Particles in Motion

Velocities and Speeds of Particles

The Maxwell-Boltzmann Distribution

- Consider a Cartesian system with orthogonal axes (x,y,z)
- $N(v_x)dv_x$ = number of particles having a velocity component along the x axis between v_x and v_x+dv_x
- N = Total Number of particles
- m = mass of the particle
- Then: $$\frac{N(v_x)dv_x}{N} = \sqrt{\frac{m}{2\pi kT}}e^{\frac{-1/2mv_x^2}{kT}}dv_x$$

Continuing

Let
$$\alpha = \sqrt{\frac{2kT}{m}}$$

Then
$$\frac{N(v_x)dv_x}{N} = \sqrt{\frac{1}{\pi}} e^{\frac{-v_x^2}{\alpha^2}} \frac{dv_x}{\alpha}$$

This is just a gaussian.

Gaussians

- Generally a gaussian is

$$y = Ae^{-ax^2}$$

- The center is at x = 0 and the amplitude is A
  - To move the center: $-a(x-x_0)^2$

$$\frac{A}{2} = Ae^{-ax^2}$$

$$\sqrt{\frac{\ln(0.5)}{-a}} = x$$

- FWHM: y = A/2 (but remember to double!)

$$FWHM = 2\sqrt{\frac{\ln(0.5)}{-a}} = \frac{1.665}{\sqrt{a}}$$

- This is the Formal Gaussian Probability Distribution where σ is the standard deviation

$$p(y) = \frac{1}{\sigma\sqrt{2\pi}} e^{\frac{-(y-a)^2}{2\sigma^2}}$$

Continuing some more

The y,z contributions are

$$\frac{N(v_y)dv_y}{N} = \sqrt{\frac{1}{\pi}} e^{\frac{-v_y^2}{\alpha^2}} \frac{dv_y}{\alpha}$$

$$\frac{N(v_z)dv_z}{N} = \sqrt{\frac{1}{\pi}} e^{\frac{-v_z^2}{\alpha^2}} \frac{dv_z}{\alpha}$$

The fraction with components along the respective axes v_x+dv_x, v_y+dv_y, v_z+dv_z

$$\frac{N(v_x)dv_x}{N}\frac{N(v_y)dv_y}{N}\frac{N(v_z)dv_z}{N} = \frac{1}{\pi^{3/2}} e^{-\left[\frac{v_x^2}{\alpha^2}+\frac{v_y^2}{\alpha^2}+\frac{v_z^2}{\alpha^2}\right]} \frac{dv_x dv_y dv_z}{\alpha^3}$$

Summation and Normalization

Probability Distributions Integrate to 1

$$\int_{-\infty}^{\infty} N(v_i)dv_i = N_i$$

Or

$$\int_{-\infty}^{\infty} \frac{N(v_x)}{N}\frac{N(v_y)}{N}\frac{N(v_z)}{N}dv_x dv_y dv_z = 1$$

The normalization on the gaussians is α

Now consider the speeds of the particles:

==> $v^2 = v_x^2 + v_y^2 + v_z^2$

Let us go to a spherical coordinate system:

==> $dv_x dv_y dv_z \rightarrow 4\pi v^2 dv$

The Speed Distribution

$$\frac{N(v_x)dv_x}{N}\frac{N(v_y)dv_y}{N}\frac{N(v_z)dv_z}{N}=\frac{1}{\pi^{3/2}}e^{-\left[\frac{v_x^2}{\alpha^2}+\frac{v_y^2}{\alpha^2}+\frac{v_z^2}{\alpha^2}\right]}\frac{dv_x dv_y dv_z}{\alpha^3}$$

$$\frac{N(v)dv}{N}=\frac{1}{\pi^{3/2}}e^{-\left[\frac{v^2}{\alpha^2}\right]}\frac{4\pi v^2}{\alpha^3}dv$$

Note that α is just the most probable speed

$$\alpha=\sqrt{\frac{2kT}{m}}$$

$$\frac{N(v)dv}{N}=\left(\frac{m}{2\pi kT}\right)^{3/2}e^{-\left[\frac{mv^2}{2kT}\right]}4\pi v^2 dv$$

NB: Velocities are normally distributed but the speeds are not!

Gas Pressure

Another way to do it!

- Pressure ≡ rate of momentum transfer normal to surface
- Consider a 3[d] orthogonal axis system
  - If the particles are confined to move along axes, then 1/6 are moving along any one axis at a single time (on the average)
  - Let the *speed* be v
  - The number crossing a unit area per second on any axis is: $N_{x+} = 1/6\ N_v$ and $N_{x-} = 1/6\ N_v$.
  - Therefore the total number of crossings is $1/3\ N_v$

Gas Pressure II

Now use the Maxwell Boltzman Distribution

- Pressure = "N * mv"
- Therefore $P_x = 1/3\ mv^2N$
- Go to a Maxwellian speed distribution:

$$P = \frac{1}{3} m \int_0^\infty N(v) v^2 dv$$

$$\int_0^\infty N(v) v^2 dv = \frac{4}{\alpha^3 \sqrt{\pi}} N \int_0^\infty e^{\frac{-v^2}{\alpha^2}} v^4 dv$$

$$= \frac{4}{\alpha^3 \sqrt{\pi}} N \frac{3}{8} \sqrt{\pi} \alpha^5$$

$$= \frac{3}{2} \alpha^2 N$$

$$P = \frac{1}{2} m \alpha^2 N$$

$$P = NkT$$

$$\therefore$$

$$kT = \frac{1}{2} m \alpha^2$$

$$\alpha = \sqrt{\frac{2kT}{m}}$$

One can either invoke the Perfect Gas Law or one can derive the Perfect Gas Law!