

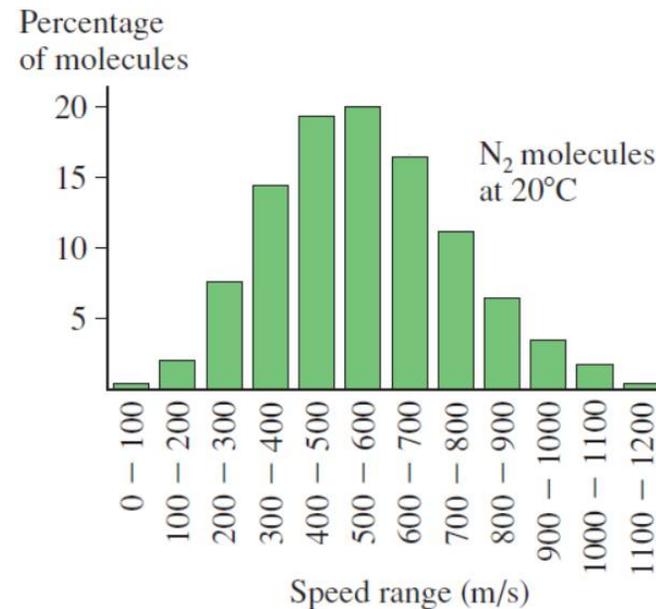
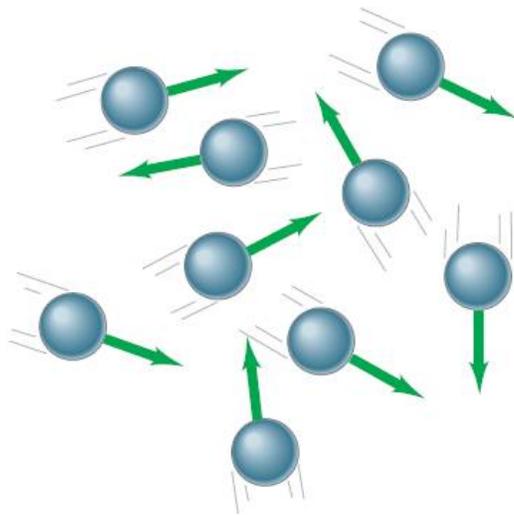
The microscopic and macroscopic connection

Subjects covered:

- Molecular collisions
- Pressure in gases
- Temperature, average kinetic energy, & root-mean-square speed
- Thermal energy and specific heat
- Thermal interactions and heat
- Irreversible process and the second law of thermodynamics

Molecular speeds and collisions

Molecules at a given temperature have a *distribution* of speeds.



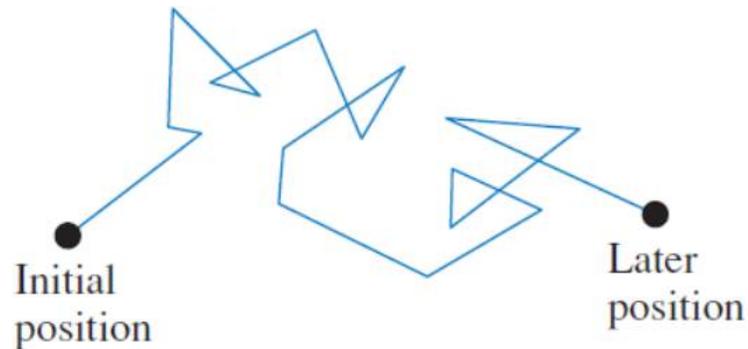
Macroscopic properties of a system, such as temperature or pressure, are related to the *average* behavior of the atoms and molecules.

Path of a molecule

Molecules are always colliding with each other in a system.

The magnitude and direction of a molecule's velocity frequently changes due to collisions with other molecules.

Thus, the path of a molecule in a system appears to be a series of short, randomly oriented motions.

