Kinetic Model of Gases

Section 1.3 of Atkins, 6th Ed.
Section 24.1 of Atkins, 7th Ed.
Section 21.1 of Atkins, 8th Ed.

Basic Assumptions

Molecular Speeds

- **RMS Speed**
- **Maxwell Distribution of Speeds**
- **Relative Mean Speed**
- **Most Probable Speed**

Collision Frequency

Mean Free Path

Properties of Gases

- Low density:

$$\rho_{gas} \ll \rho_{liquid} \approx \rho_{solid}$$

- High compressibility:

$$\beta_{gas} \gg \beta_{liquid} , \beta_{solid}$$

- Exert an external pressure:

An external pressure must be applied to contain a gas

- Different gases **diffuse** into one another:

Different gases completely mix in a **homogeneous** fashion

Kinetic Model: Basic Assumptions

In the kinetic model of gases, it is assumed that the only contribution to the energy of the gas comes from the **kinetic energies** of the atoms or molecules in the gas - interactions between molecules (**potential energy**) make no contribution

1. Gas consists of atoms or molecules of mass *m* undergoing random, neverending motion

2. Molecular size is negligible: the distances over which molecules travel are much greater than molecular size

3. Molecules are treated as **hard spheres**: they make perfectly **elastic collisions** with one another and the sides of the container - this means no energy is transferred to rotational, vibrational or electronic modes, nor to the walls - all energy is conserved for translation

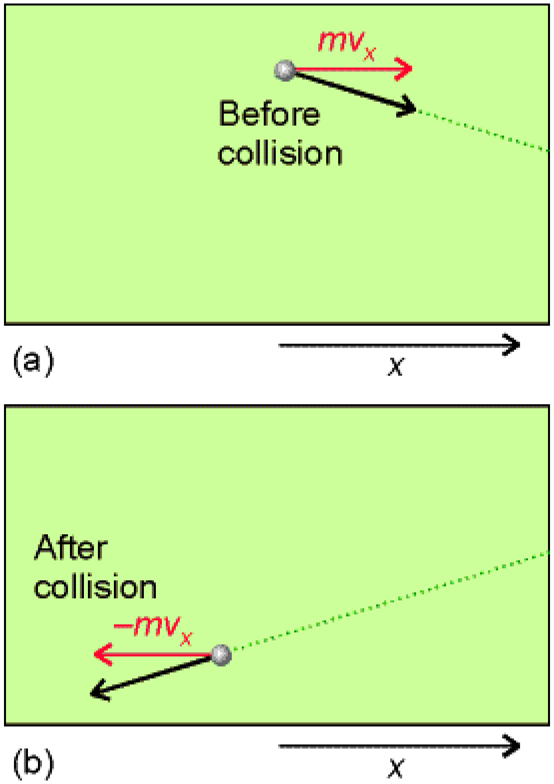
Pressure, Volume and Kinetic Energy†

We will demonstrate that under the kinetic model of gases that the pressure and volume of the gas are related by:

$$pV = \frac{1}{3}nMc^2 \quad , \qquad c = \langle v^2 \rangle^{1/2}$$

where the molar mass of the molecules, M, is $M = mN_A$, and c is the **root mean square speed** of the molecules.

We will consider a molecule of mass m with an x-component of velocity v_x. Upon colliding with the wall, its **linear momentum** $P = mv_x$ changes to $-mv_x$ (changes by $2mv_x$) (assume no changes in y and z for now)



Deriving the RMS Speed

Distance: $v_x\Delta t$

In a small time interval, Δt, a molecule with velocity v_x travels $v_x\Delta t$ along x (all molecules within this distance strike the wall during Δt)

Volume: $Av_x\Delta t$

If wall has area A, then all molecules in the volume $V = Av_x\Delta t$ hit the wall.

