Chemical Kinetics

- Chemical kinetics complements thermodynamics:
    - Thermodynamics tells us if something can happen.
    - Kinetics tells us how long it takes.
- Together they enable us to predict:
    - Rates of reactions.
    - Preference for one reaction over another.
    - Reaction conditions that will produce desired result.
    - Explosions and other dangerous conditions.
- As in the case of thermodynamics, chemical kinetics connects the microscopic and the macroscopic.

Kinetic Theory of Gases

- Properties of a typical gas:
    - Molecules constantly in motion.
    - Volume of molecules themselves small relative to the container, so that the molecules move past each other more often than colliding.
    - Uniformly move through entire volume of a container.
- History of Kinetic Theory
    - Robert Hooke (1678) postulate that collisions of gas atoms with walls of containers gave rise to pressure.
    - Daniel Bernoulli (1738) used this concept to derive Boyle's Law ($PV = \text{constant}$).
    - Waterston (1846) suggested that the mean kinetic energy of a gas was proportional to its temperature.
    - Using these ideas and classical mechanics, important contributions were made by Boltzmann, van der Waals, Maxwell, Clausius, and others from 1860 on.

Speeds and Velocities of Gases

- Recall:
    - Speed is a scalar and has only magnitude.
    - Velocity is a vector with both direction and magnitude.
- The equipartition theorem predicts that the total translational energy of a gas is $3nRT/2$ where:
    - n is the number of moles of gas
    - R is the gas constant
    - T is the temperature on a thermodynamic scale
    - For 1 mol of Ar equilibrated at 300 K, this works out to 3.741 kJ.
- But, we know that there is a distribution that has this average and that not all molecules have the same energy.

What is the nature of this distribution function?

- Consider some distributions that could give rise to the observed average energy:
- Example 1:
  - All molecules still except for one which has the entire kinetic energy.
  - That one molecule would have to move faster (10^6 times faster!) than the speed of light.
- Example 2:
  - All molecules have exactly the same velocity:

$$<\epsilon>= 3k_BT/2 = mv^2/2$$

$$v = \sqrt{\frac{3k_BT}{m}} = 432.8 \text{ m s}^{-1}$$

- Are either of these likely to be an equilibrium distribution?
  - Why?
  - Why not?

Partition Functions

- See Chapter 23 of Winn.
- We are interested in the translational partition function
- Other types of partition functions are
  - Electronic
  - Vibrational
  - Rotational
  - Combinations of the above
- Partition functions link the microscopic with the macroscopic.
  - Allow us to move from the microstate (see Chapter 3 of Winn) to the macrostate.
- Start with the quantum mechanical particle-in-a-box view of translational motion.
  - Particle-in-a-box is one of the "classic" quantum mechanical problems. (See Chapter 12, Section 12.2 if you are interested, but this is not required.)

Quantum Mechanics
and the Translational Partition Function

- Quantum mechanical formulation assumes that one particle is in an infinitely deep well.
  - Solution to the corresponding Shrodinger equation gives a wavefunction which is mathematically equivalent to a sine function and energies that are proportional to n^2 where n is the translational quantum number.

$$\epsilon_n = \frac{\hbar^2\pi^2n^2}{2mL^2}$$

- For one particle in three dimensions this becomes:

$$\epsilon_n = \frac{\hbar^2\pi^2}{2m}\left(\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}+\frac{n_z^2}{L_z^2}\right)$$

- The partition function is defined as:

$$q = \sum_1^\infty g_i e^{-\beta\epsilon_i}$$

  where:

  - g_i is the degeneracy (1 in the case of translational motion)
  - $\beta = 1/kT$
  - ϵ_i is the ith translational energy level

- Thus for the one dimensional case, the translational partition function is:

$$q_{tr} = \sum_{n=1}^\infty e^{-\beta\epsilon_n} = \sum_{n=1}^\infty exp\left(-\frac{\beta\hbar^2\pi^2n^2}{2mL^2}\right)$$

