Chapter 18. The Micro/Macro Connection

Heating the air in a hot-air balloon increases the thermal energy of the air molecules. This causes the gas to expand, lowering its density and allowing the balloon to float in the cooler surrounding air.

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

Chapter 18. The Micro/Macro Connection

Topics:

- Molecular Speeds and Collisions

- Pressure in a Gas

- Temperature

- Thermal Energy and Specific Heat

- Thermal Interactions and Heat

- Irreversible Processes and the Second Law of Thermodynamics

Chapter 18. Reading Quizzes

What is the *name* of the quantity represented as v_{rms}?

A. Random-measured-step viscosity
B. Root-mean-squared speed
C. Relative-mean-system velocity
D. Radial-maser-system volume

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✔ **B. Root-mean-squared speed**

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A. Charismatic energy
B. Translational energy
C. Heat energy
D. Rotational energy
E. Solar energy

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✔ **D. Rotational energy**
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The second law of thermodynamics says that

A. the entropy of an isolated system never decreases.
B. heat never flows spontaneously from cold to hot.
C. the total thermal energy of an isolated system is constant.
D. both A and B.
E. both A and C.

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In general,

A. both microscopic and macroscopic processes are reversible.

B. both microscopic and macroscopic processes are irreversible.

C. microscopic processes are reversible and macroscopic processes are irreversible.

D. microscopic processes are irreversible and macroscopic processes are reversible.

In general,

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✔ **C. microscopic processes are reversible and macroscopic processes are irreversible.**

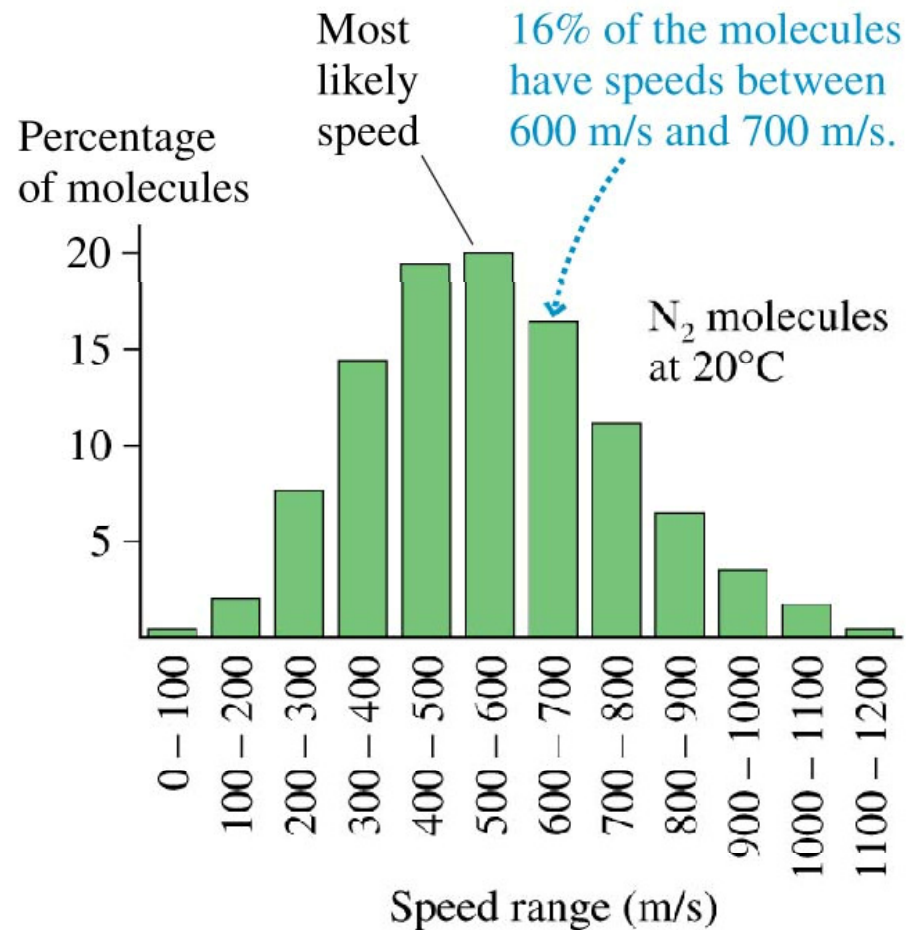D. microscopic processes are irreversible and macroscopic processes are reversible.

