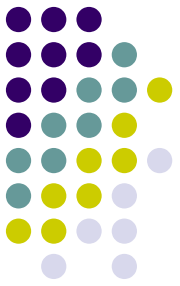
# Ideal Gas Assumptions

- The number of molecules in the gas is large, and the average separation between the molecules is large compared with their dimensions
  - The molecules occupy a negligible volume within the container
  - This is consistent with the macroscopic model where we assumed the molecules were point-like



# Ideal Gas Assumptions, 2

- The molecules obey Newton's laws of motion, but as a whole they move randomly
  - Any molecule can move in any direction with any speed
- The molecules interact only by short-range forces during elastic collisions
  - This is consistent with the macroscopic model, in which the molecules exert no long-range forces on each other



# Ideal Gas Assumptions, 3

- The molecules make elastic collisions with the walls
  - These collisions lead to the macroscopic pressure on the walls of the container
- The gas under consideration is a pure substance
  - All molecules are identical



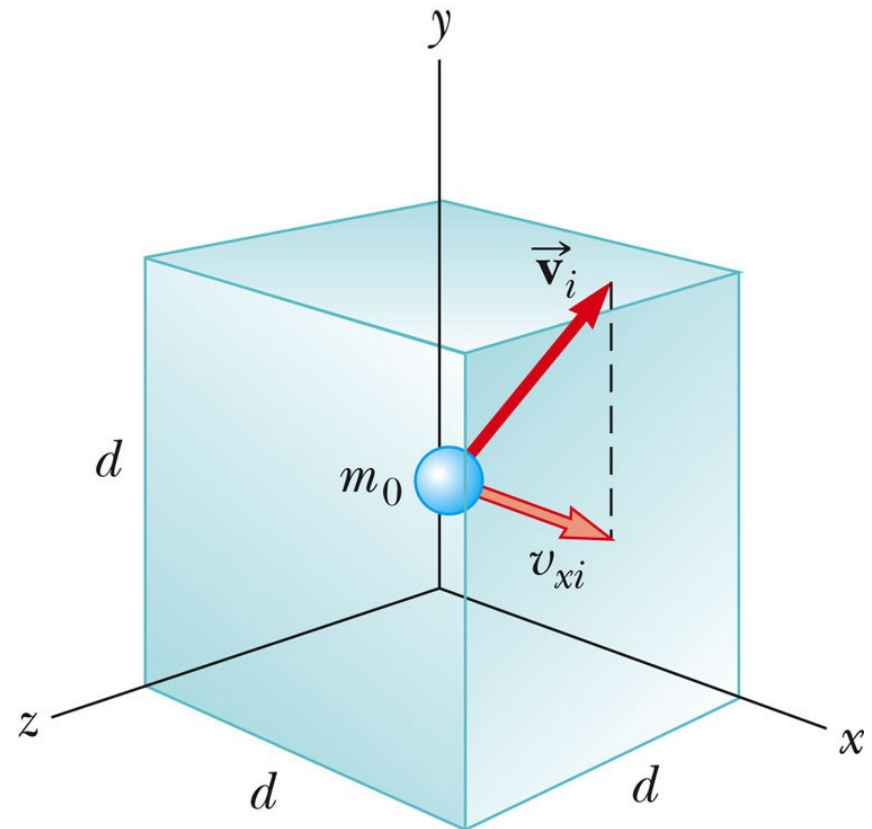
# Ideal Gas Notes

- An ideal gas is often pictured as consisting of single atoms
- However, the behavior of molecular gases approximate that of ideal gases quite well
  - At low pressures
  - Molecular rotations and vibrations have no effect, on average, on the motions considered



# Pressure and Kinetic Energy

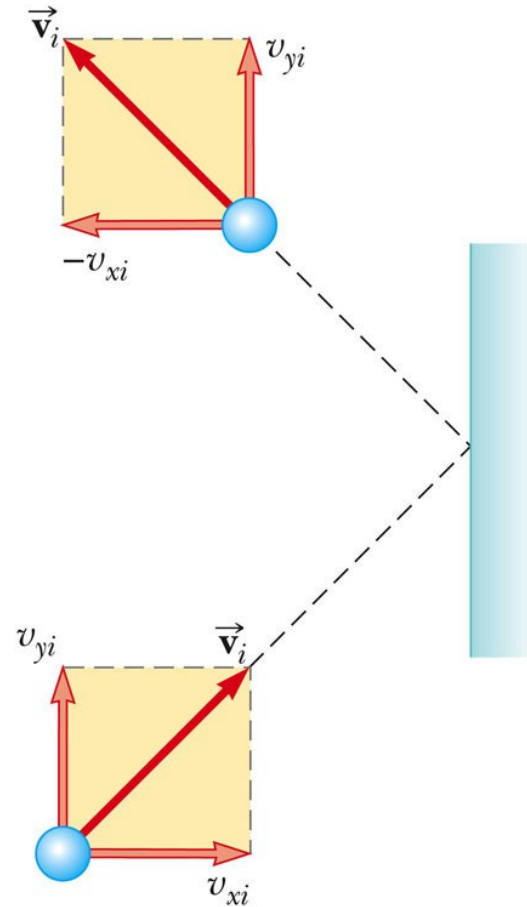
- Assume a container is a cube
  - Edges are length  $d$
- Look at the motion of the molecule in terms of its velocity components
- Look at its momentum and the average force