Density: nN_A/V

The number of particles n in the "container" of volume V, so in this small volume, there are $nN_A/V \times Av_x\Delta t$ particles

Statistics: ½

At any given time, half of the particles move left, half move right, so the average number of collisions in Δt is $\frac{1}{2}nN_AAv_x\Delta t/V$

Momentum: $2mv_x$

In the interval Δt, the total momentum change is given by the product of the average number of collisions, and total change in momentum

$$\Delta P = \frac{nN_AAv_x\Delta t}{2V} \times 2mv_x = \frac{nMAv_x^2\Delta t}{V}$$

Deriving the RMS Speed

Newton's Second Law of Motion: The rate of change of momentum is equal to force applied on an object: $\Delta P/\Delta t = F$ (kg m s^{-1}/s = kg m s^{-2})

$$F = \frac{\Delta P}{\Delta t} = \frac{nMAv_x^2}{V}$$

Pressure: Defined as force exerted over some area *A*:

$$p = \frac{F}{A} = \frac{nMv_x^2}{V} = \frac{nM\langle v_x^2\rangle}{V}$$

On the RHS of the above equation, there are angular brackets, which denote the **average** of some value (since all molecules are not travelling at an identical speed). Since molecules move randomly as well, there is similar behaviour along the *y* and *z* directions.

$$c^2 = \langle v_x^2\rangle + \langle v_y^2\rangle + \langle v_z^2\rangle = 3\langle v_x^2\rangle \text{ , } \quad \text{thus} \quad \langle v_x^2\rangle = \frac{1}{3}c^2$$

RMS Molecular Speed*

The RMS speed, c^2, depends only upon the temperature; thus at a constant temperature, pV = constant (**Boyle's Law**), so:

$$pV = nM\langle v_x^2\rangle = \frac{1}{3}nMc^2 \quad , \qquad c = \langle v^2\rangle^{1/2}$$

Under the ideal gas law, the RHS of the equation should be equal to nRT: algebraic substitution can be used to show that

$$c = \left(\frac{3RT}{M}\right)^{1/2}$$

The RMS speed is proportional to the square root of temperature, and inversely proportional to the square root of molar mass. On average:

- At higher temperatures, molecules travel faster
- Heavier molecules travel slower than light molecules (Balloons)

Maxwell Distribution of Speeds

James Clerk Maxwell (1831-1879), a Scottish physicist, did revolutionary work in electromagnetism and the **kinetic theory of gases**. By treating molecules of gases in rapid motion them statistically he was able to formulate (1866), independently of Ludwig Boltzmann, the Maxwell-Boltzmann kinetic theory of gases. **This theory showed that temperatures and heat involved only molecular movement.** Philosophically, this theory meant a change from a concept of certainty--heat viewed as flowing from hot to cold--to one of statistics--**molecules at high temperature have only a high probability of moving toward those at low temperature**. This new approach did not reject the earlier studies of thermodynamics; rather, it used a better theory of the basis of thermodynamics to explain these observations and experiments.

In a real gas the speeds of individual molecules span wide ranges, with constant collisions continually changing the molecular speeds. Maxwell showed that the distribution of speeds of molecules in a gas can be written as an **analytical equation**:

$$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}$$

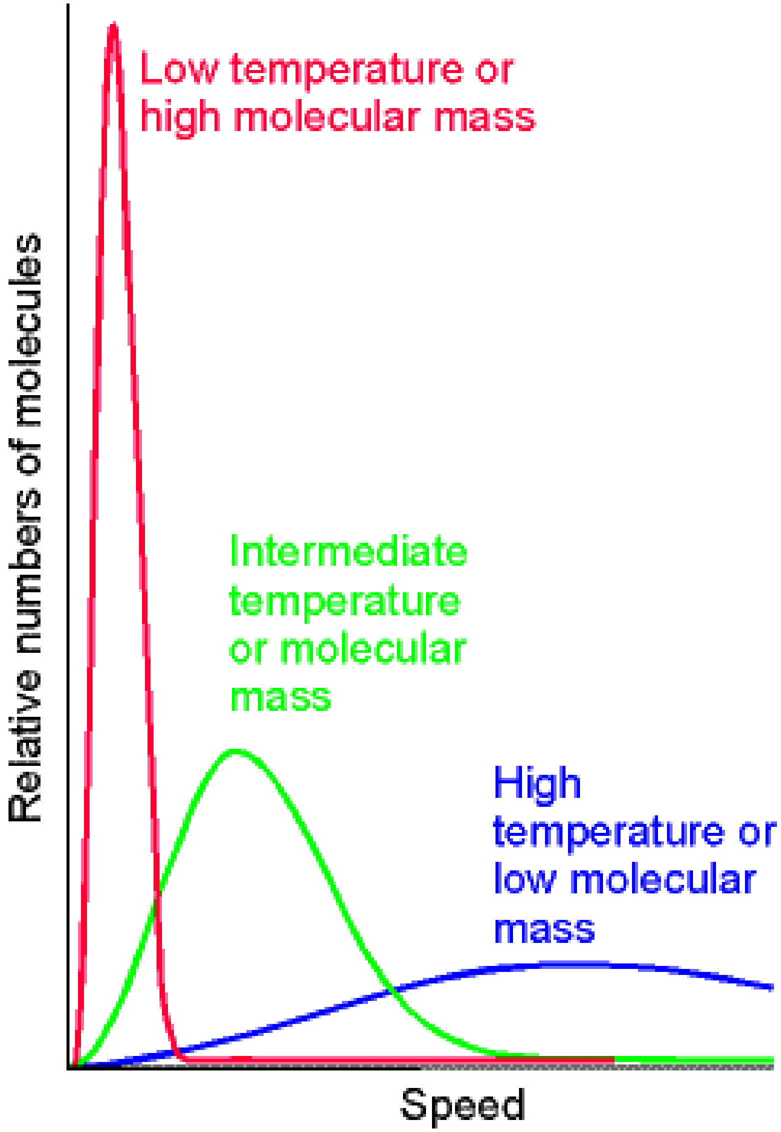
Maxwell Distribution of Speeds**

He demonstrated that the fraction of molecules that possess speeds in the range $\Delta v = v$ to $v + dv$ is proportional to the width of the range

Maxwell distributions show that:
- Higher temperatures have broader distributions of molecular speeds
- Lighter molecules have a broader distribution of speeds than heavier molecules

To use Maxwell's distribution equation, we need to multiply it by Δv, or if Δv is not infinitessimal, the **definite integral** below must be evaluated:

$$\text{Fraction between } v_1 \text{ and } v_2 = \int_{v_1}^{v_2} f(v)\, dv$$



Integral Calculus

Integrals: Give us the *"area under the curve"*

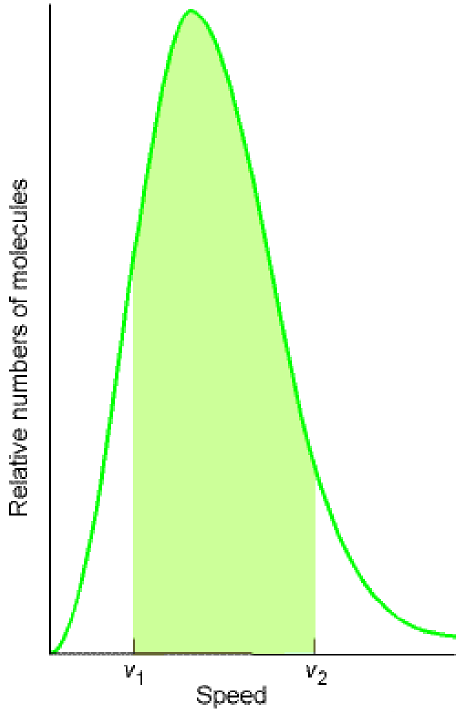
Two approaches:

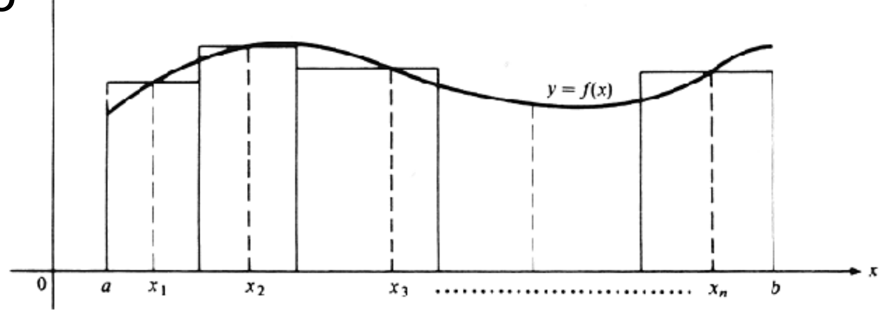
1. **Anti-derivative** - if it is possible to write a mathematical expression for a function that describes it's anti-derivative **analytically** (i.e., write a new function based on the inverse of differentiation)

   Here we mathematically generate integrals!

2. **Sum** - the area under a function may also be calculated as the sum of many small (infinitessimal) elements (these are often evaluated **numerically** by some iterative process on a computer)

   Here we give physical meaning to integrals!





