

# The Not so soft derivation of mean free path

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The precondition to understanding is *Knowing what you are doing*.

So read the section name carefully to *Know what you are doing*.

It's a confusing matter, but what **will do** is **deriving the mean free time and mean free path**, using probability and rigorous methods.

## Probability of Making a Collision in time $dt$

The path that will be swept by a molecule at speed  $v$  with cross section area  $\sigma$  in a time interval  $dt$  will cover a volume region in space,

$$dV = \sigma v dt$$

If another molecule happens to stay in that volume, then there will be a collision. Let there be  $n$  molecules per unit volume.

Let us calculate the total number of Particles in the volume  $dV$ ,

$$N = \text{Molecules per Volume} \times V \rightarrow dN = n dV = n \sigma v dt$$

**The number of molecule in this volume is the number of possible collisions that will take place with the molecule moving. The higher the number of molecule, the higher the probability of collision.** If the number of molecule is zero in the small volume, the probability of hitting one is zero. Usually the value of  $dN \approx \Delta N$  is not an integer, it's lesser than one or equal to one. Requirement is the time interval  $dt$  has to be small enough. Now, if there is a molecule in this volume, the chance of hitting is one.

The number of molecule corresponds to the probability of the Hitting or having a Collision.

$\text{Probability of Hitting someone in time interval } dt = n \sigma v dt$
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Let us now build up a variable  $P$ , which will tell the *Probability of a molecule remain free of collision up to time  $t$* , this means, if  $t$  value is high, the value of  $P$  will go close to zero; because a molecule isn't suppose to remain free of hitting other molecule for a long time. It has to hit someone.

The probability of remaining free of collision will decrease if the number of molecule per unit volume is increased.

## Probability of NOT Colliding until time $t$ and $t + dt$

So, let's say, for a molecule,  $P(t)$  is the probability of not having a collision until time  $t$ . Now, let's calculate the probability  $P$  for not having a collision until time  $t + dt$ , which is slightly more than before. Obviously, because this time the time interval is little more, the probability of remaining free of collision will decrease a bit.

By calculus, the  $P(t + dt)$  can be measured, which will be,

$$P(t + dt) = P(t) + \frac{dP}{dt}dt \tag{1}$$

Now, we will find another interpretation of  $P(t + dt)$ ,

**Probability of NOT Colliding until time  $t + dt$  using first section result**

Probability of not hitting anyone until  $t$  time is given by  $P(t)$ . But we found out before that probability of hitting some one in  $dt$  time is  $n\sigma vdt$ .

That means probability of not hitting someone until time  $dt$  is,

$$(1 - n\sigma vdt)$$

**Theorem 1** — We shall remember about the rule of probability. Let the probability of event  $A$  be  $\Pi(A)$ , and let the probability of another event that will occur after  $A$  is,  $\Pi(B)$ , now probability of the occurrence of event  $A$  and  $B$  is,

$$\Pi(A \text{ and } B) = \Pi(A) \cdot \Pi(B)$$

So, if one probability happens to be after another probability, we multiply the probability.

Now coming back to the point.

- Probability of not having collision until  $t$  is,

$$P(t)$$

- Probability of not having collision after  $t$  time for an interval  $dt$  is,

$$1 - n\sigma vdt$$

Now, together, the probability of not having a collision until  $t$  then  $dt$  time more is,

$$P(t) (1 - n\sigma vdt)$$

This is because of the probability multiplication rule.

But if the above equation means not having collision until time  $t$  then  $dt$ , then it also means not having collision for all the time  $dt + t$ , thus,

$$P(t + dt) = P(t) (1 - n\sigma vdt) \tag{2}$$

We can now use the two equations (1) and (2) and find this relation,

$$P(t) + \frac{dP}{dt}dt = P(t) (1 - n\sigma vdt)$$

Now you can solve this following the steps in **Blundell. It's a great Thermodynamics book.**

To do Blundell with it, let's rearrange the equation.

$$P(t) + \frac{dP}{dt}dt = P(t) - P(t)n\sigma vdt$$
$$\frac{1}{P} \frac{dP}{dt} = -n\sigma v$$

Let's integrate this equation, we get,

$$\int \frac{dP}{P} = - \int n\sigma v dt$$

This gives,

$$P(t) = e^{-n\sigma v t}$$

We knew probability of colliding in time  $dt$  is  $n\sigma v dt$ , Thus from here we can tell that Probability of not colliding until  $t$  but colliding in  $t + dt$  is,

$$e^{-n\sigma v t} n\sigma v dt$$

That's probability to hit in time  $dt + t$ . Integrate over  $t = 0$  to  $t = \infty$ , that means, for a particle in a span of infinite time, the probability of hitting,

$$P_{hit} = \int_0^{\infty} e^{-n\sigma v t} n\sigma v dt = 1$$

It must hit someone. This equation is true because considering  $n\sigma v t = x$  then  $dx = n\sigma v dt$ ,

$$\int_0^{\infty} e^{-x} dx = 0! = 1$$

Using an integral table we know that's the result (solving this integral takes a bit time, we don't do it here).

Now, let's finally calculate the average time elapsed between collisions for a given molecule,

If  $P(x)$  is a probability function, then average of the variable  $x$  is,

$$\text{avg}(x) = \langle x \rangle = \int x P(x) dx$$

**the average time between collisions is mean free time,**

$$\langle t \rangle = \int_0^{\infty} t P(x) dx$$

$$\langle t \rangle = \int_0^{\infty} t e^{-n\sigma v t} (n\sigma v) dt$$

We can manipulate a pattern,

$$\frac{1}{n\sigma v} \int_0^{\infty} (n\sigma v) e^{-(n\sigma v t)} d(n\sigma v t) = \frac{1}{n\sigma v} \int_0^{\infty} x e^{-x} dx$$

Using a Integral table or just solving the integral we know,

$$\int_0^{\infty} x e^{-x} dx = 1$$

So average time of between collisions,

$$\tau = \frac{1}{n\sigma v}$$

Hence,

$$\boxed{\tau = \frac{1}{n\sigma v}}$$

From this we can solve for mean free path,

$$\lambda = \langle v \rangle \tau = \langle v \rangle \frac{1}{n\sigma v}$$

What's average velocity? The problem here is we can guess  $\langle v \rangle$  to be just  $v$  but  $v$  being a vector not getting squared need to be averaged using vector principles.

It's little painful to do, I'd just directy tell you that,  $\langle v \rangle = \frac{v}{\sqrt{2}}$  Hence,

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

Here, putting appropriate matters,

$$\text{surface area } \sigma = \pi r^2 = \frac{\pi}{4} d^2$$

Then to solve for  $n$ , moles per volume,

$$pV = \nu RT \rightarrow p = \left( \frac{\nu}{V} \right) RT \rightarrow p = nRT$$

So all together, they give,

$$\lambda = \frac{1}{\sqrt{2} \left( \frac{\pi}{4} d^2 \right) \left( \frac{p}{RT} \right)}$$

$$\lambda = \frac{2\sqrt{2}RT}{\pi d^2 p}$$

By the end of this calculation, we have derived the value of the Mean Free time(the average time until a particle in gas doesn't collide), and using that, the Mean free path