Massachusetts Institute of Technology
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“Kinetic Theory of Gases: *The Maxwell-Boltzmann distribution”*

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1. Distribution of the speed of gas molecules at thermal equilibrium

Assume you are enjoying your winter vacation at a beautiful resort in Puerto Morelos, Mexico. You are drinking delicious Margarita with chilly salt on the tip of a glass at the pool bar staring at beautiful Caribbean blue. You will also see people inside the pool from kids running all around the pool area to adults drinking Margarita like you. Then you suddenly become curious about something: ‘How gas molecules will behave at a certain condition?’ I am not sure whether this is the start of the derivation of the Maxwell-Boltzmann Distribution, but the concept is somewhat similar. The only difference is that we assume that all gas molecules are identical if they are in same mass, so we can express the speed distribution of the gas molecules in terms of probability as below.

$$P\left(v_x, v_y, v_z\right) \cdot dv_x dv_y dv_z$$

since x, y and z axis are independent to each other, we can split $P\left(v_x, v_y, v_z\right)$ as below

$$P\left(v_x, v_y, v_z\right) \cdot dv_x dv_y dv_z = P(v_x)P(v_y)P(v_z) \cdot dv_x dv_y dv_z$$

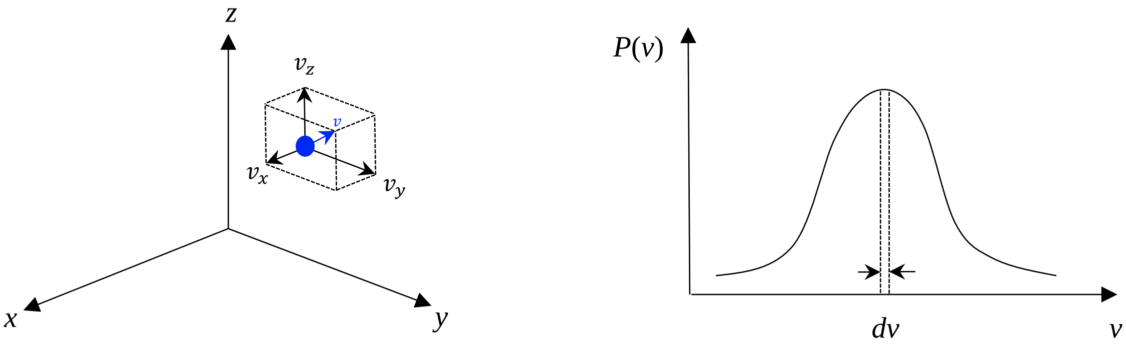

Figure 1.1 A visual expression of the velocity of a gas molecule in Cartesian coordinate (left) and the velocity probability distribution approximate as a function of velocity (right)

Since

$$v^2 = v_x^2 + v_y^2 + v_z^2,$$

(Note that v^2 is the scalar value rather than the vector value)

we can express $P(v_x)P(v_y)P(v_z)$ as the function of v by using $v^2 = v_x^2 + v_y^2 + v_z^2$

$$P\left(v_x, v_y, v_z\right) = P\left(v_x^2 + v_y^2 + v_z^2\right) = P(v_x)P(v_y)P(v_z)$$

As for the ad-hoc solution for these $P(v_x), P\left(v_y\right), P(v_z)$, we can come up with the Gaussian function that is often used in other theory (e.g., Harmonic oscillator).

Thus,

$$P(v_x) = A_x e^{-B_x v_x^2} \quad \text{and}$$

$$P(v) = P(v_x)P\left(v_y\right)P(v_z) = A_x A_y A_z e^{-B_x v_x^2 - B_y v_y^2 - B_z v_z^2}$$

The Gaussian function is very useful since it can be integrated to 1. Since the probability distribution should be integrated to 1,

$$1 = \int_{-\infty}^{\infty} P(v)\, dv = \int_{-\infty}^{\infty} A e^{-Bv^2}\, dv = A\sqrt{\frac{\pi}{B}}$$

(using the Gaussian integral)

Thus we can get,

$$A = \sqrt{\frac{B}{\pi}}$$

and we can express $P(v)$ as below

$$P(v) = \sqrt{\frac{B}{\pi}} \cdot e^{-Bv^2}$$

We call this above equation as the **Maxwell-Boltzmann distribution** and it looks pretty simple…wait! we still haven't derived what is **B**!

