

# Chapter 21

## The Kinetic Theory of Gases



# Macroscopic vs. Macroscopic Descriptions

So far we have dealt with macroscopic variables:

- Pressure
- Volume
- Temperature

These can be related to a description on a microscopic level.

- Matter is treated as a collection of molecules.
- Applying Newton's laws of motion in a statistical manner to a collection of particles provides a reasonable description of thermodynamic processes.

Pressure and temperature relate directly to molecular motion in a sample of gas.

## Ideal Gas Assumptions

1. 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 modeled the molecules as particles.
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.
3. 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, cont.

4. The molecules make elastic collisions with the walls.
  - These collisions lead to the macroscopic pressure on the walls of the container.
5. 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
- Usually, molecular rotations and vibrations have no effect, on average, on the motions considered

## Pressure and Kinetic Energy

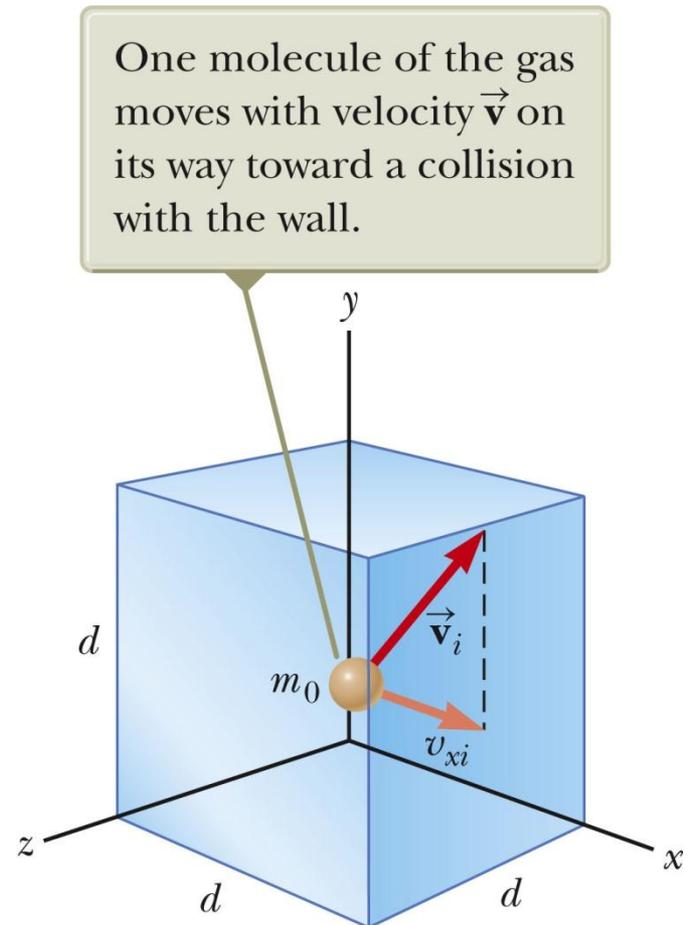
Consider a collection of  $N$  molecules of an ideal gas in a container of volume  $V$ .

Assume the 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.