Chapter 18. Basic Content and Examples

Molecular Speeds and Collisions

• A gas consists of a vast number of molecules, each moving randomly and undergoing millions of collisions every second.

• Despite the apparent chaos, *averages*, such as the average number of molecules in the speed range 600 to 700 m/s, have precise, predictable values.

• **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.**

Molecular Speeds and Collisions

FIGURE 18.2 The distribution of molecular speeds in a sample of nitrogen gas.

Percentage of molecules

Most likely speed

16% of the molecules have speeds between 600 m/s and 700 m/s.

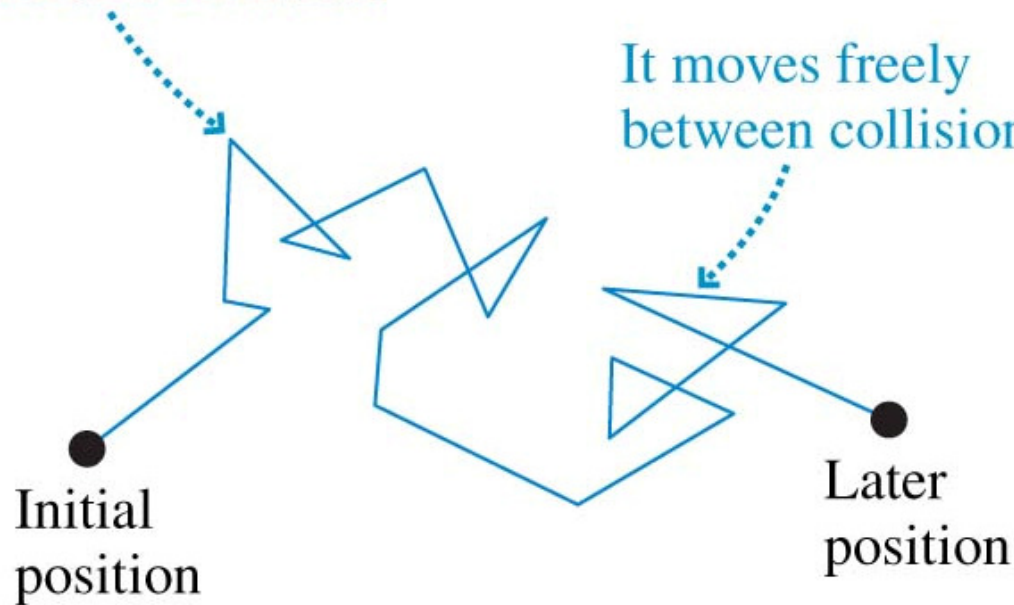N_2 molecules at 20°C

Speed range (m/s)

Molecular Speeds and Collisions

FIGURE 18.3 A single molecule follows a zig-zag path through a gas as it collides with other molecules.

The molecule changes direction and speed with each collision.

It moves freely between collisions.

Initial position

Later position

Mean Free Path

If a molecule has N_{coll} collisions as it travels distance L, the average distance between collisions, which is called the **mean free path** λ (lowercase Greek lambda), is

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

EXAMPLE 18.1 The mean free path at room temperature

QUESTION:

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)?

EXAMPLE 18.1 The mean free path at room temperature

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 $pV = Nk_\text{B}T$ to determine the number density:

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

Thus the mean free path is

$$\lambda = \frac{1}{4\sqrt{2}\pi(N/V)r^2}$$

$$= \frac{1}{4\sqrt{2}\pi(2.5 \times 10^{25} \text{ m}^{-3})(1.0 \times 10^{-10} \text{ m})^2}$$

$$= 2.3 \times 10^{-7} \text{ m} = 230 \text{ nm}$$

EXAMPLE 18.1 The mean free path at room temperature

ASSESS You learned in Example 16.5 that the average separation between gas molecules at STP is ≈ 5.7 nm. It seems that any given molecule can slip between its neighbors, which are spread out in three dimensions, and travel—on average—about 40 times the average spacing before it collides with another molecule.

Temperature in a Gas

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

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

Pressure in a Gas

The pressure on the wall of a container due to all the molecular collisions is

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

This expresses the macroscopic pressure in terms of the microscopic physics. The pressure depends on the density of molecules in the container and on how fast, on average, the molecules are moving.

EXAMPLE 18.7 Mean time between collisions

EXAMPLE 18.7 Mean time between collisions

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

EXAMPLE 18.7 Mean time between collisions

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

EXAMPLE 18.7 Mean time between collisions

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

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

EXAMPLE 18.7 Mean time between collisions

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 225 nm between collisions.