No worries, we will definitely derive **B**! This would be happening in the next section!

2. Collision – Pressure – Velocity relationship of the gas molecule

We know that the pressure of gas molecules inside a container is due to the collision between these gas molecules and the wall of a container. And the collision is the change in momentum with regard to the time difference! Based on this idea, at the end, we can get our mystery value **B**!

Now, let us consider gas molecules colliding to the wall.

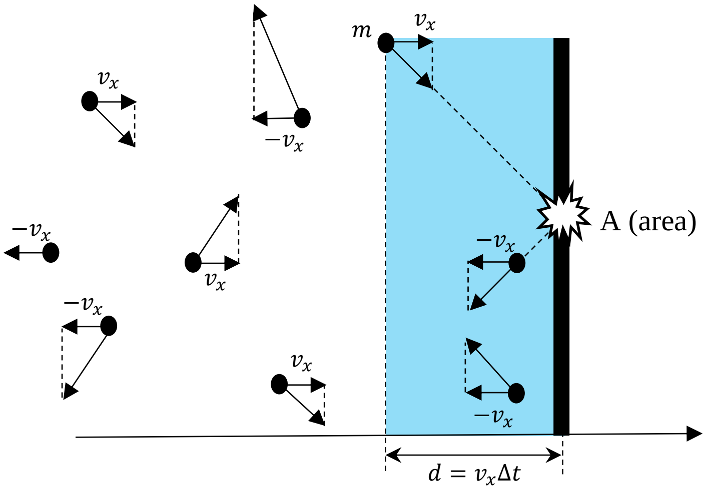

Figure 2.1 Schematic diagram of gas molecules of individual mass ***m*** and the wall whose area is ***A***.

In the figure above, we are assuming only 1 dimension that is x-axis and assuming that all the gas molecules contains same x-axis speed (absolute value of v_x). Of course, this assumption is totally wrong since what we want to derive is the distribution of speed of gas molecules at thermal equilibrium. However, we will fix this later, so let's only think about 1-dimensional problem here.

The blue-colored area indicates the range of possible region in which the gas molecules with velocity v_x to the right direction can collide with the wall within the timescale of Δt (i.e., within Δt, only gas molecules within this blue-colored region will collide with the wall). Since we are assuming that gas molecules are equally distributed inside the container with number density ***n*/*V*** [mol/m^3], we can calculate the number of the gas molecules colliding with the wall within the timescale of Δt.

$$N_{colliding} = \frac{1^*}{2} \cdot N_A \cdot \frac{n}{V} \cdot A \cdot v_x \Delta t$$

($^* \frac{1}{2}$ has been multiplied based on the assumption that a half of the gas molecules in the container will be traveling towards the wall and the rest half towards the opposite direction)

Now, the force that has been applied to each gas molecule in Δt can be derived as below

$$F_{molecule} \cdot \Delta t = \Delta p_x = p_{x,final} - p_{x,initial} = -2mv_x$$

where p_x refers to the momentum of each gas molecule. Accordingly, the force that has been applied to the wall is then the product of $N_{colliding}$ and $-F_{molecule}$:

$$F_{wall} = N_{colliding} \cdot 2mv_x = N_A \cdot \frac{n}{V} \cdot A \cdot v_x \Delta t \cdot mv_x$$