  - This infinite sum does not have a closed form (i.e. the series does not converge).
  - But for microscopic m and macroscopic L, the spacing of the energy levels is sufficiently small that the partition function can be treated as a continuum instead of a sum.

$$q_{tr} = \int_0^\infty exp\left(-\frac{\beta\hbar^2\pi^2n^2}{2mL^2}\right)dn$$

$$= \left(\frac{mk_BT}{2\pi\hbar^2}\right)^{1/2} L$$

  since

$$\int_0^\infty exp\,(-a^2n^2)dn = \sqrt{\pi}/2a$$

- Thus the three dimensional translational partition function is:

$$q_{tr} = q_{tr,x}q_{tr,y}q_{tr,z} = \left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2} L_xL_yL_z$$

$$q_{tr} = \left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2} V$$

- This gives the distribution function (back to Chapter 24):

$$f(\epsilon) = \frac{N_\epsilon}{N} = \frac{e^{-\epsilon/k_BT}}{q_{tr}} = \frac{e^{-\epsilon/k_BT}}{V(mk_BT/2\pi\hbar^2)^{3/2}}$$

  where

$$\epsilon = \frac{\hbar^2\pi^2}{2m}\left(\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}+\frac{n_z^2}{L_z^2}\right)$$

and $V = L_x L_y L_z$

- If we use the assumption that the translational energy levels are so closely spaced as to be a continuum, then the distribution function can be defined.
  - $f(\epsilon)d\epsilon$ is the fraction of molecules with energy between ϵ and $\epsilon + d\epsilon$.

- $\rho(\epsilon)d\epsilon$ is the translational density of states, the number of translational states with energy between ϵ and $\epsilon + d\epsilon$.

$$\rho(\epsilon)d\epsilon = \frac{\pi}{4}\left(\frac{2m}{\hbar^2\pi^2}\right)^{3/2} V\epsilon^{1/2}d\epsilon$$

  which can be obtained by the inverse Laplace transform of the partition function.

- Thus the distribution function becomes:

$$f(\epsilon)d\epsilon = \frac{\rho(\epsilon)e^{-\epsilon/k_BT}}{q_{tr}}d\epsilon$$

$$= 2\pi\left(\frac{1}{\pi k_BT}\right)^{3/2} \epsilon^{1/2}e^{-\epsilon/k_BT}d\epsilon$$

  which depends only on the temperature of the gas.

- Figure 24.1 shows some distributions at different temperatures.
  - The area under the curve is 1 since

$$\int_0^\infty f(\epsilon)d\epsilon = 1$$

  - At lower T, the distribution is very peaked compared to higher T.
  - The distribution is not symmetric.

Some Properties of the Distribution Function

- Consider:
  - Average energy
  - Most probable energy

- Determination of average energy
  - If a distribution function has been normalized (i.e. the integral of the distribution function over its entire range is unity), then

$$<\epsilon>= \int_0^\infty \epsilon\ f(\epsilon)d\epsilon$$

$$= 2\pi\left(\frac{1}{\pi k_BT}\right)^{3/2}\int_0^\infty \epsilon^{3/2}e^{-\epsilon/k_BT}d\epsilon$$

  - To evaluate the integral:

$$\int_0^\infty \epsilon^{3/2}e^{-\epsilon/k_BT}d\epsilon$$

    use the variable transformation $\epsilon = x^2$ and $d\epsilon = 2xdx$ and recalling that $\beta = 1/k_BT$. This gives an integral of the form:

$$\int_0^\infty x^4e^{-\beta x^2}dx = \left(\frac{1}{4}\right)\left(\frac{3}{2}\right)\pi^{1/2}\beta^{-5/2}$$

- Substitution of this into above gives

$$< \epsilon >= \frac{3}{2}\beta^{-1} = \frac{3}{2}k_BT$$

- Determination of most probable energy
  - Need to find position of the maximum of the distribution function.
  - One condition that is satisfied by the maximum is that the derivative of the function is zero.