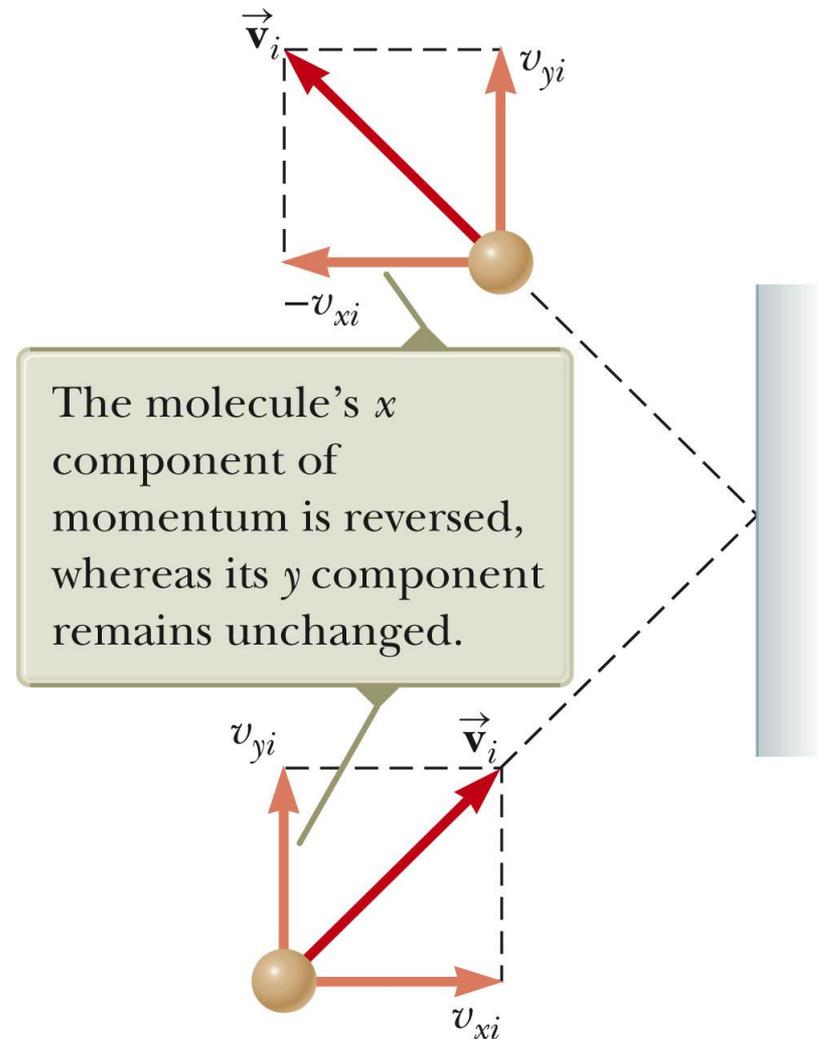
## Pressure and Kinetic Energy, 2

Assume perfectly elastic collisions with the walls of the container.

The molecule's velocity component perpendicular to the wall is reversed.

- The mass of the wall is much greater than the mass of the molecule.

The molecule is modeled as a non-isolated system for which the impulse from the wall causes a change in the molecule's momentum.



## Pressure and Kinetic Energy, 3

Analysis of the collision gives an expression for the total pressure exerted on the wall of the container .

- The total force exerted on the wall is

$$F = \frac{1}{3} N \frac{m_o \overline{v^2}}{d}$$

- The pressure is related to the kinetic energy.

The relationship is

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

This tells us that pressure:

- Is proportional to the number of molecules per unit volume ( $N/V$ )
- 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 raised by increasing the speed (kinetic energy) of the molecules.

- This can be accomplished by raising the temperature of the gas.

## 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.

$$PV = \frac{2}{3}N\left(\frac{1}{2}m_o\overline{v^2}\right) = Nk_B T$$

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

Simplifying the equation relating temperature and kinetic energy gives

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

$k_B$  is Boltzmann's Constant =  $R/N_A$

## Molecular Interpretation of Temperature, cont.

This can be applied to each direction,

$$\text{Since , } \overline{v_x^2} = \frac{1}{3} \overline{v^2}$$

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

- Similar expressions for  $v_y$  and  $v_z$  can be found.

Each translational degree of freedom contributes an equal amount to the energy of the gas,  $\frac{1}{2} k_B T$ .

- 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 translational kinetic energy is just  $N$  times the kinetic energy of each molecule.

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

$$\text{Where, } k_B = \frac{R}{N_A}$$

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

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_{\text{B}}T}{m_0}} = \sqrt{\frac{3RT}{M}}$$

$M$  is the molar mass (Kg/mol) and  $M = m_0 N_A$

Note about rms speed:

- The average is taken between the squaring and the square root steps.

$$\sqrt{(\bar{v})^2} = v_{\text{avg}} \text{ but } \sqrt{\overline{v^2}} \neq v_{\text{avg}}$$

