

# Chapter 18 The Micro/Macro Connection



**Chapter Goal:** To understand a macroscopic system in terms of the microscopic behavior of its molecules.

# Announcements

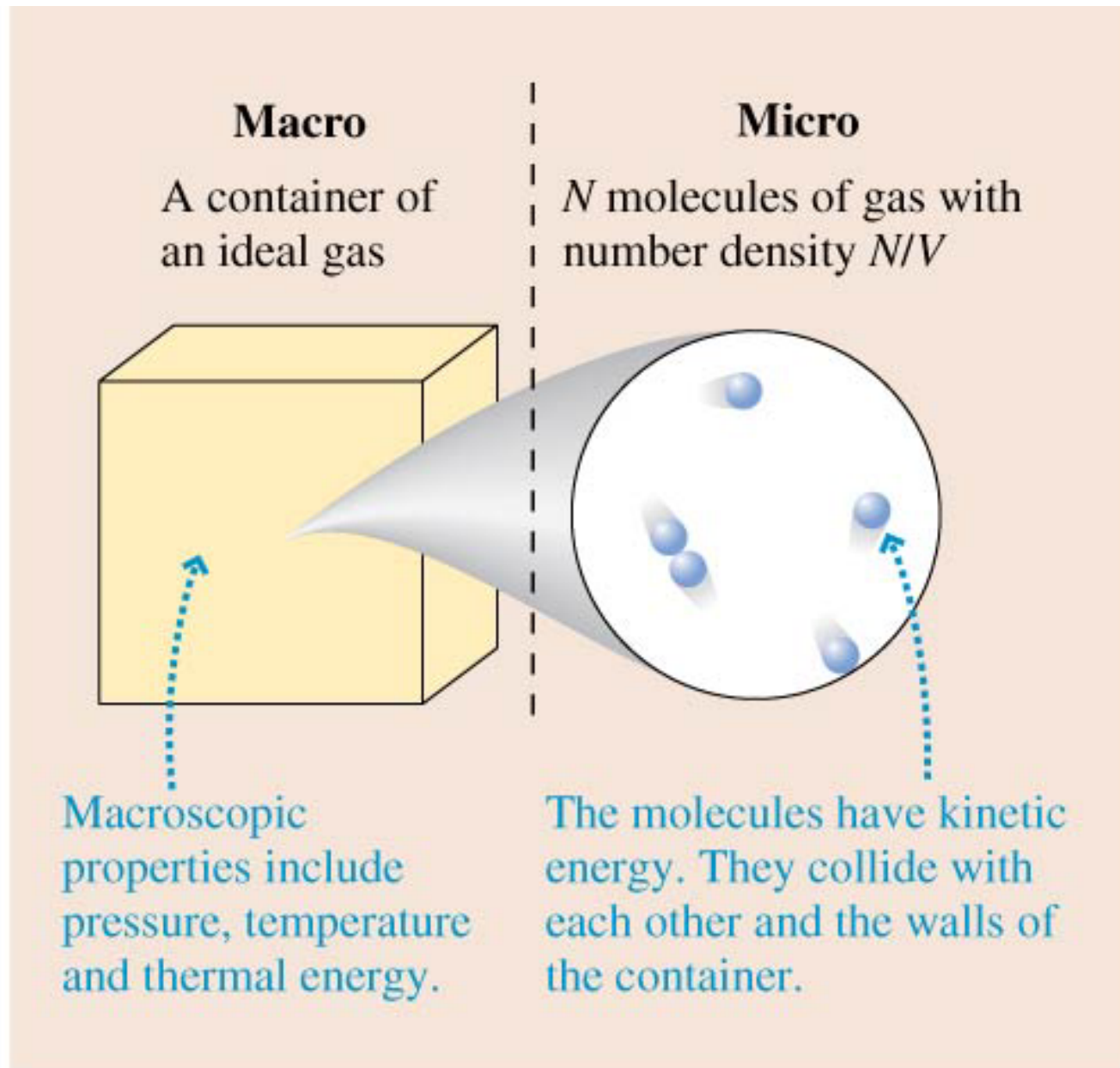
# Chapter 18 Preview

## Macro Puzzles Micro Explanations

- Why does the ideal-gas law work for every gas?
- Why is the molar specific heat for every monatomic gas the same? And for every diatomic gas and for every elemental solid?
- What does temperature measure?

These are puzzles we uncovered in the last two chapters. In this chapter, you will learn that we can resolve these puzzles and understand many of the properties of macroscopic systems by investigating the microscopic behavior of its atoms and molecules.

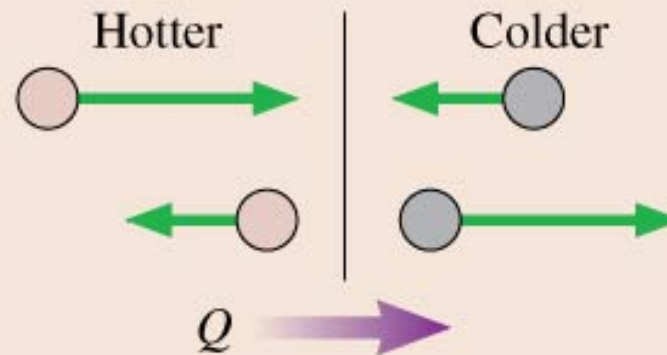
# Chapter 18 Preview



# Chapter 18 Preview

## Collisions

You will learn how to understand the pressure of a gas in terms of atomic collisions with the walls of the container.



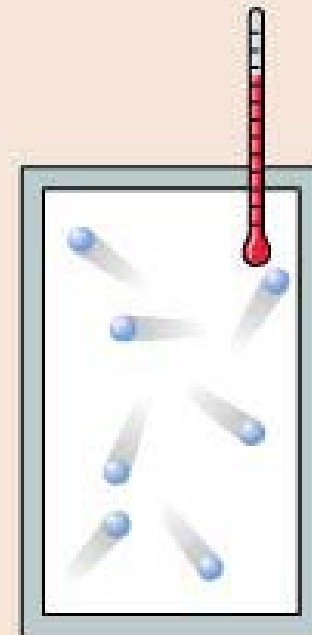
You'll also learn that heat transfer occurs via collisions at the boundary between two systems. More-energetic molecules on one side transfer their energy to less-energetic molecules on the other.

# Chapter 18 Preview

## Energy and Temperature

We'll find that the average energy of a molecule depends only on temperature.

This will allow us to interpret temperature in terms of thermal energy—the microscopic energy of the moving molecules—and then to understand why every monatomic gas has the same molar specific heat.



## The Second Law of Thermodynamics

You will learn a new law of nature, the second law of thermodynamics, that governs how systems evolve in time.

One statement of the second law is that heat energy is transferred spontaneously from a hotter system to a colder system, never from colder to hotter. Heat transfer is an *irreversible process*.

# Chapter 18 Preview



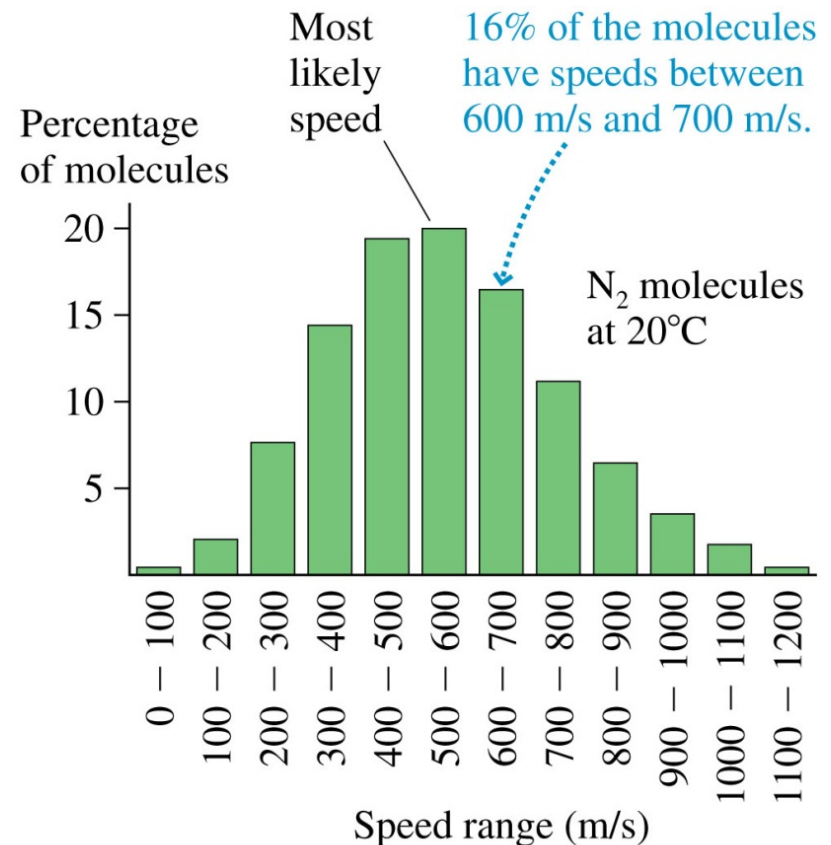
Heat goes from the burner to the teakettle, making the water hotter and the burner a little cooler. It would not violate energy conservation for heat to go from the kettle to the burner, making the water colder and the burner hotter. But it doesn't happen.

You'll learn to use the concept of **entropy** to understand why all macroscopic interactions are irreversible. Entropy explains why the future is different from the past and why there are theoretical limits to the efficiency of using energy in practical ways.



