

# 15. The Kinetic Theory of Gases

## Introduction and Summary

Previously the ideal gas law was discussed from an experimental point of view. The relationship between pressure, density, and temperature was later found to have a basis in an atomic or molecular model of gases called "the kinetic theory of gases" that was developed by Maxwell in the late 1800s. The kinetic theory of gases is a model in which molecules move freely with kinetic energy. The various properties of a gas can be accounted for (that is, can be calculated) using this molecular model. As an example, the number density  $n$  of a gas at room temperature  $T$  and one atmosphere pressure  $p$  was calculated and the result interpreted in terms of kinetic theory to give an estimate of the average distance between the gas molecules.

Here this kinetic theory of gases is extended a little further to calculate some other properties of gases. The average velocity of a molecule of a gas is obtained and it is found to be roughly the speed of sound within a gas. The collisions of the gas molecules with the walls of their container accounts for the pressure. The ideal gas model assumes the gas molecules are so far apart on average that they do not have collisions with each other. However, the gas molecules do collide and the average distance between collisions (or "mean free path") will be calculated. There are many properties of an gas, such as diffusion, viscosity, and thermal conductivity, that depend upon the collisions between molecules. Diffusion controls the speed with which an ink drop, say, spreads out in a glass of water and viscosity is the "stickiness" of a fluid. A simple formula for the diffusion coefficient will be discussed as an example of a result of using the kinetic theory of gases.

## The Average Speed of a Gas Molecule

Gas molecules have different speeds, but an average rms or "root mean square" speed

$v_{\text{rms}} = \sqrt{\overline{v^2}}$  can be calculated using what is called the "equipartition theorem," which is

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

Here T is the absolute temperature of the gas, m is the mass of a gas molecule, and  $k_B$  is the Boltzmann constant mentioned before. This formula is valid only for the gas phase, and not for liquids or solids or transitions from one phase to another.

## A Numerical Example

Suppose a gas of diatomic Nitrogen molecules is at room temperature  $T=300^\circ\text{K}$ . Diatomic Nitrogen molecules have 2 Nitrogen atoms each of which has 7 protons and 7 neutrons so the mass number is 2 atoms/molecule $\times$ 14 nucleons/atom=28 nucleons/molecule. The total mass per Nitrogen molecule is 28 neuclons $\times$  $1.67\times 10^{-27}$  kg/neucleon =  $4.68 \times 10^{-26}$  kg.

In[104]:=  $m = 28 * 1.67 * 10^{-27}$

Out[104]=  $4.676 \times 10^{-26}$

The rms speed  $v_{\text{rms}}$  is 515 m/sec

$$v_{\text{rms}} = \sqrt{v^2} = \sqrt{\frac{3 k_B T}{m}}$$

since using  $k_B = 1.38 \times 10^{-23}$  Joules/°K we get

In[100]:=  $m = 28 * 1.67 * 10^{-27};$

$T = 300.;$

$k_B = 1.38 * 10^{-23};$

$$v = \sqrt{\frac{3 * k_B * T}{m}}$$

Out[103]= 515.375

So the average speed of a gas molecule is about 500 m/sec. This is roughly the speed of sound in a gas 340 m/sec.

## The Equipartition Theorem

Basic idea: The pressure in a gas is due to microscopic collisions of the gas particles with the walls of the container.

1. Pressure Defined: The force of the gas  $F$  acting on a wall having area  $A$  produces a pressure  $P$  given by

$$P = \frac{F}{A}$$

Units of Pressure:  $\text{Nt}/\text{m}^2$  or Atmospheres where

$$1 \text{ Atm.} = 10^5 \frac{\text{Nt}}{\text{m}^2}$$

Assume the gas molecules have an average velocity  $\bar{v} = v_{\text{rms}}$  and a momentum  $p = m\bar{v}$ . The symbol  $\bar{v}$  is used instead of  $v_{\text{rms}}$  because it is simpler to write. So  $\bar{v}$  is NOT the average velocity of the  $N$  gas molecules  $\frac{V_1 + V_2 + V_3 + V_4 + \dots + V_N}{N} \simeq 0$  and this is very close to zero because of cancellations.