## 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			

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

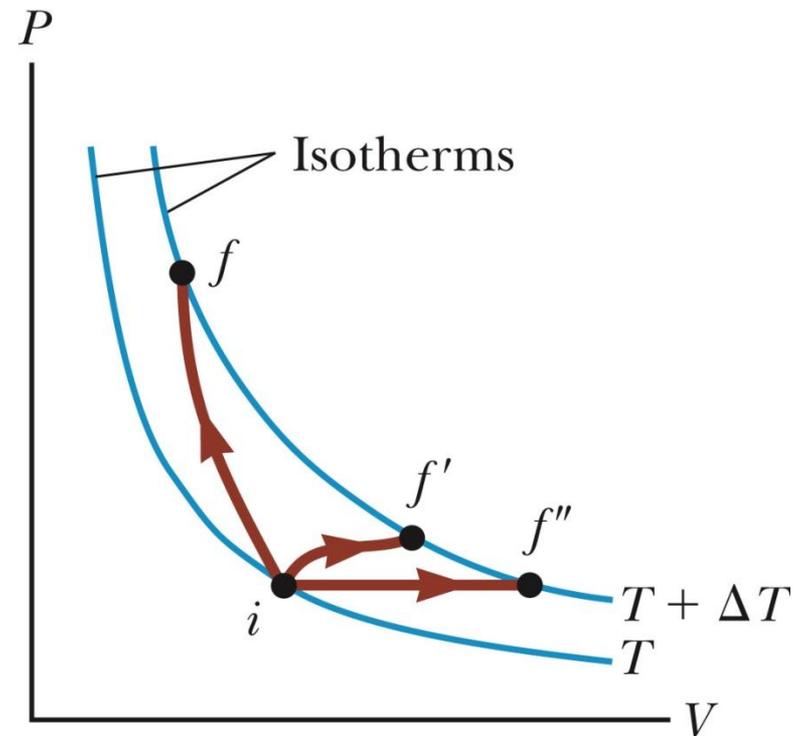
## Molar Specific Heat

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 work done on the gas is different for each path.

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, **isobaric**
- Changes with constant volume, **isovolumetric**

Using the number of moles,  $n$ , we can define molar specific heats for these processes.

## Molar Specific Heat, 3

Molar specific heats:

- $Q = n C_V \Delta T$  for constant-volume processes
- $Q = n C_P \Delta T$  for constant-pressure processes

Where,  $C_V$  and  $C_P$  are the molar specific heat at const. volume and at const. pressure, respectively.

$Q$  (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  $\Delta T$

$C_P > C_V$

## 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.

Therefore,  $E_{\text{int}} = K_{\text{tot trans}} = \frac{3}{2} nRT$

- $E_{\text{int}}$  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,  $W = 0$  and  $Q = \Delta E_{\text{int}} = nC_v \Delta T$

- This applies to all ideal gases, not just monatomic ones.

## Monatomic Gases, final

Again, for molar specific heat at constant volume is

$$C_V = \frac{1}{n} \frac{dE_{\text{int}}}{dT}$$

Solving for  $C_V$  gives for monatomic gases,

$$C_V = \frac{3}{2} R = 12.5 \text{ J/mol} \cdot \text{K}$$

- For all monatomic gases
- This is in good agreement with experimental results for monatomic gases.

## Monatomic Gases, final

In a constant-pressure process,

$$\Delta E_{\text{int}} = Q + W = nC_p \Delta T + (-P\Delta V)$$

Again, *for constant pressure*,

$$P\Delta V = nR\Delta T, \text{ and also, } \Delta E_{\text{int}} = nC_v \Delta T$$

So,

$$C_p - C_v = R$$

- 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.

All three variables in the ideal gas law ( $P$ ,  $V$ ,  $T$ ) can change during an adiabatic process.

For adiabatic conditions, change of internal energy is same as that for an isovolumetric process between the same temperature. So,

$$dE_{\text{int}} = nC_V \Delta T = -PdV$$

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.

## Adiabatic Process, cont

The PV diagram shows an adiabatic expansion of an ideal gas.