# Pressure and Kinetic Energy, 2

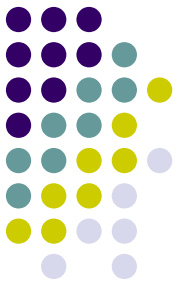
- Assume perfectly elastic collisions with the walls of the container
- The relationship between the pressure and the molecular kinetic energy comes from momentum and Newton's Laws
- Use the active figure to observe collisions



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# Pressure and Kinetic Energy, 3

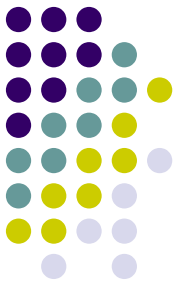


- The relationship is

$$P = \frac{2}{3} \left( \frac{N}{V} \right) \left( \frac{1}{2} m_o \overline{v^2} \right)$$

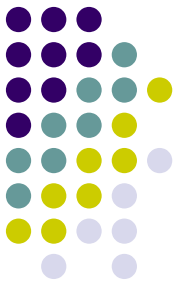
- This tells us that pressure is proportional to the number of molecules per unit volume ( $N/V$ ) and to the average translational kinetic energy of the molecules

# Pressure and Kinetic Energy, final



- This equation also relates the macroscopic quantity of pressure with a microscopic quantity of the average value of the square of the molecular speed
- One way to increase the pressure is to increase the number of molecules per unit volume
- The pressure can also be increased by increasing the speed (kinetic energy) of the molecules

# Molecular Interpretation of Temperature

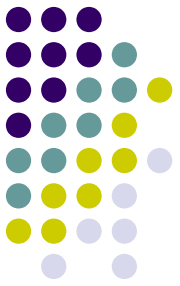


- We can take the pressure as it relates to the kinetic energy and compare it to the pressure from the equation of state for an ideal gas

$$P = \frac{2}{3} \left( \frac{N}{V} \right) \left( \frac{1}{2} m \overline{v^2} \right) = Nk_B T$$

- Therefore, the temperature is a direct measure of the average molecular kinetic energy

# Molecular Interpretation of Temperature, cont



- Simplifying the equation relating temperature and kinetic energy gives

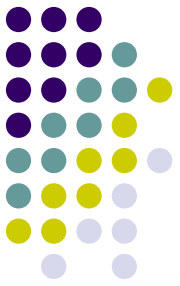
$$\frac{1}{2}m_o \overline{v^2} = \frac{3}{2}k_B T$$

- This can be applied to each direction,

$$\frac{1}{2}m \overline{v_x^2} = \frac{1}{2}k_B T$$

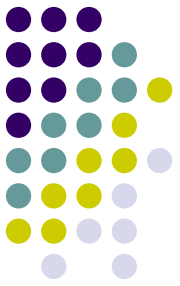
- with similar expressions for  $v_y$  and  $v_z$

# A Microscopic Description of Temperature, final



- Each translational degree of freedom contributes an equal amount to the energy of the gas
  - In general, a degree of freedom refers to an independent means by which a molecule can possess energy
- A generalization of this result is called the **theorem of equipartition of energy**

# Theorem of Equipartition of Energy



- Each degree of freedom contributes  $\frac{1}{2}k_B T$  to the energy of a system, where possible degrees of freedom are those associated with translation, rotation and vibration of molecules



# Total Kinetic Energy

- The total kinetic energy is just  $N$  times the kinetic energy of each molecule

$$K_{\text{tot trans}} = N \left( \frac{1}{2} m \overline{v^2} \right) = \frac{3}{2} N k_B T = \frac{3}{2} n R T$$

- If we have a gas with only translational energy, this is the internal energy of the gas
- This tells us that the internal energy of an ideal gas depends only on the temperature



# Root Mean Square Speed

- The root mean square (rms) speed is the square root of the average of the squares of the speeds
  - Square, average, take the square root
- Solving for  $v_{\text{rms}}$  we find

$$v_{\text{rms}} = \sqrt{\frac{3k_{\text{B}}T}{m}} = \sqrt{\frac{3RT}{M}}$$

- $M$  is the molar mass and  $M = mN_A$





# Some Example $v_{\text{rms}}$ Values

**TABLE 21.1**

Some Root-Mean-Square (rms) Speeds

Gas	Molar Mass (g/mol)	$v_{\text{rms}}$ at 20°C (m/s)	Gas	Molar Mass (g/mol)	$v_{\text{rms}}$ at 20°C (m/s)
H <sub>2</sub>	2.02	1902	NO	30.0	494
He	4.00	1352	O <sub>2</sub>	32.0	478
H <sub>2</sub> O	18.0	637	CO <sub>2</sub>	44.0	408
Ne	20.2	602	SO <sub>2</sub>	64.1	338
N <sub>2</sub> or CO	28.0	511			

