
PHAS1228/2011: Problem Set 3

- (1) The normalised probability density for the molecular speed in an ideal gas is

$$p(s) = (2/\pi)^{1/2} (m/kT)^{3/2} s^2 \exp(-ms^2/2kT),$$

where m is the molecular mass.

- (a) Sketch $p(s)$, marking the most probable, mean and root mean square speeds.
- (b) Sketch $p(s)$ at a given temperature for a large mass and a small mass.
- (c) Sketch $p(s)$ for a given mass at a large temperature and a small temperature.
- (d) Derive an equation for the most probable speed.

In Q2 and Q3, you will use the standard integral $I_n(a) = \int_0^\infty e^{-ax^2} x^n dx$. This integral takes the following values, where n is an even integer ($n > 0$):

$$I_0(a) = \sqrt{\frac{\pi}{a}},$$
$$I_n(a) = \frac{(n-1)!!}{2^{n/2} a^{n/2}} \sqrt{\frac{\pi}{a}},$$

where $(n-1)!! = (n-1) \times (n-3) \times \dots \times 5 \times 3 \times 1$.

- (2) (a) The probability density function for the x -component of the molecular velocity in an ideal gas is:

$$p(v_x) = ce^{-mv_x^2/2kT}.$$

- (a) Derive an expression for the factor c that normalises the distribution.
- (b) Derive an expression for the mean square velocity $\langle v_x^2 \rangle$.
- (c) Derive an expression for the mean kinetic energy associated with v_x .
- (d) Derive an expression for the mean kinetic energy of a molecule moving in 3 dimensions.

(3) For many systems the energy depends on a coordinate x in the following way:

$$E(x) = \frac{1}{2}Kx^2,$$

where $-\infty < x < \infty$ and K is a constant (this could represent Hooke's law, for example). According to the Boltzmann distribution:

$$p(x) = ce^{-E(x)/kT}$$

- (a) Determine the normalising factor c .
- (b) Show that the mean energy $\langle E(x) \rangle$ is equal to $\frac{1}{2}kT$.

Discussion:

Notice that when the energy depends quadratically on a coordinate e.g $E \propto v_x^2$ or $E \propto x^2$, the mean energy associated with that coordinate is always $\frac{1}{2}kT$. Thus:

- The mean energy associated with v_x or v_y or v_z is $\frac{1}{2}kT$ and therefore the mean kinetic energy of a gas molecule is $\frac{3}{2}kT$.
- The mean potential energy in a thermally excited Hooke's law system is $\frac{1}{2}kT$.

The fact that the mean energy for every quadratic energy term is $\frac{1}{2}kT$ is called *classical equipartition of energy*. It is a very powerful result that can be used to calculate the energies and specific heats of molecular systems (see forthcoming lectures). The reason that it is called 'classical' equipartition is that it is a result of classical mechanics, used in conjunction with the Boltzmann distribution. In the late 19th century and early 20th century classical equipartition was observed to break down in experiment. This directly led to the overthrow of some key principles of classical mechanics and the creation of quantum mechanics (see forthcoming lectures).