Atmospheric Aerosols

Lecture 10

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Mean Free Path of a Pure Gas

Note that even though air consists of molecules of N_2 and O_2, it is customary to talk about the mean free path of air, λ_{air}, as if air were a single chemical species.

Let us start with the simplest case, a particle suspended in a pure gas B.

If we are interested in characterizing the nature of the suspending gas relative to the particle, the mean free path that appears in the definition of the Knudsen number is λ_{BB}.

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The mean free path λ_{BB} has been defined as the average distance traveled by a B molecule between collisions with other B molecules.

The mean speed of gas molecules of B, $\vec{c}_B$ is:

$$\vec{c}_B = \sqrt{\frac{8RT}{\pi M_B}}$$

where M_B is the molecular weight of B

Note that larger molecules move more slowly, while the overall mean speed of a gas increases with temperature.

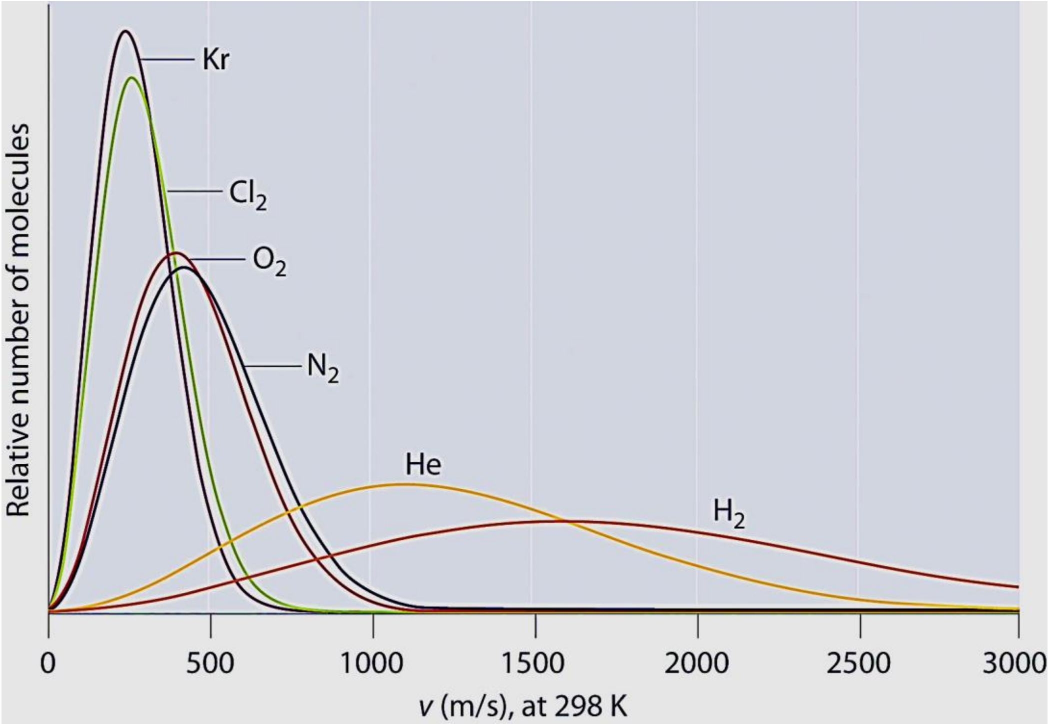
The mean speed of N_2 at 298 K is $c_{N2} = 474\ m\ s^{-1}$ and for oxygen $c_{O2} = 444\ m\ s^{-1}$

Molecular velocities of other atmospheric gases at 298 K are shown in this Table

Molecular Velocities of Some Atmospheric Gases at 298 K

Gas	Molecular Weight	Mean Velocity, m s^{-1}
NH_3	17	609
Air	28.8	468
HCl	36.5	416
HNO_3	63	316
H_2SO_4	98	254
$(CH_2)_3(COOH)_2$	132	219

Molecules with lower masses have a wider distribution of speeds and a higher average speed.



Let us estimate what happens to a B molecule during a unit of time, say, a second.