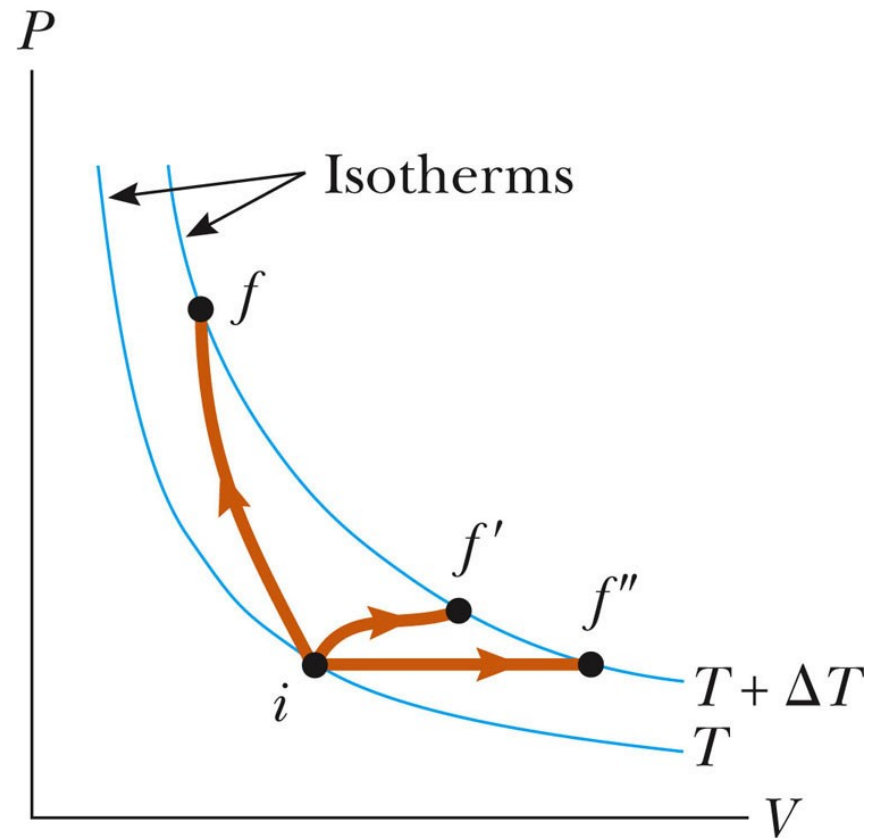
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At a given temperature, lighter molecules move faster, on the average, than heavier molecules



# Molar Specific Heat

- Several processes can change the temperature of an ideal gas
- Since  $\Delta T$  is the same for each process,  $\Delta E_{\text{int}}$  is also the same
- The heat is different for the different paths
- The heat associated with a particular change in temperature is **not** unique





# Molar Specific Heat, 2

- We define specific heats for two processes that frequently occur:
  - Changes with constant pressure
  - Changes with constant volume
- Using the number of moles,  $n$ , we can define molar specific heats for these processes



# Molar Specific Heat, 3

- Molar specific heats:
  - $Q = nC_V \Delta T$  for constant-volume processes
  - $Q = nC_P \Delta T$  for constant-pressure processes
- $Q$  (constant pressure) must account for both the increase in internal energy and the transfer of energy out of the system by work
- $Q_{\text{constant } P} > Q_{\text{constant } V}$  for given values of  $n$  and  $\Delta T$



# Ideal Monatomic Gas

- A monatomic gas contains one atom per molecule
- When energy is added to a monatomic gas in a container with a fixed volume, all of the energy goes into increasing the translational kinetic energy of the gas
  - There is no other way to store energy in such a gas



# Ideal Monatomic Gas, cont

- Therefore,  $\Delta E_{\text{int}} = \frac{3}{2} nRT$ 
  - $\Delta E$  is a function of  $T$  only
- In general, the internal energy of an ideal gas is a function of  $T$  only
  - The exact relationship depends on the type of gas
- At constant volume,  $Q = \Delta E_{\text{int}} = nC_V \Delta T$ 
  - This applies to all ideal gases, not just monatomic ones



# Monatomic Gases, final

- Solving for  $C_V$  gives  $C_V = 3/2 R = 12.5 \text{ J/mol} \cdot \text{K}$ 
  - For all monatomic gases
  - This is in good agreement with experimental results for monatomic gases
- In a constant-pressure process,  $\Delta E_{\text{int}} = Q + W$  and  $C_P - C_V = R$ 
  - This also applies to any ideal gas
  - $C_p = 5/2 R = 20.8 \text{ J/mol} \cdot \text{K}$



# Ratio of Molar Specific Heats

- We can also define the ratio of molar specific heats

$$\gamma = \frac{C_P}{C_V} = \frac{5R/2}{3R/2} = 1.67$$

- Theoretical values of  $C_V$ ,  $C_P$ , and  $\gamma$  are in excellent agreement for monatomic gases
- But they are in serious disagreement with the values for more complex molecules
  - Not surprising since the analysis was for monatomic gases