$$f(\epsilon) = 2\pi\left(\frac{1}{\pi k_BT}\right)^{3/2}\epsilon^{1/2}e^{-\epsilon/k_BT}$$

$$\frac{df(\epsilon)}{d\epsilon} = 0 = \frac{d(\epsilon^{1/2}e^{-\epsilon/k_BT})}{d\epsilon}$$

$$= \epsilon^{1/2}\frac{d(e^{-\epsilon/k_BT})}{d\epsilon} + e^{-\epsilon/k_BT}\frac{d\epsilon^{1/2}}{d\epsilon}$$

$$= \epsilon^{1/2}\left(\frac{-1}{k_BT}\right)e^{-\epsilon/k_BT} + e^{-\epsilon/k_BT}\left(\frac{1}{2}\right)\epsilon^{-1/2}$$

Therefore:

$$0 = \epsilon^{1/2}e^{-\epsilon/k_BT}\left(\frac{-1}{k_BT} + \frac{\epsilon^{-1}}{2}\right)$$

and:

$$\epsilon = \frac{k_BT}{2}$$

N. B. The condition that the first derivative is zero is a **necessary** condition for a maximum, but not a **sufficient** condition. It must now be shown that this is a maximum. There are two approaches to this:

- Find the second derivative and show that it is negative at the maximum.
- Characterize the function.

Characterizing the energy distribution function

- Is the first derivative zero at only one value?
  - If not, then another method must be used to prove the maximum
  - If so, then this method can be used.
- Must show that points on either side of the maximum have values of $f(\epsilon)$ less than the value at the maximum.
  - Appropriate choices to test for maximum are

$$\epsilon = 0$$

and

$$\epsilon = \infty$$

  - Consider $f(\epsilon)$ at each of these values:

$$f(\epsilon = 0) = 0$$

$$f(\epsilon = \infty) = 0$$

  - Therefore $\epsilon = \frac{k_BT}{2}$ is a maximum.

- Note that the average energy is three times the most probable energy.

Properties of the Speed Distribution

- Consider the relationship between energy, speed, and velocity.

$$\epsilon = \frac{1}{2}mv^2 = \frac{1}{2}m\ \mathbf{v}\cdot\mathbf{v} = \frac{1}{2}m\left(v_x^2 + v_y^2 + v_z^2\right)$$

  - Energy is a scalar. Distributions in energy are directly proportional to distributions of the square of the speed.

$$\langle\epsilon\rangle = \left\langle\frac{1}{2}mv^2\right\rangle = \frac{1}{2}m\langle v^2\rangle$$

  - Since $\langle\epsilon\rangle = 3k_BT/2$, the root mean square (rms) speed may be determined:

$$v_{rms} = \langle v^2\rangle^{1/2} = \sqrt{\frac{2\langle\epsilon\rangle}{m}} = \sqrt{\frac{3k_BT}{m}}$$

Transformation of the Kinetic Energy Distribution Function into a Speed Distribution Function

- Start with the kinetic energy distribution function:

$$f(\epsilon)d\epsilon = 2\pi\left(\frac{1}{\pi k_BT}\right)^{3/2}\epsilon^{1/2}e^{-\epsilon/k_BT}d\epsilon$$

- Transform the variable from ϵ to v

$$\epsilon = \frac{1}{2}mv^2$$

$$d\epsilon = mvdv$$

$$\epsilon^{1/2} = \frac{m^{1/2}v}{\sqrt{2}}$$

- This substitution gives the Maxwell-Boltzmann distribution:

$$f(v)dv = 4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2}v^2e^{-mv^2/2k_BT}dv$$

- From this can be determined the most probable speed, the average speed, and the median speed.