# Molecular Speeds and Collisions

- A gas consists of a vast number of molecules, each moving randomly and undergoing millions of collisions every second.
- Shown is the distribution of molecular speeds in a sample of nitrogen gas at 20°C.
- **The micro/macro connection is built on the idea that the macroscopic properties of a system, such as temperature or pressure, are related to the *average* behavior of the atoms and molecules.**



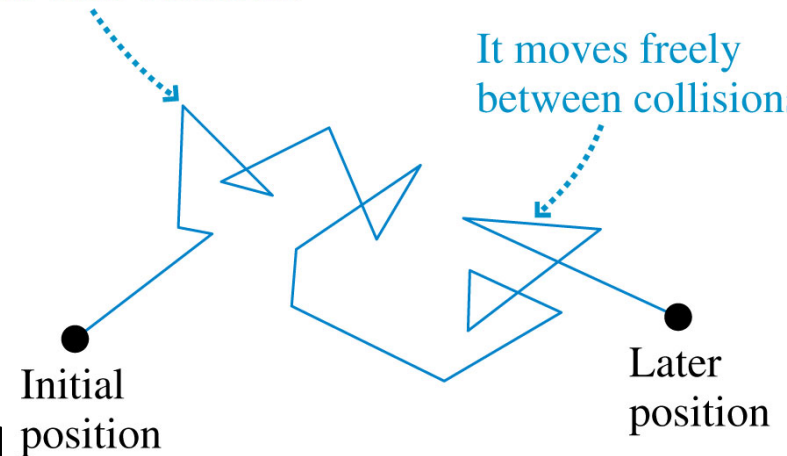
# Mean Free Path

- A single molecule follows a zig-zag path through a gas as it collides with other molecules.
- The average distance between the collisions is called the **mean free path**:

$$\lambda = \frac{1}{4\sqrt{2}\pi(N/V)r^2} \quad (\text{mean free path})$$

The molecule changes direction and speed with each collision.

It moves freely between collisions.



- $(N/V)$  is the number density of the gas in  $\text{m}^{-3}$ .
- $r$  is the the radius of the molecules when modeled as hard spheres; for many common gases  $r \approx 10^{-10}$  m.

## QuickCheck 18.1

The temperature of a rigid container of oxygen gas ( $O_2$ ) is lowered from  $300^\circ\text{C}$  to  $0^\circ\text{C}$ . As a result, the mean free path of oxygen molecules

- A. Increases.
- B. Is unchanged.
- C. Decreases.

## QuickCheck 18.1

The temperature of a rigid container of oxygen gas ( $O_2$ ) is lowered from  $300^\circ\text{C}$  to  $0^\circ\text{C}$ . As a result, the mean free path of oxygen molecules

- A. Increases.
- ✓ **B. Is unchanged.**       *$\lambda$  depends only on  $N/V$ , not  $T$ .*
- C. Decreases.

# Example 18.1 The Mean Free Path at Room Temperature

## EXAMPLE 18.1 The mean free path at room temperature

What is the mean free path of a nitrogen molecule at 1.0 atm pressure and room temperature (20°C)?

**SOLVE** Nitrogen is a diatomic molecule, so  $r \approx 1.0 \times 10^{-10}$  m. We can use the ideal-gas law in the form  $pV = Nk_B T$  to determine the number density:

$$\frac{N}{V} = \frac{p}{k_B T} = \frac{101,300 \text{ Pa}}{(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K})} = 2.5 \times 10^{25} \text{ m}^{-3}$$

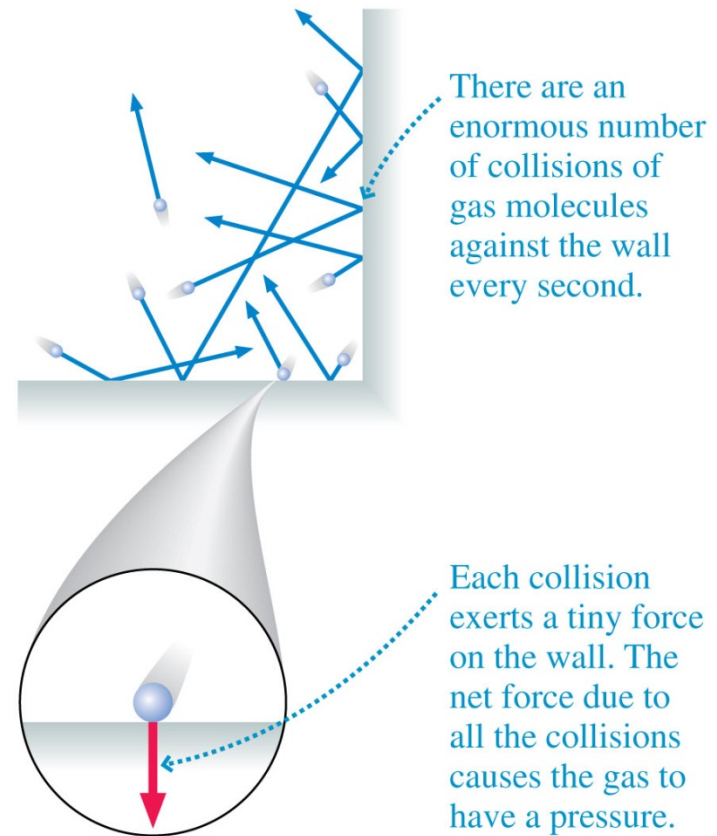
Thus the mean free path is

$$\begin{aligned}\lambda &= \frac{1}{4\sqrt{2}\pi(N/V)r^2} \\ &= \frac{1}{4\sqrt{2}\pi(2.5 \times 10^{25} \text{ m}^{-3})(1.0 \times 10^{-10} \text{ m})^2} \\ &= 2.3 \times 10^{-7} \text{ m} = 230 \text{ nm}\end{aligned}$$

**ASSESS** You learned in Example 16.5 that the average separation between gas molecules at STP is  $\approx 4$  nm. It seems that any given molecule can slip between its neighbors, which are spread out in three dimensions, and travel—on average—about 60 times the average spacing before it collides with another molecule.

# Pressure in a Gas

- Why does a gas have pressure?
- In Chapter 15 we suggested that the pressure in a gas is due to collisions of the molecules with the walls of its container.
- The steady rain of a vast number of molecules striking a wall each second exerts a measurable **macroscopic** force.
- The gas pressure is the force per unit area ( $p = F/A$ ) resulting from these molecular collisions.



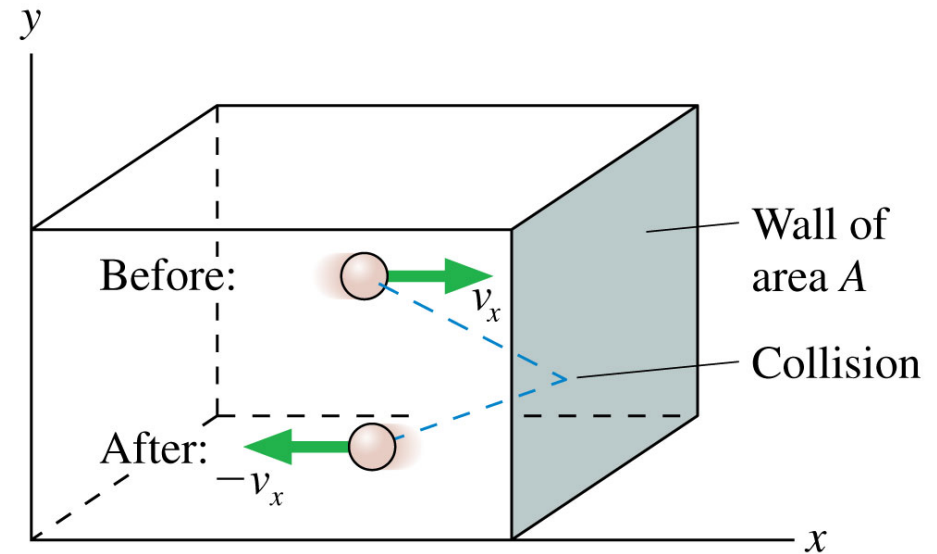
# Pressure in a Gas

- The figure shows a molecule which collides with a wall, exerting an impulse on it.
- The  $x$ -component of the impulse from a **single collision** is:

$$(J_x)_{\text{molecule on wall}} = +2mv_x$$

- If there are  $N_{\text{coll}}$  such collisions during a small time interval  $\Delta t$ , the net impulse is:

$$J_{\text{wall}} = N_{\text{coll}} \times (J_x)_{\text{molecule on wall}} = 2N_{\text{coll}}mv_x$$



# Pressure in a Gas

- The figure reminds you that impulse is the area under the force-versus-time curve and thus

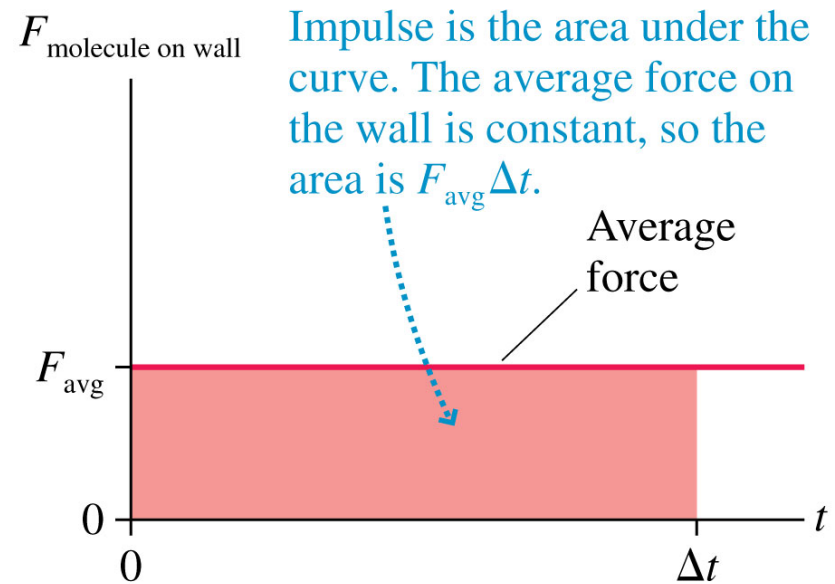
$$J_{\text{wall}} = F_{\text{avg}} \Delta t.$$