# Sample Values of Molar Specific Heats



**TABLE 21.2**

**Molar Specific Heats of Various Gases**

Gas	Molar Specific Heat (J/mol · K) <sup>a</sup>			$\gamma = C_P/C_V$
	$C_P$	$C_V$	$C_P - C_V$	
<i>Monatomic gases</i>				
He	20.8	12.5	8.33	1.67
Ar	20.8	12.5	8.33	1.67
Ne	20.8	12.7	8.12	1.64
Kr	20.8	12.3	8.49	1.69
<i>Diatomic gases</i>				
H <sub>2</sub>	28.8	20.4	8.33	1.41
N <sub>2</sub>	29.1	20.8	8.33	1.40
O <sub>2</sub>	29.4	21.1	8.33	1.40
CO	29.3	21.0	8.33	1.40
Cl <sub>2</sub>	34.7	25.7	8.96	1.35
<i>Polyatomic gases</i>				
CO <sub>2</sub>	37.0	28.5	8.50	1.30
SO <sub>2</sub>	40.4	31.4	9.00	1.29
H <sub>2</sub> O	35.4	27.0	8.37	1.30
CH <sub>4</sub>	35.5	27.1	8.41	1.31

<sup>a</sup> All values except that for water were obtained at 300 K.

# Molar Specific Heats of Other Materials



- The internal energy of more complex gases must include contributions from the rotational and vibrational motions of the molecules
- In the cases of solids and liquids heated at constant pressure, very little work is done, since the thermal expansion is small, and  $C_p$  and  $C_v$  are approximately equal

# Adiabatic Processes for an Ideal Gas

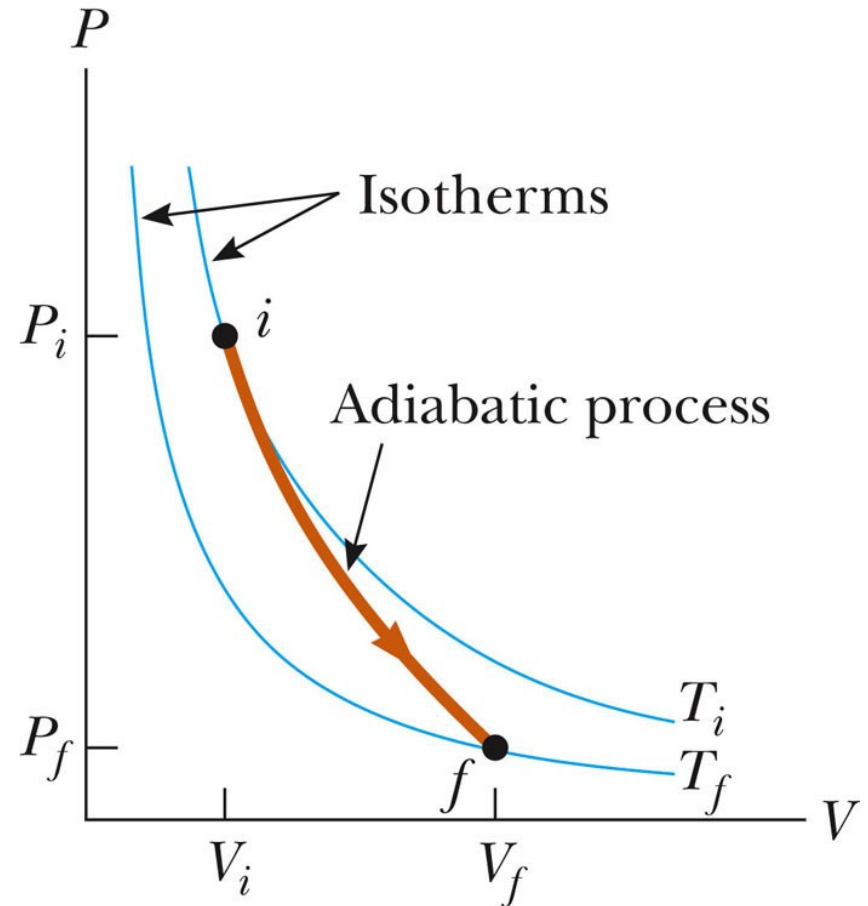


- An adiabatic process is one in which no energy is transferred by heat between a system and its surroundings
- Assume an ideal gas is in an equilibrium state and so  $PV = nRT$  is valid
- The pressure and volume of an ideal gas at any time during an adiabatic process are related by  $PV^\gamma = \text{constant}$
- $\gamma = C_p / C_v$  is assumed to be constant during the process
- All three variables in the ideal gas law ( $P, V, T$ ) can change during an adiabatic process



# Adiabatic Process, cont

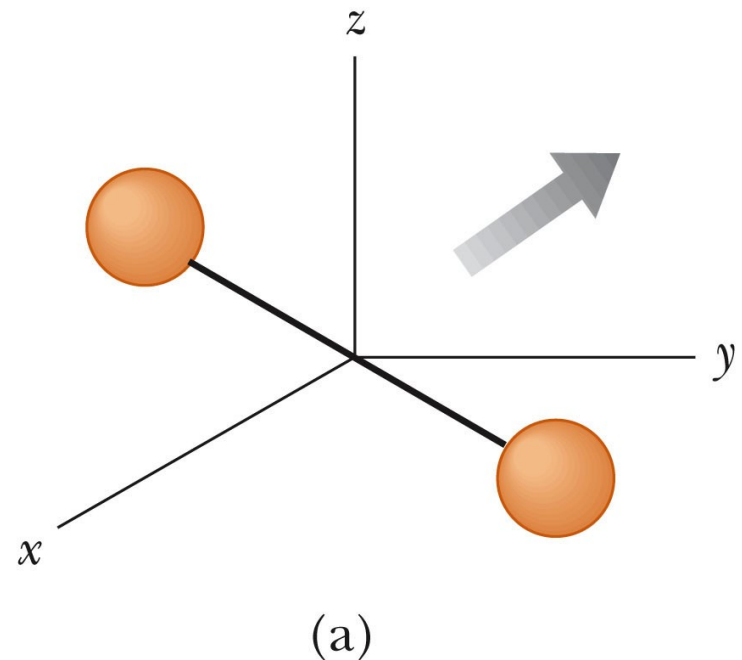
- The PV diagram shows an adiabatic expansion of an ideal gas
- The temperature of the gas decreases
  - $T_f < T_i$  in this process
- For this process
$$P_i V_i^\gamma = P_f V_f^\gamma \text{ and}$$
$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$$