Monatomic and Diatomic Gases

The thermal energy of a monatomic gas of N atoms is

$$E_{th} = \frac{3}{2}Nk_BT = \frac{3}{2}nRT \qquad \text{(thermal energy of a monatomic gas)}$$

A diatomic gas has more thermal energy than a monatomic gas at the same temperature because the molecules have rotational as well as translational kinetic energy.

$$E_{th} = \frac{5}{2}Nk_BT = \frac{5}{2}nRT$$

$$\text{(diatomic gases)}$$

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

Thermal Interactions and Heat

• Consider a rigid, insulated container divided into two   sections by a very thin, stiff membrane. The left side,   which we'll call system 1, has N_1 atoms at an initial   temperature T_{1i}. System 2 on the right has N_2 atoms at an   initial temperature T_{2i}.

• The membrane is so thin that atoms can collide at the   boundary as if the membrane were not there, yet it is a   barrier that prevents atoms from moving from one side to   the other.

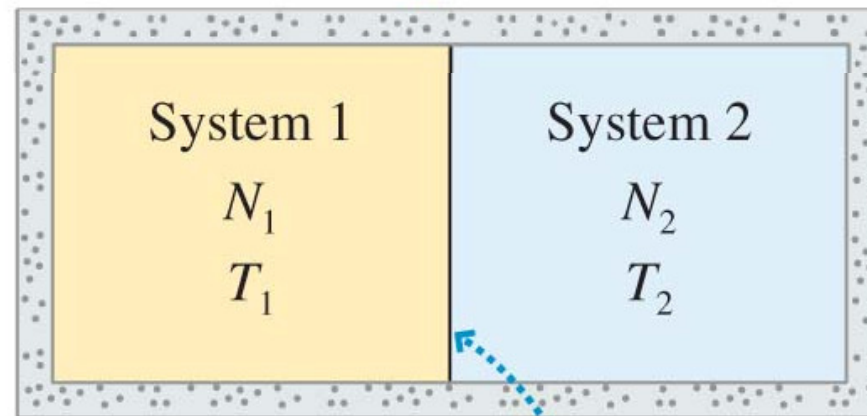• System 1 and system 2 begin with thermal energies

$$E_{1i} = \frac{3}{2}N_1 k_B T_{1i} = \frac{3}{2}n_1 R T_{1i}$$

$$E_{2i} = \frac{3}{2}N_2 k_B T_{2i} = \frac{3}{2}n_2 R T_{2i}$$

Thermal Interactions and Heat

FIGURE 18.14 Two gases can interact thermally through a very thin barrier.

Insulation prevents heat from entering or leaving the container.

System 1
N_1
T_1

System 2
N_2
T_2

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 condition for thermal equilibrium is that the average translational kinetic energies of the atoms in both systems are equal.

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

Because the average energies are directly proportional to the final temperatures, thermal equilibrium is characterized by the macroscopic condition as follows:

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

The final thermal energies of the two systems are

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

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

EXAMPLE 18.9 A thermal interaction

QUESTIONS:

EXAMPLE 18.9 A thermal interaction

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 18.9 A thermal interaction

SOLVE a. Let the helium be system 1. Helium has molar mass $M_{mol} = 4\,g/mol$, so $n_1 = M/M_{mol} = 0.50\,mol$.

Similarly, argon has $M_{mol} = 40\,g/mol$, so $n_2 = 0.25\,mol$. The initial thermal energies of the two monatomic gases are

$$E_{1i} = \frac{3}{2}n_1 R T_{1i} = 225R = 1870\,J$$

$$E_{2i} = \frac{3}{2}n_2 R T_{2i} = 225R = 1870\,J$$

The systems start with *equal* thermal energies, but they are not in thermal equilibrium. The total energy is $E_{tot} = 3740\,J$. In equilibrium, this energy is distributed between the two systems as

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

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

EXAMPLE 18.9 A thermal interaction

The heat entering or leaving each system is

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

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

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 18.9 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