- The average force on the wall is:

$$F_{\text{avg}} = 2 \frac{N_{\text{coll}}}{\Delta t} m v_x$$

- where the rate of collisions is:

$$\frac{N_{\text{coll}}}{\Delta t} = \frac{1}{2} \frac{N}{V} A v_x$$





# Pressure in a Gas

- The pressure is the average force on the walls of the container per unit area:

$$p = \frac{F}{A} = \frac{1}{3} \frac{N}{V} m v_{\text{rms}}^2$$

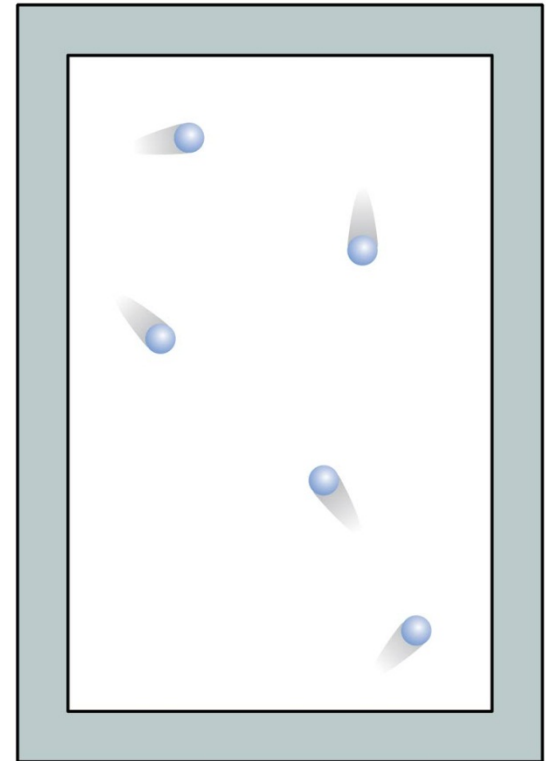
- $(N/V)$  is the number density of the gas in  $\text{m}^{-3}$ .
- Note that the average velocity of many molecules traveling in random directions is *zero*.
- $v_{\text{rms}}$  is the root-mean-square speed of the molecules, which is the square root of the average value of the *squares* of the speeds of the molecules:

$$v_{\text{rms}} = \sqrt{(v^2)_{\text{avg}}} \quad (\text{root-mean-square speed})$$

## QuickCheck 18.2

A rigid container holds oxygen gas ( $O_2$ ) at  $100^\circ\text{C}$ . The average velocity of the molecules is

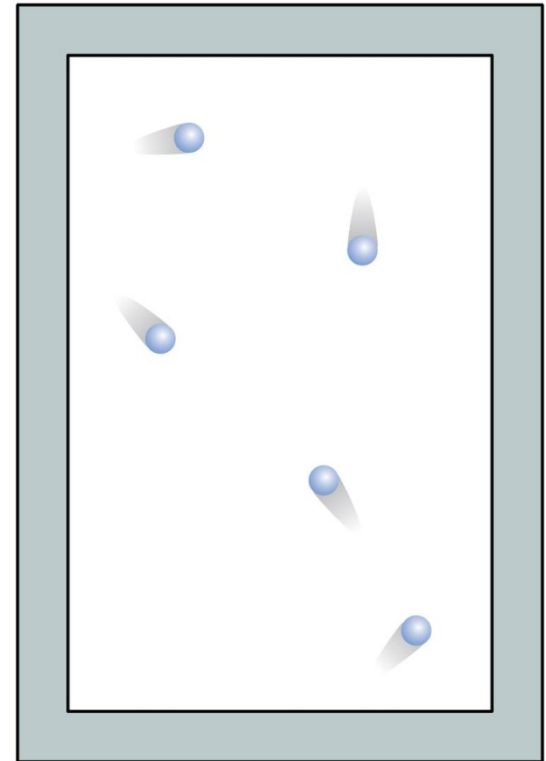
- A. Greater than zero.
- B. Zero.
- C. Less than zero.



## QuickCheck 18.2

A rigid container holds oxygen gas ( $O_2$ ) at  $100^\circ\text{C}$ . The average velocity of the molecules is

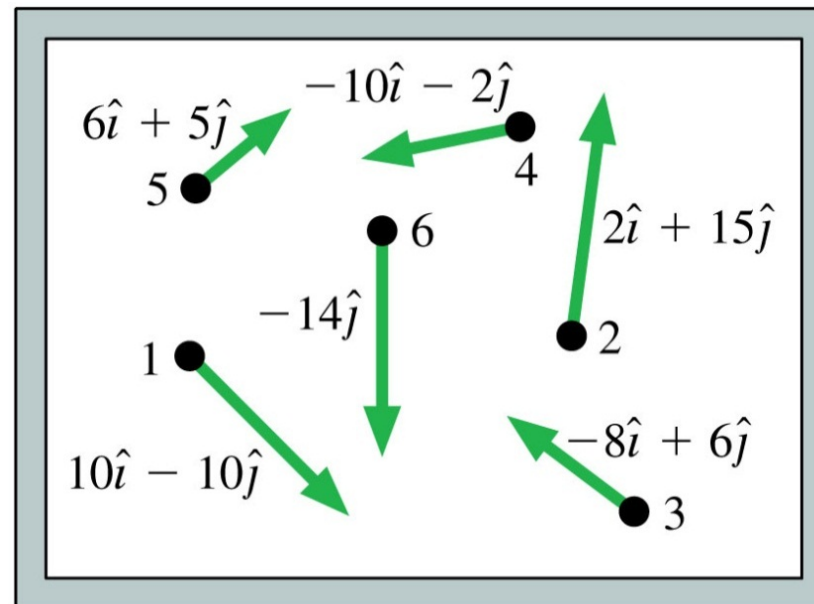
- A. Greater than zero.
- ✓ B. **Zero.**
- C. Less than zero.



# Example 18.2 Calculating the Root-Mean-Square Speed

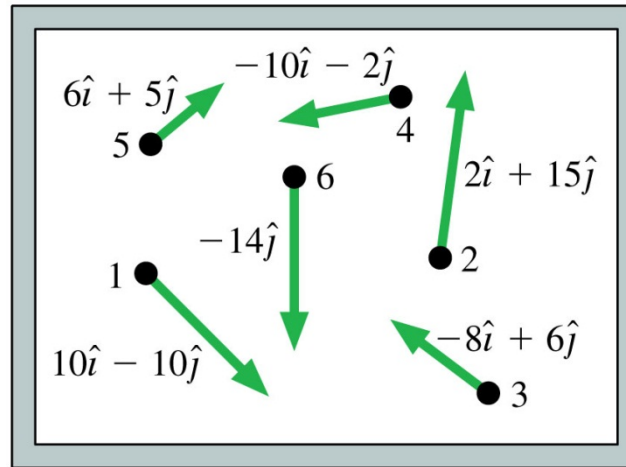
## EXAMPLE 18.2 Calculating the root-mean-square speed

The figure shows the velocities of all the molecules in a six-molecule, two-dimensional gas. Calculate and compare the average velocity  $\vec{v}_{\text{avg}}$ , the average speed  $v_{\text{avg}}$ , and the rms speed  $v_{\text{rms}}$ .



Units of velocity are m/s.

# Example 18.2 Calculating the Root-Mean-Square Speed



Molecule	$v_x$	$v_y$	$v_x^2$	$v_y^2$	$v^2$	$v$
1	10	-10	100	100	200	14.1
2	2	15	4	225	229	15.1
3	-8	6	64	36	100	10.0
4	-10	-2	100	4	104	10.2
5	6	5	36	25	61	7.8
6	0	-14	0	196	196	14.0
Average	0	0			148.3	11.9

# Example 18.2 Calculating the Root-Mean-Square Speed

## EXAMPLE 18.2 Calculating the root-mean-square speed

**SOLVE** The table on the previous slide shows the velocity components  $v_x$  and  $v_y$  for each molecule, the squares  $v_x^2$  and  $v_y^2$ , their sum  $v^2 = v_x^2 + v_y^2$ , and the speed  $v = (v_x^2 + v_y^2)^{1/2}$ . Averages of all the values in each column are shown at the bottom. You can see that the average velocity is  $\vec{v}_{\text{avg}} = \vec{0}$  m/s and the average speed is

$v_{\text{avg}} = 11.9$  m/s. The rms speed is

$$v_{\text{rms}} = \sqrt{(v^2)_{\text{avg}}} = \sqrt{148.3 \text{ m}^2/\text{s}^2} = 12.2 \text{ m/s}$$

**ASSESS** The rms speed is only 2.5% greater than the average speed.

# Example 18.3 The RMS Speed of Helium Atoms

## EXAMPLE 18.3 The rms speed of helium atoms

A container holds helium at a pressure of 200 kPa and a temperature of 60.0°C. What is the rms speed of the helium atoms?