# Equipartition of Energy

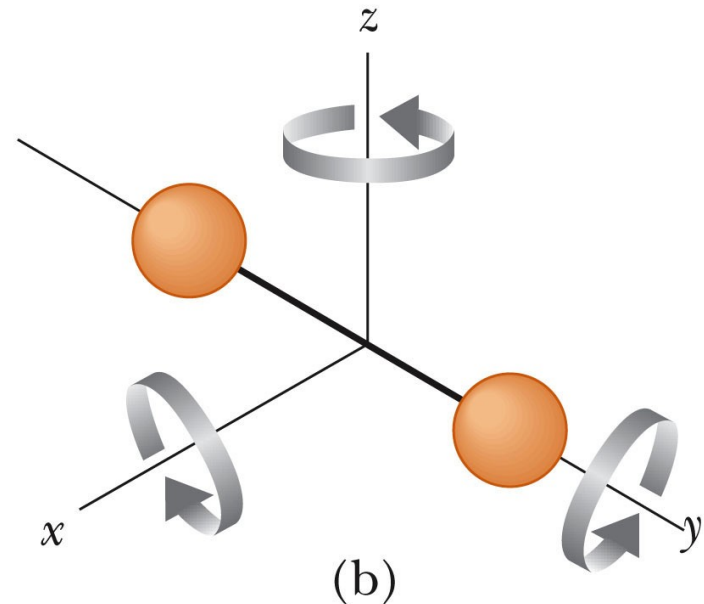
- With complex molecules, other contributions to internal energy must be taken into account
- One possible energy is the translational motion of the center of mass

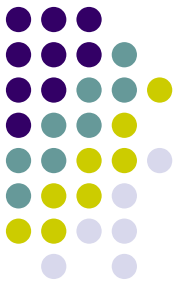


# Equipartition of Energy, 2



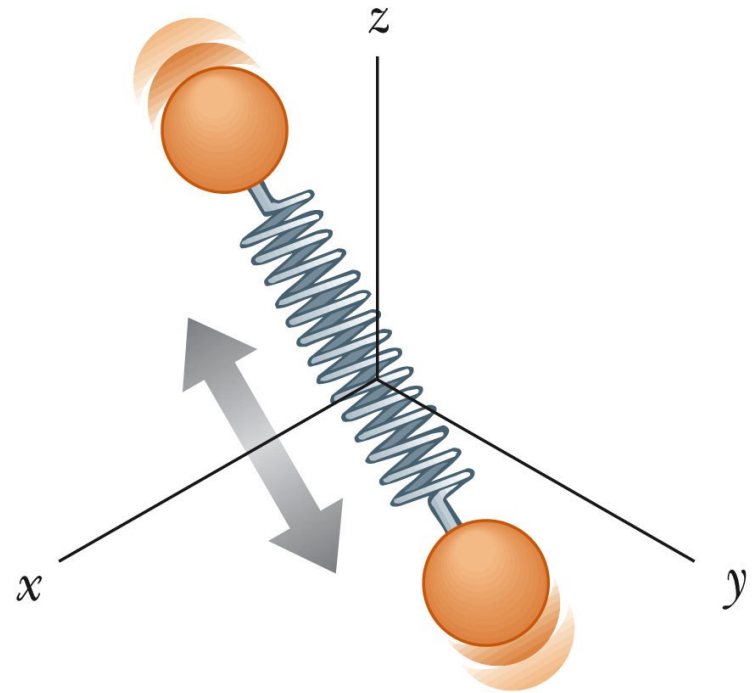
- Rotational motion about the various axes also contributes
  - We can neglect the rotation around the  $y$  axis since it is negligible compared to the  $x$  and  $z$  axes
    - For this molecule, there are only rotational d.o.f.