Thus,

$$F_{wall} = \frac{nmN_A A {v_x}^2}{V}$$

Surely, the pressure on the wall would be

$$P_{wall} = {F_{wall}}/{A} = \frac{nmN_A {v_x}^2}{V}$$

Do you remember that the assumption of all the gas molecules containing same x-axis speed is wrong? Now it is time to fix it. In statistics, we use the mean value (or expectation value) for expressing a certain property of the certain population. Thus, we can replace ${v_x}^2$ with $\langle {v_x}^2 \rangle$.

$$P_{wall} = \frac{nmN_A \langle {v_x}^2 \rangle}{V}$$

This allows us to define root mean square speed as below,

$$v_{rms} = \left[\langle {v_x}^2 \rangle + \langle {v_y}^2 \rangle + \langle {v_z}^2 \rangle\right]^{1/2}$$

Since x, y, and z are orthogonal and square value becomes scalar,

$$\langle {v_x}^2 \rangle = \langle {v_y}^2 \rangle = \langle {v_z}^2 \rangle$$

Then we will get

$$\langle {v_x}^2 \rangle = \frac{1}{3} {v_{rms}}^2$$

$$P = P_{wall} = \frac{nmN_A {v_{rms}}^2}{3V}$$

which is,

$$PV = \frac{nmN_A {v_{rms}}^2}{3}$$

FYI, if you couple the above equation with the ideal gas law (i.e., $PV = nRT$), you can get:

$$\frac{3}{2} k_B T = \frac{1}{2} m v_{rms}^2$$

which corresponds to the kinetic energy of the individual gas molecule at the temperature *T*.

Now we are ready to derive the ***Maxwell-Boltzmann Distribution!***

3. The Maxwell-Boltzmann Distribution

From section 2, we derived,

$$PV = nmN_A\langle {v_x}^2\rangle$$

From the ideal gas law,

$$PV = nmN_A\langle {v_x}^2\rangle = nRT$$

From the above,

$$\langle {v_x}^2\rangle = \frac{k_BT}{m}$$

Another way to calculate $\langle {v_x}^2\rangle$ is using the probability function that we derived from section 1.

$$\langle {v_x}^2\rangle = \int_{-\infty}^{\infty} {v_x}^2 P(v_x)\,dv_x$$

since

$$P(v_x) = \sqrt{\frac{B_x}{\pi}} \cdot e^{-B_x{v_x}^2}$$

(Be aware that P now indicates the probability function rather than the pressure.)

Then,

$$\langle {v_x}^2\rangle = \sqrt{\frac{B_x}{\pi}} \int_{-\infty}^{\infty} {v_x}^2 \cdot e^{-B_x{v_x}^2}\,dv_x$$

Since the solution for modified Gaussian function is as below,

$$\int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx = \frac{\sqrt{\pi}}{2}\alpha^{-3/2} \ \ (see\ appendix\ for\ derivation)$$

$$\langle {v_x}^2\rangle = \sqrt{\frac{B_x}{\pi}} \times \frac{\sqrt{\pi}}{2} \times {B_x}^{-3/2} = \frac{1}{2B_x} = \frac{k_BT}{m}$$

$$B_x = \frac{m}{2k_BT}$$

$$P(v_x) = \sqrt{\frac{m}{2\pi k_BT}} \cdot e^{-\frac{m{v_x}^2}{2k_BT}}$$

$$\therefore P\left(v_x^2 + v_y^2 + v_z^2\right) = P(v_x)P\left(v_y\right)P(v_z) = \frac{m}{2\pi k_BT}^{3/2} \cdot e^{-\frac{m}{2k_BT}\left({v_x}^2+{v_y}^2+{v_z}^2\right)}$$

$$= \frac{m}{2\pi k_BT}^{3/2} \cdot e^{-\frac{mv^2}{2k_BT}}$$

Finally,

$$P\left(v_x^2+v_y^2+v_z^2\right)dv_x dv_y dv_z = {\frac{m}{2\pi k_B T}}^{3/2} \cdot e^{-\frac{mv^2}{2k_BT}}\, dv_x dv_y dv_z$$