During this second the molecule travels on average ($\vec{c}_B$ X 1 s) m

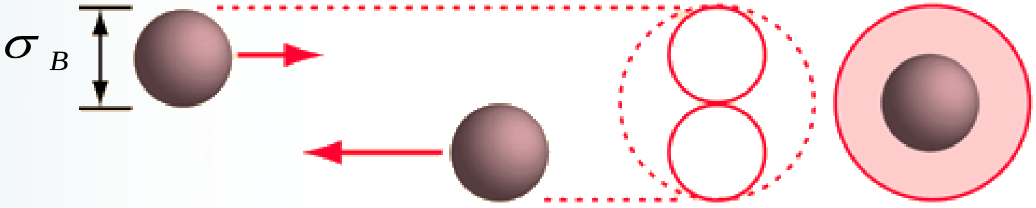
If during the same second it undergoes Z_{BB} collisions, then its mean free path will be by definition

$$\lambda_{BB} = \frac{\vec{c}_B}{Z_{BB}}$$

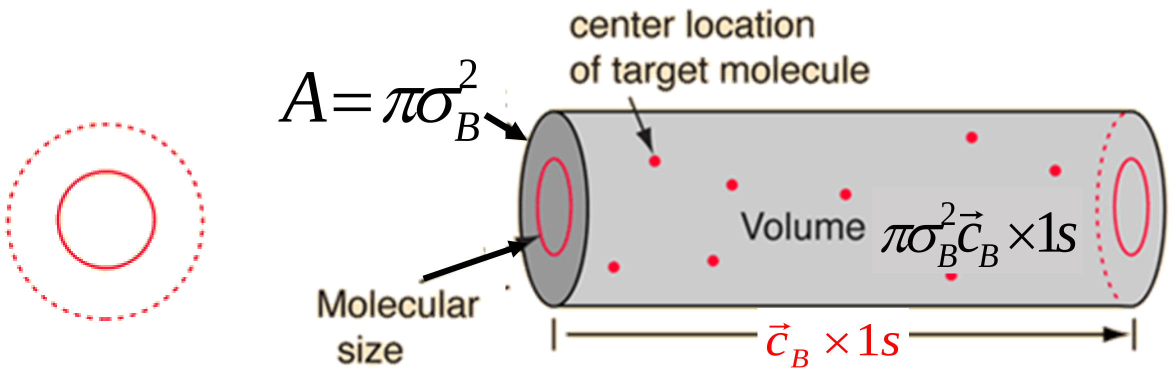
Thus to calculate λ_{BB} we need to first calculate the collision rate of B molecules, Z_{BB}.

Let σ_B be the diameter of a B molecule.

In 1 s a molecule travels a distance c_B and collides with all molecules whose centers are in the cylinder of radius σ_B and height c_B.



$$A = \pi\sigma_B^2$$



N_B = molecules per unit volume

The mean free path could then be taken as the length of the path divided by the number of collisions.

$$\text{Mean free path estimate } \frac{\vec{c}_B \times 1s}{\pi\sigma_B^2\vec{c}_B \times 1s N_B} = \frac{1}{\pi\sigma_B^2 N_B}$$

The problem with this expression is that the average molecular velocity is used, but the target molecules are also moving. The frequency of collisions depends upon the average relative velocity of the randomly moving molecules.

Note that two molecules of diameter σ_B collide when the distance between their centers is σ_B.

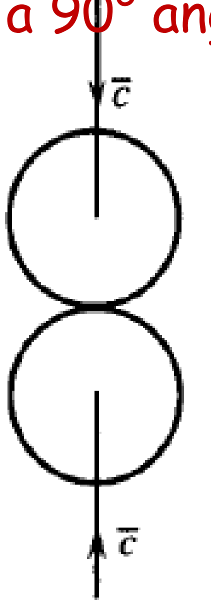
If N_B is the number of B molecules per unit volume, then the number of molecules in the cylinder is:

$$\pi \sigma_B^2 \vec{c}_B N_B$$

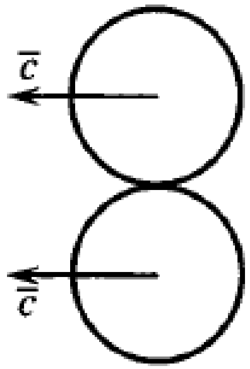
Above we have calculated the number of collisions assuming that one molecule of B is moving while the rest are immobile and in the process we have underestimated the frequency of collisions.

If two particles move in opposite directions, their relative speed is 2 $\vec{c}_B$

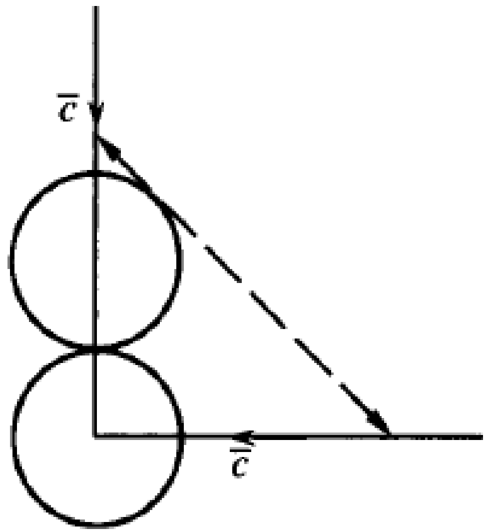
If they move in the same direction, their relative speed is zero, while for a 90° angle their relative velocity of approach is $\sqrt{2}\vec{c}_B$



relative speed
2 $\vec{c}_B$



relative speed
0



relative speed
$\sqrt{2}\vec{c}_B$

One can prove that the latter situation represents the average, so we can write

$$Z_{BB} = \sqrt{2}\ \pi\ \sigma_B^2\ \vec{c}_B\ N_B$$

and the mean free path λ_{BB} is given by path length divided by collision numbers:

$$\lambda_{BB} = \frac{\vec{c}_B}{Z_{BB}} \qquad \lambda_{BB} = \frac{1}{\sqrt{2}\ \pi\ \sigma_B^2\ N_B}$$