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

$$\Delta T_{Ar} = \frac{Q_{Ar}}{\frac{3}{2}nR} = \frac{-623 \text{ J}}{1.5(0.25 \text{ mol})(8.31 \text{ J/mol K})} = -200 \text{ K}$$
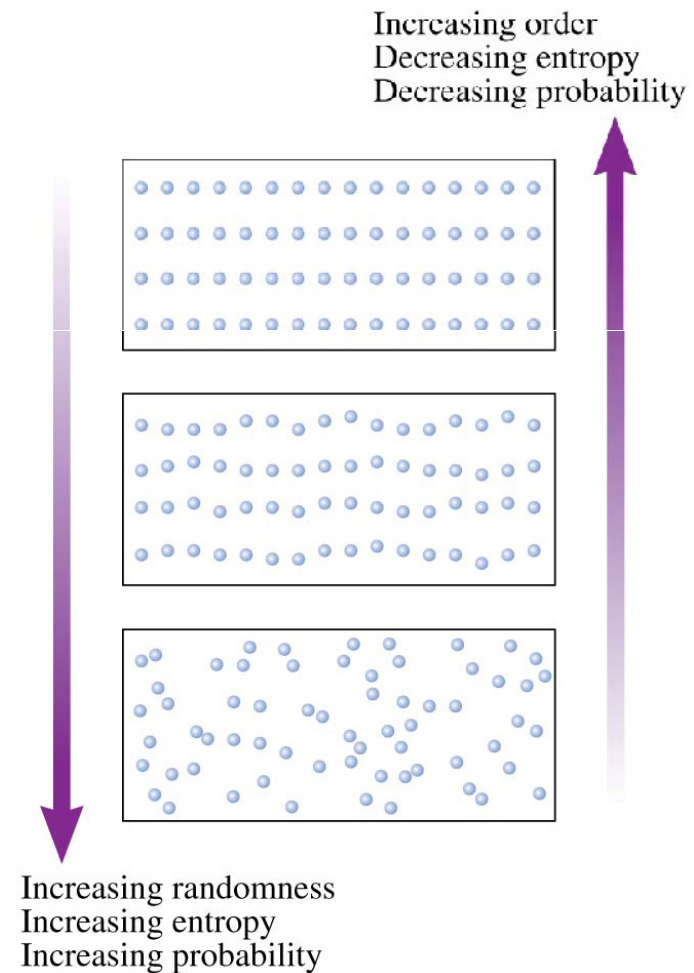
EXAMPLE 18.9 A thermal interaction

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

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.

FIGURE 18.20 Ordered and disordered systems.

Increasing order
Decreasing entropy
Decreasing probability

Increasing randomness
Increasing entropy
Increasing probability

The Second Law of Thermodynamics

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.

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.

Chapter 18. Summary Slides

General Principles

Kinetic theory, 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, $\frac{1}{2}nRT$.

## 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:

$$p = \frac{1}{3}\frac{N}{V}mv_{rms}^2 = \frac{2}{3}\frac{N}{V}\epsilon_{avg}$$
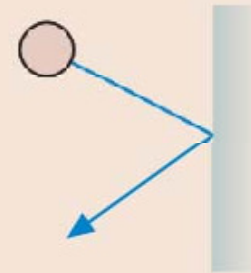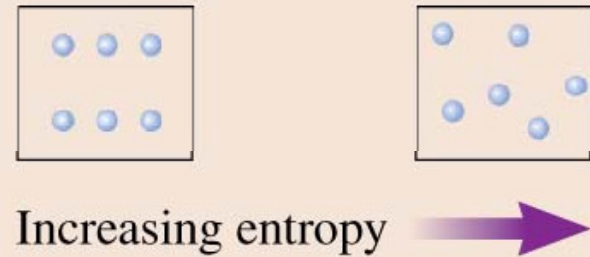
Important Concepts

The **average translational kinetic energy** of a molecule is $\epsilon_{avg} = \frac{3}{2}k_B T$. The temperature of the gas $T = \frac{2}{3k_B}\epsilon_{avg}$ 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.

Increasing entropy

Important Concepts

The **thermal energy** of a system is

E_{th} = translational kinetic energy + rotational kinetic energy + vibrational energy

- **Monatomic gas** $E_{th} = \frac{3}{2}Nk_BT = \frac{3}{2}nRT$
- **Diatomic gas** $E_{th} = \frac{5}{2}Nk_BT = \frac{5}{2}nRT$
- **Elemental solid** $E_{th} = 3Nk_BT = 3nRT$

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 $(\epsilon_1)_{avg} = (\epsilon_2)_{avg}$, which implies $T_{1f} = T_{2f}$.

