5.62 Physical Chemistry II
Spring 2008

Kinetic Theory of Gases:
Maxwell-Boltzmann Distribution

"Collision Theory" was invented by Maxwell (1831 - 1879) and Boltzmann (1844 - 1906) in the mid to late 19th century. Viciously attacked until ~1900-1910, when Einstein and others showed (1910) that it explained many new experiments. It is key to describing collisions in dilute gases which kinetic theory relates to transport properties such as diffusion and viscosity. Collision Theory provides an alternative to standard Statistical Mechanics for the computation of thermodynamic quantities.

In Statistical Mechanics, we make simplifying assumptions about energy levels, degeneracies, and inter-particle interactions in order to compute Q(N,V,T).

In Collision Theory, we start with the Maxwell-Boltzmann velocity distribution for a gas, then compute everything from Newton's Laws. *Stoss-zahl ansatz*: each collision is independent of previous events. Get a classical mechanical picture for the properties of gases:

* pressure
* transport (mean free path, thermal conductivity, diffusion, viscosity, electrical conductivity)
* reactions.

We begin with the usual independent, distinguishable particle kinetic energy distribution function.

Maxwell-Boltzmann Distribution Function

For a single free particle the distribution of energy is proportional to the kinetic energy. Thus:

$$F(\vec{v}) \propto e^{-\frac{mv^2}{2kT}} = e^{-\frac{m}{2kT}\left(v_x^2+v_y^2+v_z^2\right)}.$$

The velocity is a three dimensional vector with components along the Cartesian coordinates: $\vec{v} = (v_x, v_y, v_z)$. The values of the three velocity components are uncorrelated and each velocity component takes on values between $-\infty$ to $+\infty$. $F(\vec{v})$ is the probability density for finding that a gas molecule has a velocity in the range $\vec{v}$ to $\vec{v}+d\vec{v}$; here $d\vec{v} = dv_x dv_y dv_z$. This probability distribution must be properly normalized.

$$\int_{-\infty}^{+\infty} F(\vec{v})d\vec{v} = 1 = C^{-1}\left(\int_{-\infty}^{+\infty} e^{-\frac{mv_x^2}{2kT}}dv_x\right)\left(\int_{-\infty}^{+\infty} e^{-\frac{mv_y^2}{2kT}}dv_y\right)\left(\int_{-\infty}^{+\infty} e^{-\frac{mv_z^2}{2kT}}dv_z\right)$$

where C is the normalization constant. This involves three Gaussian integrals of the form:

$$\int_0^{\infty} e^{-\alpha x^2}dx = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}}$$

We find the normalization constant to be $C = \left(\frac{2\pi kT}{m}\right)^{\frac{3}{2}}$. <u>The normalized Maxwell Boltzmann distribution for molecular velocities is</u>:

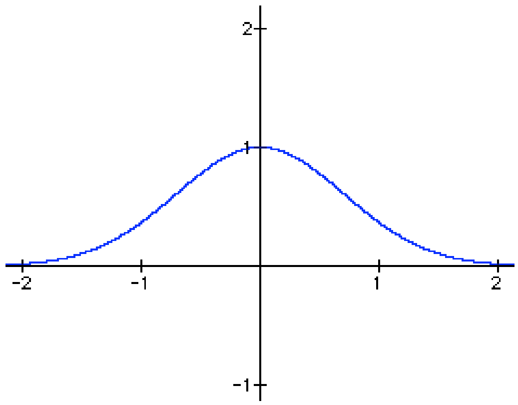
$$F(\vec{v})\,d\vec{v} = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2kT}}dv_x dv_y dv_z \quad .$$

This is a three dimensional probability density. Since the gas dynamics is isotropic (no favored direction) we should expect, and indeed find, that this three dimensional distribution is the product of independent probability distributions in the three Cartesian directions:

$$F(\vec{v})d\vec{v} = f(v_x)dv_x f(v_y)dv_y f(v_z)dv_z$$

where the normalized one-dimensional distributions are of the form:

$$f(u)=\left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mu^2/2kT}$$



In the above formula u denotes one of the velocity components.

Note well: the MB distribution is strongly peaked around u = 0. The width of the distribution is related to the square root of the temperature.