Most Probable Speed

- Find the maximum of the distribution function.

$$\frac{df(v)}{dv} = 4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2}\frac{d\left(v^2e^{-mv^2/2k_BT}\right)}{dv} = 0$$

  - Therefore there is an extremum (a maximum or minimum) when:

$$\frac{d\left(v^2 e^{-mv^2/2k_BT}\right)}{dv} = 0$$

$$2v\ e^{-mv^2/2k_BT} + \left(\frac{-2mv}{2k_BT}\right)\ v^2\ e^{-mv^2/2k_BT} = 0$$

$$2v\ - \left(\frac{mv^3}{k_BT}\right)\ = 0$$

$$\left(\frac{2k_BT}{m}\right) = v^2$$

$$v = \left(\frac{2k_BT}{m}\right)^{1/2}$$

- Now prove that this is a maximum or minimum by characterizing the distribution function.

$$v \rightarrow 0, f(v) \rightarrow 0$$

$$v \rightarrow \infty, f(v) \rightarrow 0$$

  - Therefore it is a maximum and the most probable speed is:

$$v = \left(\frac{2k_BT}{m}\right)^{1/2}$$

The Average Speed

- Determine the average speed by integration of:

$$\langle v\rangle = \int_0^\infty vf(v)dv =$$

$$4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2}\int_0^\infty v^3 e^{-mv^2/2k_BT}\ dv$$

- This involves a definite integral of the form:

$$\int_0^\infty x^m e^{-ax^2} dx$$

which may be looked up in a standard table of integrals.

A Mathematical Aside

- If m is even, then write the integral in the form:

$$\int_0^\infty x^{2n} e^{-ax^2} dx$$

$$\int_0^\infty x^{2n} e^{-ax^2} dx = \frac{1}{2}\sqrt{\pi}\ \frac{(2n)!a^{-(n+1/2)}}{2^{2n}n!}$$

- If m is odd, then write the integral in the form:

$$\int_0^\infty x^{2n+1} e^{-ax^2} dx$$

$$\int_0^\infty x^{2n+1} e^{-ax^2} dx = \frac{1}{2}(n!)a^{-(n+1)}$$

- If $m = 3$ then the integral is:

$$\int_0^\infty x^3 e^{-ax^2} dx = \frac{1}{2}(1!)a^{-2} = \frac{1}{2a^2}$$

  - Therefore the average speed is:

$$\langle v \rangle = \int_0^\infty v f(v)\ dv$$

$$= 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \int_0^\infty v^3 e^{-mv^2/2k_B T}\ dv$$

$$= 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \frac{1}{2} \left(\frac{2k_B T}{m}\right)^2$$

$$\langle v \rangle = \left(\frac{8k_B T}{\pi m}\right)^{1/2}$$

Characteristic Speeds of an Equilibrium Gas

- So far we have determined:
  - Root-mean-square speed

$$v_{rms} = \sqrt{\frac{3k_B T}{m}}$$

  - Most probable

$$v_{mp} = \sqrt{\frac{2k_B T}{m}}$$

  - Average

$$\langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}}$$

- Also of interest are:
  - Median

$$v_{med} = 1.5382\sqrt{\frac{k_B T}{m}}$$

  - Speed of sound

$$v_s = \sqrt{\frac{\gamma k_B T}{m}}$$

(Recall that $\gamma = C_P/C_V$)

Velocity Distributions

- We know that $v^2 = v_x^2 + v_y^2 + v_z^2$

  - From equipartition of energy, we can infer that:

$$\langle v_x^2\rangle = \langle v_y^2\rangle = \langle v_z^2\rangle = \frac{1}{3}\langle v^2\rangle = \frac{v_{rms}^2}{3} = \frac{k_BT}{m}$$

- We also now that the average value of each velocity component must correspond with the components of velocity of the center of mass.
  - If the center of mass is at rest, then the velocity distribution must be symmetric about zero.
- Starting with

$$f(v)dv = 4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2} v^2 e^{-mv^2/2k_BT}dv$$

we must be able to break it into:

$$f(v_x)f(v_y)f(v_z)dv_xdv_ydv_z$$

How do we do this?

Mathematical Aside #2

Transformation from Cartesian to Spherical Polar Coordinates

See p. 412 in your text.