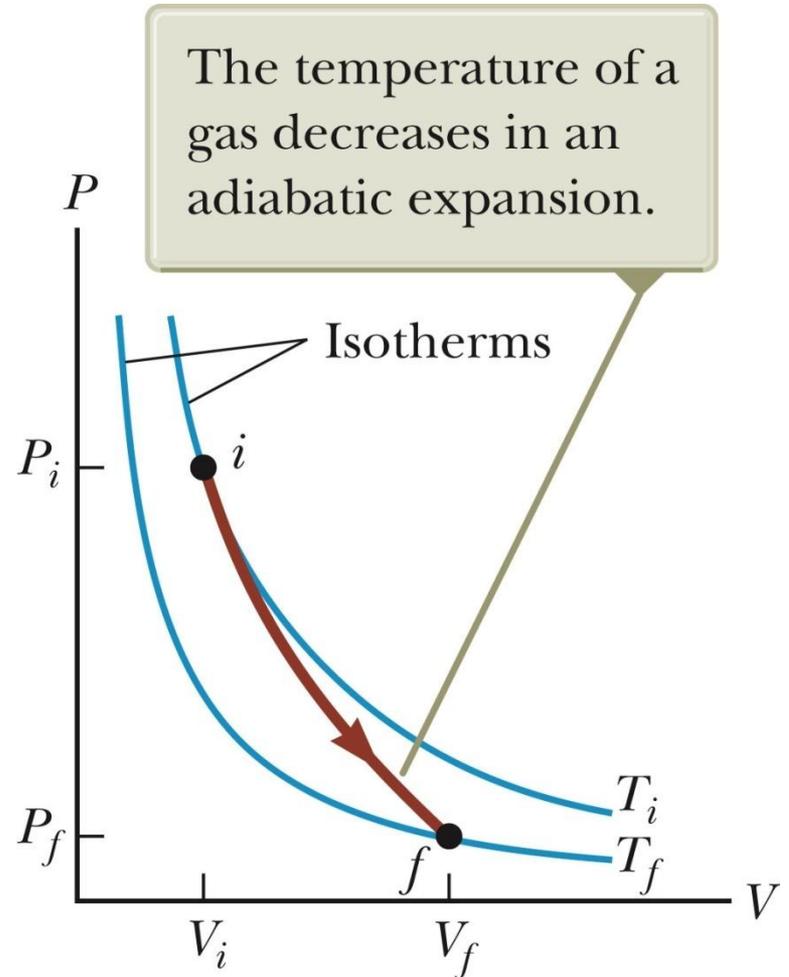
The temperature of the gas decreases

- $T_f < T_i$  in this process

For this process

$$P_i V_i^\gamma = P_f V_f^\gamma \text{ and}$$

$$T V^{\gamma-1} = \text{constant}$$



## Equipartition of Energy

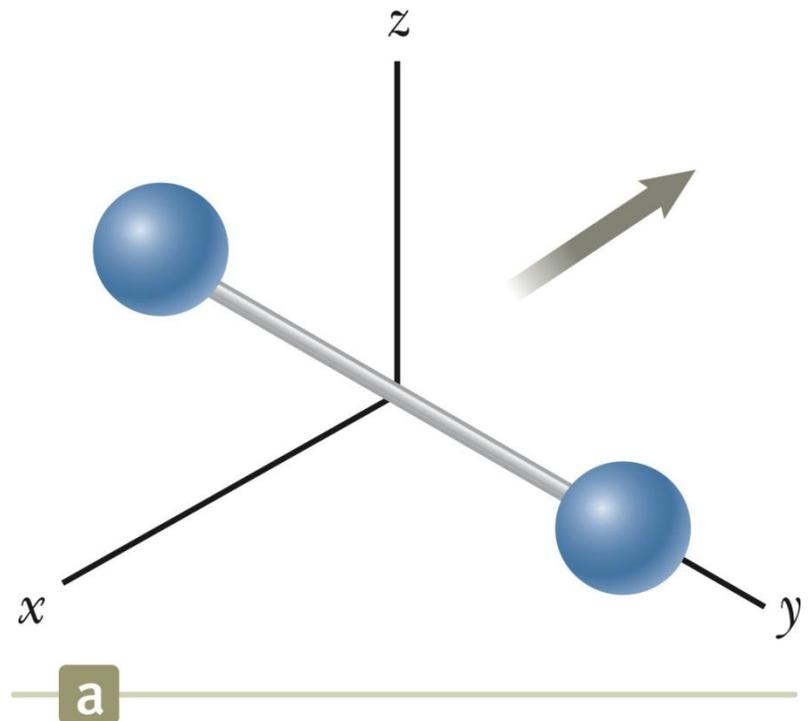
With complex molecules, other contributions to internal energy must be taken into account.

One possible energy is the translational motion of the center of mass.

The center of mass can translate in the  $x$ ,  $y$ , and  $z$  directions.

This gives three degrees of freedom for translational motion.