Deriving the Maxwell Distribution: 1

The probability that a molecule has velocity in the range:
v_x to v_x+dv_x, v_y to v_y+dv_y, v_z to v_z+dv_z is proportional to widths and depends on velocity components:

$$f(v_x, v_y, v_z)\,dv_x\,dv_y\,dv_z$$

Cartesian (x,y,z) velocity components are **orthogonal** (independent)

$$f(v_x, v_y, v_z) = f(v_x)f(v_y)f(v_z)$$

Equal probability of molecule having velocity $+|v_x|$ to $+|v_x|dv_x$ or $-|v_x|$ to $-|v_x|dv_x$, so $f(v_x)$ must be related to square of v_x

$$f(v_x) = f(v_x^2), \qquad f(v_x, v_y, v_z) = f(v_x^2)f(v_y^2)f(v_z^2)$$

Molecular speed is independent of direction of invidual components

$$\begin{aligned} f(v_x, v_y, v_z) &= f(v_x^2 + v_y^2 + v_z^2), \\ \text{thus } f(v_x^2 + v_y^2 + v_z^2) &= f(v_x^2)f(v_y^2)f(v_z^2) \end{aligned}$$

Deriving the Maxwell Distribution: 2

An exponential function is ideal here, since: $e^a e^b = e^{(a+b)}$; thus,

$$f(v_x) = Ke^{\pm\zeta v_x^2}$$

where K and ζ (zeta) are constants, and $f(v_x) = f(v_x^2)$ (same for y and z)

Probability that a molecule has an extremely high velocity is low, therefore we can discard the solution with $\underline{+\zeta v_x^2}$ in the exponent

To determine K, molecule must have v in range $-\infty$ to ∞:

$$\int_{-\infty}^{\infty} f(v_x)\, dv_x = 1$$

Substitute above expression for $f(v_x)$ and integrate wrt v_x:

$$1 = K\int_{-\infty}^{\infty} e^{-\zeta v_x^2}\, dv_x = K\left(\frac{\pi}{\zeta}\right)^{1/2}$$

Therefore, $K = (\zeta/\pi)^{1/2}$ (solution of above **definite integral** comes from a table of integrals, found in CRC Handbook or basic calculus textbooks)

Deriving the Maxwell Distribution: 3

In order to find ζ, the **RMS Speed** must be calculated. In the next step, we calculate the **expectation value** for v_x^2:

$$\langle v_x^2\rangle = \int_{-\infty}^{\infty} v_x^2 f(v_x)\,dv_x = \left(\frac{\zeta}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} v_x^2 e^{-\zeta v_x^2}\,dv_x$$

$$= \left(\frac{\zeta}{\pi}\right)^{1/2} \times \frac{1}{2}\left(\frac{\pi}{\zeta^3}\right)^{1/2} = \left(\frac{1}{2\zeta}\right)$$

$$c = (\langle v_x^2\rangle + \langle v_x^2\rangle + \langle v_x^2\rangle)^{1/2} = \left(\frac{3}{2\zeta}\right)^{1/2}$$

Since we know $c = (3RT/M)^{1/2}$, $\zeta = M/2RT$. Therefore

$$f(v_x) = \left(\frac{M}{2\pi RT}\right)^{1/2} e^{-Mv_x^2/2RT}$$

We are very close to the final solution now!

Deriving the Maxwell Distribution: 4

Probability that a molecule has speed in the range v_i to v_i+dv_i ($i = x,y,z$)

$$\begin{aligned} f(v_x,v_y,v_z)dv_x dv_y dv_z &= f(v_x)f(v_y)f(v_z)dv_x dv_y dv_z \\ &= \left(\frac{M}{2\pi RT}\right)^{3/2} e^{-Mv^2/2RT} dv_x dv_y dv_z \end{aligned}$$

Since speed is not dependent upon direction, the probabilities that the velocities are in the **volume element** $dv_x dv_y dv_z$ on the RHS can be written as the volume of a spherical shell of radius v, $4\pi v^2 dv$. Thus,

$$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}$$

The **mean speed**, $\overline{c}$, and the **most probable speed**, c^*, can be evaluated by similar methods (please try Example and Self Test 1.6 in Atkins, 6th Ed. or Example and Self Test 24.1 in Atkins, 7th Ed., 21.1 in 8th Ed.)