# Equipartition of Energy, 3

- The molecule can also vibrate
- There is kinetic energy and potential energy associated with the vibrations



(c)



# Equipartition of Energy, 4

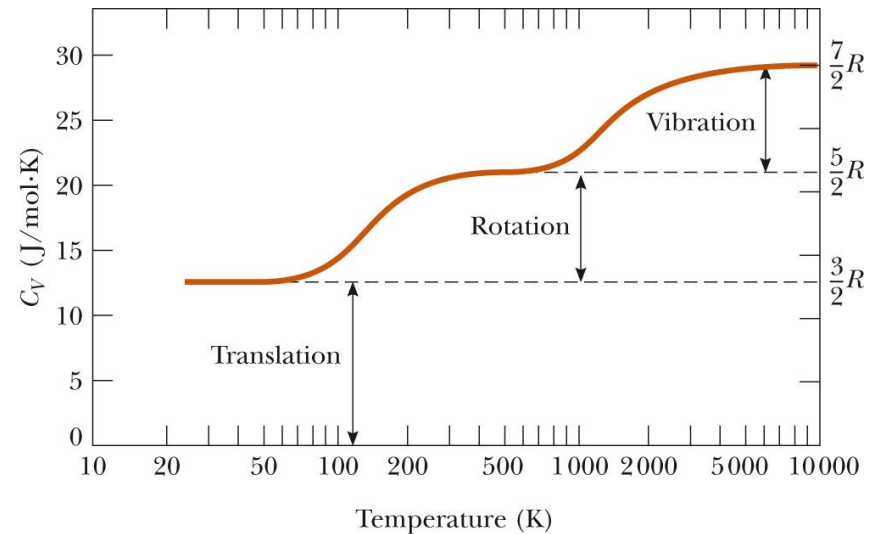
- The translational motion adds three degrees of freedom
- The rotational motion adds two degrees of freedom
- The vibrational motion adds two more degrees of freedom
- Therefore,  $E_{\text{int}} = 7/2 nRT$  and  $C_v = 7/2 R$
- This is inconsistent with experimental results



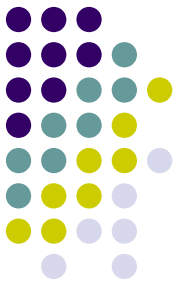
# Agreement with Experiment



- Molar specific heat is a function of temperature
- At low temperatures, a diatomic gas acts like a monatomic gas
  - $C_V = 3/2 R$



# Agreement with Experiment, cont



- At about room temperature, the value increases to  $C_V = 5/2 R$ 
  - This is consistent with adding rotational energy but not vibrational energy
- At high temperatures, the value increases to  $C_V = 7/2 R$ 
  - This includes vibrational energy as well as rotational and translational



# Complex Molecules

- For molecules with more than two atoms, the vibrations are more complex
- The number of degrees of freedom is larger
- The more degrees of freedom available to a molecule, the more “ways” there are to store energy
  - This results in a higher molar specific heat



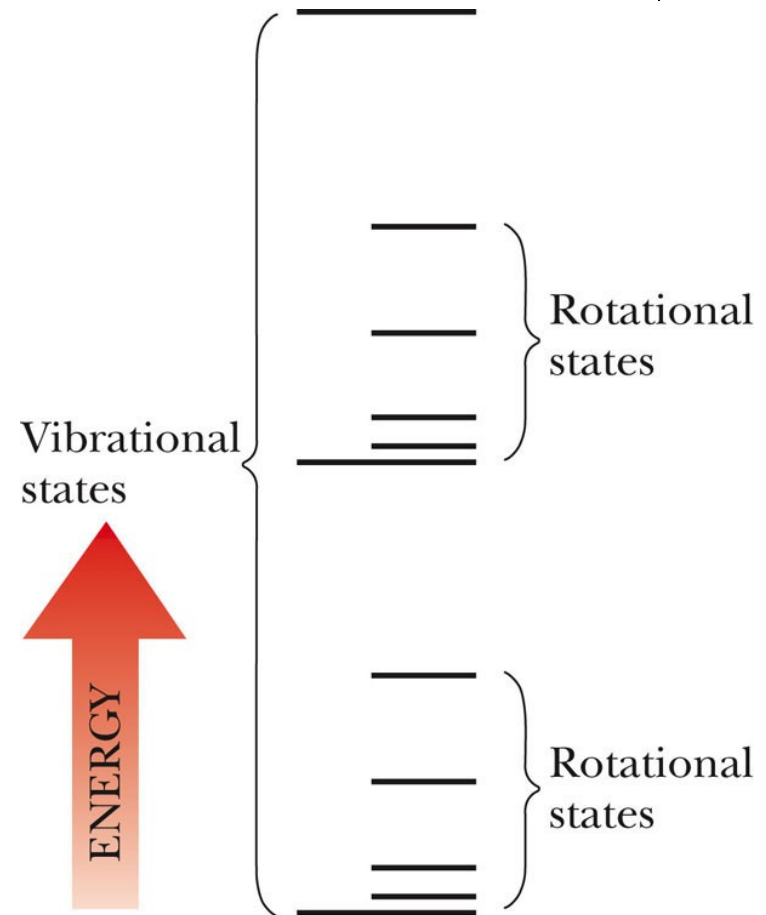
# Quantization of Energy

- To explain the results of the various molar specific heats, we must use some quantum mechanics
  - Classical mechanics is not sufficient
- In quantum mechanics, the energy is proportional to the frequency of the wave representing the frequency
- The energies of atoms and molecules are quantized



# Quantization of Energy, 2

- This energy level diagram shows the rotational and vibrational states of a diatomic molecule
- The lowest allowed state is the **ground state**





