

# The Physical Basis Of Chemistry

## Classical Mechanics

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This course introduces the physical principles you will need to describe the translational, rotational, and vibrational motion of molecules. We will then use these concepts to describe the molecular properties of gases.

### List of Lectures

1. **Translational Motion I.** Newton's laws of motion, collisions and momentum.
2. **Translational Motion II.** Work and energy.
3. **Rotational Motion.** Angular momentum and moments of inertia.
4. **Vibrational Motion.** Simple harmonic motion.
5. **Ideal & Real Gases.**
6. **The Kinetic Theory of Gases & Classical Equipartition.**
7. **The Distribution of Molecular Speeds.**
8. **Applications of Kinetic Theory.** Diffusion, Viscosity & Thermal Conductivity.

### Recommended Textbooks

**Foundations of Physics for Chemists.** Ritchie & Sivia. Oxford Chemistry Primer.

**Elements of Physical Chemistry.** Atkins & de Paula.

### Online Material

Handouts, slides, and problem sets can be found at [wallace.chem.ox.ac.uk](http://wallace.chem.ox.ac.uk)

## Translational Motion I

### Equations of Motion

The motion of a particle is defined by its position, velocity, and acceleration.

Position /m                     $r(t)$

Velocity /ms<sup>-1</sup>               $v(t) = \frac{dr}{dt} \equiv \dot{r}$

Acceleration /ms<sup>-2</sup>           $a(t) = \frac{dv}{dt} = \frac{d^2r}{dt^2} \equiv \ddot{r}$

### An Example: Calculating Acceleration

We can calculate the acceleration of a particle from its time dependent position. Let's choose an arbitrary function describing particle motion:

$$r(t) = At^3 \quad v(t) = \frac{dr}{dt} = 3At^2 \quad a(t) = \frac{dv}{dt} = 6At$$

### An Example: Calculating Position

We can do the previous example in reverse, and calculate the position of a particle given its time dependent acceleration. If  $a(t)=6At$ ,  $v(t)$  is obtained by integration.

Let's set  $r=0$  at  $t=0$  and  $v=0$  at  $t=0$ .

$$v(t) = \int_0^t a(t) dt = \int_0^t 6At dt = 3At^2$$

Integrating again gets us back to the position:

$$r(t) = \int_0^t v(t) dt = \int_0^t 3At^2 dt = At^3$$

### Equation of Motion For Constant Acceleration

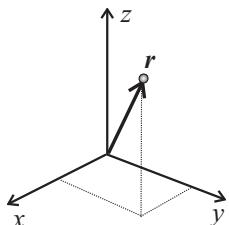
For constant acceleration ( $a(t)=a$ ) we can integrate as we did above to show that the particle's position is described by

$$r(t) = r_0 + v_0 t + \frac{1}{2} a t^2$$

where  $r_0$  and  $v_0$  describe the initial position and velocity of the particle.

### Equations of Motion in Three Dimensions

We need to be able to describe particles that move in more than one dimension



Motion in each **orthogonal direction** can be decomposed into a separate set of equations. This is often a useful tool for breaking down a problem into more manageable parts. We can also combine these equations by describing the motion as a **vector**.

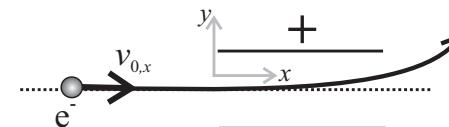
$$\vec{a}(t) = \vec{a}_0$$

$$\vec{v}(t) = \vec{v}_0 + \vec{a}_0 t$$

$$\vec{r}(t) = \vec{r}_0 + \vec{v}_0 t + \frac{1}{2} \vec{a}_0 t^2$$

### An Example: The Cathode Ray Tube

Electrons, initially travelling at  $2.4 \times 10^6 \text{ ms}^{-1}$  in the horizontal direction, enter a region between two horizontal charged plates of length 2 cm where they experience an acceleration of  $4 \times 10^{14} \text{ ms}^{-2}$  vertically upwards. Find (a) the vertical position as they leave the region between the plates, and (b) the angle at which they emerge from between the plates.



For motion along the  $x$  co-ordinate,

$$a_x = 0$$

$$v_x = v_{0x} = 2.4 \times 10^6 \text{ m s}^{-1}$$

$$r_x = r_{0x} + v_{0x} t \quad (r_{0x} = 0)$$

$$r_x = 2.4 \times 10^6 t = 0.02 \text{ m}$$

$$\therefore t = 8.33 \times 10^{-9} \text{ s}$$

For motion along the  $y$  co-ordinate,

$$a_y = 4 \times 10^{14} \text{ m s}^{-2}$$

$$v_y = v_{0y} + a_y t \quad (v_{0y} = 0)$$

$$r_y = r_{0y} + \frac{1}{2} a_y t^2 \quad (r_{0y} = 0)$$

Substitute for the time the electron spends between the plates,

$$r_y = \frac{1}{2} a_y t^2 = 0.0139 \text{ m}$$

For the angle at which the electrons depart,

$$\tan \theta = \frac{v_y}{v_x} = \frac{a_y t}{v_{0x}} \quad \theta = 54.2^\circ$$

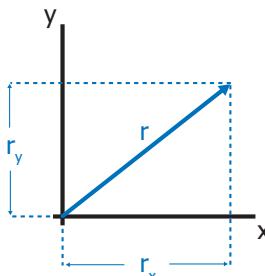
## Vectors

A vector is a quantity with both magnitude and direction. Vectors are covered in detail in your mathematics course. A brief guide to vectors is given here for reference.

As this course precedes the vectors material, where possible, the examples and questions in this lecture course will not require a full vectorial treatment.

### An Example: 2D Vectors

Consider a position vector  $\vec{r}$  with magnitude  $r$  and direction  $\theta$  with respect to the  $x$  axis. We can decompose this vector into two orthogonal components  $r_x$  and  $r_y$ .



