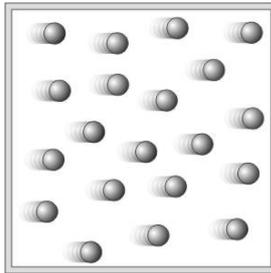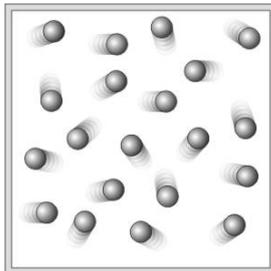# The Equipartition Theorem

The equipartition theorem states that energy is shared equally amongst all energetically accessible degrees of freedom of a system. This is not a particularly surprising result, and can be thought of as another way of saying that a system will generally try to maximise its entropy (i.e. how 'spread out' the energy is in the system) by distributing the available energy evenly amongst all the accessible modes of motion.

To give a rather contrived example, consider a container in which we have placed a number of ping-pong balls. Initially the balls are stationary. Imagine we now throw some energy randomly into our box, which will be shared out amongst the ping-pong balls in some way such that they begin to move about. While you might not realise it, intuitively you know what this motion will look like. For example, you would be very surprised if the particle motion looked like this:

You would probably predict something more like this:

i.e. completely random motion of the ping-pong balls. This is exactly the same result as predicted by the equipartition theorem – the energy is shared out evenly amongst the x, y, and z translational degrees of freedom.

The equipartition theorem can go further than simply predicting that the available energy will be shared evenly amongst the accessible modes of motion, and can make quantitative predictions about how much energy will appear in each degree of freedom. Specifically, it states that each quadratic degree of freedom will, on average, possess an energy $\frac{1}{2}kT$. A 'quadratic degree of freedom' is one for which the energy depends on the square of some property. Consider the kinetic and potential energies associated with translational, rotational and vibrational energy.

Translational degrees of freedom	$K = \frac{1}{2}mv^2$	
Rotational degrees of freedom	$K = \frac{1}{2}I\omega^2$	
Vibrational degrees of freedom	$K = \frac{1}{2}mv^2$	$V = \frac{1}{2}kx^2$

These three types of degrees of freedom all have a quadratic dependence on the velocity (or angular velocity in the case of rotation) and therefore all follow the equipartition theorem.   Note that when

considering vibration in a harmonic oscillator potential (V, above), we consider both the kinetic energy and the potential energy i.e the potential energy counts as an additional degree of freedom. Another point about vibrations is that vibrational motion in molecules is highly quantised, and at room temperature most molecules are in their ground vibrational state and higher levels are not thermally accessible. As a consequence, equipartition contributions from vibrational degrees of freedom need only usually be considered at very high temperatures. Conversely, at room temperature many rotational and translational states are occupied, and they can be treated classically (i.e. as if their energy levels were not quantised) to a very good approximation.

<u>A simple derivation of the equipartition result for translational motion</u>

We can use the Maxwell-Boltzmann distribution of molecular speeds to determine the average kinetic energy of a particle in a gas, and show that it agrees with the equipartition result.

The Maxwell-Boltzmann distribution of molecular speeds is:

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

The average kinetic energy of a particle in the gas is then

$$\langle K \rangle = \langle \tfrac{1}{2} mv^2 \rangle = \int_0^\infty \tfrac{1}{2} mv^2 \, f(v) \, dv$$

Substituting for f(v) and taking all constant terms outside the integral gives

$$\langle K \rangle = \tfrac{1}{2} m \, 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty v^4 \exp\left(\frac{-mv^2}{2kT}\right) dv$$

We can evaluate the integral by using the general result that

$$\int_0^\infty x^{2s} \exp(-ax^2) = \frac{(2s-1)!!}{2^{s+1} a^s} \left(\frac{\pi}{a}\right)^{1/2}$$

where n!! indicates a double factorial, n(n-2)(n-4)... etc. Identifying x = v and a = m/2kT in our integral above gives

$$\int_0^\infty v^4 \exp\left(\frac{-mv^2}{2kT}\right) dv = \frac{3!!}{8(m/2kT)^2}\left(\frac{2\pi kT}{m}\right)^{1/2} = \frac{3}{2}\left(\frac{kT}{m}\right)^2\left(\frac{2\pi kT}{m}\right)^{1/2}$$

Substituting back into our expression for < K > gives

$$\langle K \rangle = \tfrac{1}{2} m \, 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \frac{3}{2}\left(\frac{kT}{m}\right)^2\left(\frac{2\pi kT}{m}\right)^{1/2} = \frac{3}{2} kT$$

The average translational kinetic energy of a particle in a gas is therefore $\tfrac{3}{2}kT$, or $\tfrac{1}{2}kT$ per translational degree of freedom, in agreement with the equipartition theorem.