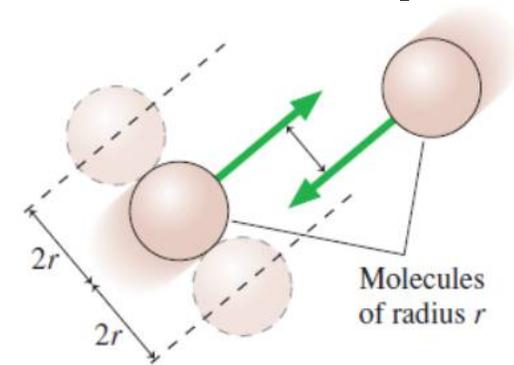


For a molecule that travels a distance of L that experiences N_{coll} number of collisions, the mean free path is defined as

$$\lambda = \frac{L}{N_{\text{coll}}}$$

Molecular collisions and mean free path

Two of the same type of molecules will collide if their center-of-masses are within twice the radius of each other.



The cross-sectional area for impact to occur is $A_{\text{impact}} = \pi (2r)^2$. The volume of space where a collision can occur is the area multiplied by the length traveled by the molecule, $V_{\text{impact}} = 4\pi r^2 L$.

The number density is the total number of gas molecules divided by the total volume, $\frac{N}{V}$. The number of collisions is then given by

$$N_{\text{coll}} = \frac{N}{V} V_{\text{impact}} = 4\pi r^2 N \frac{L}{V}$$

Therefore, the mean free path is

$$\lambda = \frac{L}{N_{\text{coll}}} = \frac{1}{4\pi r^2 (N/V)}$$

What happens to the mean free path if the pressure of an ideal gas is doubled while volume and temperature are held constant?

(a) It would change by a factor of $\frac{1}{2}$.

(b) It would change by a factor of $\sqrt{2}$.

(c) It would change by a factor of 2.

(d) The mean free path will remain the same.

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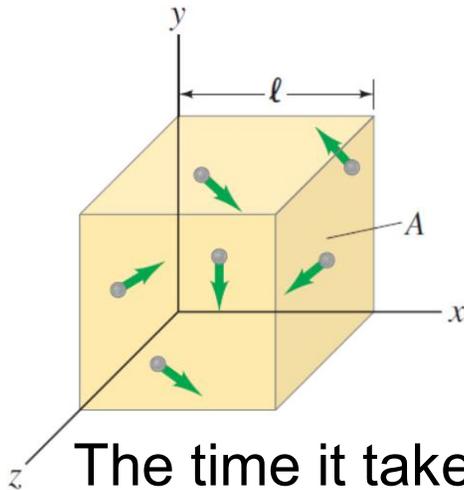
(a) It would change by a factor of 2.

(d) The mean free path will remain the same.

Molecular gases and pressure

When a gas molecule strikes a container wall, the wall exerts an force back onto the molecule with equal magnitude.

According to Newton's 2nd law, $F = ma = m \frac{\Delta v}{\Delta t} = \frac{\Delta (mv)}{\Delta t}$



Assuming only elastic collisions, the only change in momentum is in along the normal direction to the container wall. For the left wall in the yz -plane,

$$\Delta (mv) = mv_x - (-mv_x) = 2mv_x$$

The time it takes the molecule to travel across the container and back again is

$$\Delta t = \frac{2L}{v_x}$$

The molecule moves back and forth rapidly, and so the average force is

$$F = \frac{\Delta (mv)}{\Delta t} = \frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{L}$$

Molecular gases and pressure (cont.)

Summing up all of the molecules colliding with the wall gives

$$F_{\text{net}} = \frac{m}{L} (v_{x1}^2 + v_{x2}^2 + \cdots + v_{xN}^2)$$

We know that the average velocity squared is

$$(v_x^2)_{\text{avg}} = \frac{1}{N} (v_{x1}^2 + v_{x2}^2 + \cdots + v_{xN}^2)$$

and that the volume is area multiplied by the length, $V = AL$.

Therefore, we may write the net force of the wall on the molecules as

$$F_{\text{net}} = \frac{A}{V} N m (v_x^2)_{\text{avg}}$$

Molecular gases and pressure (cont.)