# Quantization of Energy, 3

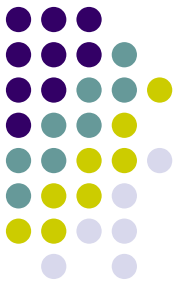
- The vibrational states are separated by larger energy gaps than are rotational states
- At low temperatures, the energy gained during collisions is generally not enough to raise it to the first excited state of either rotation or vibration



# Quantization of Energy, 4

- Even though rotation and vibration are classically allowed, they do not occur
- As the temperature increases, the energy of the molecules increases
- In some collisions, the molecules have enough energy to excite to the first excited state
- As the temperature continues to increase, more molecules are in excited states

# Quantization of Energy, final



- At about room temperature, rotational energy is contributing fully
- At about 1000 K, vibrational energy levels are reached
- At about 10 000 K, vibration is contributing fully to the internal energy





# Boltzmann Distribution Law

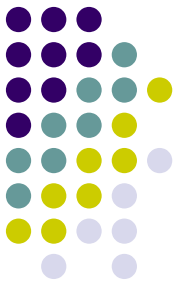
- The motion of molecules is extremely chaotic
- Any individual molecule is colliding with others at an enormous rate
  - Typically at a rate of a billion times per second
- We add the **number density**  $n_V(E)$ 
  - This is called a distribution function
  - It is defined so that  $n_V(E) dE$  is the number of molecules per unit volume with energy between  $E$  and  $E + dE$

# Number Density and Boltzmann Distribution Law

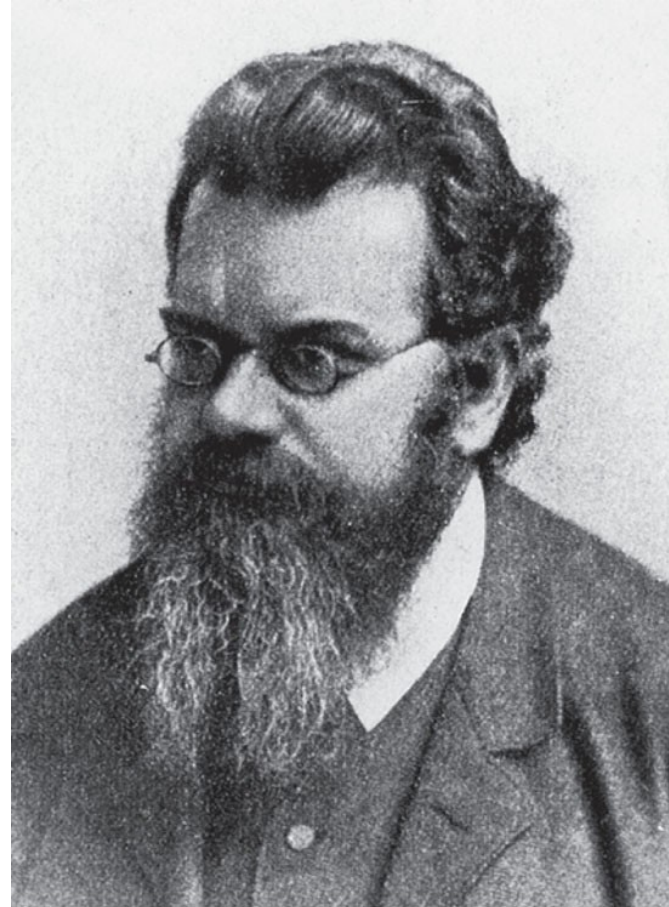


- From statistical mechanics, the number density is  $n_V(E) = n_0 e^{-E/k_B T}$
- This equation is known as the Boltzmann distribution law
- It states that the probability of finding the molecule in a particular energy state varies exponentially as the negative of the energy divided by  $k_B T$

# Ludwig Boltzmann



- 1844 – 1906
- Austrian physicist
- Contributed to
  - Kinetic Theory of Gases
  - Electromagnetism
  - Thermodynamics
- Pioneer in statistical mechanics