#### Components

$$r_x = |r| \cos \theta \quad r_y = |r| \sin \theta$$

#### Magnitude

$$|r| = \sqrt{(r_x^2 + r_y^2)}$$

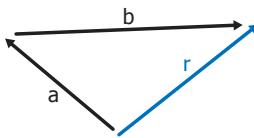
#### Direction

$$\tan \theta = \frac{r_y}{r_x}$$

The vector  $\vec{r}$  can be described as the sum of its two components,  $r_x$  and  $r_y$ , each multiplied by their respective unit vectors  $\hat{i}$  and  $\hat{j}$ . Unit vectors are vectors with a magnitude of 1 in their respective directions.

$$\vec{r} = r_x \hat{i} + r_y \hat{j}$$

## Vector Addition



## Vector Sum

$$\vec{r} = \vec{a} + \vec{b}$$

## Components

$$r_x = a_x + b_x \quad r_y = a_y + b_y$$

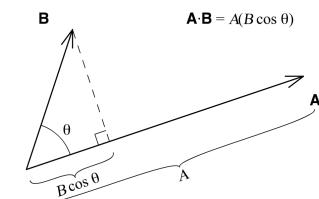
## Vector Multiplication

Multiplication of one vector by another is not uniquely defined, as when two vectors are multiplied we must deal with not only the magnitudes, but also the directions of the two vectors. Consider two vectors  $\vec{A}$  and  $\vec{B}$ .

### Scalar (Dot) Product

$$\vec{A} \cdot \vec{B} = |A||B| \cos \theta$$

The dot product is a **scalar**. It is the product of the magnitude of one vector ( $A$ ), and the magnitude of the projection of a second vector ( $B$ ) along the first.

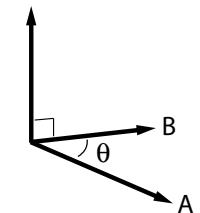


### Vector (Cross) Product

$$\vec{A} \times \vec{B} = \hat{n}|A||B| \sin \theta$$

The cross product is a vector quantity.  $\hat{n}$  is a unit vector perpendicular to the plane containing  $\vec{A}$  and  $\vec{B}$ .

$A \times B$



## Forces

A force is any influence which tends to change the motion of an object. Forces are inherently vector quantities.

### Types of Force

Fundamental Force	Relative Strength	Range	Comments
Strong	1	$10^{-15}$ m	Holds the nucleus together
Electromagnetic	$10^{-2}$	$\infty$	<b>Chemistry!</b>
Weak	$10^{-6}$	$10^{-17}$ m	Associated with radioactivity
Gravitational	$10^{-38}$	$\infty$	Causes apples to fall

For most problems in chemistry, we only need worry about electromagnetic forces.

### Gravitational Forces

The gravitational force between point or spherical masses,  $m_1$  and  $m_2$ , is

$$F = -\frac{Gm_1m_2}{r^2} \quad G = 6.67 \times 10^{-11} \text{ N m}^2 \text{ kg}^{-2}$$

The **weight** of an object is the net gravitational force acting on it. For objects close to the earth's surface:

$$F = mg \quad g = \frac{Gm_E}{R_e^2} \simeq 9.8 \text{ m s}^{-2}$$

where  $g$  is the acceleration due to gravity and  $r = R_e$ , the radius of the earth.

### Electrostatic Forces

In a vacuum, the **Coulomb force** between point or spherical charges,  $q_1$  and  $q_2$ , is

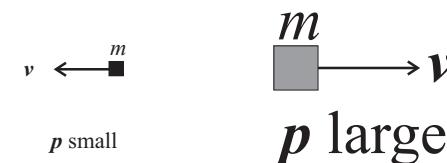
$$F = \frac{q_1q_2}{4\pi\epsilon_0 r^2} \quad \frac{1}{4\pi\epsilon_0} = 9.0 \times 10^9 \text{ N m}^2 \text{ C}^{-2}$$

Unlike gravity (which is always attractive), the Coulomb force can be either attractive or repulsive depending on the sign of the charges. Electrostatics will be covered in detail in your Electricity and Magnetism course.

## Linear Momentum

Linear Momentum,  $\vec{p}$  is the product of an object's mass times its velocity.

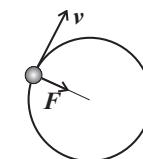
$$\vec{p} = m\vec{v}$$



## Newton's 1st Law

**An object in motion will remain in motion unless acted upon by a net force.**

This implies that changes in velocity (i.e. acceleration) arise from forces. Note that velocity is a **vector**, so a change in velocity could be a change in the **direction** of particle velocity, as well as its **magnitude**.



## Newton's 2nd Law

**A force acting on an object is proportional to its rate of change of momentum.**

Newton's second law describes the observation that the acceleration of an object depends directly upon the net force acting upon the object, and inversely upon the mass of the object. Newton's Second Law can be expressed in terms of the **linear momentum**:

$$\vec{F} = \frac{d\vec{p}}{dt}$$

We can rewrite Newton's second law in a more familiar form knowing that momentum,  $\mathbf{p}=m\mathbf{v}$  and for cases where the mass of our object does not change:

$$\vec{F} = \frac{d\vec{p}}{dt} = \frac{d(m\vec{v})}{dt} = m\frac{d\vec{v}}{dt} = m\vec{a}$$

$$\vec{F} = m\vec{a}$$

Force has units of **Newtons** ( $1 \text{ N} = 1 \text{ kg m s}^{-2}$ ). Force is a **vector** quantity, and can therefore be decomposed into orthogonal components. If more than one force acts on a particle, the **net force** determines the acceleration of the particle

$$\sum_i \vec{F}_i = m\vec{a}$$

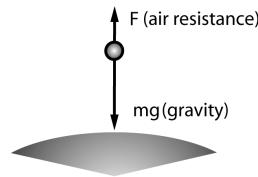
#### An Example: The Hydrogen Atom

The force of attraction between the electron and the proton in a hydrogen atom is  $8.2 \times 10^{-8} \text{ N}$ . The mass of the electron is  $9.109 \times 10^{-31} \text{ kg}$  and that of the proton is  $1.672 \times 10^{-27} \text{ kg}$ . Calculate the acceleration of each particle due to their mutual interaction assuming their initial velocity is zero. [ $9.0 \times 10^{22} \text{ ms}^{-2}$ ,  $4.9 \times 10^{19} \text{ ms}^{-2}$ ]

#### An Example: Skydiving!

Can we describe the motion of a skydiver using Newton's second law? If we know all the forces acting on an object, we can calculate the equations of motion describing the fall.

$$m\vec{a} = \sum_i \vec{F}_i = mg - F_{air}$$



Let us assume in this example that the retarding force due to air resistance can be described by  $F_{air}=kv$ , where  $k$  is a constant, and  $v$  is the velocity. We can use this to calculate the terminal velocity,  $v_T$  of the skydiver.

$$a = \frac{dv}{dt} = \frac{mg}{m} - \frac{kv}{m}$$

You will become very used to solving differential equations like this in your mathematics course. We can solve this separating the variables  $v$  and  $t$ , and integrating:

$$\int \frac{dv}{g - \frac{k}{m}v} = \int dt + C$$

$$-\frac{m}{k} \ln \left( g - \frac{k}{m}v \right) = t + C$$

Setting  $v=0$  when  $t=0$  and rearranging for  $v$  gives us

$$v = \frac{mg}{k} (1 - e^{-\frac{k}{m}t})$$

as  $t \rightarrow \infty$ ,  $v \rightarrow v_T$  so  $v_T = mg/k$ .

