Mean free path

How far can a molecule travel without bumping into another? Of course, it is different each time, because the thermal motion in molecules are random. However, we can say of its average called "mean free path." In this article, we will derive a formula for mean free path. For simplicity, we will assume that there are only one type of molecules.

What would the mean free path depend on? Certainly, if the molecules are densely populated, they won't be able to travel far before bumping into other ones. Therefore, it should depend on the number density (i.e., the number of molecules per unit volume). Also, it should depend on the size of molecules. If a molecule is very small, it won't bump into other molecules unless they pass very close.

Would the mean free path depend on the mean speed of the molecules? Suppose you videotape molecules moving around and bumping one another. Then, by closely measuring each free path in the video, you will be able to calculate the mean free path. Suppose now you play the video twice faster. The molecules will move twice faster, but each free path will remain the same. Therefore, we see that the mean free path cannot depend on the mean speed of molecules.



So, let's try to calculate λ the mean free path from the size of molecules and the number density n. Let's say the radius of each molecule is r. Then, if the distance between two molecules is bigger than 2r, they won't collide. If it is smaller than 2r they will collide. So, we can think of a molecule as having "personal space" of 2r. See the above figure. As a molecule travels the distance L, it swipes the personal space drawn as cylinder. Whenever another molecule intrudes this space, there is a collision. So, what is the volume of personal space as it travels L? It is $\pi(2r)^2L$. As the number density n is average number of molecules per volume there are $\pi(2r)^2Ln$ molecules in this personal space, and there are $\pi (2r)^2 Ln$ collisions while traveling the distance L. Therefore, on average, for 1 collision to happen, a molecule has to travel λ which satisfies

$$1 = \pi (2r)^2 \lambda n \tag{1}$$

So, we get

$$\lambda = \frac{1}{\pi (2r)^2 n} \tag{2}$$

This is almost correct. There is one caveat though. We have assumed that only the molecule of which the personal space is drawn in the previous figure is moving while the other molecules are not moving. In reality, the other molecules are not just sitting there. So, the actual mean free path is smaller. So, let's correct our answer. We will assume that all molecules move at the speed v, to simplify the calculation. Then, what is the average relative speed between two molecules? Let's say that each velocity is \vec{v}_1 and \vec{v}_2 . Of course we have,

$$|\vec{v}_1|^2 = |\vec{v}_2|^2 = v^2 \tag{3}$$

The relative speed squared is given by

$$|\vec{v}_1 - \vec{v}_2|^2 = |\vec{v}_1|^2 + |\vec{v}_2|^2 - 2\vec{v}_1 \cdot \vec{v}_2 = 2v^2 - 2\vec{v}_1 \cdot \vec{v}_2 \tag{4}$$

However, remember that both \vec{v}_1 and \vec{v}_2 point random directions. So, on average, $\vec{v}_1 \cdot \vec{v}_2 = 0$. Let me explain the reason why. There is an equal probability that $\vec{v}_1 \cdot \vec{v}_2 = a$ happens and that $\vec{v}_1 \cdot \vec{v}_2 = -a$ happens, as there is an equal probability that \vec{v}_1 goes on certain direction and that \vec{v}_1 goes on its direct opposite direction. Therefore, on average, the last term in (4) is zero. Thus, we conlcude that the relative speed between molecules is $|\vec{v}_1 - \vec{v}_2| = \sqrt{2}v$.

Then, it is easy to see that a molecule swipes the relative distance $\sqrt{2v\Delta t}$ between itself and another during the time Δt . Therefore, for one collision to happen, it takes on average Δt that satisfies

$$(\sqrt{2v\Delta t})\pi(2r)^2 n = 1 \tag{5}$$

So, we have

$$\Delta t = \frac{1}{\pi (2r)^2 nv} \tag{6}$$

However, during such Δt , the molecule travels $v\Delta t$, which is the exact definition of mean free path. Thus, we conclude

$$\lambda = \frac{1}{\sqrt{2\pi}(2r)^2 n} \tag{7}$$

In actual physics, instead of talking about the size of molecule r, we use what is called "cross section" or "scattering cross section." In our example, the cross section σ is $\pi(2r)^2$. Therefore, the above formula can be re-expressed as

$$\lambda = \frac{1}{\sqrt{2}\sigma n} \tag{8}$$

Experimental particle physicists collide particles in accelerators, and measure the cross sections between particles and compare them with theoretical predictions. However, that the radiuses of two colliding particles are both r doesn't necessarily mean that the cross section is $\pi(2r)^2$, because they can scatter each other by forces even though they don't directly touch each other.

Nonetheless, if you want to calculate how many colliding (i.e., scattering) events should happen, given the cross section of colliding particles and the intensity of beam, you can just remember the basic idea you learned in this article through the concept of "personal space" and calculate accordingly. Then, the answer is correct.

Summary

• The mean free path is inversely proportional to the cross section and the number density. It doesn't depend on the speed of colliding particles.