**SOLVE** The rms speed can be found from the pressure and the number density. Using the ideal-gas law gives us the number density:

$$\frac{N}{V} = \frac{p}{k_B T} = \frac{200,000 \text{ Pa}}{(1.38 \times 10^{-23} \text{ J/K})(333 \text{ K})} = 4.35 \times 10^{25} \text{ m}^{-3}$$

The mass of a helium atom is  $m = 4 \text{ u} = 6.64 \times 10^{-27} \text{ kg}$ . Thus

$$v_{\text{rms}} = \sqrt{\frac{3p}{(N/V)m}} = 1440 \text{ m/s}$$

Using  $pV = Nk_B T$ ,

$$v_{\text{rms}} = \sqrt{\frac{3k_B T}{m}}$$

# Temperature in a Gas

- The thing we call *temperature* measures the average translational kinetic energy  $\epsilon_{\text{avg}}$  of molecules in a gas.
- A higher temperature corresponds to a larger value of  $\epsilon_{\text{avg}}$  and thus to higher molecular speeds.
- *Absolute zero* is the temperature at which  $\epsilon_{\text{avg}} = 0$  and all molecular motion ceases.
- By definition,  $\epsilon_{\text{avg}} = \frac{1}{2}mv_{\text{rms}}^2$ , where  $v_{\text{rms}}$  is the root mean squared molecular speed; using the ideal-gas law, we found  $\epsilon_{\text{avg}} = \frac{3}{2}k_B T$ .
- By equating these expressions we find that the rms speed of molecules in a gas is:

$$\epsilon_{\text{avg}} \equiv \frac{1}{2}mv_{\text{rms}}^2 = \frac{3}{2}k_B T$$

$$v_{\text{rms}} = \sqrt{\frac{3k_B T}{m}}$$




## QuickCheck 18.3

A rigid container holds both hydrogen gas ( $\text{H}_2$ ) and nitrogen gas ( $\text{N}_2$ ) at  $100^\circ\text{C}$ . Which statement describes their rms speeds?

- A.  $v_{\text{rms}}$  of  $\text{H}_2 < v_{\text{rms}}$  of  $\text{N}_2$ .
- B.  $v_{\text{rms}}$  of  $\text{H}_2 = v_{\text{rms}}$  of  $\text{N}_2$ .
- C.  $v_{\text{rms}}$  of  $\text{H}_2 > v_{\text{rms}}$  of  $\text{N}_2$ .

## QuickCheck 18.3

A rigid container holds both hydrogen gas ( $\text{H}_2$ ) and nitrogen gas ( $\text{N}_2$ ) at  $100^\circ\text{C}$ . Which statement describes their rms speeds?

- A.  $v_{\text{rms}}$  of  $\text{H}_2 < v_{\text{rms}}$  of  $\text{N}_2$ .
  - B.  $v_{\text{rms}}$  of  $\text{H}_2 = v_{\text{rms}}$  of  $\text{N}_2$ .
  -  C.  $v_{\text{rms}}$  of  $\text{H}_2 > v_{\text{rms}}$  of  $\text{N}_2$ .
- $v_{\text{rms}} \sim 1/\sqrt{m}$

For nitrogen ( $\text{N}_2$ ,  $m = 28 \text{ u}$ ),  $v_{\text{rms}} = 1440/(7)^{1/2} = 1440/2.65 = 540 \text{ m/s}$ .  
Speed of sound =  $340 \text{ m/s}$ .


## QuickCheck 18.4

A rigid container holds both hydrogen gas ( $\text{H}_2$ ) and nitrogen gas ( $\text{N}_2$ ) at  $100^\circ\text{C}$ . Which statement describes the average translational kinetic energies of the molecules?

- A.  $\epsilon_{\text{avg}}$  of  $\text{H}_2 < \epsilon_{\text{avg}}$  of  $\text{N}_2$ .
- B.  $\epsilon_{\text{avg}}$  of  $\text{H}_2 = \epsilon_{\text{avg}}$  of  $\text{N}_2$ .
- C.  $\epsilon_{\text{avg}}$  of  $\text{H}_2 > \epsilon_{\text{avg}}$  of  $\text{N}_2$ .

## QuickCheck 18.4

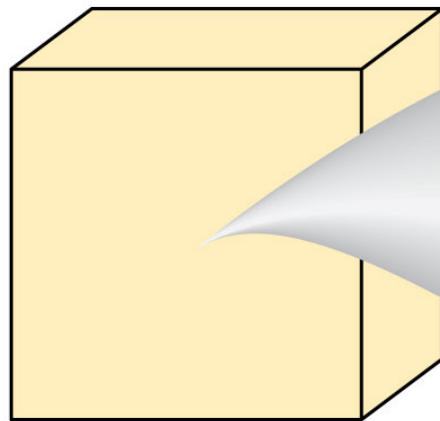
A rigid container holds both hydrogen gas ( $\text{H}_2$ ) and nitrogen gas ( $\text{N}_2$ ) at  $100^\circ\text{C}$ . Which statement describes the average translational kinetic energies of the molecules?

- A.  $\epsilon_{\text{avg}}$  of  $\text{H}_2 < \epsilon_{\text{avg}}$  of  $\text{N}_2$ .
-  B.  $\epsilon_{\text{avg}}$  of  $\text{H}_2 = \epsilon_{\text{avg}}$  of  $\text{N}_2$ .
- C.  $\epsilon_{\text{avg}}$  of  $\text{H}_2 > \epsilon_{\text{avg}}$  of  $\text{N}_2$ .

# The Micro/Macro Connection for Pressure and Temperature

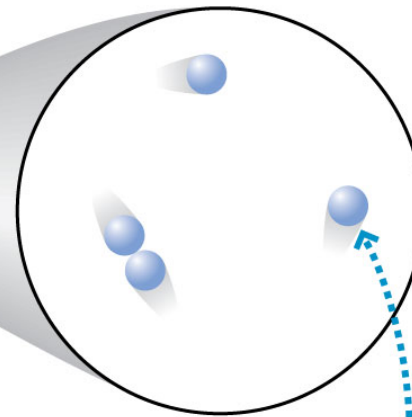
## Macro

A container of an ideal gas



## Micro

$N$  molecules of gas with number density  $N/V$



The average translational kinetic energy of a molecule is

$$\epsilon_{\text{avg}} = \frac{1}{2} m v_{\text{rms}}^2 = \frac{3}{2} k_B T.$$

$$\text{Pressure, } p = \frac{2}{3} \frac{N}{V} \epsilon_{\text{avg}}$$

$$\text{Temperature, } T = \frac{2}{3 k_B} \epsilon_{\text{avg}}$$

# Example 18.4 Total Microscopic Kinetic Energy

## EXAMPLE 18.4 Total microscopic kinetic energy

What is the total translational kinetic energy of the molecules in 1.0 mol of gas at STP?

**SOLVE** The average translational kinetic energy of each molecule is

$$\begin{aligned}\epsilon_{\text{avg}} &= \frac{3}{2}k_{\text{B}}T = \frac{3}{2}(1.38 \times 10^{-23} \text{ J/K})(273 \text{ K}) \\ &= 5.65 \times 10^{-21} \text{ J}\end{aligned}$$

1.0 mol of gas contains  $N_{\text{A}}$  molecules; hence the total kinetic energy is

$$K_{\text{micro}} = N_{\text{A}}\epsilon_{\text{avg}} = 3400 \text{ J}$$

**ASSESS** The energy of any one molecule is incredibly small. Nonetheless, a macroscopic system has substantial thermal energy because it consists of an incredibly large number of molecules.

# Example 18.5 Calculating an RMS Speed

## EXAMPLE 18.5 Calculating an rms speed

What is the rms speed of nitrogen molecules at room temperature (20°C)?

**SOLVE** The molecular mass is  $m = 28 \text{ u} = 4.68 \times 10^{-26} \text{ kg}$  and  $T = 20^\circ\text{C} = 293 \text{ K}$ . It is then a simple calculation to find

$$v_{\text{rms}} = \sqrt{\frac{3(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K})}{4.68 \times 10^{-26} \text{ kg}}} = 509 \text{ m/s}$$

Some speeds will be greater than this and others smaller, but 509 m/s will be a typical or fairly average speed. This is in excellent agreement with the experimental results of Figure 18.2.

# Example 18.6 Mean Time Between Collisions

## EXAMPLE 18.6 Mean time between collisions

Estimate the mean time between collisions for a nitrogen molecule at 1.0 atm pressure and room temperature (20°C).

**MODEL** Because  $v_{\text{rms}}$  is essentially the average molecular speed, the *mean time between collisions* is simply the time needed to travel distance  $\lambda$ , the mean free path, at speed  $v_{\text{rms}}$ .

**SOLVE** We found  $\lambda = 2.3 \times 10^{-7}$  m in Example 18.1 and  $v_{\text{rms}} = 509$  m/s in Example 18.5. Thus the mean time between collisions is

$$\tau_{\text{coll}} = \frac{\lambda}{v_{\text{rms}}} = \frac{2.3 \times 10^{-7} \text{ m}}{509 \text{ m/s}} = 4.5 \times 10^{-10} \text{ s}$$

**ASSESS** The air molecules around us move very fast, they collide with their neighbors about two billion times every second, and they manage to move, on average, only about 230 nm between collisions.