Translational motion of the center of mass



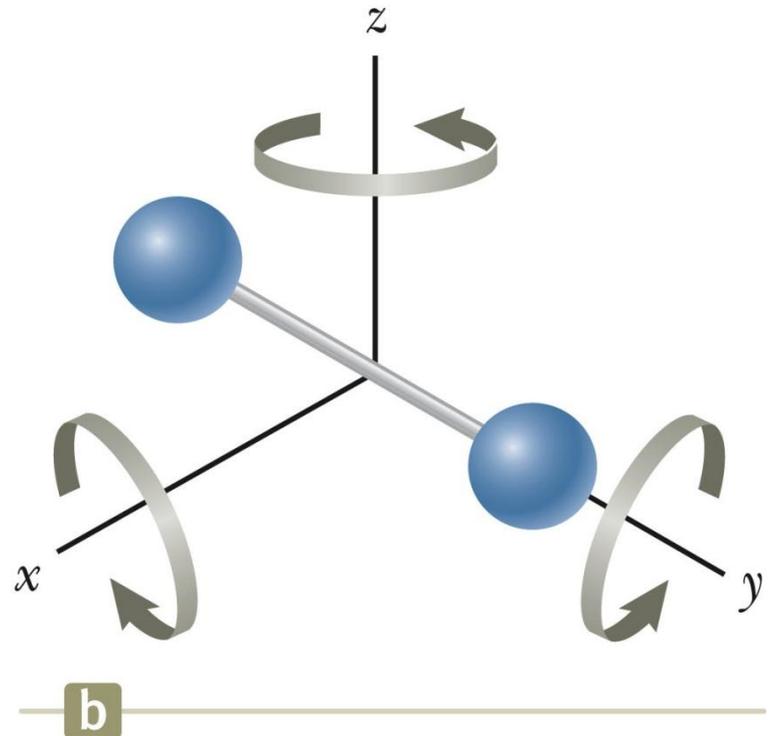
## Equipartition of Energy, 2

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.
  - Ideally, if the two atoms can be modeled as particles,  $I_y$  is zero.

Rotational motion contributes two degrees of freedom.

Rotational motion about the various axes



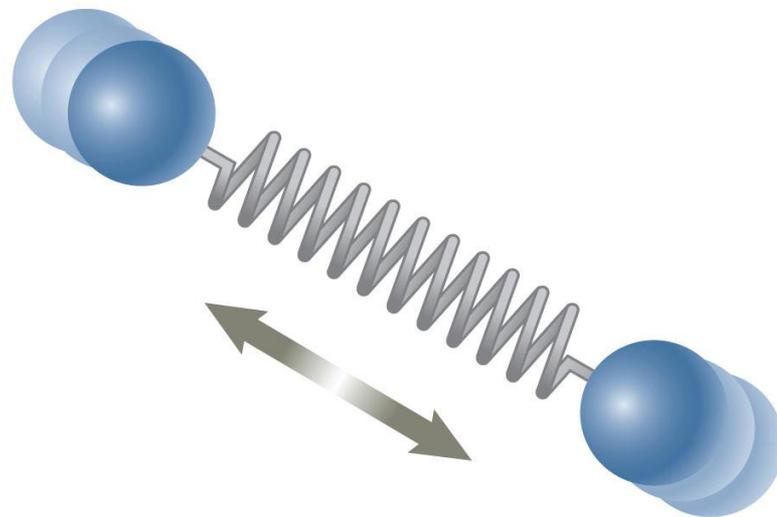
## Equipartition of Energy, 3

The molecule can also vibrate.

There is kinetic energy and potential energy associated with the vibrations.

The vibrational mode adds two more degrees of freedom.

Vibrational motion along the molecular axis



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## Equipartition of Energy, 4

Taking into account the degrees of freedom from just the translation and rotation contributions.

- $E_{\text{int}} = 5/2 NK_{\text{B}} T = 5/2 n R T$  and  $C_V = 5/2 R$
- This gives  $C_P = C_V + R = 7/2 R$
- Combining,  $\gamma = C_P / C_V = 1.40$
- This is in good agreement with data for diatomic molecules.
  - See table 21.1

However, 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.

## Molar Specific Heat: Agreement with Experiment

Molar specific heat is a function of temperature.

At low temperatures, a diatomic gas acts like a monatomic gas.