And

$$dv_x dv_y dv_z = \frac{4}{3}\pi\left[(v+dv)^3 - v^3\right] \sim 4\pi v^2 dv$$

$${\frac{m}{2\pi k_B T}}^{3/2} \cdot e^{-\frac{m}{2k_BT}(v^2)}\, dv_x dv_y dv_z = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} \cdot v^2 \cdot e^{-\frac{mv^2}{2k_BT}} \cdot dv$$

Thus,

$$P(v)dv = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} \cdot v^2 \cdot e^{-\frac{mv^2}{2k_BT}} \cdot dv$$

The Maxwell-Boltzmann Distribution of gas molecular speed at thermal equilibrium is

$$P(v)_T = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} \cdot v^2 \cdot e^{-\frac{mv^2}{2k_BT}}$$

If you plot the equation above, these will look like as below

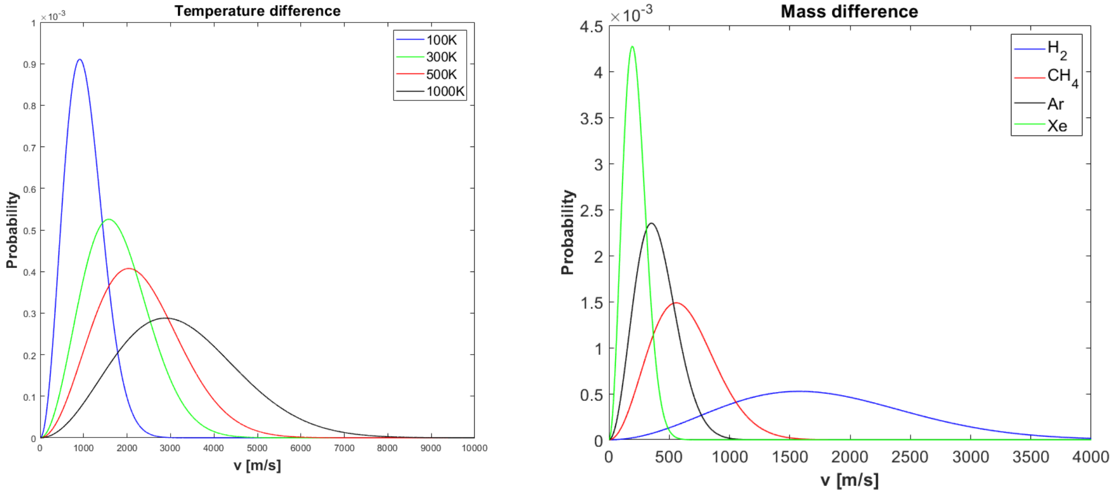

Figure 3.1 Maxwell-Boltzmann distribution with regard to different temperature of H_2 (left) and with regard to different mass at 300K (right)

As you can see from figure 3.1, with lighter mass and higher temperature, gas molecules can be distributed wider reaching to high speed region.

4. Appendix: Derivation of $\int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx = \frac{\sqrt{\pi}}{2} \alpha^{-3/2}$

$$\int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx = \frac{\sqrt{\pi}}{2} \alpha^{-3/2}$$

From above,

$$x^2 e^{-\alpha x^2} = -\frac{d(e^{-\alpha x^2})}{d\alpha}$$

Thus,

$$\int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx = \int_{-\infty}^{\infty} -\frac{d(e^{-\alpha x^2})}{d\alpha} dx = -\frac{d}{d\alpha} \int_{-\infty}^{\infty} e^{-\alpha x^2} dx$$

Now we got simple Gaussian integral: $\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}$

$$\therefore -\frac{d}{d\alpha} \int_{-\infty}^{\infty} e^{-\alpha x^2} dx = -\frac{d}{d\alpha}\left(\sqrt{\frac{\pi}{\alpha}}\right) = \frac{\sqrt{\pi}}{2} \alpha^{-3/2}$$