- Cartesian Coordinates are (x, y, z)
- Spherical Polar Coordinates are (r, θ, ϕ)
  - θ is the polar angle
  - ϕ is the azimuthal angle
- x, y, z in terms of (r, θ, ϕ):

$$x = r\sin\theta\cos\phi$$

$$y = r\sin\theta\sin\phi$$

$$z = r\cos\theta$$

- (r, θ, ϕ) in terms of x, y, z

$$r = (x^2 + y^2 + z^2)^{1/2}$$

$$\theta = cos^{-1}(z/r)$$

$$\phi = tan^{-1}(y/z)$$

Transforming a differential element

- Need to take into account the change is shape of the differential element.

$$dx\ dy\ dz\ \ =\ \ |J\left(\frac{x, y, z}{r, \theta, \phi}\right)|\ dr\ d\theta\ d\phi$$

where $|J\left(x, y, z/r, \theta, \phi\right)|$ is the determinant of the Jacobian matrix.

$$J\left(\frac{x, y, z}{r, \theta, \phi}\right) = \begin{pmatrix} \left(\frac{\partial x}{\partial r}\right)_{\theta,\phi} & \left(\frac{\partial x}{\partial \theta}\right)_{r,\phi} & \left(\frac{\partial x}{\partial \phi}\right)_{r,\theta} \\ \left(\frac{\partial y}{\partial r}\right)_{\theta,\phi} & \left(\frac{\partial y}{\partial \theta}\right)_{r,\phi} & \left(\frac{\partial y}{\partial \phi}\right)_{r,\theta} \\ \left(\frac{\partial z}{\partial r}\right)_{\theta,\phi} & \left(\frac{\partial z}{\partial \theta}\right)_{r,\phi} & \left(\frac{\partial z}{\partial \phi}\right)_{r,\theta} \end{pmatrix}$$

- Therefore, we need to get all the derivatives:

$$\left(\frac{\partial x}{\partial r}\right)_{\theta,\phi} = \sin\theta\cos\phi$$

$$\left(\frac{\partial x}{\partial \theta}\right)_{r,\phi} = r\cos\theta\cos\phi$$

$$\left(\frac{\partial x}{\partial \phi}\right)_{r,\theta} = -r\sin\theta\sin\phi$$

$$\left(\frac{\partial y}{\partial r}\right)_{\theta,\phi} = \sin\theta\sin\phi$$

$$\left(\frac{\partial y}{\partial \theta}\right)_{r,\phi} = r\cos\theta\sin\phi$$

$$\left(\frac{\partial y}{\partial \phi}\right)_{r,\theta} = r\sin\theta\cos\phi$$

$$\left(\frac{\partial z}{\partial r}\right)_{\theta,\phi} = \cos\theta$$

$$\left(\frac{\partial z}{\partial \theta}\right)_{r,\phi} = -r\sin\theta$$

$$\left(\frac{\partial z}{\partial \phi}\right)_{r,\theta} = 0$$

- Evaluation of the Jacobian shows:

$$\left|J\left(\frac{x,y,z}{r,\theta,\phi}\right)\right| = r^2 \ \sin\theta$$

- Therefore

$$dx\ dy\ dz \ = \ r^2 \ \sin\theta \ dr\ d\theta\ d\phi$$

- Since the range of θ is 0 to π and the range of ϕ is 0 to 2π, integration of the angles over these ranges gives:

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dx\ dy\ dz \ = \int_0^{\infty} \ 4\pi r^2\ dr$$

- On this basis, we can say that

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dv_x dv_y dv_z = \int_0^{\infty} \ 4\pi v^2 dv$$

  and

$$\int_0^{\infty} 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-mv^2/2k_BT} dv$$
$$= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f(v_x)f(v_y)f(v_z)dv_x dv_y dv_z$$
$$= \left[\int_{-\infty}^{\infty}\left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-mv_x^2/2k_BT} dv_x\right] \cdot$$

$$\left[\int_{-\infty}^{\infty}\left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-mv_y^2/2k_BT}dv_y\right]\cdot$$

$$\left[\int_{-\infty}^{\infty}\left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-mv_z^2/2k_BT}dv_z\right]$$

