Kinetic Theory of Gases

Physics 1425 Lecture 31
Bernoulli’s Picture

• Daniel Bernoulli, in 1738, was the first to understand air pressure in terms of molecules—he visualized them shooting around very rapidly in a closed container, supporting a weight as shown by constantly bouncing off the underside of the piston.

• Given more room, they would rush in to fill the new space, just as a gas is observed to do.

• No-one believed him.

Applet here.
One Dimensional, One Molecule Gas

• The molecule roundtrips in time $2L/v$, so it bounces off the piston $v/2L$ times per sec, each time delivering momentum $2mv$, so the piston will pick up momentum from this “gas” at rate $2mv \times v/2L$ per second.

• Force from gas on piston:
  
  $F = \text{rate of change of momentum} = mv^2/L$. An equal opposite force must be supplied from outside to keep the piston at rest.

• Animation!
Molecule in a Two-Dimensional Box

• Assume perfectly elastic collisions with all walls.
• The molecule will follow a zigzag path, the time between collisions with the same end, say the end at \( x = L \), is now \( 2L/v_x \), and the momentum transferred per collision is \( 2mv_x \), so the average force on the end is \( mv_x^2/L \).
• This will still hold good in *three* dimensions.
N Molecules in an $L \times L \times L$ Cube

• Assume first that we have a very large number $N$ of molecules bouncing around, so small that they don’t hit each other, each follows its own zigzag path.

• The force on the right-hand wall at $x = L$ is just the sum of the forces from each one, so

$$F = \frac{mv_{x_1}^2}{L} + \frac{mv_{x_2}^2}{L} + \frac{mv_{x_3}^2}{L} + \ldots + \frac{mv_{x_N}^2}{L}.$$
Bar Means Average

• The force on the wall depends on the sum

\[ v_{x1}^2 + v_{x2}^2 + v_{x3}^2 + \ldots + v_{xN}^2 \]

• We don’t need the \textit{individual} values \( v_{x1}^2 \), etc., just the \textit{average}, written \textbf{with a bar}:

\[ \bar{v}_x^2 = \frac{v_{x1}^2 + v_{x2}^2 + v_{x3}^2 + \ldots + v_{xN}^2}{N} \]

• So the force on the wall is:

\[ F = \frac{Nm\bar{v}_x^2}{L} \]
Gas Molecules Have *Random* Velocities...

- Gravity has a negligible effect on the speeds, so all directions look the same to the gas molecules.
- This means: \( \overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} \)

and since the molecular speed squared

\[ v^2 = v_x^2 + v_y^2 + v_z^2 \]

it follows that

\[ \overline{v_x^2} = \frac{1}{3} \overline{v^2} \]
Relating Pressure to Molecular Energy

• Our gas of molecules is in an $L \times L \times L$ cube, the force on one wall (which has area $L^2$) is

\[ F = \frac{N m \overline{v_x^2}}{L} = \frac{N m \overline{v^2}}{3L} \]

• So the pressure $P$, force per unit area, is $(V = L^3)$

\[ P = \frac{F}{L^2} = \frac{N m \overline{v^2}}{3L^3} = \frac{2N \left( \frac{1}{2} m \overline{v^2} \right)}{3V} \]

• Now we’ll multiply both sides by $V$ ...
Finding the Ideal Gas Law

- We’ve established that \[ PV = \frac{2}{3} N \left( \frac{1}{2} m v^2 \right) \]
  and we know that for very weakly interacting gases, \( PV = nRT \). These two equations must be the same!

- The equivalence is most simply expressed using Boltzmann’s constant, \( k = \frac{R}{N_A} (= 1.38 \times 10^{-23} \text{ J/K}) \).

\[ PV = nRT = nN_A kT = NkT, \text{ so } \]

\[ \frac{1}{2} m v^2 = \frac{3}{2} kT \]

- Absolute temperature is proportional to average molecular kinetic energy.
Average Speed of Air Molecules

• Maxwell and co were very smart guys—they figured out accurately the average speed of air molecules before they had any idea how big the molecules were!

• They just used

\[ PV = \frac{2}{3} N \left( \frac{1}{2} m \overline{v^2} \right) = \frac{1}{3} N m \overline{v^2} = \frac{1}{3} M \overline{v^2} \]

where \( M \) is the total mass of the gas in the box.
Average Speed of Air Molecules

• Let’s see what $PV = \frac{1}{3} M \bar{v}^2$ gives for the speed of air molecules in this room (we are, of course, averaging here over oxygen and nitrogen plus a tiny amount of other stuff).