We define the root-mean-square speed as

$$v_{\text{rms}} = \sqrt{(v^2)_{\text{avg}}} \quad \text{or} \quad v_{\text{rms}}^2 = (v_x^2)_{\text{avg}} + (v_y^2)_{\text{avg}} + (v_z^2)_{\text{avg}}$$

Also, a gas has no preferred direction, which means that

$$(v_x^2)_{\text{avg}} = (v_y^2)_{\text{avg}} = (v_z^2)_{\text{avg}}$$

Therefore, $v_{\text{rms}}^2 = (v_x^2)_{\text{avg}} + (v_x^2)_{\text{avg}} + (v_x^2)_{\text{avg}} = 3 (v_x^2)_{\text{avg}}$

The net force of the wall on the molecules becomes

$$F_{\text{net}} = \frac{N}{3} \frac{A}{V} m v_{\text{rms}}^2$$

Pressure is defined as force per unit area, which gives

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

Connection to kinetic energy

We can multiply both sides of our equation for pressure to get

$$pV = \frac{1}{3}Nmv_{\text{rms}}^2$$

This expression can be rewritten as

$$pV = \frac{2}{3}N \left(\frac{1}{2}mv_{\text{rms}}^2 \right)$$

Thus, the pressure multiplied by the volume can be written in terms of the average molecular kinetic energy, ϵ_{avg} , which gives

$$pV = \frac{2}{3}N\epsilon_{\text{avg}}$$

Two samples of the same ideal gas have the same pressure and density. Sample B has twice the volume of sample 1. What is the rms speed of the molecules in sample 2?

(a) Twice that in sample 1.

(b) Equal to that in sample 1.

(a) Half that in sample A.

(d) Impossible to determine.

Temperature as related to rms speed

Recall the ideal gas law

$$pV = NkT$$

We may substitute our expression, $pV = \frac{2}{3}N\epsilon_{\text{avg}}$, into the ideal gas law to obtain

$$\epsilon_{\text{avg}} = \frac{3}{2}kT$$

which, in terms of the rms speed, becomes

$$\frac{1}{2}mv_{\text{rms}}^2 = \frac{3}{2}kT$$

Solving for the rms speed gives

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

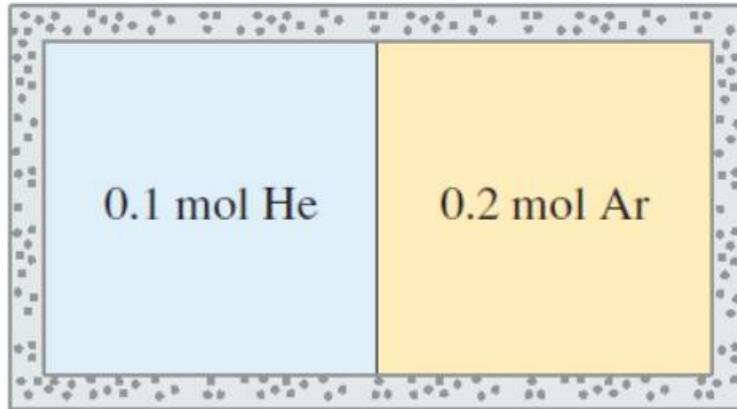
Suppose that the speed of every molecule in a gas increases by a factor of 2. What would happen?

(a) The temperature would increase by a factor of $\sqrt{2}$.

(b) The temperature would increase by a factor of 2.

(a) The temperature would increase by a factor of 4.

(d) The temperature would remain the same.



He	2	Ar	18
4.002 6		39.948	
$1s^2$		$3p^6$	

The two containers of gas are in good thermal contact with each other but well insulated from the environment. They have been in contact for a long time and are in thermal equilibrium. The v_{rms} of helium is

- A. greater than the v_{rms} of argon.
- B. the same as the v_{rms} of argon.
- C. less than the v_{rms} of argon.