- Now consider

$$f(v_x)dv_x = \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-mv_x^2/2k_BT}dv_x$$

- From this may be shown:
  - $\langle v_x \rangle = 0$
  - $\langle v_x^2 \rangle = k_B T/m$

Pressure and the velocity distribution

- Pressure is defined as force per unit area
- Force is defined as the change in momentum with respect to time.

$$P = \frac{force}{unit\ area} = \frac{dp/dt}{unit\ area}$$

- Considering pressure in terms of collisions with the wall of the container.

$$P = (momentum\ change\ per\ wall\ collision)\cdot$$

$$\frac{(number\ of\ wall\ collisions)}{(unit\ wall\ area)(unit\ time)}$$

- Consider elastic collisions with the wall perpendicular to the x direction.
  - The x component of the velocity is the same magnitude after the collision with the wall as it was before, but opposite in direction. Therefore the change in momentum is:

$$m|v_x| - (-m|v_x|) = 2m|v_x|$$

  - The number of molecules per unit volume with velocities between v_x and $v_x + dv_x$ is:

$$\frac{Nf(v_x)dv_x}{V}$$

  - Let A be an area on the wall
  - Let τ be an arbitrary time period.
  - Define a volume $v_x\tau A$ extending a distance $v_x\tau$ from the wall. Molecules within this volume will hit the wall within time τ.
  - Assume density is so low that molecule-molecule collisions do not occur within this volume during time τ.
  - The number of molecules striking unit area per unit time is:

$$\frac{(v_x\tau)A(N/V)f(v_x)dv_x}{\tau A} = \frac{v_x N f(v_x)dv_x}{V}$$

- Thus the pressure contribution due to molecules with velocities between v_x and $v_x + dv_x$ is:

$$(2mv_x)\left(\frac{v_x N f(v_x)}{V}\right) dv_x$$

- Thus the total pressure due to velocities directed toward the wall is:

$$P = \int_0^\infty (2mv_x)\left(\frac{v_x N f(v_x)}{V}\right) dv_x$$

$$= \left(\frac{N}{V}\right) m \int_{-\infty}^{\infty} v_x^2 f(v_x) dv_x = \left(\frac{N}{V}\right) m\langle v_x^2\rangle$$

- But $mv_x^2/2 = k_BT/2$, therefore:

$$P = \left(\frac{N}{V}\right) m\langle v_x^2\rangle = \frac{Nk_BT}{V} = \frac{nN_Ak_BT}{V} = \frac{nRT}{V}$$

- Related to this derivation of pressure is the wall collision rate, J_x, the number of molecules hitting a unit area per unit time.

$$J_x = \frac{N}{V}\int_0^\infty v_x f(v_x) dv_x$$

$$= \frac{N}{V}\left(\frac{m}{2\pi k_BT}\right)^{1/2}\int_0^\infty v_x e^{-mv_x^2/2k_BT} dv_x$$

$$= \frac{N}{V}\left(\frac{k_BT}{2\pi m}\right)^{1/2}$$

  - Since $P = Nk_BT/V$, then

$$J_x = \frac{P}{(2\pi m k_BT)^{1/2}}$$

  - Since mean speed is $\langle v\rangle = (8k_BT/\pi m)^{1/2}$, J_x becomes

$$J_x = \frac{N}{V}\left(\frac{k_BT}{2\pi m}\right)^{1/2} = \frac{1}{4}\frac{N}{V}\left(\frac{8k_BT}{\pi m}\right)^{1/2} = \frac{1}{4}\frac{N}{V}\langle v\rangle$$

- A flow expressed as amount per unit time per unit area is a *flux*, therefore J_x is a flux of molecules.
- Consider a container with a hole of small area, A. The rate of escape through that hole is AJ_x, if there is an appropriate relationship between the hole and the density of the gas.
  - Collisions between molecules and the wall are independent, isolated events. (i.e. The density is so low that molecules do not collide with each other as they are going through the hole.)