Full Width at Half Maximum (FWHM) of f(u)

$$\text{FWHM} \equiv 2u_{1/2}$$

$$\frac{1}{2} \equiv \frac{f(u_{1/2})}{f(0)} = e^{-mu_{1/2}^2/2kT}$$

$$u_{1/2} = \left[\frac{2kT\ln 2}{m}\right]^{1/2} \propto T^{1/2}$$

Distribution of molecular speed. The speed (a quantity distinct from u) of a molecule in the gas is the magnitude of the velocity vector:

$$v = |\vec{v}| = \sqrt{v_x^2 + v_y^2 + v_z^2}\ .$$

We can obtain an expression for the probability distribution of the speed by transforming the 3-D distribution into a distribution of the magnitude of the velocity vector (averaged over direction). This is accomplished by use of spherical coordinates for the velocity vector:

$$v_x = v\sin\theta\cos\phi,\ \ v_y = v\sin\theta\sin\phi,\ \ v_z = v\cos\theta\ .$$

In spherical coordinates the 3-D differential volume element is:

$$d\vec{v} = v^2 dv \sin\theta d\theta d\phi\ .$$

Thus we have:

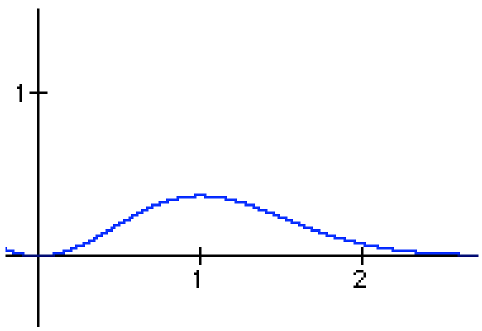
$$F(\vec{v})d\vec{v} = F(v,\theta,\phi)v^2 dv \sin\theta d\theta d\phi = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2kT}} v^2 \; dv\sin\theta d\theta d\phi$$

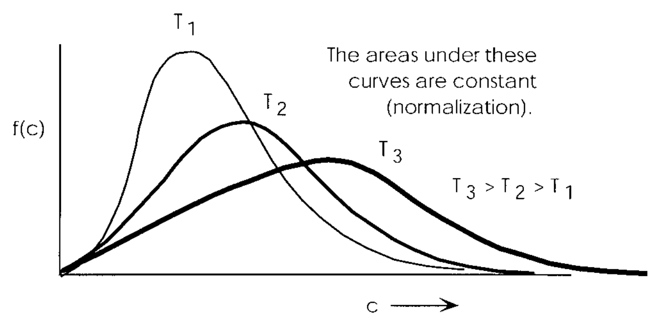
The ranges of the variables are: $0 < v < \infty, \;\; 0 < \theta < \pi, \;\; 0 < \phi < 2\pi$.

The distribution of the speed is found by integrating over angles. The result is:

$$h(v)dv = 4\pi\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2kT}} v^2 \; dv \;\; .$$

The speed distribution is drawn below. We also give a sketch of how the distribution shifts – it broadens and moves to higher speeds - as the temperature increases.





We shall determine several characteristics of the speed distribution

1 The most probable speed: The most probable speed $\hat{v}$ is the speed which has the maximum likelihood. This speed is determined from the condition $h'(\hat{v}) = 0$.

$$\hat{v} = \left(\frac{2kT}{m}\right)^{\frac{1}{2}}$$

2 The average speed: The average speed $\bar{v}$ is determined from the formula:

$$\bar{v} = \int_0^\infty v h(v) dv = \left(\frac{8kT}{\pi m}\right)^{1/2}$$

3 <u>The Root Mean Square (rms) speed</u>: This quantity is determined from the formula:

$$\left(\overline{v^2}\right)^{\frac{1}{2}} = \left[\int_0^\infty v^2 h(v)dv\right]^{\frac{1}{2}} = \left(\frac{3kT}{m}\right)^{\frac{1}{2}}$$

Note : $\overline{\varepsilon} = \frac{1}{2}m\overline{v^2} \neq \frac{1}{2}m\left(\overline{v}\right)^2$ and since $\overline{v^2} \propto \frac{3kT}{m}$ we have $\overline{\varepsilon} \propto \frac{3}{2}kT$.

$\hat{v}$	$4.07(T/m)^{1/2}$m/s
$\overline{v}$	$4.59(T/m)^{1/2}$m/s
$\left[\overline{v^2}\right]^{1/2}$	$4.98(T/m)^{1/2}$m/s

@ 300K

species	m	$\overline{v}$
N_2	28	4.8×10^2m/s **= 5 × 10⁴ cm/s**
H_2	2	1.8×10^3m/s
Hg	201	1.8×10^2m/s

} only a factor of 10 for a factor of 100 in mass

How is velocity distribution measured?

shutter, Time-of-Flight (TOF) distribution
rotating sectors

effusive molecular beam
supersonic jet (skimmed)