Q
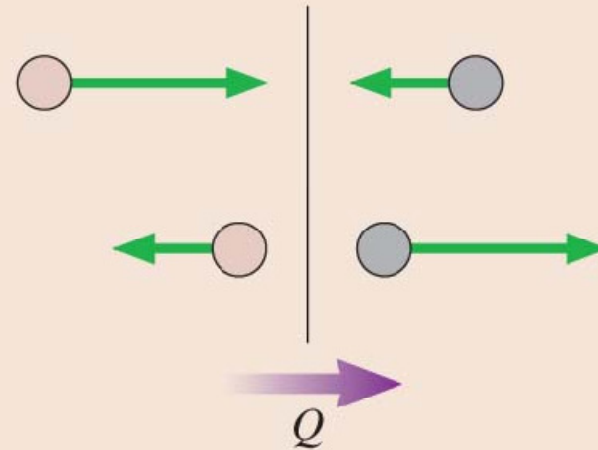
Applications

The **root-mean-square speed** v_{rms} is the square root of the average of the squares of the molecular speeds:

$$v_{rms} = \sqrt{(v^2)_{avg}}$$

For molecules of mass m at temperature T, $v_{rms} = \sqrt{\dfrac{3k_B T}{m}}$

Applications

Molar specific heats can be predicted from the thermal energy because $\Delta E_{th} = nC\Delta T$.

- **Monatomic gas** $C_V = \frac{3}{2}R$
- **Diatomic gas** $C_V = \frac{5}{2}R$
- **Elemental solid** $C = 3R$

Chapter 18. Questions

The table shows the properties of four gases, each having the same number of molecules. Rank in order, from largest to smallest, the mean free paths λ_A to λ_D of molecules in these gases.

Gas	A	B	C	D
Volume	V	$2V$	V	V
Atomic mass	m	m	$2m$	m
Atomic radius	r	r	r	$2r$

1. $\lambda_B > \lambda_A = \lambda_C > \lambda_D$
2. $\lambda_B > \lambda_A = \lambda_C = \lambda_D$
3. $\lambda_B = \lambda_C > \lambda_A = \lambda_D$
4. $\lambda_C > \lambda_D > \lambda_A = \lambda_B$
5. $\lambda_C > \lambda_A = \lambda_B = \lambda_D$

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3. $\lambda_B = \lambda_C > \lambda_A = \lambda_D$
4. $\lambda_C > \lambda_D > \lambda_A = \lambda_B$
5. $\lambda_C > \lambda_A = \lambda_B = \lambda_D$

The speed of every molecule in a gas is suddenly increased by a factor of 4. As a result, v_{rms} increases by a factor of

A. 2.

B. <4, but not necessarily 2.

C. 4.

D. >4 but not necessarily 16.

E. 16.

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✔ C. 4.
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Which system has the largest average translational kinetic energy per molecule?

A. 2 mol of He at $p = 2$ atm, $T = 300$ K
B. 2 mol of N_2 at $p = 0.5$ atm, $T = 450$ K
C. 1 mol of He at $p = 1$ atm, $T = 300$ K
D. 1 mol of N_2 at $p = 0.5$ atm, $T = 600$ K
E. 1 mol of Ar at $p = 0.5$ atm, $T = 450$ K

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✔ **D. 1 mol of N_2 at $p = 0.5$ atm, $T = 600$ K**
E. 1 mol of Ar at $p = 0.5$ atm, $T = 450$ K

How many degrees of freedom does a bead on a wire have?

A. 1

B. 4

C. 3

D. 5

E. 2

How many degrees of freedom does a bead on a wire have?

A. 1

B. 4

C. 3

D. 5

✔ E. 2

Systems A and B are interacting thermally. At this instant of time,

A	B
$N = 1000$	$N = 2000$
$\epsilon_{avg} = 1.0 \times 10^{-20}\,\text{J}$	$\epsilon_{avg} = 0.5 \times 10^{-20}\,\text{J}$
$E_{th} = 1.0 \times 10^{-17}\,\text{J}$	$E_{th} = 1.0 \times 10^{-17}\,\text{J}$

A. $T_A > T_B$.

B. $T_A < T_B$.

C. $T_A = T_B$.

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✔ **A. $T_A > T_B$.**

B. $T_A < T_B$.

C. $T_A = T_B$.

Two identical boxes each contain 1,000,000 molecules. In box A, 750,000 molecules happen to be in the left half of the box while 250,000 are in the right half. In box B, 499,900 molecules happen to be in the left half of the box while 500,100 are in the right half. At this instant of time,

    A. the entropy of box A is larger than the entropy of box B.

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