Note that the larger the molecule size, σ_B, and the higher the gas concentration, the smaller the mean free path.

$$\lambda_{BB} = \frac{2\mu_B}{p\sqrt{8M_B / \pi R / T}}$$

where μ_B is the gas viscosity (in kg $m^{-1}s^{-1}$), p is the gas pressure (in Pa), and M_B is the molecular weight of B.

The mean free path of air varies with height above the Earth's surface as a result of pressure and temperature changes.

This change for standard atmospheric conditions is shown in Figure. The net result is an increase of the air mean free path with altitude, to roughly 0.2 μm at 10 km.

Mean free path of air as a function of altitude for the standard U.S. Atmosphere (Hinds 1999).

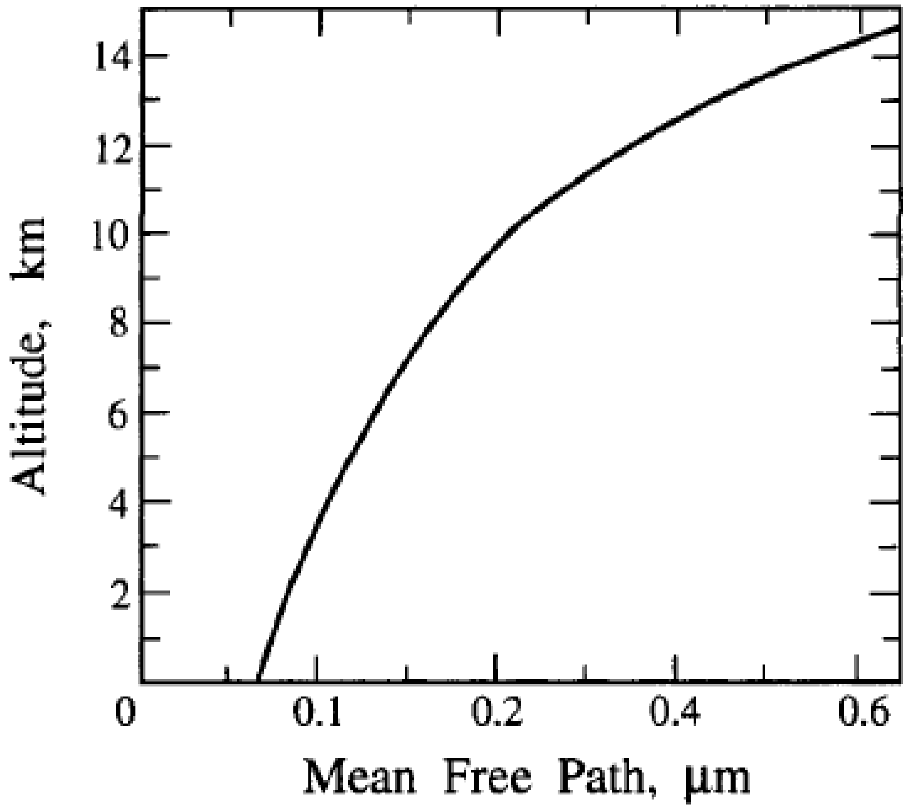


TABLE A.7 Properties of the Atmosphere[a]

