

4.12: The Frequency of Collisions between Unlike Gas Molecules

Thus far in our theoretical development of the properties of gases, we have assumed that ideal gas molecules are point masses. While they can collide with the walls of their container, point masses cannot collide with one another. As we saw in our discussion of [van der Waals equation](#), the deviation of real gases from ideal gas behavior is one indication that an individual gas molecule occupies a finite volume.

To develop a model for molecular collisions, we need to know the size and shape of the colliding molecules. For a general model, we want to use the simplest possible size and shape. Accordingly, we consider a model in which gas molecules are spheres with well-defined radii. We let the radii of molecules 1 and 2 be σ_1 and σ_2 , respectively. See Figure 10. When such molecules collide, their surfaces must come into contact, and the distance between their centers must be $\sigma_{12} = \sigma_1 + \sigma_2$. We call σ_{12} the **collision radius**.

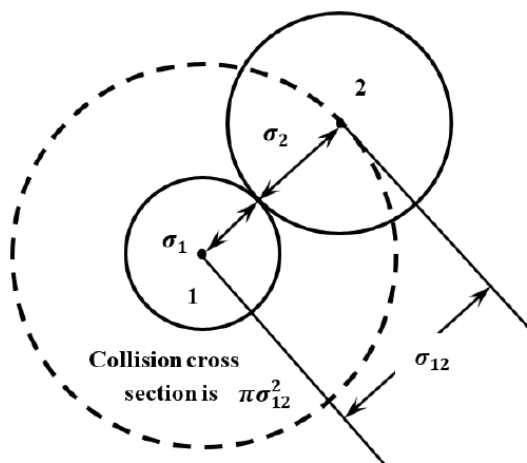


Figure 10. The molecular collision radius.

Let us consider a molecule of type 1 in a container with a large number of molecules of type 2. We suppose that there are N_2 molecules of type 2 per unit volume. Every molecule of type 2 has some velocity, v_{12} , relative to the molecule of type 1. From our development above, we know both the probability density function for v_{12} and the expected value $\langle v_{12} \rangle$. Both molecule 1 and all of the molecules of type 2 are moving with continuously varying speeds. However, it is reasonable to suppose that—on average—the encounters between molecule 1 and molecules of type 2 are the same as they would be if all of the type 2 molecules were fixed at random locations in the volume, and molecule 1 moved among them with a speed equal to the average relative velocity, $\langle v_{12} \rangle$.

Under this assumption, a molecule 1 travels a distance equal to $\langle v_{12} \rangle$ in unit time. As it does so, it collides with any type 2 molecule whose center is within a distance σ_{12} of its own center. For the moment, let us suppose that the trajectory of molecule 1 is unaffected by the collisions it experiences. Then, in unit time, molecule 1 sweeps out a cylinder whose length is $\langle v_{12} \rangle$ and whose cross-sectional area is $\pi\sigma_{12}^2$. The volume of this cylinder is $\pi\sigma_{12}^2 \langle v_{12} \rangle$. (See Figure 11.)

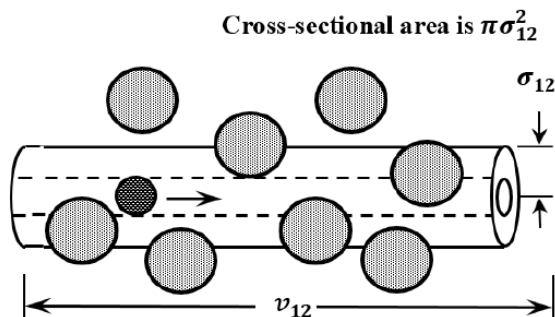


Figure 11. The collision volume of a gas molecule in unit time.

Since there are N_2 molecules of type 2 per unit volume, the number of type 2 molecules in the cylinder is $N_2 \pi \sigma_{12}^2 \langle v_{12} \rangle$. Each of these molecules is a molecule of type 2 that experiences a collision with molecule 1 in unit time. Letting $\bar{\nu}_{12}$ be the frequency (number of collision per unit time) with which molecule 1 collides with molecules of type 2, we have

$$\begin{aligned}\tilde{\nu}_{12} &= N_2 \pi \sigma_{12}^2 \langle v_{12} \rangle = N_2 \pi \sigma_{12}^2 \left(\frac{8kT}{\pi \mu} \right)^{1/2} \\ &= N_2 \sigma_{12}^2 \left(\frac{8\pi kT}{\mu} \right)^{1/2}\end{aligned}$$

Two additional parameters that are useful for characterizing molecular collisions are τ_{12} , the **mean time between collisions**, and λ_{12} , the **mean distance** that molecule 1 travels between collisions with successive molecules of type 2. λ_{12} is called the **mean free path**. The mean time between collisions is simply the reciprocal of the collision frequency,

$$\tau_{12} = 1/\tilde{\nu}_{12}$$

and the mean free path for molecule 1 is the distance that molecule 1 actually travels in this time, which is $\langle v_1 \rangle$, not $\langle v_{12} \rangle$, so that

$$\lambda_{12} = \langle v_1 \rangle \tau_{12} = \frac{(\mu/m)^{1/2}}{N_2 \pi \sigma_{12}^2}$$

Now, we need to reevaluate the assumption that the trajectory of a molecule of a molecule 1 is unaffected by its collisions with molecules of type 2. Clearly, this is not the case. The path of molecule 1 changes abruptly at each collision. The actual cylinder that molecule 1 sweeps out will have numerous kinks, as indicated in Figure 12. The kinked cylinder can be produced from a straight one by making a series oblique cuts (one for each kink) across the straight cylinder and then rotating the ends of each cut into convergence. If we think of the cylinder as a solid rod, its volume is unchanged by these cuttings and rotations. The volume of the kinked cylinder is the same as that of the straight cylinder. Thus, our conclusions about the collision frequency, the mean time between collisions, and the mean free path are not affected by the fact that the trajectory of molecule 1 changes at each collision.

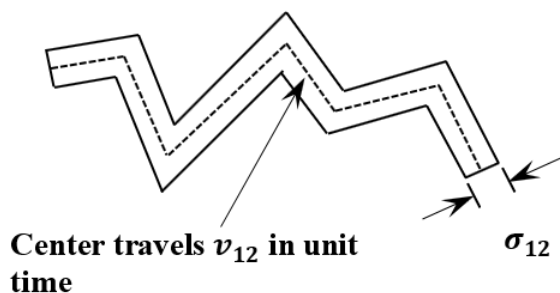


Figure 12. The collision volume is unaffected by collisions.

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