<u>A more general derivation of the equipartition theorem</u>

A general derivation of the equipartition theorem requires statistical mechanics, which is covered in the second year of the M.Chem. course. I will try and provide enough explanation here so that those of you in the first year can also follow what's going on.

The partition function in statistical mechanics tells us the number of quantum states of a system that are thermally accessible at a given temperature. It is defined as:

$$q = \sum_i \exp(-E_i/kT)$$

where E_i are the energies of the quantum states i.

Once we know the partition function, we can calculate many of the macroscopic properties of our system using standard equations from statistical mechanics. Of particular relevance here, in deriving the equipartition theorem we will use the partition function to calculate the internal energy U associated with a single degree of freedom of the system. Before we do this though, we need to consider the difference between a quantum and a classical system.

If we are treating the particle motions classically (which we should do if we're expecting to derive the classical equipartition theorem), then it doesn't make much sense to express the partition function as a sum of discrete terms as we have above. Classically, the position and momentum of a particle can vary continuously, and the 'energy levels' are also continuous. As a result, the classical partition function takes the form of an integral rather than a sum.

$$q = \int \exp\left(\frac{-E(x_1,x_2...,p_1,p_2...)}{kT}\right) dx_1 \, dx_2... \, dp_1 \, dp_2...$$

where the energy E can be a function of the particle positions x_i and momenta p_i.

If we assume that we can write the energy as a sum of contributions from each degree of freedom, then the exponential functional dependence on the energy means that we can separate the integral into the product of integrals over each degree of freedom. i.e.

$$E(x_1,x_2,...p_1,p_2...) = E(x_1) + E(x_2) + ... + E(p_1) + E(p_2) + ...$$

so
$$\exp\left(\frac{-E(x_1,x_2,...p_1,p_2...)}{kT}\right) = \exp\left(\frac{-E(x_1) - E(x_2) - ... - E(p_1) - E(p_2) ...}{kT}\right)$$
$$= \exp\left(\frac{-E(x_1)}{kT}\right) \exp\left(\frac{-E(x_2)}{kT}\right) ... \exp\left(\frac{-E(p_1)}{kT}\right) \exp\left(\frac{-E(p_2)}{kT}\right) ...$$

and the integral may be written

$$q = \int \exp\left(\frac{-E(x_1)}{kT}\right) dx_1 \int \exp\left(\frac{-E(x_2)}{kT}\right) dx_2 ... \int \exp\left(\frac{-E(p_1)}{kT}\right) dp_1 \int \exp\left(\frac{-E(p_2)}{kT}\right) dp_2 ...$$

$$= q(x_1) \, q(x_2) ... q(p_1) \, q(p_2) ...$$

The consequence of this is that we have separated the partition function into the product of partition functions for each degree of freedom.   In general, we may write the partition function for a single degree of freedom in which the energy depends quadratically on the coordinate x (i.e. $E(x) = cx^2$ with c a constant) as

$$q(x) = \int_{-\infty}^{\infty} \exp\left(\frac{-E(x)}{kT}\right) dx = \int_{-\infty}^{\infty} \exp\left(\frac{-cx^2}{kT}\right) dx = \left(\frac{\pi\, kT}{c}\right)^{1/2}$$

where we have used the standard integral $\int_{-\infty}^{\infty} \exp(-ax^2)\, dx = \left(\frac{\pi}{a}\right)^{1/2}$

Once we know the partition function, we can calculate the internal energy of the system according to the standard result from statistical mechanics:

$$U = kT^2 \frac{d(\ln q)}{dT}$$

Substituting in our partition function, the internal energy associated with one degree of freedom is therefore

$$U = kT^2 \frac{d}{dT} \ln\left(\frac{\pi kT}{c}\right)^{1/2}$$

$$= \frac{1}{2} kT^2 \frac{d}{dT} \ln\left(\frac{\pi kT}{c}\right) \qquad \text{(since } \ln x^n = n \ln x\text{)}$$

$$= \frac{kT^2}{2} \frac{c}{\pi kT} \frac{\pi k}{c} \qquad \text{(since } \frac{d\ln y}{dx} = \frac{1}{y}\frac{dy}{dx} \text{)}$$

$$= \frac{1}{2} kT$$

The energy associated with each quadratic degree of freedom is therefore $\tfrac{1}{2}kT$, and we have proved the equipartition theorem.