Standard temperature	$T_0 = 0°C = 273.15\,K$
Standard pressure	$p_0 = 760\,mm\,Hg$
	$= 1013.25$ millibar (mbar)
Standard gravity	$g_0 = 9.807\,m\,s^{-2}$
Air density	$\rho_0 = 1.29\,kg\,m^{-3}$
Molecular weight	$M_0 = 28.97\,g\,mol^{-1}$
Mean molecular mass	$= 4.81 \times 10^{-23}\,g$
Molecular root-mean-square velocity $(3RT_0/M_0)^{1/2}$	$= 4.85 \times 10^4\,cm\,s^{-1}$
Speed of sound $(\gamma RT_0/M_0)^{1/2}$	$= 3.31 \times 10^4\,cm\,s^{-1}$
Specific heats[b]	$\hat{c}_p = 1005\,J\,K^{-1}\,kg^{-1}$
	$\hat{c}_v = 717\,J\,K^{-1}\,kg^{-1}$
Ratio	$\hat{c}_p/\hat{c}_v = \gamma = 1.401$
Air molecules per cm^3	$N = 2.688 \times 10^{19}$ (at 273 K)
	$= 2.463 \times 10^{19}$ (at 298 K)
Air molecular diameter	$\sigma = 3.46 \times 10^{-8}\,cm$
Air mean free path $(\sqrt{2}\pi N\sigma^2)^{-1}$	$\lambda_a = 6.98 \times 10^{-6}\,cm$
Viscosity	$\mu = 1.72 \times 10^{-4}\,g\,cm^{-1}\,s^{-1}$
Thermal conductivity	$k = 2.40 \times 10^{-2}\,J\,m^{-1}\,s^{-1}\,K^{-1}$
Refractive index (real part)	$(n-1) \times 10^8 = 6.43 \times 10^3$
	$+ \frac{2.95 \times 10^6}{146 - \lambda^{-2}} + \frac{2.55 \times 10^4}{41 - \lambda^{-2}}$ (λ in μm)

[a] Dry air at $T = 273\,K$ and 1 atm.

Mean Free Path of a Gas in a Binary Mixture

The Knudsen number in the case of interest is given by

$$Kn = \frac{2\lambda_{AB}}{D_p}$$

and we need to estimate λ_{AB}

Jeans showed that the effective mean free path of molecules of *A*, λ_{AB}, in a binary mixture of *A* and B is (Davis 1983)

$$\lambda_{AB} = \frac{1}{\sqrt{2}\pi N_A \sigma_A^2 + \pi(1+z)^{1/2} N_B \sigma_{AB}^2}$$

where N_A and N_B are the molecular number concentrations of *A* and B, σ_A and σ_{AB} are the collision diameters for binary collisions between molecules of *A* and molecules of *A* and B, respectively, where

$$\lambda_{AB} = \frac{1}{\sqrt{2}\pi N_A \sigma_A^2 + \pi(1+z)^{1/2} N_B \sigma_{AB}^2} \qquad \sigma_{AB} = \frac{\sigma_A + \sigma_B}{2}$$

and $z = m_A/m_B = M_A/M_B$ is the ratio of molecular masses (or molecular weights) of A and B.

The first term in the denominator accounts for the collisions between A molecules, while the second for the collisions between A and B molecules.

If the concentration of species A is very low (a good assumption for almost all atmospheric situations), $N_A \ll N_B$ and equation can be simplified by neglecting the collisions between A molecules as

$$\lambda_{AB} = \frac{1}{\pi(1+z)^{1/2} N_B \sigma_{AB}^2}$$

Note that the molecular concentration N_B can be calculated from the ideal-gas law $N_B = p/kT$, where p is the pressure of the system.

$$D_{AB} = \frac{3}{8\pi} \frac{[\pi k^3 T^3 (1+z)/(2m_A)]^{1/2}}{\rho \sigma_{AB}^2 \Omega_{AB}^{(1,1)}}$$

$\Omega_{AB}^{(1,1)}$ the collision integral

which has been tabulated by Hirschfelder et al. (1954) as a function of the reduced temperature

$$T^* = kT/\varepsilon_{AB}$$

ε_{AB} is the Lennard-Jones molecular interaction parameter.

For hard spheres $\Omega_{AB}^{(1,1)} = 1$

and for this case the following relationship connects the mean free path λ_{AB} , and the binary diffusivity D_{AB}

$$\lambda_{AB} = \frac{32}{3\pi(1+z)} \frac{D_{AB}}{\bar{c}_A}$$

Note the appearance of the molecular mass ratio $z = M_A/M_B$

Many investigators have assumed $z \ll 1$ either explicitly or implicitly and this has been the source of some confusion. We can identify certain limiting cases for above equation

$$\lambda_{AB} = 3.397 \frac{D_{AB}}{\bar{c}_A} \qquad z \ll 1$$

$$= 1.7 \frac{D_{AB}}{\bar{c}_A} \qquad z = 1$$

$$= \frac{3.397}{z} \frac{D_{AB}}{\bar{c}_A} \qquad z \gg 1$$

Additional relationships have been proposed to determine the mean free path in terms of D_{AB}.

From zero-order kinetic theory, Fuchs and Sutugin (1971) showed that

$$\lambda_{AB} = 3 \frac{D_{AB}}{\bar{c}_A}$$

while Loyalka et al. (1989) used $\lambda_{AB} = \frac{4}{\sqrt{\pi}} \frac{D_{AB}}{\bar{c}_A} = 2.257 \frac{D_{AB}}{\bar{c}_A}$