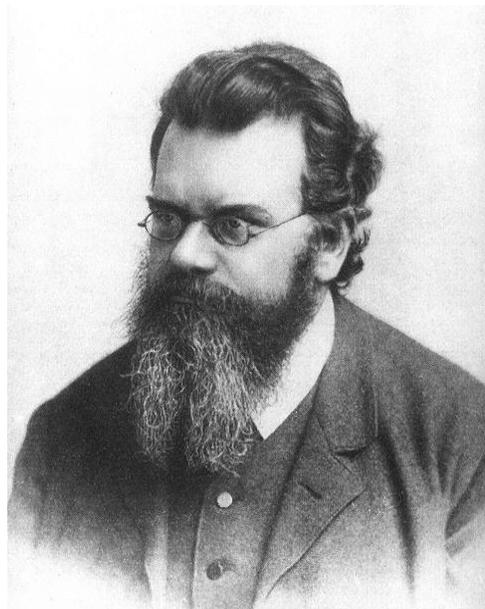# Boltzmann's Statistical Mechanics

- Please work through the exercises and simulated lab activities at
http://aspire.cosmic-ray.org/labs/gas_particles/

Ludwig Boltzmann (1844-1906) proposed that the
macroscopic properties of a gas or fluid can be deduced from
the statistical behavior of random motion.   In particular, the
(infamous) gas laws,

  (1) Boyle's Law (1622): at constant temperature, the
      product of an ideal gas's pressure and volume is
      always constant;
  (2) Charles' Law (1787): for an ideal gas at constant
      pressure, the volume is proportional to the absolute
      temperature (in kelvins),
  (3) Gay-Lussac's Law (1809): the pressure exerted on a
      container's sides by an ideal gas is proportional to the
      absolute temperature of the gas,

can all be explained in terms of random motion of gas molecules. These three laws can be combined
into a single equation, usually referred to as the Ideal Gas Law:

$$PV = nRT = n\left(N_A \frac{R}{N_A}\right)T = (nN_A)\left(\frac{R}{N_A}\right)T \equiv NkT$$

Where P V, and T are the pressure, volume, and absolute temperature of a gas in a closed container, n is
the number of moles (one mole = N_A or Avogadro's number = 6.02×10^{23}) of molecules in the container,
and R is the (measured) Universal Gas Constant (R=8.31 J/K).   Alternatively, the right hand side of the
equation can be written in terms of the total number of molecules $N=nN_A$, and a redefined/rescaled gas
constant, $k \equiv R/N_A$=1.38×10^{-23} J/K, also known as the Boltzmann Constant.

You see the triple bar equal sign, which is used to indicate either an identity (an equation that is true for
all values of one or more variables contained therein), or a definition.   I have used it here to define the
Boltzmann Constant. Experimentalists think of R as the more basic quantity since it is measured directly,
whereas theorists prefer k as the more fundamental (i.e. per molecule) quantity. Textbooks beyond the
Elementary (College) level Physics or Chemistry nearly always use k rather than R. This whole subject of
using statistical analysis of random systems to infer macroscopically measureable quantities (such as
pressure) is known as *Statistical Mechanics*.

Kinetic Theory of Ideal Gases in ONE dimension

A key postulate of Boltzmann's theory is that the heat (obviously related to the temperature) of a gas is
entirely found in the kinetic energy (i.e. energy associated with motion) of the gas molecules.   In

Newtonian mechanics (for objects moving at speeds much lower than the speed of light), the kinetic energy of a particle is given by

$$E = \frac{mv^2}{2},$$

where *m* is the mass of a particle and *v* its speed. A key result of Boltzmann's statistical mechanics is that on average (over many particles and over times), every *degree of freedom* in a system at (absolute) temperature T that has a squared term in the energy contains an amount of energy equal to

$$E = \frac{kT}{2}.$$

We now imagine a cubic box of side *L* containing *N* particles that are all moving along only the *x* direction. Motion along the *x* direction in each particle constitutes one degree of freedom, so that on average the particles have speed (in the ±x direction) given by

$$\frac{mv^2}{2} = \frac{kT}{2} \rightarrow v = \sqrt{\frac{kT}{m}}.$$

So far we have specified the volume *V*, the temperature *T*, and the number of particles *N* in the system. We are now in a position to calculate the pressure P on the two end faces.

What exactly is pressure anyway? BY definition, the pressure is the (averaged) force exerted by the particles on the wall. We assume the collisions between the particles on the wall to be perfectly elastic: that a particle hitting the wall with speed *v* leaves the wall with speed *v* in the opposite direction. So the change in the velocity $\vec{v}$ (which not only describes the speed. But also the direction) of the particle is

$$|\Delta\vec{v}| = 2v.$$

Why are we concerned with change in speed? It's because this is related to acceleration and acceleration is related to force. In the collision the particle exerts a force on the wall. By Newton's Third Law, the wall exerts an equal and opposite force on the particle, causing the change of velocity. Over long periods of time, many collisions occur, so that the effective time Δt over which the force acts on each particle is equal to the average time, τ, between collisions. The average acceleration of the particles is then

$$a = \frac{|\Delta\vec{v}|}{\Delta t} = \frac{2v}{\tau}.$$

And by Newton's Second Law: force = mass x acceleration (mass here is the one the force acts on):

$$F = ma = \frac{2mv}{\tau}.$$

The problem here then is to find the mean time τ, between collisions. To do this we imagine that the $N/2$ particles moving, say, to the right, are arranged along a straight line with equal spacing Δx. Then the time between collisions is just the time it takes for a particle to travel at the average speed $v=\sqrt{kT/m}$ through a distance $\Delta x = L/(N/2)$:

$$v\tau = \Delta x \rightarrow \tau = \frac{\Delta x}{v} = \frac{L/(N/2)}{v} = \frac{2L}{Nv} = \frac{2L}{N\sqrt{kT/m}} = \frac{2L\sqrt{m}}{N\sqrt{kT}}$$

We now substitute this expression back into the force, and dividing by area $A=L^2$ to get the pressure:

$$P = \frac{F}{A} = \frac{2mv}{\tau L^2} = \frac{2m\sqrt{kT}}{\sqrt{m}L^2} \div \frac{2L\sqrt{m}}{N\sqrt{kT}} = \frac{2\sqrt{mkT}}{L^2} \times \frac{N\sqrt{kT}}{2L\sqrt{m}} = \frac{NkT}{L^3}$$

Noting that L^3 is in fact the volume V of the box, we then have

$$PV = NkT$$