- $C_V = 3/2 R$

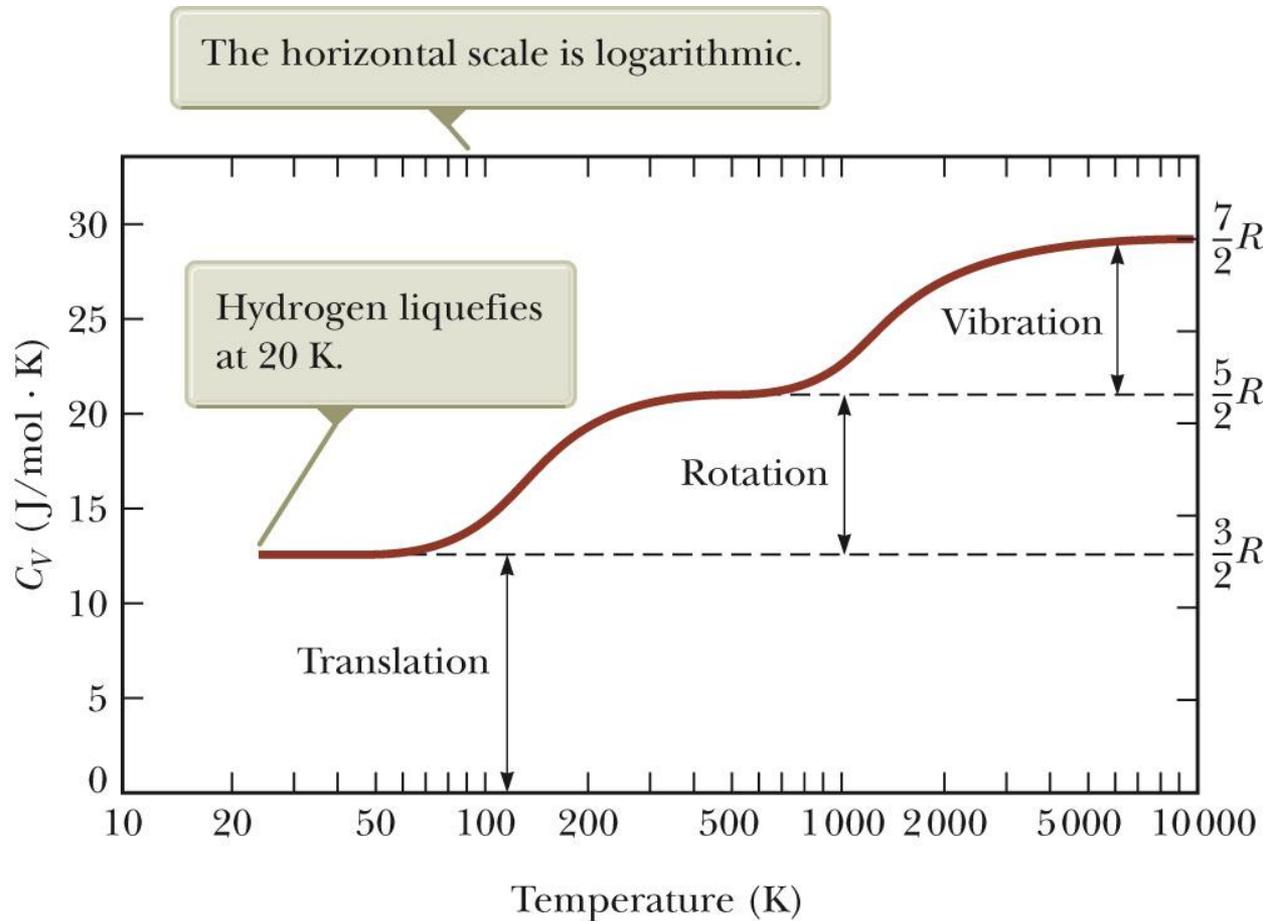
At about room temperature, the value increases to  $C_V = 5/2 R$ .

- 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.

## Agreement with Experiment, cont



## 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 of a system is proportional to the frequency of the wave representing the system.

So the energies of atoms and molecules are quantized.