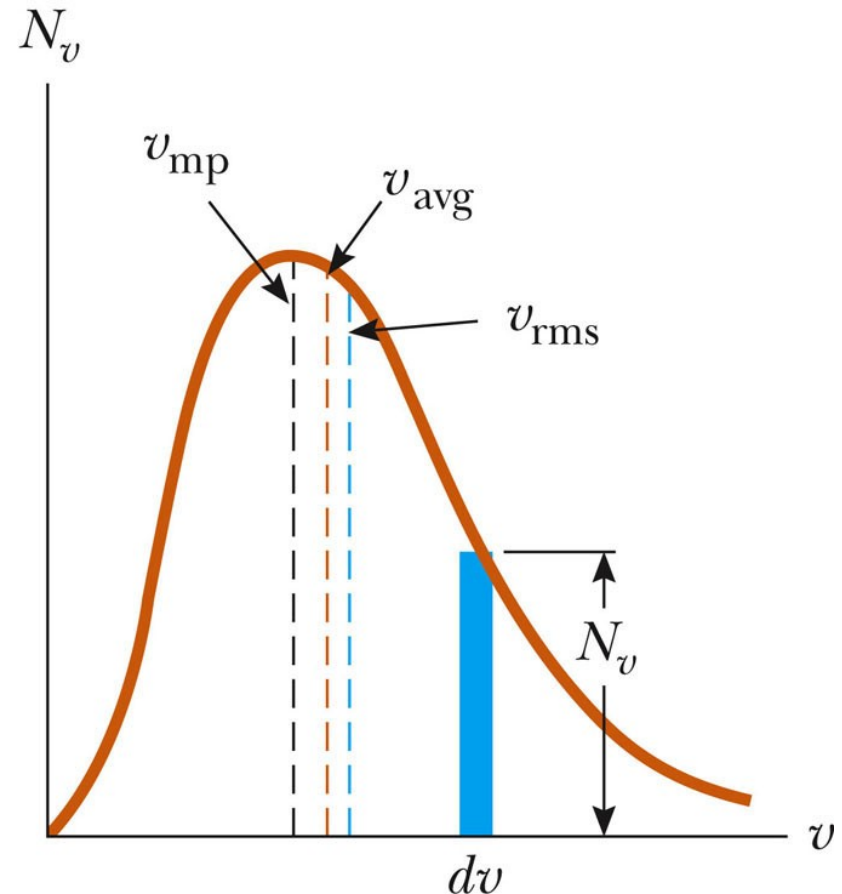


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# Distribution of Molecular Speeds



- The observed speed distribution of gas molecules in thermal equilibrium is shown at right
- $N_v$  is called the **Maxwell-Boltzmann speed distribution function**
- Use the active figure to measure the number of molecules in the blue bar





# Distribution Function

- The fundamental expression that describes the distribution of speeds in  $N$  gas molecules is

$$N_V = 4\pi N \left( \frac{m_o}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2 / 2k_B T}$$

- $m_o$  is the mass of a gas molecule,  $k_B$  is Boltzmann's constant and  $T$  is the absolute temperature



# Speed Summary

- Root mean square speed

$$v_{\text{rms}} = \sqrt{\frac{3k_{\text{B}}T}{m_o}} = 1.73 \sqrt{\frac{k_{\text{B}}T}{m_o}}$$

- The average speed is somewhat lower than the rms speed

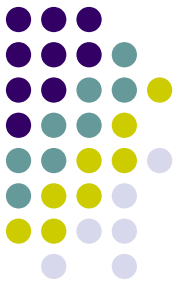
$$v_{\text{avg}} = \sqrt{\frac{8k_{\text{B}}T}{\pi m_o}} = 1.60 \sqrt{\frac{k_{\text{B}}T}{m_o}}$$

- The most probable speed,  $v_{\text{mp}}$  is the speed at which the distribution curve reaches a peak

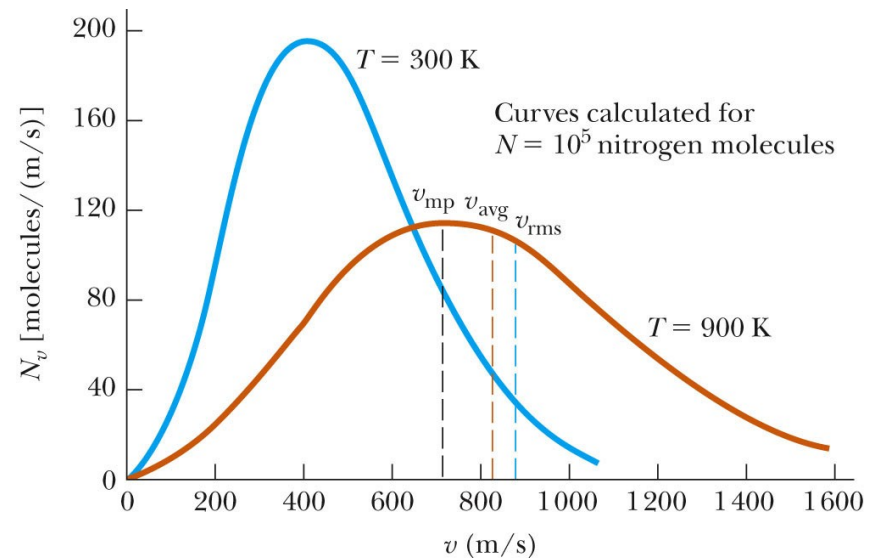
$$v_{\text{mp}} = \sqrt{\frac{2k_{\text{B}}T}{m}} = 1.41 \sqrt{\frac{k_{\text{B}}T}{m}}$$

- $v_{\text{rms}} > v_{\text{avg}} > v_{\text{mp}}$

# Speed Distribution



- The peak shifts to the right as  $T$  increases
  - This shows that the average speed increases with increasing temperature
- The asymmetric shape occurs because the lowest possible speed is 0 and the highest is infinity
- Use the active figure to set the temperature and observe the distribution curve





# Speed Distribution, final

- The distribution of molecular speeds depends both on the mass and on temperature
- The speed distribution for liquids is similar to that of gases





# Evaporation

- Some molecules in the liquid are more energetic than others
- Some of the faster moving molecules penetrate the surface and leave the liquid
  - This occurs even before the boiling point is reached
- The molecules that escape are those that have enough energy to overcome the attractive forces of the molecules in the liquid phase
- The molecules left behind have lower kinetic energies
- Therefore, evaporation is a cooling process