## Newton's 3rd Law

To every action there is an equal and opposite reaction.

$$F_{AB} = -F_{BA}$$

Newton's third law describes the phenomenon that if a force is exerted by one object on another, there is an equal and opposite force acting on the first object.

### An Example: More Skydiving!

Ignoring air resistance, calculate the change in position of the earth just before impact when an unlucky skydiver falls from a position 1 km above the surface of the earth.

Using NIII and then NII:

$$F_{AE} = -F_{EA}$$

$$m_A a_A = -m_E a_E$$

$$a_E = g \frac{m_A}{m_E}$$

$$a_E = 1.07 \times 10^{-22} \text{ ms}^{-2}$$

So how long until the skydiver hits?

$$r = r_0 + v_0 t + \frac{1}{2} a t^2$$

$$0 = 1000 + 0 - \frac{1}{2} g t^2$$

$$t = 14.3 \text{ s}$$

How far did the earth move in that time?

$$r = r_0 + v_0 t + \frac{1}{2} a t^2$$

$$r = 0 + 0 + \frac{1}{2} a_E t^2$$

$$r = 10^{-20} \text{ m}$$

Unsurprisingly, not very far!



## Conservation of Momentum

The total momentum of an isolated system of particles is constant.

Newton's laws embed the idea of conservation of linear momentum. In a closed system, momentum is always conserved. The principle of conservation of momentum can be stated in its most general form as:

$$\vec{P} = \sum_i \vec{p}_i = \vec{p}_1 + \vec{p}_2 + \vec{p}_3 + \dots = \text{constant}$$

### An Example: Inelastic Collisions

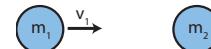
In an **inelastic collision**, momentum is conserved, but kinetic energy is not. (We will deal with kinetic energy in the next section).

For example, consider a particle of mass  $m$  travelling at a velocity  $v$  that hits a stationary particle of the same mass and sticks to it. What is the final velocity  $v_f$  of the two particles after they collide?

Momentum before collision?

$$\sum_i p_i = m_1 v_1 + m_2 v_2 = mv + 0 = mv$$

Momentum after collision?



$$\sum_i p_i = (m_1 + m_2) v_f = 2mv_f$$

Applying conservation of momentum



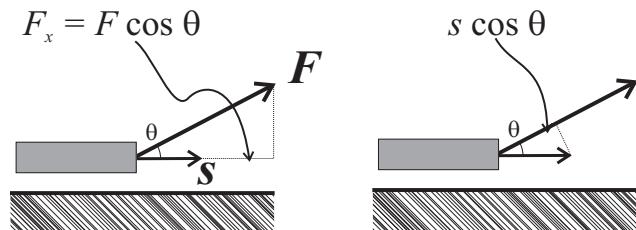
$$mv = 2mv_f$$

$$\text{Hence } v_f = v/2.$$

## Translational Motion II

### Work

The concept of mechanical work provides the link between **force** and **energy**. Work is done on an object when a force acts on it in the direction of motion.



The mechanical work,  $W$ , done by a constant force,  $F$ , is simply the force times the total displacement,  $s$ , in the direction of the force. This is most generally described using vector notation as a scalar product.

$$W = \vec{F} \cdot \vec{s}$$

Notice that the resultant work done is a **scalar** quantity not a vector. Also notice that if there is no displacement in the direction of the force, no work is done. Conversely, if the displacement is **in** the direction of the force the work done is simply  $W=Fs$ .

The work done can also be written as

$$W = |F||s| \cos \theta$$

where  $|F|$  and  $|s|$  are the magnitudes of the Force and displacement, and  $\theta$  is the angle between the two vectors. Again, notice that **work done is a scalar**.

For the above definitions, we have assumed the force applied is constant. If the force is not constant we need to extend our definition of work. The work done by a force acting on an object moving in a fixed direction is

$$W = \int_{x_1}^{x_2} F_x dx$$

where  $dx$  is the infinitesimal displacement along  $x$ .

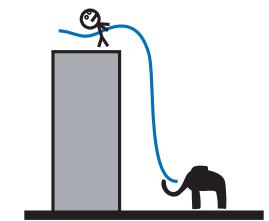
If the movement is not in a constant direction, again we need to extend our mathematical description to integrate over the path taken during the motion.

$$W = \int_C \vec{F} \cdot d\vec{s}$$

Here  $C$  describes the path taken during the motion. We also need to include the scalar product as now we must treat both force and displacement as vectors. **We will not deal with path integrals in this lecture course.**

### An Example: Lifting Elephants

Your lecturer decides to haul an Asian Bull Elephant to the roof of the Chemistry Research Laboratory, using a steel cable weighing 500 g per metre. Assuming the CRL is 100 m high, and that the average weight of an Asian Bull Elephant is 2300 kg, calculate the work done.



Dealing with the elephant first:

$$W = F s = (mg)s = 2300 \times 9.8 \times 100 = 2.25 \times 10^6 \text{ J}$$

Now the cable:

$$W = \int_0^{100} F ds = \int_0^{100} (mg)s ds = 0.5 \times 9.8 \left[ \frac{s^2}{2} \right]_0^{100} = 2.45 \times 10^4 \text{ J}$$

So in total:

$$W = 2.28 \times 10^6 \text{ J}$$

## Kinetic Energy

The kinetic energy,  $K$ , of a particle is the energy a particle possesses by virtue of its motion. For a particle of mass  $m$  moving along  $x$  with velocity  $v_x$

$$K = \frac{1}{2}mv_x^2$$

Returning to the equation for the work done on a particle

$$W = \int F_x dx$$

We can use Newton's 2nd Law to rewrite

$$F_x dx = ma_x dx = m \frac{dv_x}{dt} dx = mv_x dv_x$$

which gives

$$W = \int_{v_1}^{v_2} mv_x dv_x = \frac{1}{2}m(v_2^2 - v_1^2)$$

The work done on the particle is equal to its change in kinetic energy.

$$W = \Delta K$$

## An Example: The Cathode Ray Tube

An electron accelerated in a TV tube reaches the screen with a kinetic energy of 10000 eV. Find the velocity of the electron.