Specific heat of ideal gases

The thermal energy of an ideal gas is the sum each element's translational kinetic energy

$$E_{\text{th}} = \epsilon_1 + \epsilon_2 + \cdots + \epsilon_N = N\epsilon_{\text{avg}}$$

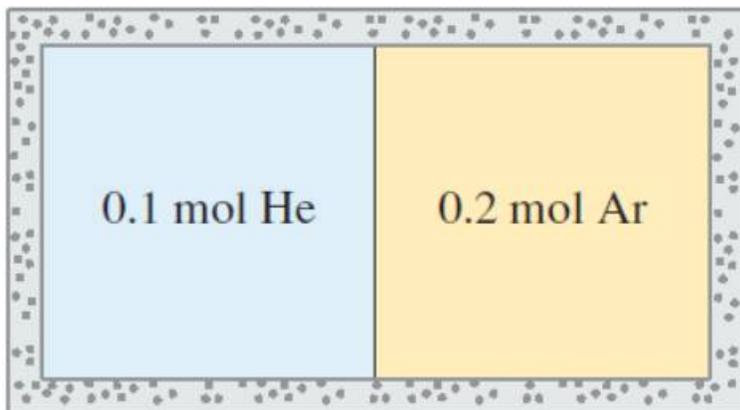
This can be then be written as $E_{\text{th}} = \frac{3}{2}NkT$, where the difference in thermal energy from an ideal gas being raised by a temperature ΔT is given by

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

The change in thermal energy for a gas at constant volume was previously given as $\Delta E_{\text{th}} = NC_V \Delta T$, where we may substitute this expression into the above equation to get

$$C_V = \frac{3}{2}k \quad \text{or} \quad C_V = \frac{3}{2}R$$

(for an ideal gas only)



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4.002 6
 $1s^2$

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- B. the same as the thermal energy of argon.
- C. less than the thermal energy of argon.

Equipartition Theorem

Degrees of freedom: 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.

Consequence, For a system of N particles at temperature T , the energy stored in each mode (each degree of freedom) is $\frac{1}{2}NkT$ or, in terms of moles, $\frac{1}{2}nRT$.

Specific heat of real gases

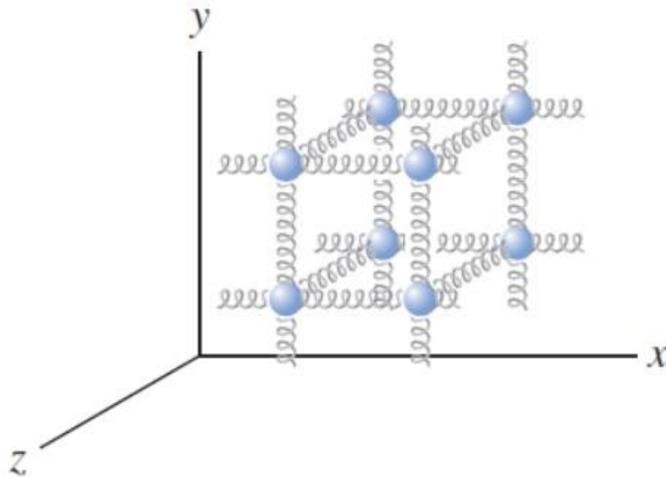
Molar specific heats of gases (J/mol K)

Gas	C_p	C_v	$C_p - C_v$
Monatomic Gases			
He	20.8	12.5	8.3
Ne	20.8	12.5	8.3
Ar	20.8	12.5	8.3
Diatomic Gases			
H ₂	28.7	20.4	8.3
N ₂	29.1	20.8	8.3
O ₂	29.2	20.9	8.3

- The noble gases behave like ideal gases with $C_v = \frac{3}{2}R$.
- The diatomic gases are more complicated than the monatomic gases, where the translational kinetic energy alone is not sufficient to describe the thermal properties.