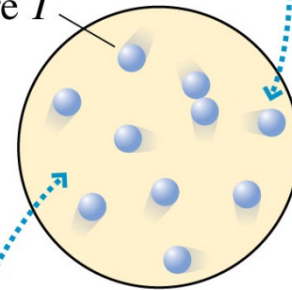


# Thermal Energy and Specific Heat

- The thermal energy of a system is  $E_{\text{th}} = K_{\text{micro}} + U_{\text{micro}}$ .
- The figure shows a monatomic gas such as helium or neon.
- The atoms in a monatomic gas have no molecular bonds with their neighbors, hence  $U_{\text{micro}} = 0$ .
- Since the average kinetic energy of a single atom in an ideal gas is  $\epsilon_{\text{avg}} = 3/2 k_{\text{B}}T$ , the total thermal energy is:

Atom  $i$  has translational kinetic energy  $\epsilon_i$  but no potential energy or rotational kinetic energy.

$N$  atoms in a gas at temperature  $T$



The thermal energy of the gas is  $E_{\text{th}} = \epsilon_1 + \epsilon_2 + \epsilon_3 + \dots = N\epsilon_{\text{avg}}$ .

$$E_{\text{th}} = \frac{3}{2}Nk_{\text{B}}T = \frac{3}{2}nRT \quad (\text{thermal energy of a monatomic gas})$$

# Thermal Energy and Specific Heat

- If the temperature of a monatomic gas changes by  $\Delta T$ , its thermal energy changes by:

$$\Delta E_{\text{th}} = \frac{3}{2}nR\Delta T$$

- In Chapter 17 we found that the change in thermal energy for *any* ideal-gas process is related to the molar specific heat at constant volume by:

$$\Delta E_{\text{th}} = nC_V\Delta T$$

- Combining these equations gives us a prediction for the molar specific heat for a monatomic gas:

$$C_V = \frac{3}{2}R = 12.5 \text{ J/mol K} \quad (\text{monatomic gas})$$

- This prediction is confirmed by experiments.

# The Equipartition Theorem

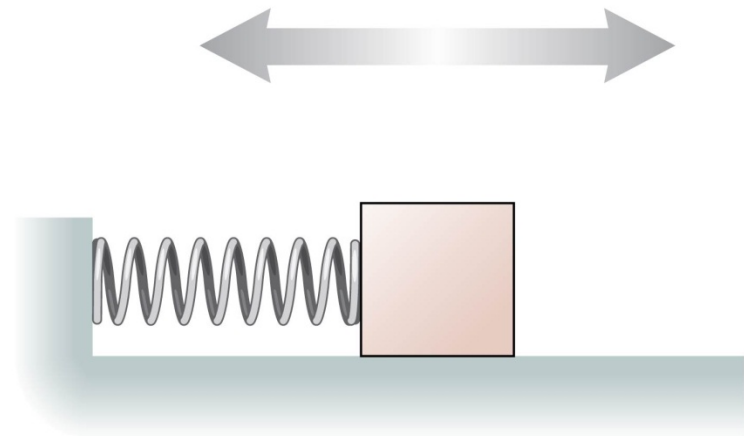
- Atoms in a monatomic gas carry energy exclusively as translational kinetic energy (3 degrees of freedom).
- Molecules in a gas may have additional modes of energy storage, for example, the kinetic and potential energy associated with vibration, or rotational kinetic energy.
- We define the number of **degrees of freedom** as the number of distinct and independent modes of energy storage.

**Equipartition theorem** The thermal energy of a system of particles is equally divided among all the possible degrees of freedom. For a system of  $N$  particles at temperature  $T$ , the energy stored in each mode (each degree of freedom) is  $\frac{1}{2}Nk_B T$  or, in terms of moles,  $\frac{1}{2}nRT$ .

## QuickCheck 18.5

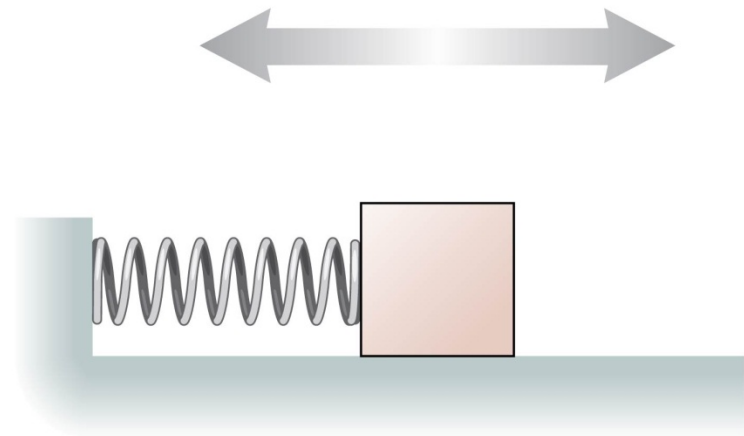
A mass on a spring oscillates back and forth on a frictionless surface. How many degrees of freedom does this system have?

- A. 1.
- B. 2.
- C. 3.
- D. 4.
- E. 6.



## QuickCheck 18.5

A mass on a spring oscillates back and forth on a frictionless surface. How many degrees of freedom does this system have?



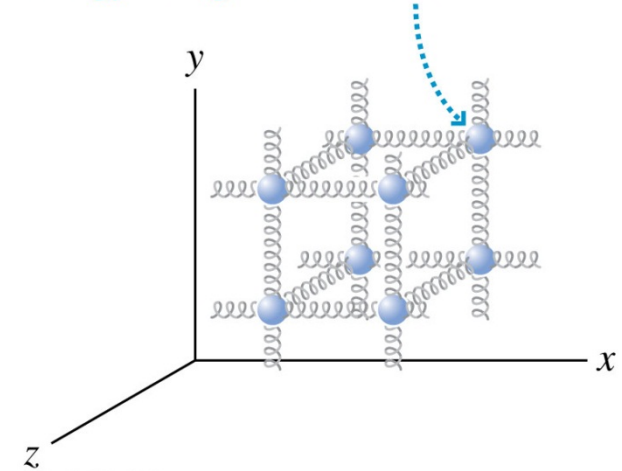
- A. 1.
- ✓ B. 2. *It can hold energy as kinetic energy or potential energy.*
- C. 3.
- D. 4.
- E. 6.

# Thermal Energy of a Solid

- The figure reminds you of the “bedspring model” of a solid with particle-like atoms connected by spring-like molecular bonds.
- There are 3 degrees of freedom associated with kinetic energy + 3 more associated with the potential energy in the molecular bonds = 6 degrees of freedom total.
- The energy stored in each degree of freedom is  $\frac{1}{2} Nk_B T$ , so:

$$E_{\text{th}} = 3Nk_B T = 3nRT \quad (\text{thermal energy of a solid})$$

Each atom has microscopic translational kinetic energy *and* microscopic potential energy along all three axes.



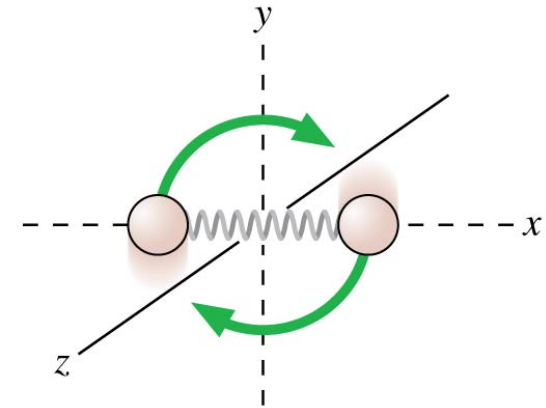
# Diatomic Molecules

- In addition to the 3 degrees of freedom from translational kinetic energy, a diatomic gas at commonly used temperatures has 2 additional degrees of freedom from end-over-end rotations.
- This gives 5 degrees of freedom total:

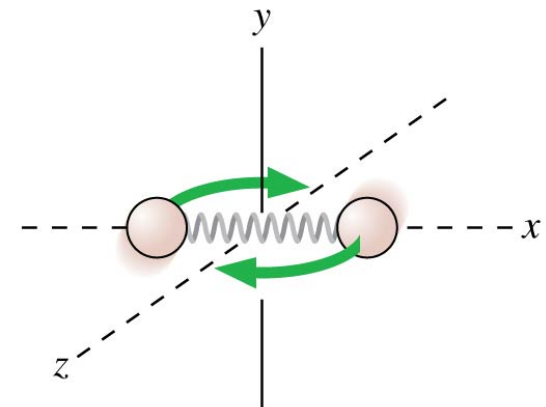
$$E_{\text{th}} = \frac{5}{2} Nk_{\text{B}}T = \frac{5}{2} nRT$$

(diatomic gases)

$$C_{\text{V}} = \frac{5}{2} R = 20.8 \text{ J/mol K}$$



Rotation end-over-end  
about the z-axis



Rotation end-over-end  
about the y-axis

# Thermal Energy and Specific Heat

**TABLE 18.2** Kinetic theory predictions for the thermal energy and the molar specific heat

System	Degrees of freedom	$E_{\text{th}}$	$C_V$
Monatomic gas	3	$\frac{3}{2}Nk_{\text{B}}T = \frac{3}{2}nRT$	$\frac{3}{2}R = 12.5 \text{ J/mol K}$
Diatomic gas	5	$\frac{5}{2}Nk_{\text{B}}T = \frac{5}{2}nRT$	$\frac{5}{2}R = 20.8 \text{ J/mol K}$
Elemental solid	6	$3Nk_{\text{B}}T = 3nRT$	$3R = 25.0 \text{ J/mol K}$



## QuickCheck 18.6

Systems A and B are both monatomic gases. At this instant,

A	B
$N = 1000$	$N = 2000$
$E_{\text{th}} = 2 \times 10^{-17} \text{ J}$	$E_{\text{th}} = 3 \times 10^{-17} \text{ J}$

- A.  $T_A > T_B$ .
- B.  $T_A = T_B$ .
- C.  $T_A < T_B$ .
- D. There's not enough information to compare their temperatures.