We must first convert from eV into Joules.

$$K = 10^4 \text{ eV} = 10^4 \times 1.6 \times 10^{-19} \text{ J} = 1.6 \times 10^{-15} \text{ J}$$

Before calculating the velocity

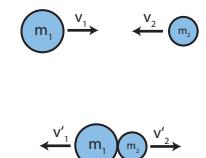
$$v = \sqrt{\frac{2K}{m}} = \sqrt{\frac{2 \times 1.6 \times 10^{-15}}{9.109 \times 10^{-31}}} = 5.93 \times 10^7 \text{ ms}^{-1}$$

Pretty fast!

## An Example: Elastic Collisions

In an elastic collision, **kinetic energy is conserved**, along with total energy and momentum which are always conserved.

Consider the head-on collision between two atoms. Derive an expression for the final velocity of both particles in terms of their masses and initial velocities assuming the collision is elastic.



First let's set up what we know about the system.

Initial momentum of system:

$$p_i = m_1 v_{i1} + m_2 v_{i2}$$

Final momentum of the system:

$$p_f = m_1 v_{f1} + m_2 v_{f2}$$

Initial kinetic energy of system:

$$K_i = \frac{1}{2}m_1 v_{i1}^2 + \frac{1}{2}m_2 v_{i2}^2$$

Final kinetic energy of the system:

$$K_f = \frac{1}{2}m_1 v_{f1}^2 + \frac{1}{2}m_2 v_{f2}^2$$

Now let's apply conservation of momentum,

$$\begin{aligned} m_1 v_{i1} + m_2 v_{i2} &= m_1 v_{f1} + m_2 v_{f2} \\ m_1 (v_{i1} - v_{f1}) &= m_2 (v_{f2} - v_{i2}) \end{aligned} \quad -\bullet$$

and similarly, conservation of kinetic energy, as it is an elastic collision.

$$\begin{aligned} m_1 v_{i1}^2 + m_2 v_{i2}^2 &= m_1 v_{f1}^2 + m_2 v_{f2}^2 \\ m_1 (v_{i1}^2 - v_{f1}^2) &= m_2 (v_{f2}^2 - v_{i2}^2) \end{aligned} \quad -\bullet$$

We can solve these two simultaneous equations ( $\bullet$  and  $\bullet$ ) to determine the final velocities, however it may not be immediately obvious how to do so. One route is to note that  $a^2 - b^2 = (a+b)(a-b)$  and substitute into  $\bullet$ .

$$m_1(v_{i1} + v_{f1})(v_{i1} - v_{f1}) = m_2(v_{f2} + v_{i2})(v_{f2} - v_{i2}) \quad -\text{③}$$

③ / ① then gives us

$$v_{i1} + v_{f1} = v_{f2} + v_{i2} \quad -\text{④}$$

Thus the difference in initial velocities is equal to the difference in final velocities. We can then substitute this expression into ① or ② to retrieve the final velocities in terms of the initial conditions:

For example, take ④ and multiply by  $m_1$

$$m_1 v_{i1} + m_1 v_{f1} = m_1 v_{f2} + m_1 v_{i2}$$

Add this to ① giving

$$\begin{aligned} m_1 v_{i1} + m_1 v_{f1} + m_1 v_{i1} - m_1 v_{f1} &= m_1 v_{f2} + m_1 v_{i2} + m_2 v_{f2} - m_2 v_{i2} \\ 2m_1 v_{i1} &= (m_1 + m_2) v_{f2} + (m_1 - m_2) v_{i2} \end{aligned}$$

So our expression for the final velocity of particle 2 is

$$v_{f2} = \frac{2m_1}{m_1 + m_2} v_{i1} + \frac{m_2 - m_1}{m_1 + m_2} v_{i2}$$

The equivalent expression for particle 1 is straightforward to derive.

## Potential Energy

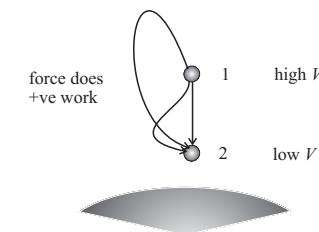
The potential energy,  $V$ , is the energy associated with the position of a particle. Potential energy may be thought of as stored energy, or the capacity to do work.

## The Link Between Force, Work and Potential Energy.

For some forces the work done by the force is **independent of the path** taken. Such forces are called **conservative forces** and include gravity and electrostatic forces.

Conservative forces can be represented by potential energy functions because they depend solely on position. For non-conservative forces, such as friction, the work done and the force depends on the path taken.

Consider gravity as an example of a conservative force:



The work done  $dW$  by the gravitational force  $F$  is independent of the path. In moving the particle from position 1 to 2 its capacity to do work (i.e. potential energy) is reduced. The fixed amount of work is therefore minus the change in potential energy:

$$dV = -dW$$

As we already know that  $W = \int F_x dx$ , we can combine these equations to yield

$$F = -\frac{dV}{dx}$$

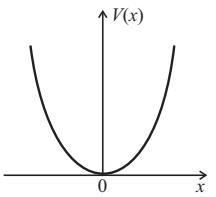
Therefore, the (finite) change in potential energy between points  $x_1$  and  $x_2$  is

$$V(x_2) - V(x_1) = \Delta V = - \int_1^2 F_x dx = -W$$

**An Example: The Harmonic Spring**

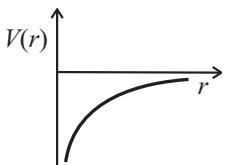
$$V(x) = \frac{1}{2}kx^2$$

$$F(x) = -\frac{dV}{dx} = -kx$$

**An Example: Gravitational Potential Energy**

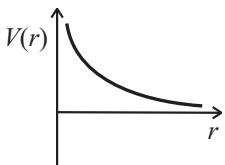
$$V(r) = -\frac{Gm_1m_2}{r}$$

$$F(r) = -\frac{dV}{dr} = -\frac{Gm_1m_2}{r^2}$$

**An Example: Electrostatic Potential Energy**

$$V(r) = \frac{q_1q_2}{4\pi\epsilon_0 r}$$

$$F(r) = -\frac{dV}{dr} = \frac{q_1q_2}{4\pi\epsilon_0 r^2}$$



(In this plot  $q_1$  and  $q_2$  have been given the same sign)

**Conservation of Energy**

**The total energy in a closed system of particles is constant.**

As we showed above, the work done by a force is related to changes in both the kinetic and potential energy. Note that again we focus exclusively on conservative forces.

$$W = \Delta K = -\Delta V$$

Rearranging  $\Delta K = -\Delta V$  yields  $\Delta K + \Delta V = 0$ . Therefore, the sum of these energies, called the total energy,  $E$ , must be constant:

$$E = K + V$$

**Frames of Reference**

Take the previous example of an elastic collision between two particles. In applying conservation of momentum we had to pick a frame of reference. We measured the velocity of  $m_1$  and  $m_2$  relative to a fixed reference. We can link velocity of an object in one frame of reference ( $v$ ) with motion in another ( $v'$ ) by simply subtracting the relative velocity between the two frames ( $v_{rel}$ ).

$$\vec{v}' = \vec{v} - \vec{v}_{rel}$$

Conservation of momentum can only be applied within a specific frame of reference. This concept is often useful for simplifying collisions; in particular in the **centre of mass frame of reference** the total momentum is zero.