Simple model for solids

A simple model of a solid is a “bedspring” model, where a crystal lattice has an atom at each lattice site. The atoms are connected to their nearest neighbors by springs.



$$E_{\text{th}} = 6 \left(\frac{1}{2} NkT \right) \\ = 3NkT$$

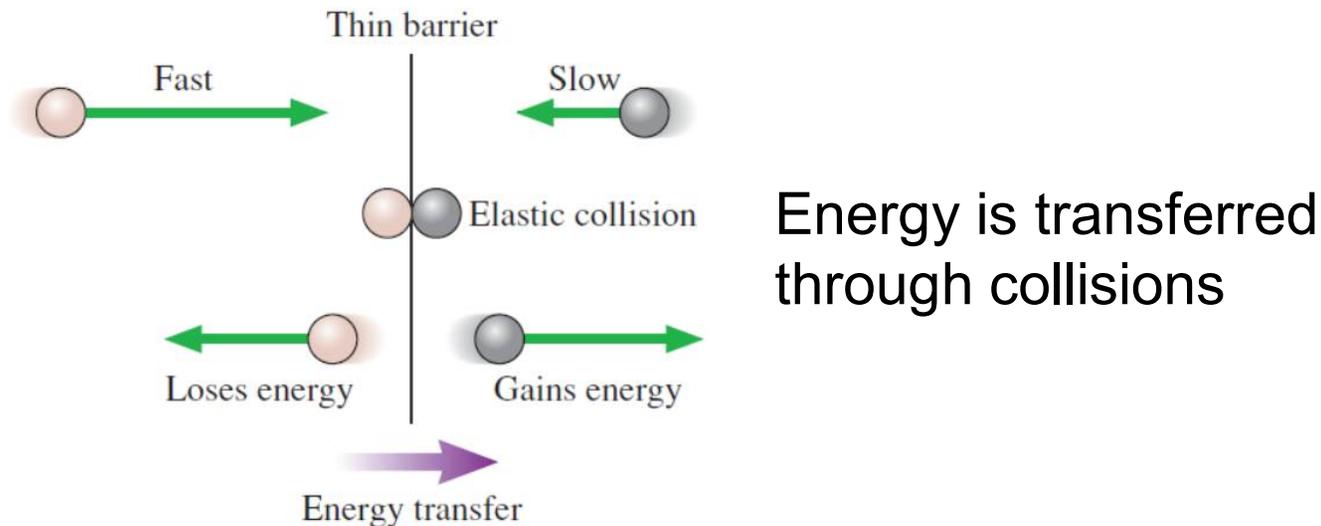
$$\left(C = 3k \quad \text{or} \quad C = 3R \right)$$

There are **three** independent spatial directions that the atoms can move along just as in gases. There are also **three** directions of vibrational motion caused by the spring-like potential energy.

Thus, there are six degrees of freedom in this model of a solid.

Exchange of thermal energy

If two systems are at different temperatures and come into thermal contact, then thermal energy will be transferred until these systems are both at a common temperature.



The temperature is proportional to the average translational kinetic energy of the molecules.

Therefore, thermal equilibrium is achieved when the two systems in thermal contact have constituents with the same average kinetic energy.

$$\epsilon_{\text{avg},1} = \epsilon_{\text{avg},2}$$

Entropy on the microscopic scale

For equally probable microscopic configurations, the entropy is a measure of the number of these configurations.

Example: consider a system of two states,



-If we throw a yellow ball in the system, then it can either be in the left state or the right state (2 possibilities).