Mean Free Path

- The mean free path, λ, is the average distance that a molecule travels between collisions with other molecules.
- The derivation of this involves molecules that are nonideal.

  - Collisions occur only between molecules that have size.
  - The hard-sphere gas consists of molecules that are spheres of radius r.
- Collisions between two hard-sphere molecules occur when their centers are separated by a distance of d where $d = 2r$.
  - Therefore the hard-sphere cross section is:

$$\sigma = \pi d^2$$

  - Any other molecule that comes within the distance d of the center of this molecule will collide with it.
- Consider first the case in which all the other molecules are still with just the molecule of interest moving.
  - On average the molecule will move the distance λ before hitting another molecule.
  - The volume swept out will be $\sigma\lambda$.
  - This volume will also be V/N, the average volume per molecule.
- But in a real gas, all the molecules are moving.
  - Therefore we must consider the average *relative* velocity, not the average velocity of the molecule with respect to the observer.

Mathematical Aside # 3

Conversion to center-of-mass coordinates

- Consider two particles, one of mass m_a, the other of mass m_b with position x_a and x_b
- X, the position of the center-of-mass, satisfies:

$$m_a(X - x_a) = m_b(x_b - X)$$

$$X = \frac{m_a x_a + m_b x_b}{m_a + m_b}$$

- x, the separation of the two particles is:

$$x = x_b - x_a$$

- Therefore

$$x_a = X - \frac{m_b x}{m_a + m_b}$$

$$x_b = X + \frac{m_a x}{m_a + m_b}$$

- The moment of inertia about the center-of-mass is:

$$I = m_a(X - x_a)^2 + m_b(x_b - X)^2$$

$$I = m_a\left(\frac{m_b x}{m_a + m_b}\right)^2 + m_b\left(\frac{m_a x}{m_a + m_b}\right)^2$$

$$I = \frac{m_a m_b^2 + m_a^2 m_b}{(m_a + m_b)^2} x^2$$

$$I = \frac{m_a m_b}{m_a + m_b} x^2 = \mu x^2$$

where

$$\mu = \frac{m_a m_b}{m_a + m_b}$$

- If $m_a = m_b = m$ then

$$\mu = \frac{m^2}{m + m} = \frac{m}{2}$$

- Instead of distance, this approach may be applied to any vector including velocity.

- The mean relative speed for identical particles is:

$$\langle g \rangle = \left(\frac{8 k_B T}{\pi \mu} \right)^{1/2} = \sqrt{2} \left(\frac{8 k_B T}{\pi m} \right)^{1/2} = \sqrt{2} \langle v \rangle$$

  - Note that the mean relative speed is greater than the mean speed. Therefore the volume swept out between collisions is smaller by the factor $\sqrt{2}$

$$\sigma \lambda = \frac{V}{\sqrt{2} N}$$

  or

$$\lambda = \frac{V}{\sqrt{2} N \sigma}$$

- But $V/N = k_B T/P$ and

$$\lambda = \frac{k_B T}{\sqrt{2} P \sigma}$$

  - λ gets smaller as the density or pressure of the gas increases.
  - λ gets larger as the density or pressure of the gas decreases.
- Returning to our consideration of gas escaping through a hole, if λ is larger than the characteristic diameter, then the gas will escape through the hole without hitting another molecule.
- If the diameter of the hole is D then the Knudsen number, Kn is the ratio λ/D
  - If $Kn >> 1$, then the molecules will pass through the hole without colliding with each other. This process is known as effusion.
- The rate at which molecules leave the container is:

$$-\frac{dN}{dt} = A J_x = \frac{\pi D^2}{4} \frac{P}{(2 \pi m k_B T)^{1/2}}$$

  - Thus the rate of effusion permits the experimental determination of vapour pressure.