## Centre of Mass

The centre of mass of a system is the point where the system responds as if it were a point with a mass equal to the sum of the masses of its constituent parts. In one-dimension for  $N$  particles in a system this is described by

$$Mx_{CM} = \sum_{i=1}^N m_i x_i \quad M = \sum_{i=1}^N m_i$$

where  $x_{CM}$  is the distance to the centre of mass,  $m_i$  is a particles mass and  $x_i$  is its position. For two particles (such as in a diatomic molecule) this simplifies to

$$(m_1 + m_2) x_{CM} = m_1 x_1 + m_2 x_2$$

### An Example: COM Frame in Collisions

Take the previous example of an elastic collision between two particles, we could've simplified our calculation by working in the centre of mass frame.



In the centre of mass frame, the velocity of the frame is zero, as is the total momentum. Let's denote the velocities in the new frame as  $v'$



Initial momentum of system:

$$0 = m_1 v'_{i1} + m_2 v'_{i2}$$

Final momentum of the system:

$$0 = m_1 v'_{f1} + m_2 v'_{f2}$$

Initial kinetic energy of system:

$$K_i = \frac{1}{2} m_1 v'^2_{i1} + \frac{1}{2} m_2 v'^2_{i2}$$

Final kinetic energy of the system:

$$K_f = \frac{1}{2} m_1 v'^2_{f1} + \frac{1}{2} m_2 v'^2_{f2}$$

Now it's much more straightforward to show

$$\begin{aligned} m_1 v'^2_{i1} + m_2 v'^2_{i2} &= m_1 v'^2_{f1} + m_2 v'^2_{f2} \\ m_1 v'^2_{i1} + m_2 \left( -\frac{m_1}{m_2} v_{i1} \right)^2 &= m_1 v'^2_{f1} + m_2 \left( -\frac{m_1}{m_2} v_{f1} \right)^2 \\ v'^2_{i1} \left( m_1 + \frac{m_1^2}{m_2} \right) &= v'^2_{f1} \left( m_1 + \frac{m_1^2}{m_2} \right) \\ v'^2_{i1} &= v'^2_{f1} \end{aligned}$$

This equation has two solutions. Either  $v'_{i1}=v'_{f1}$  which is pretty boring; nothing's happened. Or  $v'_{i1}=-v'_{f1}$  (and  $v'_{i2}=-v'_{f2}$ ) which tells us that after the collision the particles have reversed their velocities.

## Rotational Motion

### Motion in a Circle

The radian,  $\theta$  is defined by the equation,

$$\theta = \frac{s}{r}$$

and the angular velocity,  $\omega$  (units: rad s<sup>-1</sup>), by the equation

$$\omega = \frac{d\theta}{dt} \quad \left( \text{cf. } v = \frac{dr}{dt} \right)$$

Similarly, we can also have an angular acceleration,  $\alpha$

$$\alpha = \frac{d\omega}{dt} \quad \left( \text{cf. } a = \frac{dv}{dt} \right)$$

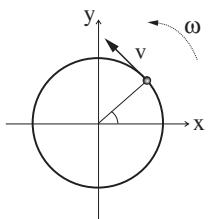
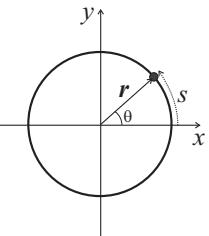
For uniform circular motion, we can define a rotational period,  $T$ , and rotational frequency,  $f$  related to  $\omega$  by the equations

$$\omega = \frac{2\pi}{T} = 2\pi f$$

### Vectors in Circular Motion

For a fixed angular velocity,  $\omega$ , the velocity of a rotating particle,  $v$ , must be directly proportional to the radius of rotation,  $R$ .

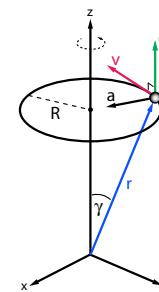
$$v = \omega R$$



However, both angular velocity and the particle position are vectors. To deal with this problem fully, we must be able to deal with the product of two vectors.

In the case shown above, angular velocity and particle position vectors were orthogonal, so the angular velocity vector is simply a vector of magnitude  $\omega R$  in a direction perpendicular to the plane of motion (into the page for the diagram above).

To deal with the more general case, we must consider vectors from a point of reference that is not simply the centre of rotation.



$$\vec{v} = \vec{\omega} \times \vec{r}$$

or

$$\vec{v} = \hat{n}|\omega||r| \sin \gamma$$

Remember that  $\hat{n}$  describes a unit vector orthogonal to the plane containing the vectors  $\omega$  and  $r$  (as defined by the right hand rule).

### Centripetal Acceleration

For uniform circular motion (constant  $\omega$ ) the centripetal acceleration is therefore

$$\vec{a} = \frac{d\vec{v}}{dt} = \vec{\omega} \times \frac{d\vec{r}}{dt} \quad \text{or} \quad \vec{a} = \vec{\omega} \times \vec{v}$$

The centripetal acceleration points radially inwards. It is constant in magnitude but not in direction. As  $\omega$  is perpendicular to  $v$  we can write  $a = \omega v$ . Remembering that  $v = \omega R$  for this case

$$a = \omega^2 R = \frac{v^2}{R}$$

Using Newton's second law, the magnitude of the centripetal force is thus

$$F = ma = \frac{mv^2}{R}$$

### An Example: Circular Motion of an Electron

Earlier, we learnt that the force of attraction between an electron and a proton in a hydrogen atom is approximately  $8.2 \times 10^{-8}$  N. Assuming that it is centripetal motion that prevents the electron from plummeting into the nucleus (n.b. it is not that simple in reality), we can calculate the velocity of the electron. The mass of the electron is  $9.109 \times 10^{-31}$  kg, and the radius of a hydrogen atom is  $5.29 \times 10^{-11}$  m. [ $v=2.2 \times 10^6$  ms $^{-1}$ ]