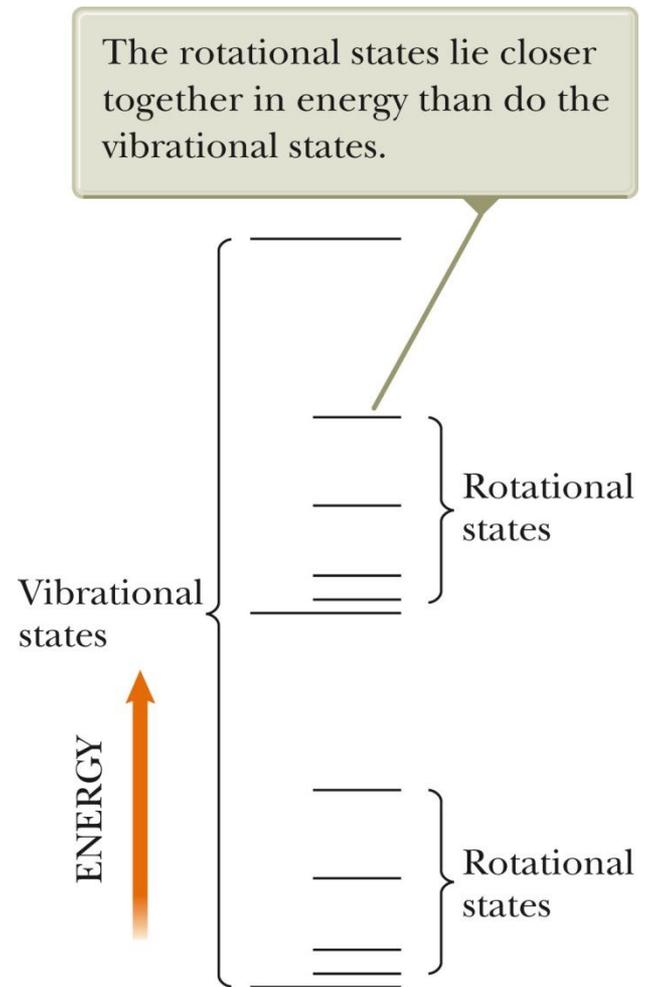
## Quantization of Energy, cont.

This energy level diagram shows the rotational and vibrational states of a diatomic molecule.

The lowest allowed state is the **ground state**.

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, final

Even though rotation and vibration are classically allowed, they do not occur at low temperatures.

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.

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 (Distribution of Energies)

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.

**What is relative number of molecules that possess some characteristic such as energy within a certain range?**

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  $E + dE$ .
- This definition is used since the number of molecules is finite and the number of possible values of the energy is infinite.
  - The number of molecules with an exact energy of  $E$  may be zero.

## Number Density and Boltzmann Distribution Law

From statistical mechanics, the number density is  $n_V(E) = n_0 e^{-E/k_B T}$ .

Where  $n_0$  is defined such that  $n_0 dE$  is the number of molecules per unit volume having energies between  $E = 0$  and  $E = dE$ .

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  $k_B T$ .

All the molecules would fall into the lowest energy level if the thermal agitation at a temperature  $T$  did not excite them to higher energy levels.

# Ludwig Boltzmann

1844 – 1906

Austrian physicist

Contributed to

- Kinetic Theory of Gases
- Electromagnetism
- Thermodynamics

Pioneer in statistical mechanics



# Distribution of Molecular Speeds

The observed speed distribution of gas molecules in thermal equilibrium is shown at right.