Summary of Speeds

Root mean square speed:

$$c = \left(\frac{3RT}{M}\right)^{1/2}$$

Maxwell distribution of speeds:

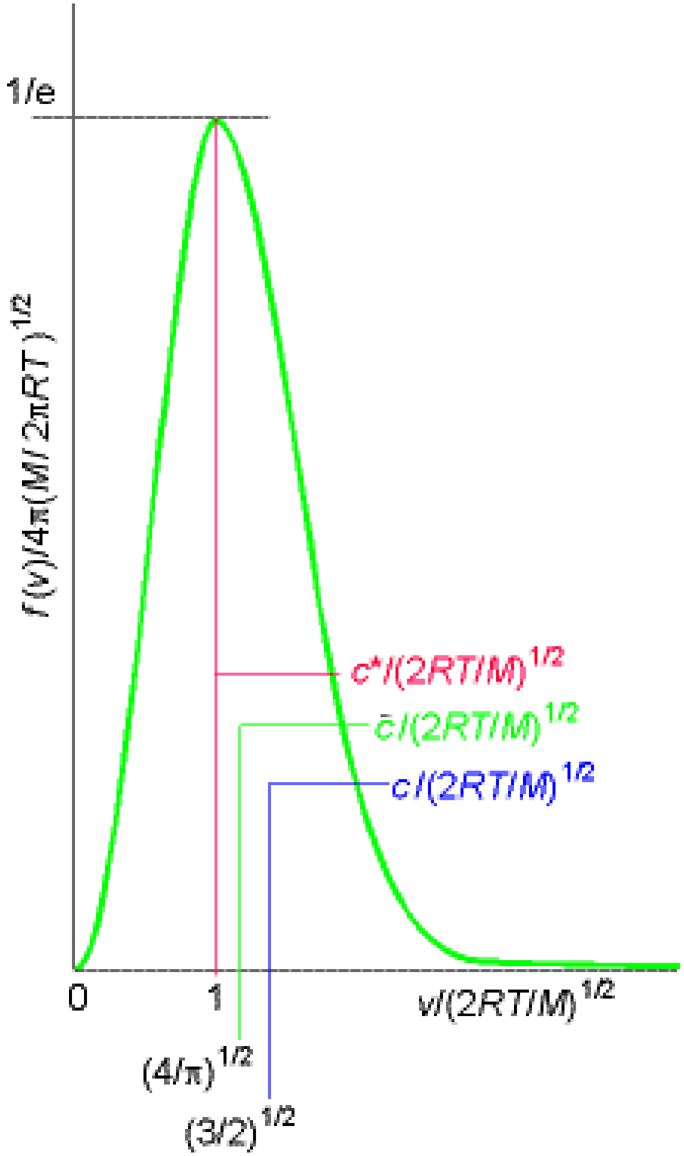
$$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}$$

Mean speed:

$$\bar{c} = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

Most probable speed:

$$c^* = \left(\frac{2RT}{M}\right)^{1/2}$$



Relative Mean Speed

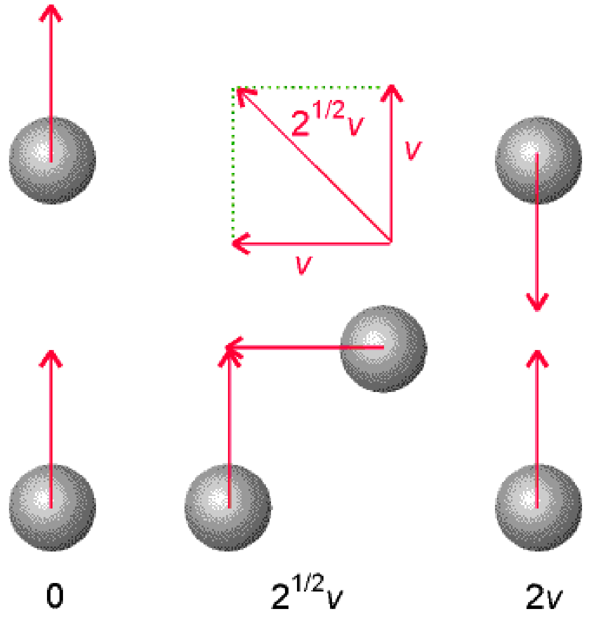
The **relative mean speed** is the speed with which one molecule approaches another, and is given by

$$\bar{c}_{\mathrm{rel}} = 2^{1/2}\bar{c} = \left(\frac{8kT}{\pi\mu}\right)^{1/2}, \qquad \mu = \frac{m_A m_B}{m_A + m_B}$$

where k is the **Boltzmann constant**, $k = R/N_A$, and μ is called the **reduced mass** (expression is used for molecules of different masses)

What does $\bar{c}_{\mathrm{rel}}$ tell us?