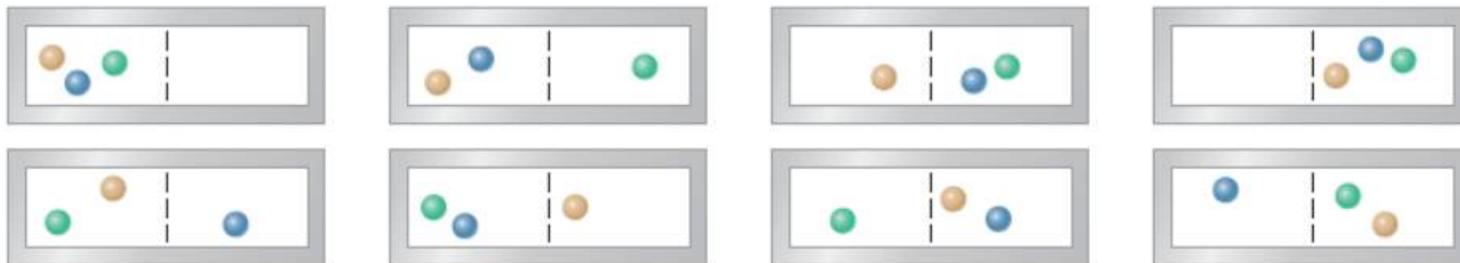
-If we throw a yellow ball and a blue ball in the system, then there are 4 possible configurations.





A container has a left state and a right state.

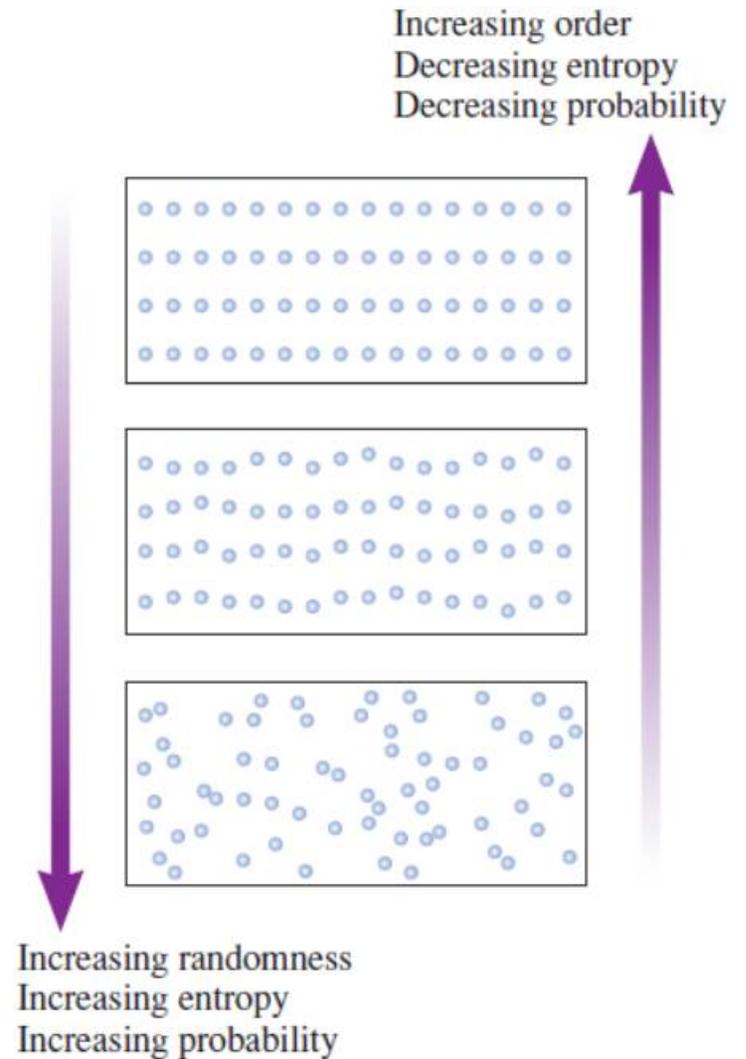
How many configurations are there when a yellow ball, blue ball, and green ball are placed in the container?



Entropy and order of a system

As the entropy increases, the order of a system decreases.

Consequently, the disorder must increase as the entropy increases.



Irreversible processes

The spontaneous transfer of heat energy from a hot object to a cold object is allowed, but this spontaneous flow cannot happen in the opposite direction.

We call this type of process irreversible.

Thus, we can rewrite the second law of thermodynamics to state:
The time direction in which the entropy of an isolated macroscopic system increases is “the future.”