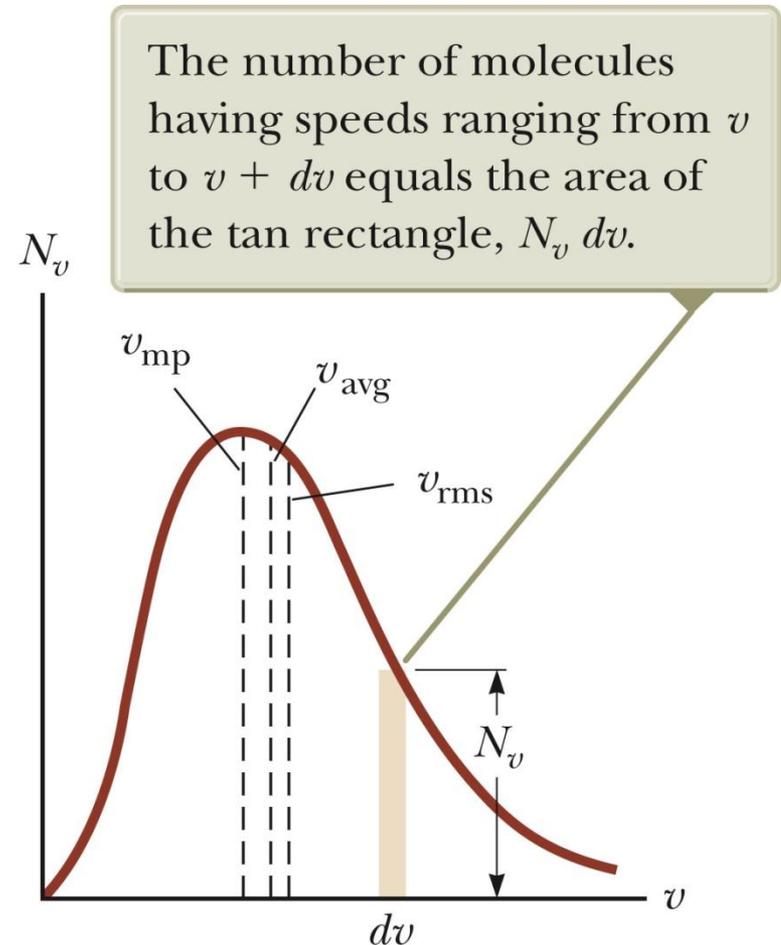
$N_v$  is called the **Maxwell-Boltzmann speed distribution function**.

If  $N$  is total number of molecules, the number of molecules with speeds between  $v$  and  $v + dv$  is

$$dN = N_v dv = \text{Shaded Rectangle Area}$$

Again, the fraction of molecules with speed between  $v$  and  $v + dv$  is

$$N_v dv / N$$



## 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

$$v_{\text{rms}} = \sqrt{v^2} = \sqrt{\frac{3k_{\text{B}}T}{m_o}} = 1.73 \sqrt{\frac{k_{\text{B}}T}{m_o}}$$

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.

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

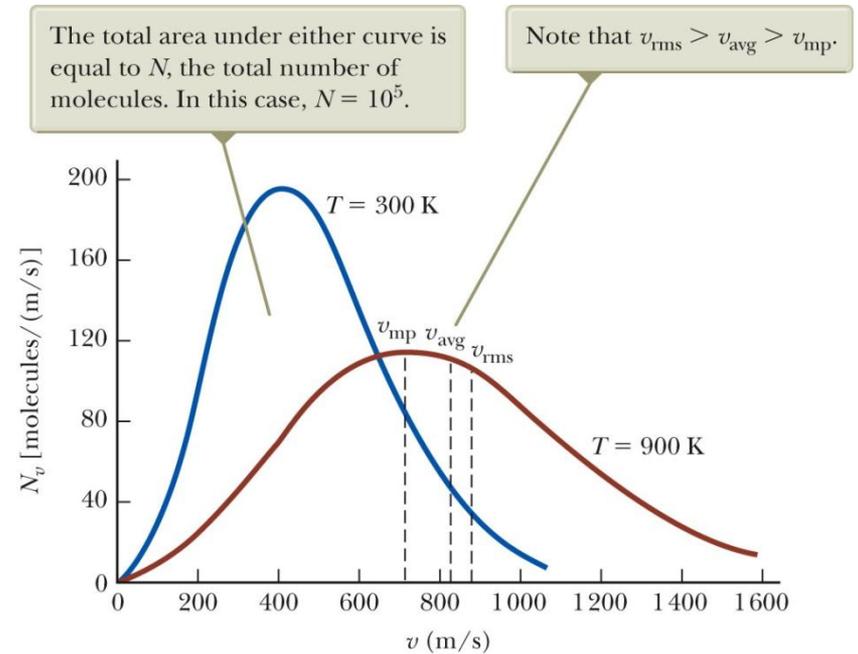
$$v_{\text{rms}} > v_{\text{avg}} > v_{\text{mp}}$$

# Speed Distribution – Nitrogen Example

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.



## Speed Distribution, final

The distribution of molecular speeds depends both on the mass and on temperature.

At a given temperature, the fraction of molecules with speeds exceeding a fixed value increases as the mass decreases.

- This explains why lighter molecules escape into space from the Earth's atmosphere more easily than heavier molecules.

# Evaporation

The speed distribution for liquids is similar to that of gases.

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.