Instead what is meant is  $\bar{v} = v_{\text{rms}} = \sqrt{\frac{V_1^2 + V_2^2 + V_3^2 + V_4^2 + \dots + V_N^2}{N}}$  which is not zero but was 515 m/s in the above example.

2. When a gas molecule has a collision with a wall, the change in momentum of the gas molecule is  $\Delta p = 2m\bar{v}$  assuming each collision is elastic.

3. The number density of the gas is  $n$  molecules/ $\text{m}^3$ . The gas is inside a container having a volume

$\Omega=L^3$  where L is the length of a side of the cube.

4. The number of gas molecules hitting one wall having area  $A=L^2$  of a cube in a time  $\Delta t$  is

$$\frac{1}{6} n (\bar{v} \Delta t A)$$

5. The total momentum exerted by all the molecules hitting the wall during a time  $\Delta t$  is

$$\Delta p_{\text{total}} = \frac{1}{6} n (\bar{v} \Delta t A) 2m\bar{v}$$

6. The force F on the wall is the total momentum of all the molecules hitting the wall during a time  $\Delta t$  is

$$F = \frac{\Delta p_{\text{total}}}{\Delta t}$$

This is just Newton's 2nd Law written in terms of the momentum change instead of the acceleration.

7. Combining 5 & 6 yields (after canceling the  $\Delta t$  and with  $2/6=1/3$ )

$$F = \frac{\frac{1}{6} n (\bar{v} \Delta t A) 2m\bar{v}}{\Delta t} = \frac{1}{3} n m \bar{v}^2 A$$

8. Remember the pressure  $P=F/A$  so from step 7 we get

$$P = \frac{1}{3} n m \bar{v}^2$$

9. Remember the ideal gas law  $PV=Nk_B T$ , which can be written

$$P = nk_B T \quad \text{with } n = \frac{N}{V} \text{ the number density}$$

Combining this with 8 yields

$$n k_B T = \frac{1}{3} n m \bar{v}^2 \text{ or } 3 k_B T = m \bar{v}^2$$

Finally

$$\frac{1}{2} m \bar{v}^2 = \frac{3}{2} k_B T \text{ or } \overline{\text{KE}} = \frac{3}{2} k_B T$$

To be clear about what is meant,  $\bar{v} = v_{\text{rms}}$  so that  $\bar{v}^2 = v_{\text{rms}}^2 = \frac{v_1^2 + v_2^2 + v_3^2 + v_4^2 + \dots + v_N^2}{N}$ .

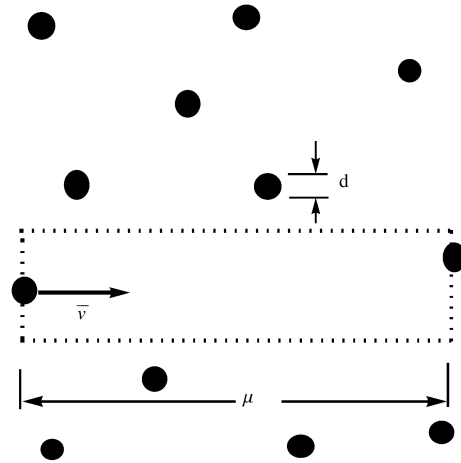
So the average kinetic energy of the gas molecules is related to the temperature of the gas.

This equation does not work at a phase transition. Also this equation does not work for liquids or solids.

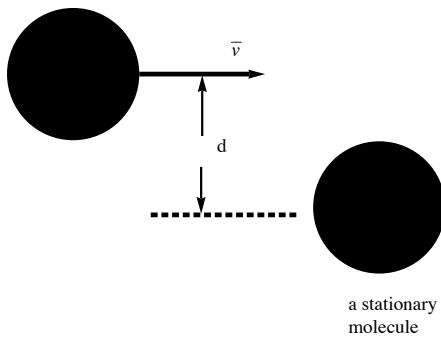
## The Mean Free Path $\mu$

The ideal gas model assumes that gas molecules have no collisions with one another. The only collisions the gas molecules have are with the walls of the container and this produces the gas pressure. Nonetheless, there are phenomena, like diffusion, that depend upon the molecules colliding among themselves. It is these molecular collisions that are responsible for the slowness of the diffusion process compared with the speed of sound. So it is important to know how far molecules travel between collisions ( $\mu$ ). Also, the time between collisions  $\tau$  (the so-called "collision time") is given by  $\mu = \bar{v} \tau$  where  $\bar{v}$  is the average velocity of a molecule.