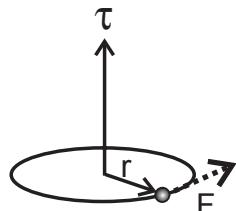
### Torque

A torque can (roughly) be considered to be the rotational equivalent of a force. For

$$\tau = rF$$

a force applied perpendicular to  $r$ , the torque,  $\tau$ , is  $\tau = rF$  or more generally,

$$\vec{\tau} = \vec{r} \times \vec{F}$$



### Angular Momentum

Is it possible to define the torque in terms of a derivative of a momentum, like with linear forces? Let us define the angular momentum,  $\vec{l}$

$$\vec{l} = \vec{r} \times \vec{p}$$

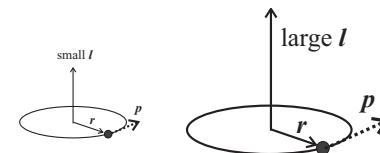
Then taking the time derivative we obtain

$$\frac{d\vec{l}}{dt} = \vec{r} \times \vec{F} = \vec{\tau}$$

i.e.

$$\vec{\tau} = \frac{d\vec{l}}{dt} \quad \left( \text{cf. } \vec{F} = \frac{d\vec{p}}{dt} \right)$$

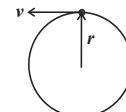
**Angular momentum is a vector directed perpendicular to the plane of rotation (as defined by the right hand rule).**



### Angular momentum for uniform motion in a circle

For uniform motion in a circle (i.e. no angular acceleration)  $p$  and  $v$  are constant in magnitude and always directed perpendicular to  $r$ , and the angular momentum has a constant magnitude

$$l = pr = mvr = mr^2\omega = I\omega$$



### Conservation of Angular Momentum

If there is no external torque acting on a system, the total angular momentum is constant in magnitude and direction.

Angular momentum applies in almost all cases that we are interested in describing in Chemistry. Be sure you understand this concept, you will be seeing it a lot!

### An Example: N<sub>2</sub> Rotation

The bond length of N<sub>2</sub> changes from 1.22 Å to 1.287 Å upon electronic excitation. Using conservation of angular momentum, calculate the fractional change in rotational period of the molecule. [11.3% increase in rotational period]

## Rotational Kinetic Energy

The kinetic energy of a particle,  $i$ , rotating with a constant angular frequency  $\omega$  about a fixed axis is (using  $v = \omega R_i$  where  $R_i$  is the particle's distance from the axis of rotation).

$$K_{i,\text{ang}} = \frac{1}{2}m_i v_i^2 = \frac{1}{2}m_i \omega^2 R_i^2$$

For a system of particles all rotating with frequency  $\omega$ , the rotational (angular) kinetic energy is therefore

$$K_{\text{ang}} = \sum_i K_{i,\text{ang}} = \frac{1}{2} \sum_i m_i \omega^2 R_i^2$$

## Moments of Inertia

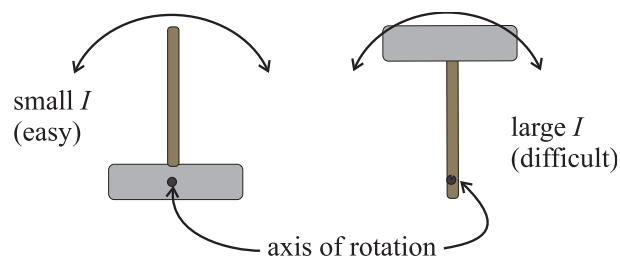
Defining the moment of inertia,  $I$ , as

$$I = \sum_i m_i r_i^2$$

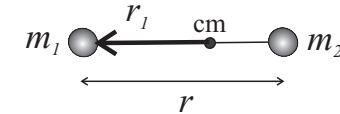
the rotational kinetic energy can be written

$$K_{\text{ang}} = \frac{1}{2} I \omega^2 \quad (\text{cf. } K_{\text{lin}} = \frac{1}{2} m v^2)$$

The moment of inertia plays a similar role in rotational motion as mass does in linear motion. The magnitude of  $I$  depends on the axis of rotation.



## Classical rotation of diatomic molecules

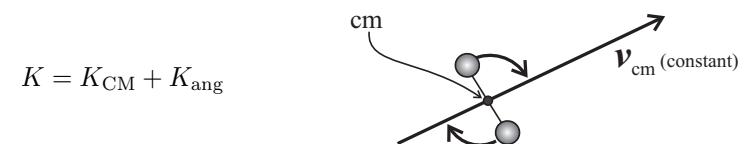


For a diatomic molecule with a bond length  $r$ , rotation must occur about the centre-of-mass, and the moment of inertia can be written

$$I = \sum_i m_i r_i^2 = \mu r^2 \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

$\mu$  is the reduced mass. Reduced mass is the 'effective' inertial mass. Rather than considering the motion of the molecule, by using the reduced mass we can focus only on the motion of each atom relative to the centre of mass. We can prove this by considering the relative acceleration between the two atoms ( $a = a_1 - a_2$ ) from Newton's third law.

In the absence of external forces on the molecule, the motion of the centre-of-mass is conserved, and the total kinetic energy of the molecule can be factored



Because both atoms rotate with the same frequency  $\omega$  about the CM, the angular momentum and the angular kinetic energy of the molecule may be written as

$$l = \sum_i m_i r_i^2 \omega = I \omega \quad K_{\text{ang}} = \frac{1}{2} \sum_i m_i r_i^2 \omega^2 = \frac{l^2}{2I}$$

## Vibrational Motion

### The Wave Equation

In one dimension wave motion can be described by

$$\frac{\partial^2 \psi}{\partial t^2} = v^2 \frac{\partial^2 \psi}{\partial x^2}$$

Where  $\psi$  is a function that describes the wave (the wave function) and  $v$  is the speed of the wave. This equation tells us about how a wave propagates in space and time.



The general solutions to this equation can be expressed as the superposition of two waves propagating in opposite directions.

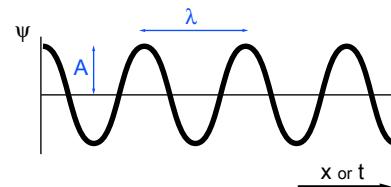
$$\psi(x, t) = f_1(x - vt) + f_2(x + vt)$$

where  $f_1$  and  $f_2$  are arbitrary functions. The fluctuations in a wave can be perpendicular to the direction of motion (a **transverse** wave), or parallel to the direction of motion (**longitudinal** wave).

### Sinusoidal Waves

We can verify that this differential equation really does describe a wave. Let's start with the simplest of waves, a sinusoid.