## QuickCheck 18.6

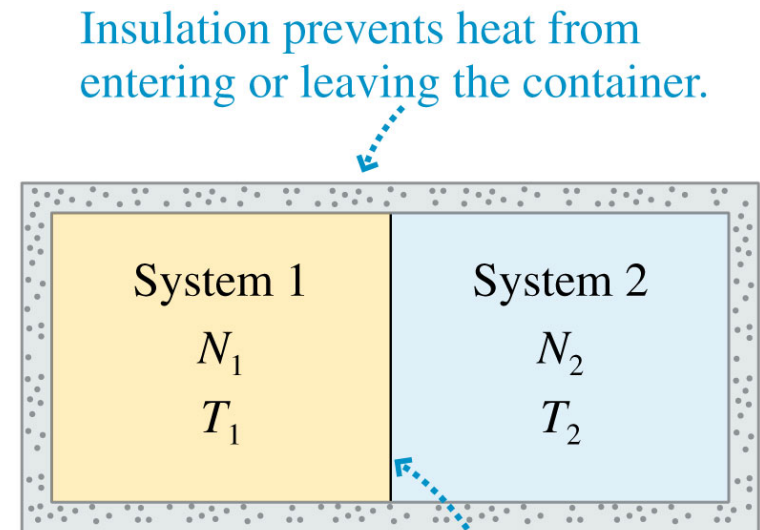
Systems A and B are both monatomic gases. At this instant,

A	B
$N = 1000$	$N = 2000$
$E_{\text{th}} = 2 \times 10^{-17} \text{ J}$	$E_{\text{th}} = 3 \times 10^{-17} \text{ J}$

- ✓ **A.**  $T_A > T_B$ . *A has the larger average energy per atom.*
- B.  $T_A = T_B$ .
- C.  $T_A < T_B$ .
- D. There's not enough information to compare their temperatures.

# Thermal Interactions and Heat

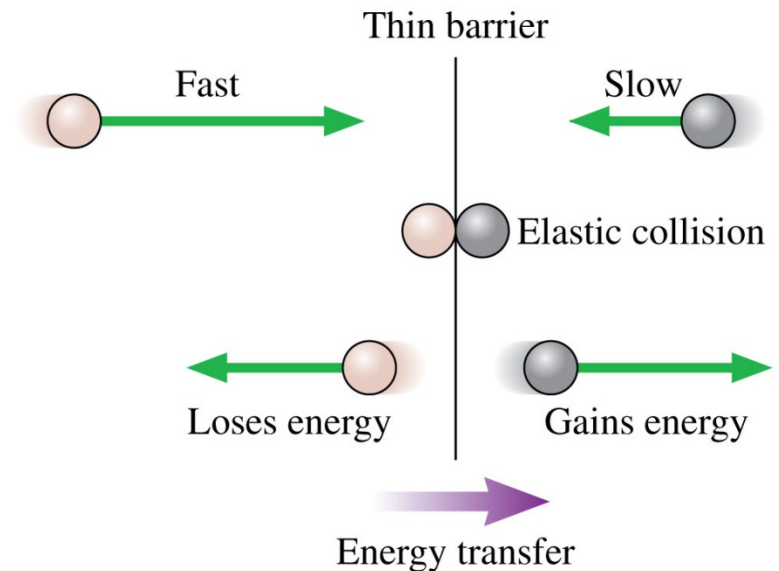
- Consider two gases, initially at different temperatures  
 $T_{1i} > T_{2i}$ .
- They can interact thermally through a very thin barrier.
- The membrane is so thin that atoms can collide at the boundary as if the membrane were not there, yet atoms cannot move from one side to the other.
- The situation is analogous, on an atomic scale, to basketballs colliding through a shower curtain.



A thin barrier prevents atoms from moving from system 1 to 2 but still allows them to collide. The barrier is clamped in place and cannot move.

# Thermal Interactions and Heat

- The figure shows a fast atom and a slow atom approaching the barrier from opposite sides.
- During the collision, there is an *energy transfer* from the faster atom's side to the slower atom's side.



**Heat is the energy transferred via collisions between the more-energetic (warmer) atoms on one side and the less-energetic (cooler) atoms on the other.**

# Thermal Interactions and Heat

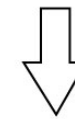
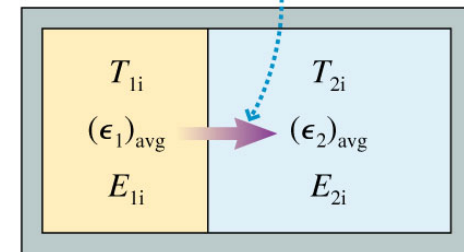
- Equilibrium is reached when the atoms on each side have, on average, equal energies:

$$(\epsilon_1)_{\text{avg}} = (\epsilon_2)_{\text{avg}} \quad (\text{thermal equilibrium})$$

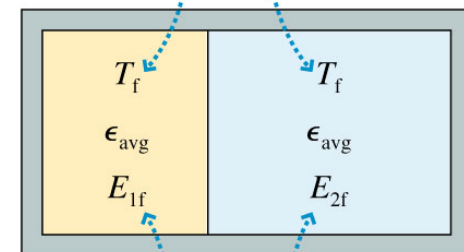
- Because the average energies are directly proportional to the final temperatures,

$$T_{1f} = T_{2f} = T_f \quad (\text{thermal equilibrium})$$

Collisions transfer energy from the warmer system to the cooler system as more-energetic atoms lose energy to less-energetic atoms.



Thermal equilibrium occurs when the systems have the same average translational kinetic energy and thus the same temperature.



In general, the thermal energies  $E_{1f}$  and  $E_{2f}$  are *not* equal.

# Thermal Interactions and Heat

The final thermal energies of the two systems are:

$$E_{1f} = \frac{N_1}{N_1 + N_2} E_{\text{tot}} = \frac{n_1}{n_1 + n_2} E_{\text{tot}}$$

$$E_{2f} = \frac{N_2}{N_1 + N_2} E_{\text{tot}} = \frac{n_2}{n_1 + n_2} E_{\text{tot}}$$

No work is done on either system, so the first law of thermodynamics is:

$$Q_1 = \Delta E_1 = E_{1f} - E_{1i}$$

$$Q_2 = \Delta E_2 = E_{2f} - E_{2i}$$

Conservation of energy requires that  $Q_1 = -Q_2$ .

# Example 18.8 A Thermal Interaction

## EXAMPLE 18.8 A thermal interaction

A sealed, insulated container has 2.0 g of helium at an initial temperature of 300 K on one side of a barrier and 10.0 g of argon at an initial temperature of 600 K on the other side.

- How much heat energy is transferred, and in which direction?
- What is the final temperature?

**MODEL** The systems start with different temperatures, so they are not in thermal equilibrium. Energy will be transferred via collisions from the argon to the helium until both systems have the same average molecular energy.

# Example 18.8 A Thermal Interaction

## EXAMPLE 18.8 A thermal interaction

**SOLVE** a. Let the helium be system 1. Helium has molar mass  $M_{\text{mol}} = 0.004 \text{ kg/mol}$ , so  $n_1 = M/M_{\text{mol}} = 0.50 \text{ mol}$ . Similarly, argon has  $M_{\text{mol}} = 0.040 \text{ kg/mol}$ , so  $n_2 = 0.25 \text{ mol}$ . The initial thermal energies of the two monatomic gases are

$$E_{1i} = \frac{3}{2}n_1RT_{1i} = 225R = 1870 \text{ J}$$

$$E_{2i} = \frac{3}{2}n_2RT_{2i} = 225R = 1870 \text{ J}$$

The systems start with *equal* thermal energies, but they are not in thermal equilibrium. The total energy is  $E_{\text{tot}} = 3740 \text{ J}$ .



# Example 18.8 A Thermal Interaction

## EXAMPLE 18.8 A thermal interaction

In equilibrium, this energy is distributed between the two systems as

$$E_{1f} = \frac{n_1}{n_1 + n_2} E_{\text{tot}} = \frac{0.50}{0.75} 3740 \text{ J} = 2493 \text{ J}$$

$$E_{2f} = \frac{n_2}{n_1 + n_2} E_{\text{tot}} = \frac{0.25}{0.75} 3740 \text{ J} = 1247 \text{ J}$$

The heat entering or leaving each system is

$$Q_1 = Q_{\text{He}} = E_{1f} - E_{1i} = 623 \text{ J}$$

$$Q_2 = Q_{\text{Ar}} = E_{2f} - E_{2i} = -623 \text{ J}$$

The helium and the argon interact thermally via collisions at the boundary, causing 623 J of heat to be transferred from the warmer argon to the cooler helium.

# Example 18.8 A Thermal Interaction

## EXAMPLE 18.8 A thermal interaction

b. These are constant-volume processes, thus  $Q = nC_V\Delta T$ .  
 $C_V = \frac{3}{2}R$  for monatomic gases, so the temperature changes are

$$\Delta T_{\text{He}} = \frac{Q_{\text{He}}}{\frac{3}{2}nR} = \frac{623 \text{ J}}{1.5(0.50 \text{ mol})(8.31 \text{ J/mol K})} = 100 \text{ K}$$

$$\Delta T_{\text{Ar}} = \frac{Q_{\text{Ar}}}{\frac{3}{2}nR} = \frac{-623 \text{ J}}{1.5(0.25 \text{ mol})(8.31 \text{ J/mol K})} = -200 \text{ K}$$

Both gases reach the common final temperature  $T_f = 400 \text{ K}$ .