Suppose the number density  $n$  of the gas is known as well as the diameter of a gas molecule. The model for the calculation of  $\mu$  assumes (for simplicity) that all the molecules are at rest except for one, which is moving with speed  $\bar{v}$ . So all the molecules are "frozen in space" except for one molecule. Below is a picture of what is going on in the gas.



The mean free path  $\mu$  is the average distance a molecule travels in the gas between collisions. Suppose the molecules have diameter  $d$ . The moving molecule will collide with or hit a stationary molecule when the area of the moving molecule overlaps the area of one of the stationary molecules.



1. If the two molecules each having radius  $R$  overlap then there will be a collision. The area covered by a circle with diameter  $d=2R$  indicates when two molecules overlap. The area covered by the moving molecule and one stationary molecule is therefore  $\pi d^2$ .

2.  $\mu \pi d^2$  is the volume of the cylinder "covered" by the moving molecule.

$n (\mu \pi d^2)$  is the number density times the volume and this equals the number of molecules (besides the moving molecule) in the volume  $\mu \pi d^2$ .

3. The mean free path is the distance  $\mu$  such that there is at least one molecule inside the volume  $\mu \pi d^2$ , since then we know there is at least one collision. So we make  $n (\mu \pi d^2) = 1$  molecule.

4. Solving for  $\mu$ , we have a formula for the mean free path  $\mu$  which is the average distance a molecule travels between collisions:

$$\mu = \frac{1}{n \pi d^2}$$

5. This formula makes some intuitive sense. For example, if the density  $n$  of the gas is increased we would expect the average distance between collisions  $\mu$  to decrease. Also, if you have fatter molecules with a larger diameter  $d$ , you would also expect the average distance between collisions  $\mu$  to be smaller.

## A numerical example

Previously we mentioned that atoms have a size roughly  $d=10^{-10}$  m which is an Angstrom. Also the average distance between atoms is roughly  $\ell = \frac{1}{n^{\frac{1}{3}}} = 3.5 \times 10^{-9}$  m (for a gas at one atmosphere pressure and room temperature, which is called STP or Standard Temperature and Pressure).  $\ell$  is something like 35 times the diameter of an atom  $d$ . If you take the gas density  $n=2.4 \times 10^{25}$  molecules /  $m^3$  and a typical diameter  $d=2 \times 10^{-10}$  m of a molecule and calculate  $\mu$  you get



```
In[109]:= ℓ = 3.5 * 10-9;
n = 2.4 * 1025;
d = 2 * 10-10;
μ =  $\frac{1}{n * \pi * d^2}$ 
```

```
Out[112]= 3.31573 * 10-7
```

So the average distance between collisions (which is called the "mean free path") is roughly

$$\mu = 3.3 \times 10^{-7} \text{ m}$$

**IMPORTANT OBSERVATIONS:** Size comparisons that agree with your intuition of a gas

1. The mean free path  $\mu$  should be compared with  $\ell$  the average distance between molecules

$$\ell = 3.5 \times 10^{-9} \text{ m}$$

```
In[113]:= μ / ℓ
```

```
Out[113]= 94.7351
```

So the average distance between collisions is much greater than the average distance between atoms  $\mu \gg \ell$ .

2. The average distance  $\ell$  between atoms compared with the typical size of an atom  $d$  is

```
In[114]:= ℓ / d
```

```
Out[114]= 17.5
```

So the average distance  $\ell$  between atoms is large compared with the size of an atom  $d$ .

## Transport Processes in a Gas

Mass is transported (that is, moved) by the process of diffusion. For example, if a bottle of perfume is opened in a room, the smell of the perfume will spread throughout the room by diffusion. This diffusion process is ***much*** slower than the average speed  $\bar{v}$  of the molecules, which is comparable to the speed of sound.