We can draw two equivalent sine waves, one describing oscillations in position ( $x$ ), and another describing oscillations in time ( $t$ ).



The equation for this wave can be written as

$$\psi(x, t) = A \sin(kx - \omega t + \phi)$$

We can vary either time or position in this equation, and we would see a sinusoidal variation in amplitude of the wave function.

#### Wavelength, $\lambda$

The distance between successive peaks.

#### Amplitude, $A$

The maximum value of the wave function

#### Frequency, $\nu$

The number of cycles per second.

#### Phase, $\varphi$

The initial offset of the wave in  $x$  at time  $t=0$ .

#### Angular Wavenumber,<sup>1,2</sup> $k$

The number of wavelengths in the distance  $2\pi$ .  $k = 2\pi/\lambda$ .

#### Angular Frequency, $\omega$

The number of cycles per second, measured in radians.  $\omega = 2\pi\nu$ .

#### Wave Velocity<sup>3</sup>, $v$

The speed of the wave.  $v = \lambda\nu = \omega/k$ .

<sup>1</sup> Thus far we have only considered 1D waves, so we don't have to resort to vectors. In the case of multidimensional waves,  $k$  is called the wave vector and also specifies the direction of propagation of the wave.

<sup>2</sup> Don't confuse **angular wavenumber** ( $k=2\pi/\lambda$ ) used when talking about waves, and **wavenumber** used in spectroscopy. In spectroscopy, wavenumber is the number of wavelengths in one unit of length. It is the spatial analogue of frequency and usually expressed in units of  $\text{cm}^{-1}$ .

<sup>3</sup> There are actually several kinds of wave velocity, here we are talking about the group velocity.

### So is this sinusoid a solution to the general wave equation?

Differentiate the wave function with respect to  $t$  at fixed  $x$ , twice

$$\psi(x, t) = A \sin(kx - \omega t + \phi)$$

$$\frac{\partial^2 \psi}{\partial t^2} = -A\omega^2 \sin(kx - \omega t + \phi) = -\omega^2 \psi(x, t)$$

Repeat the (partial) differentiation of the wave function, but now with respect to  $x$  at fixed  $t$ :

$$\frac{\partial^2 \psi}{\partial x^2} = -Ak^2 \sin[kx - \omega t + \phi] = -k^2 \psi(x, t)$$

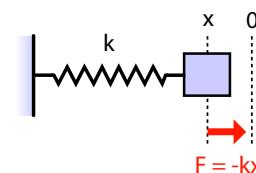
Combining these two equations, making use of the definition of the wave velocity,  $v = \omega/k$ , gets us back to the linear wave equation.

$$\frac{\partial^2 \psi}{\partial t^2} = v^2 \frac{\partial^2 \psi}{\partial x^2}$$

### Simple harmonic motion

One easy example of a wave equation is from simple harmonic motion. SHM is present where there is a restoring force that is proportional to the displacement of the system (e.g a pendulum, springs, molecular vibrations, sound waves, etc).

#### An Example: Mass and Spring



Consider the forces on the mass when it is displaced from its resting position by a distance  $x$ . We know that  $F=ma$ . The spring also applies a force given by **Hooke's law** proportional to the displacement  $F_{\text{restoring}} = -kx$ . Here  $k$  is the spring constant.

$$m \frac{d^2 x}{dt^2} = -kx$$

Another second order differential equation! Let's tidy up:

$$\frac{d^2 x}{dt^2} + \frac{k}{m} x = 0$$

You will learn how to solve such equations in your mathematics course. We can quote the solution and check it really works:

$$x(t) = A \sin(\omega t + \phi)$$

Where  $\omega$  is the angular frequency  $\omega^2 = k/m$ . If we substitute this into the differential equation, we can check it is a solution and gives us the result.

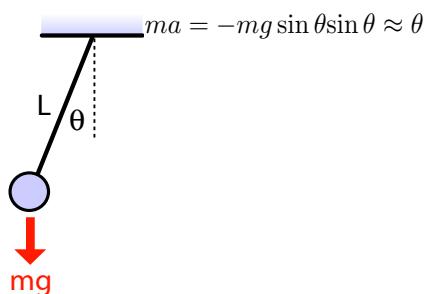
$$T = \frac{2\pi}{\omega} = 2\pi \sqrt{\frac{m}{k}}$$

Interestingly, the period is independent of the initial displacement.

#### An Example: Simple Pendulum

The equation of motion for a simple pendulum is given by

We can approximate for small angles with



So the equation of motion becomes

$$ma = -mg\theta$$

The easiest way to solve this is to convert  $a$  to an angular form ( $a=\alpha L$ )

$$m\alpha L = -mg\theta$$

Giving us the second order differential equation

$$\frac{d^2\theta}{dt^2} + \frac{g}{L}\theta = 0$$

Just as in the previous example, we can substitute in a sinusoidal solution to show that this gives a period of oscillation of

$$T = 2\pi \sqrt{\frac{L}{g}}$$

## Energy in Simple Harmonic Motion

### Potential Energy

$$\begin{aligned} V(t) &= \frac{1}{2}kx^2 \\ x(t) &= A \sin(\omega t + \phi) \\ V(t) &= \frac{1}{2}kA^2 \sin^2(\omega t + \phi) \end{aligned}$$

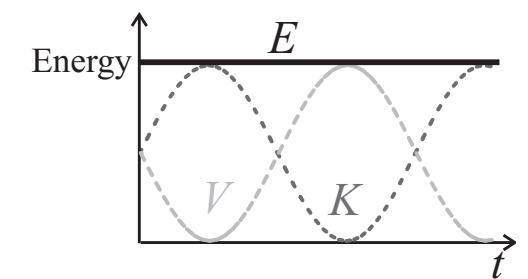
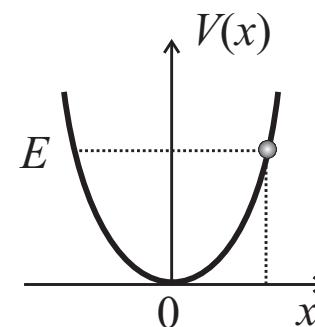
### Kinetic Energy

$$\begin{aligned} K(t) &= \frac{1}{2}mv^2 \\ v(t) &= A\omega \cos(\omega t + \phi) \\ K(t) &= \frac{1}{2}mA^2\omega^2 \cos^2(\omega t + \phi) \\ K(t) &= \frac{1}{2}kA^2 \cos^2(\omega t + \phi) \end{aligned}$$