**ASSESS**  $E_{1f} = 2E_{2f}$  because there are twice as many atoms in system 1.

# Irreversible Processes and the Second Law of Thermodynamics

- When two gases are brought into thermal contact, heat energy is transferred from the warm gas to the cold gas until they reach a common final temperature.
- Energy could still be conserved if heat was transferred in the opposite direction, but this *never happens*.
- The transfer of heat energy from hot to cold is an example of an **irreversible process**, a process that can happen only in one direction.

## QuickCheck 18.7

A large  $-20^{\circ}\text{C}$  ice cube is dropped into a super-insulated container holding a small amount of  $5^{\circ}\text{C}$  water, then the container is sealed. Ten minutes later, is it possible that the temperature of the ice cube will be colder than  $-20^{\circ}\text{C}$ ?

- A. Yes.
- B. No.
- C. Maybe. It would depend on other factors.

## QuickCheck 18.7

A large  $-20^{\circ}\text{C}$  ice cube is dropped into a super-insulated container holding a small amount of  $5^{\circ}\text{C}$  water, then the container is sealed. Ten minutes later, is it possible that the temperature of the ice cube will be colder than  $-20^{\circ}\text{C}$ ?

- A. Yes.
- B. **No.**
- C. Maybe. It would depend on other factors.

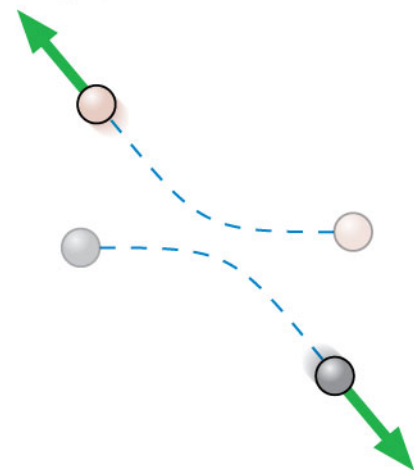
# Molecular Collisions Are Reversible

(a) Forward movie

Before:

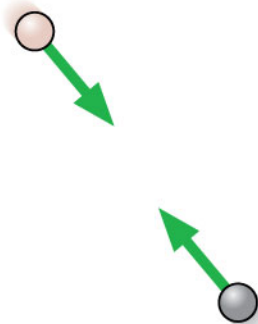


After:

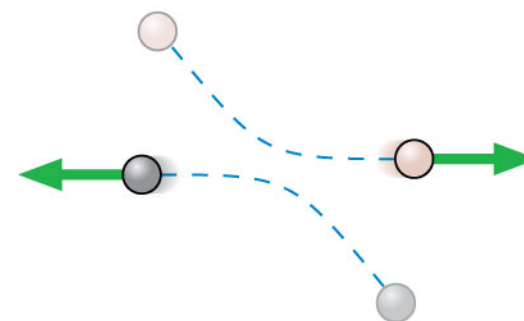


(b) The backward movie is equally plausible.

Before:



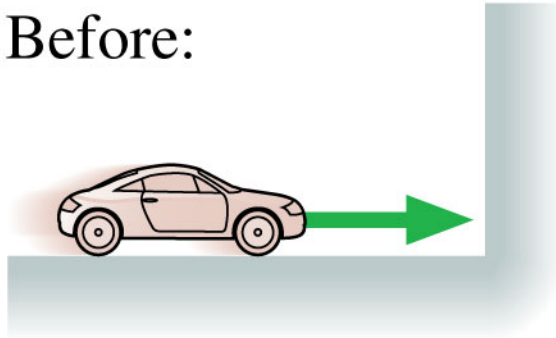
After:



# A Car Crash Is Irreversible

(a) Forward movie

Before:

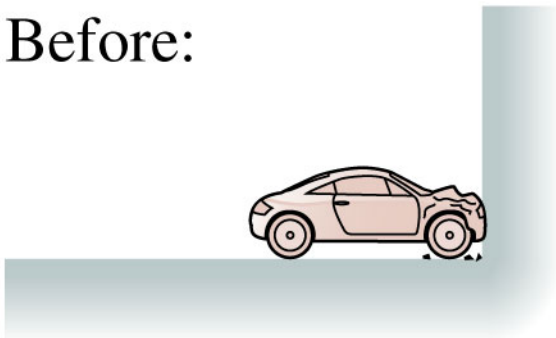


After:

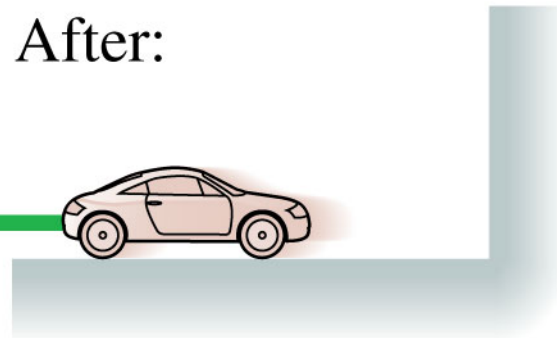


(b) The backward movie is physically impossible.

Before:

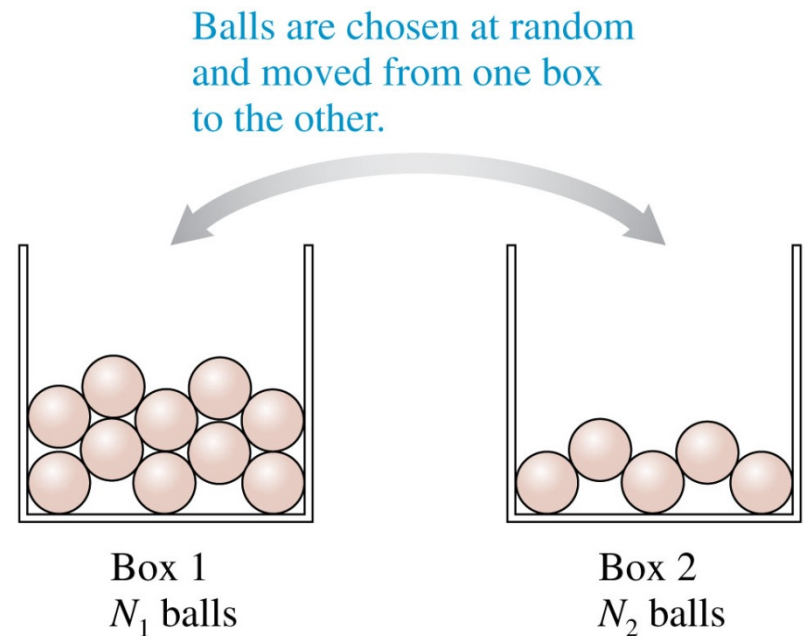


After:



# Which Way to Equilibrium?

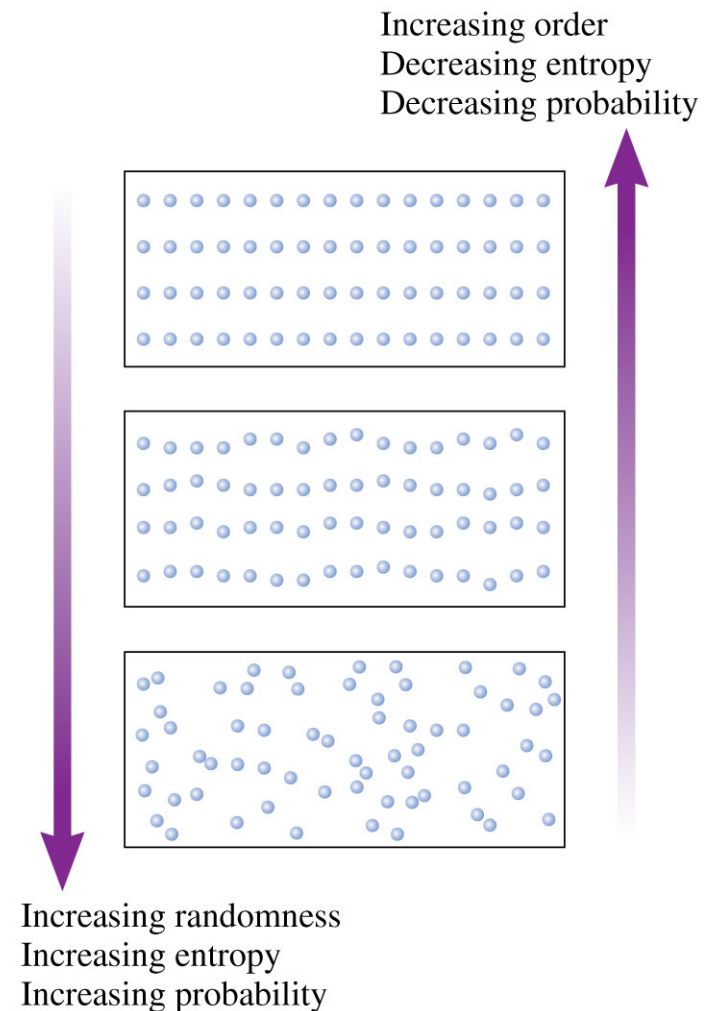
- The figure shows two boxes containing identical balls.
- Once every second, one ball is chosen at random and moved to the other box.
- What do you expect to see if you return several hours later?
- Although each transfer is reversible, it is more likely that the system will evolve toward a state in which  $N_1 \approx N_2$  than toward a state in which  $N_1 \gg N_2$ .
- The macroscopic drift toward equilibrium is **irreversible**.