ASIDE: Sound will travel a distance  $x = \bar{v}t$  in a time  $t$  where  $\bar{v} = 300$  m/sec. How far will sound travel in one hour? In one hour there are  $t = 1 \text{ hour} \times 60 \text{ min/hr} \times 60 \text{ sec/min} = 3,600$  sec. So in one hour sound travels  $x = 300 \text{ m/sec} \times 3600 \text{ sec} = 1.08 \times 10^6$  meters = 1,080 kilometers.

Keep this distance 1,000 meters that sound travels in one hour in mind for later comparison.

In[105]:= 300. \* 3600

Out[105]= 1.08 × 10<sup>6</sup>

DIFFUSION: The diffusion coefficient  $D$  controls the speed of diffusion by means of the equation

$$\bar{x}^2 = 2Dt \text{ or } x_{\text{rms}} = \sqrt{2Dt}$$

where the rms or "root mean square" distance is  $x_{\text{rms}} = \sqrt{\bar{x}^2}$ . A typical value for a diffusion coefficient is  $D = 1.8 \times 10^{-5} \text{ m}^2/\text{sec}$  for perfume in air (more on this in a moment). So how far is the distance  $x_{\text{rms}}$  the perfume will diffuse in one hour or  $t = 3,600$  sec? Answer:

$$x_{\text{rms}} = \sqrt{2 \times 1.8 \times 10^{-5} \text{ m}^2 / \text{sec} \times 3,600 \text{ sec}} = 0.4 \text{ meters !!!!}$$

So in the same time, sound has traveled a much greater distance than the perfume has diffused.

Another way of putting this is to calculate the time for sound to travel a given distance and then compare this with the time it would take perfume to diffuse the same distance. The latter time would be much longer and that is why it is said that diffusion is a much slower process than sound travel.

## A Simple Formula for the Diffusion Coefficient D

The kinetic theory of gases gives a simple formula for the diffusion coefficient:  $D = \frac{1}{3} \mu \bar{v}$

where  $\mu$  is the mean free path and  $\bar{v}$  is the average speed of an atom in the gas. (The derivation of this formula will not be given here.) Using typical values we get

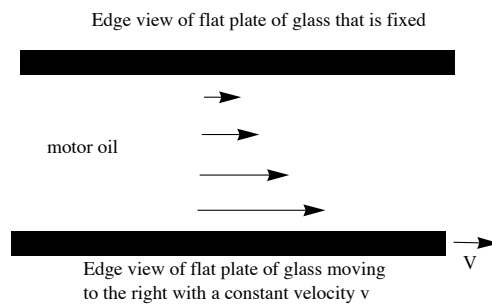
```
In[115]:=  $\mu = 3.3 \times 10^{-7};$ 
 $v = 515.;$ 
 $D = \frac{1}{3} * \mu * v$ 
```

```
Out[117]= 0.00005665
```

So the formula gives  $D=5.7 \times 10^{-5} \text{ m}^2 / \text{sec} = 0.57 \text{ cm}^2 / \text{sec}$  which is not too far from the experimental value  $0.18 \text{ cm}^2 / \text{sec}$  used above to calculate this diffusion distance in one hour.

Diffusion coefficients in water are much smaller--even as small as  $2.1 \times 10^{-7} \text{ m}^2 / \text{sec}$ . You have probably looked at a tea bag in hot water and seen how the tea produced stays near the tea bag. Unless you stir the mixture (and this is NOT diffusion) the tea does not spread out very far by diffusion alone.

There is also the "transport of momentum," which is governed by the shear viscosity or stickiness of the fluid. Suppose for example, motor oil between parallel, flat plates of glass which a distance apart. Also, suppose one of the plates of glass is pulled with a velocity  $v$  as indicated in the diagram below:



The oil near the moving plate sticks to the plate and moves almost with the same velocity as the plate. The fluid velocity decreases the further away you get from the moving plate to the plate at rest. The fluid is almost at rest next the fixed plate. But suppose the fixed plate is free to move horizontally. Then the momentum of the fluid will cause the originally stationary plate to move horizontally too. We say momentum has been "transported" by the viscosity of the fluid from the moving plate on the bottom to the top plate. Different fluids have different viscosity or ability to transport momentum. Honey is said to be more viscous than water, for example. There also is "transport of energy," and this is controlled by the heat conductivity coefficient.

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