If molecules move in same direction, the relative mean speed is 0.
If molecules are on a direct collision course, relative mean speed is $2v$.
If molecules have orthogonal pathways, the relative mean speed is $2^{1/2}v$ (this is the most typical speed)



Collision frequency

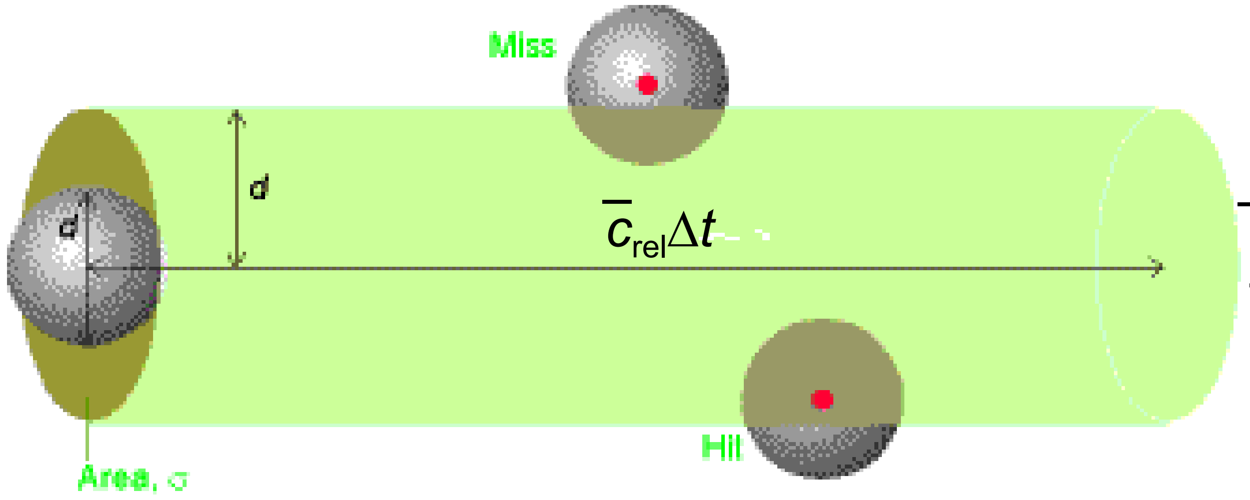
Kinetic model allows us to:

- calculate the frequency with which molecules collide
- calculate the distance traveled by molecules between collisions
- calculate molecular transport properties and reactivities in gases

When molecules are within distance *d*, the **collision diameter**, they are said to collide with one another. The kinetic model gives the **collision frequency**, *z*, which is the number of collisions in some time interval

$$z = \frac{\sigma \bar{c}_{\mathrm{rel}} N}{V} = \frac{\sigma \bar{c}_{\mathrm{rel}} p}{kT}, \qquad \sigma = \pi d^2$$

σ is the **collision cross-section** of the molecules



In interval Δt, molecule sweeps a tube of diameter 2*d* and length $\bar{c}_{\mathrm{rel}}\Delta t$. Each hit changes the direction of the path, but the “volume” of the path is the same

Mean Free Path

If the collision frequency is known, then one can calculate the **mean free path**, λ, which is the average distance between collisions

If a molecule collides with frequency z, it is in traveling at a mean speed of c for a time $1/z$ (substituting in for z):

$$\lambda = \frac{\bar{c}}{z} = \frac{kT}{2^{1/2}\sigma p}$$

The kinetic model works if $d \ll \lambda$ (molecules are far from one another)

Example: For N_2 gas at 1 atm and 25°C ($\sigma = 0.43\ \text{nm}^2$)

$z = 7 \times 10^9\ \text{s}^{-1}$ (collisions about every ns or so)

$\lambda = 70$ nm (10^3 molecular diameters)

$c = 350\ \text{m s}^{-1}$