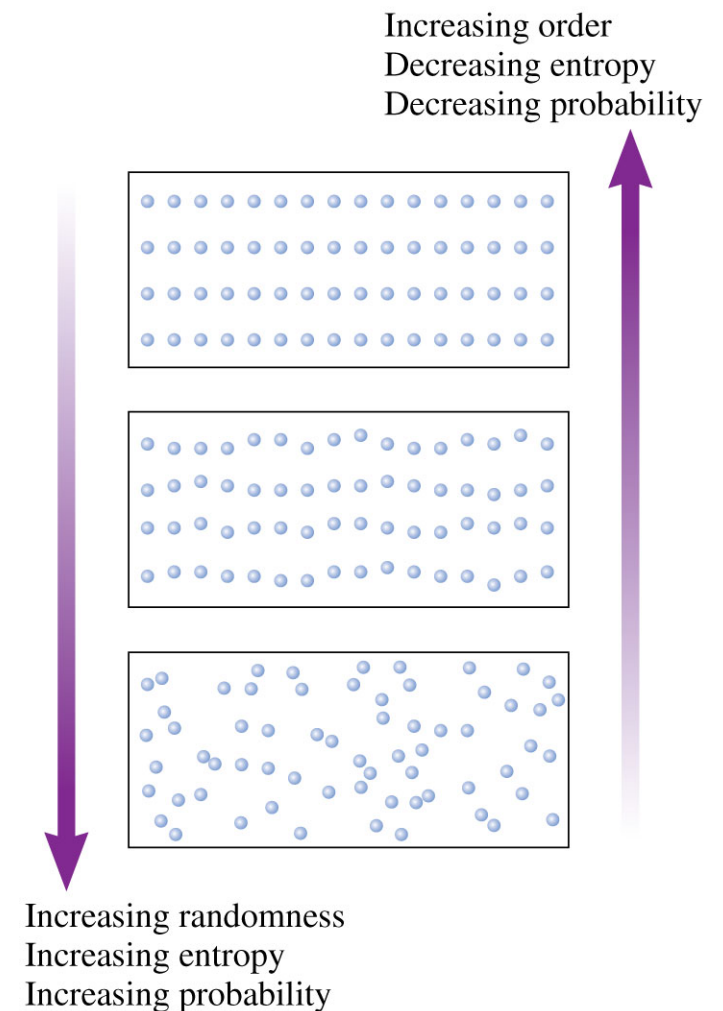
# Order, Disorder, and Entropy

- Scientists and engineers use a state variable called **entropy** to measure the probability that a macroscopic state will occur spontaneously.
- It is often said that entropy measures the amount of *disorder* in a system.



# Order, Disorder, and Entropy

- In principle, any number of heads are possible if you throw  $N$  coins in the air and let them fall.
- If you throw four coins, the odds are 1 in  $2^4$ , or 1 in 16 of getting four heads; this represents fairly low entropy.
- With 10 coins, the probability that  $N_{\text{heads}} = 10$  is  $0.5^{10} \approx 1/1000$ , which corresponds to much lower entropy.
- With 100 coins, the probability that  $N_{\text{heads}} = 100$  has dropped to  $10^{-30}$ ; it is safe to say it will never happen.
- Entropy is highest when  $N_{\text{heads}} \approx N_{\text{tails}}$ .



# The Second Law of Thermodynamics

- Macroscopic systems evolve irreversibly toward equilibrium in accordance with the following law:

**Second law, formal statement** The entropy of an isolated system (or group of systems) never decreases. The entropy either increases, until the system reaches equilibrium, or, if the system began in equilibrium, stays the same.

- This law tells us what a system does *spontaneously*, on its own, without outside intervention.
- Order turns into disorder and randomness.
- Information is lost rather than gained.
- The system “runs down.”

# The Second Law of Thermodynamics

- The second law of thermodynamics is often stated in several equivalent but more informal versions:

**Second law, informal statement #1** When two systems at different temperatures interact, heat energy is transferred spontaneously from the hotter to the colder system, never from the colder to the hotter.

**Second law, informal statement #2** The time direction in which the entropy of an isolated macroscopic system increases is “the future.”

- Establishing the “arrow of time” is one of the most profound implications of the second law of thermodynamics.

## QuickCheck 18.8

A large  $-20^{\circ}\text{C}$  ice cube is dropped into a super-insulated container holding a small amount of  $5^{\circ}\text{C}$  water, then the container is sealed. Ten minutes later, the temperature of the ice (and any water that has melted from the ice) will be warmer than  $-20^{\circ}\text{C}$ . This is a consequence of

- A. The first law of thermodynamics.
- B. The second law of thermodynamics.
- C. The third law of thermodynamics.
- D. Both the first and the second laws.
- E. Joule's law.

## QuickCheck 18.8

A large  $-20^{\circ}\text{C}$  ice cube is dropped into a super-insulated container holding a small amount of  $5^{\circ}\text{C}$  water, then the container is sealed. Ten minutes later, the temperature of the ice (and any water that has melted from the ice) will be warmer than  $-20^{\circ}\text{C}$ . This is a consequence of

- A. The first law of thermodynamics.
- ✓ **B. The second law of thermodynamics.**
- C. The third law of thermodynamics.
- D. Both the first and the second laws.
- E. Joule's law.



# Chapter 18 Summary Slides

# General Principles

The **micro/macro connection** relates the macroscopic properties of a system to the motion and collisions of its atoms and molecules.

## The Equipartition Theorem

Tells us how collisions distribute the energy in the system. The energy stored in each mode of the system (each **degree of freedom**) is  $\frac{1}{2}Nk_B T$  or, in terms of moles,  $\frac{1}{2}nRT$ .



# General Principles

The **micro/macro connection** relates the macroscopic properties of a system to the motion and collisions of its atoms and molecules.

## The Second Law of Thermodynamics

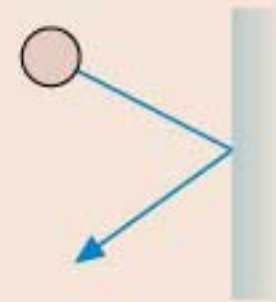
Tells us how collisions move a system toward equilibrium. The entropy of an isolated system can only increase or, in equilibrium, stay the same.

- Order turns into disorder and randomness.
- Systems run down.
- Heat energy is transferred spontaneously from a hotter to a colder system, never from colder to hotter.

# Important Concepts

**Pressure** is due to the force of the molecules colliding with the walls:

$$p = \frac{1}{3} \frac{N}{V} m v_{\text{rms}}^2 = \frac{2}{3} \frac{N}{V} \epsilon_{\text{avg}}$$



# Important Concepts

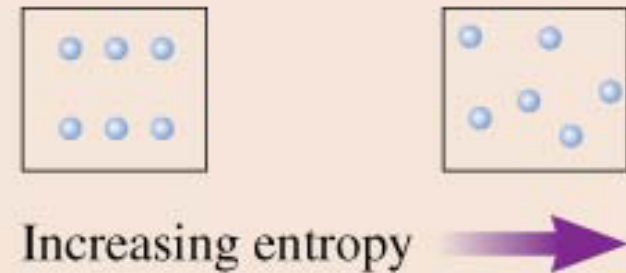
The **average translational kinetic energy** of a molecule is

$$\epsilon_{\text{avg}} = \frac{3}{2} k_{\text{B}} T. \text{ The temperature of the gas } T = \frac{2}{3k_{\text{B}}} \epsilon_{\text{avg}}$$

measures the average translational kinetic energy.

# Important Concepts

**Entropy** measures the probability that a macroscopic state will occur or, equivalently, the amount of disorder in a system.



# Important Concepts

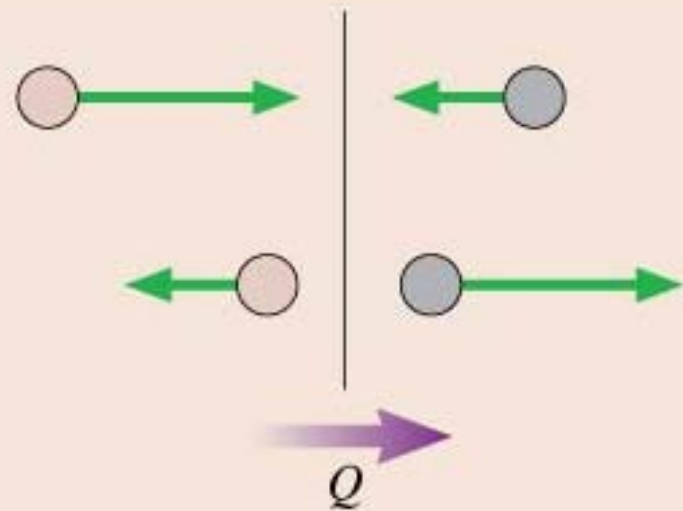
The **thermal energy** of a system is

$E_{\text{th}}$  = translational kinetic energy + rotational kinetic energy + vibrational energy

- **Monatomic gas**       $E_{\text{th}} = \frac{3}{2}Nk_{\text{B}}T = \frac{3}{2}nRT$
- **Diatomic gas**       $E_{\text{th}} = \frac{5}{2}Nk_{\text{B}}T = \frac{5}{2}nRT$
- **Elemental solid**       $E_{\text{th}} = 3Nk_{\text{B}}T = 3nRT$

# Important Concepts

**Heat** is energy transferred via collisions from more-energetic molecules on one side to less-energetic molecules on the other. Equilibrium is reached when  $(\epsilon_1)_{\text{avg}} = (\epsilon_2)_{\text{avg}}$ , which implies  $T_{1f} = T_{2f}$ .



# End of chapter problems

- Concept questions, page 522.