• Let’s take a one meter cube: it will contain about 1.3 kg of air. The pressure $P = 10^5$ N/m$^2$, close enough, so

$$PV = 10^5 = \frac{1}{3} (1.3) \bar{v}^2$$

giving the root mean square value $\sqrt{\bar{v}^2} = 480$ m/s.
Clicker Question

• Since oxygen, nitrogen and helium all satisfy the same gas law $PV = nRT$ at room temperature, we conclude that:

A. All have the same (rms) root mean square average molecular speed
B. All have the same average molecular kinetic energy
C. Neither of the above is true.
Clicker Question

• If we take the average speed of oxygen molecules in this room to be 480 m/s, what would be the average speed of helium atoms that leaked from a balloon into the room?

A. 480 m/s  
B. 960 m/s  
C. 1360 m/s  
D. 1920 m/s
The Speed Distribution

- Although the molecules fly freely almost all of the time, they do collide occasionally.
- Assuming random elastic collisions, there will be transfer of energy, typically of order $kT$, from one to another in a collision.
- The chances of a particular molecule picking up $kT n$ times in a row is similar to the chances of a coin toss coming up heads $n$ times in a row.... that is, high energies are exponentially unlikely.
Maxwell’s Speed Distribution

• Maxwell did the math precisely, and found the probability of a molecule having a high energy at a given moment did drop exponentially with energy:

\[
\text{Probability (speed } = v) \propto e^{-\frac{1}{2}mv^2/kT}
\]

meaning that for each extra \(kT\) of energy, the probability of finding a particle with that energy drops by \(1/e \approx 0.37\) —more than a factor of 2, because the average amount picked up per collision is less than \(kT\).

• (Maxwell’s exact result is \(f(v) = 4\pi N \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} v^2 e^{-\frac{1}{2}mv^2/kT} \).)
Escaping from a Planet

- Maxwell’s speed distribution makes it quite easy to predict which gases can escape from planetary atmospheres.
- For the Earth, $v_{\text{escape}} = 11 \text{ km/sec.}$
- The upper atmosphere has parts as hot as 1000K.
- The speed distribution includes $e^{-\frac{mv^2}{2kT}} = e^{-\frac{3v_{\text{escape}}^2}{2v^2}}$ where we’ve used $\frac{1}{2}mv^2 = \frac{3}{2}kT$.
- For $\text{H}_2$, at 1000K, the fraction of molecules at escape velocity is of order $10^{-6}$, for $\text{He} \ 10^{-12}$, for $\text{O}_2 \ 10^{-79}$. This means the $\text{H}_2$ will escape almost instantly, the He pretty quickly, and the $\text{O}_2$ never.
Clicker Question

• Which of the following gases would you expect to be dominant in the Martian atmosphere?
  A. $H_2$
  B. He
  C. $N_2$
  D. $H_2O$
  E. $CO_2$
Real Gases

- (This is of course chemistry.)
- **Water** has the three phases as shown on this pressure/temperature graph.
- They meet at the “**triple point**” a definite $P$ and $T$, useful as a reference point in fixing temperatures.
- Freezing and boiling points vary with pressure.
- At the **critical point**, liquid and vapor become the same.

The solid-liquid dividing line slopes *forwards* for almost all substances—water is an exception.
Vapor Pressure and Humidity

• The H₂O molecules in liquid water strongly attract each other, holding the liquid together. But these molecules are still jiggling around, with a Maxwell speed distribution. This means a fraction of them near the surface are moving fast enough to escape, forming a vapor above the surface.

• In a closed container, with enough water present, an equilibrium situation is reached between escaping and returning molecules.
Water and Vapor in Equilibrium

• In equilibrium in a closed container, the molecules in the vapor have the same average kinetic energy as the air molecules, so exert pressure on the walls of the container proportionate to their numbers.

• This is the saturated vapor pressure. It varies with temperature like $e^{-a/T}$, not surprising since its origin is molecules fast enough to escape.
Water Vapor Pressure

• At room temperature, saturated vapor pressure is about 2.5% of atmospheric pressure.
• At 100°C, it **equals** atmospheric pressure: this means small bubbles formed in the liquid by fast moving molecules coming together are no longer crushed by the surrounding atmospheric pressure, the water boils.
• In mountain resorts like Aspen, water boils at a lower temperature, producing inferior tea.
Relative Humidity and Dew Point

• If water is constantly boiled off in a closed room, it is not possible to establish an equilibrium situation with vapor pressure above the saturated value for that temperature — further water will condense out on the walls, etc. At this point, relative humidity = 100%.

• Relative humidity = vapor pressure/saturated vapor pressure

Dew point: temperature at which dew forms—that is, water condenses out as the air cools.