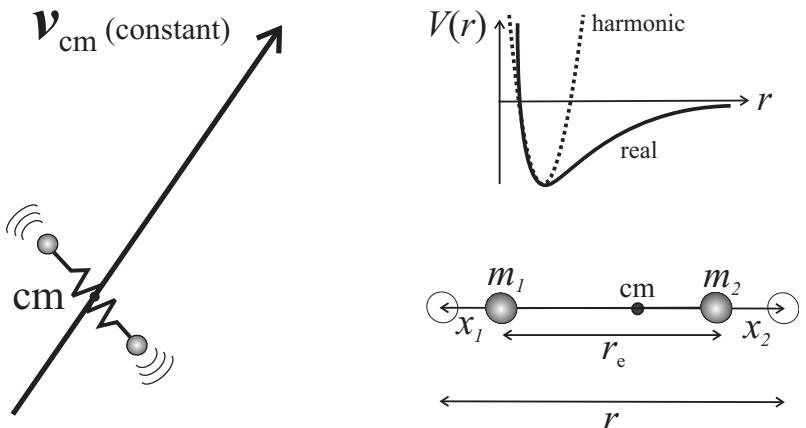
### Total Energy

$$\begin{aligned} E &= K + V \\ E &= \frac{1}{2}kA^2 [\sin^2(\omega t + \phi) + \cos^2(\omega t + \phi)] = \frac{1}{2}kA^2 \end{aligned}$$

The vibrational frequency of a harmonic oscillator is independent of the total energy.



### Vibration Motion of a Diatomic Molecule

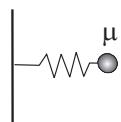


In the absence of external forces, the motion of the centre of mass (CM) of a molecule can be treated separately from the relative motion of the two atoms. The relative motion describes the time-dependent changes in bond length of the molecule

In this case, we have an analogous system to a mass on a spring. The only difference here is that we must again use the relative or **reduced mass**,  $\mu$ , of the system rather than the actual mass, as we are only considering the internal motion.

$$\mu = \frac{m_1 m_2}{(m_1 + m_2)}$$

$$\omega = \sqrt{\frac{k}{\mu}}$$



$\mu$  is the reduced mass of the oscillator and  $\omega$  is the angular frequency.

#### An Example: Vibrational Frequency of HBr

Treating HBr as a simple harmonic oscillator with force constant  $412 \text{ N m}^{-1}$ , calculate the expected vibrational wavelength of the molecule. [ $3.76 \mu\text{m}$ ] (The actual vibrational wavenumber is  $2649.7 \text{ cm}^{-1} = 3.77 \mu\text{m}$ ). Not bad for just SHM.

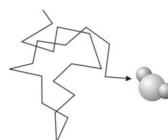
# Properties Of Gases

We can use classical mechanics to describe the properties and behaviour of gases. As the interactions between gas particles are relatively weak, we can describe the gas phase using relatively simple models.

## Characteristics of the Gas Phase

### 1. A gas is a collection of particles in constant random motion.

**motion.** The particles in a gas continually undergoing collisions with each other and with the walls of the container.



### 2. A gas fills any container it occupies.

This is consistent with the second law of thermodynamics, gas expansion is a spontaneous process due to the accompanying increase in entropy.

### 3. The effects of intermolecular forces in a gas are generally small.

For many gases over a wide range of temperatures and pressures, they can be ignored entirely.

## States of Gases

The physical state of a pure gas (as opposed to a mixture) may be defined by four physical properties:

$p$  – the pressure of the gas.

$T$  – the temperature of the gas.

$V$  – the volume of the gas.

$n$  – the number of moles of substance present.

The **equation of state** for a gas is simply an expression that relates these four variables.

## Gases & Vapours

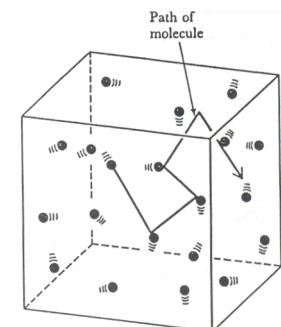
The difference between a 'gas' and a 'vapour' is sometimes a source of confusion. When a gas phase of a substance is present under conditions when the substance would typically be a solid or liquid then we call this a vapour phase.

For example, at the surface of a liquid an equilibrium exists between the liquid and gas phases. At a temperature below the boiling point of the substance, the gas is termed a vapour, and its pressure is known as the 'vapour pressure' of the substance at that temperature. As the temperature is increased, the vapour pressure also increases. The boiling point is the temperature at which the vapour pressure of the substance is equal to the ambient pressure.

This is in contrast to a 'fixed gas', which is a gas for which no liquid or solid phase exists at the temperature of interest (e.g. gases such as N<sub>2</sub>, O<sub>2</sub> or He at room temperature).

## Pressure

Pressure is a measure of the **force** exerted by a gas **per unit area**. In a gas, these force arise from collisions of the particles in the gas with the surface at which the pressure is being measured, often the walls of the container. The SI units of pressure is Newtons per square metre (Nm<sup>-2</sup>), or Pascals (Pa). Several other units of pressure are in common usage (1 Torr = 1 mmHg = 133.3 Pa) (1 bar = 100 000 Pa).



## Dalton's Law of Partial Pressures

As the measured pressure arises from collisions of individual gas particles with the container walls, the total pressure  $p$  exerted by a mixture of gases is simply the sum of the contributing parts of the pressure coming from the component gases: the **partial pressure**  $p_i$  is simply the pressure that gas  $i$  would exert if it alone occupied the container. This result is known as **Dalton's law**.

$$p = \sum_i p_i$$

We can also write this in terms of mole fractions,  $x_i$

$$p_i = x_i p \quad \text{where} \quad x_i = \frac{n_i}{\sum_i n_i}$$

### Barometric Pressure

Static fluid pressure is determined by the density and depth of a fluid. Consider a U-tube filled with a non-volatile liquid: One end of the tube provides a reference pressure ( $p_2$ ) and is either open to atmospheric pressure or sealed and evacuated to very low pressure. The other end of the U-tube is exposed to the system pressure to be measured ( $p_1$ ). The gas at each end of the tube applies a force to the liquid column through collisions with the liquid surface. If the pressures at each end of the tube are unequal then these forces are unbalanced, and the liquid will move along the tube until the forces are balanced.

At equilibrium, the liquid exerts a pressure,

$$\Delta p = -\rho g \Delta h$$

where  $\rho$  is the density of the liquid,  $g$  is the acceleration due to gravity, and  $\Delta h$  is the height difference between the two arms of the U-tube.

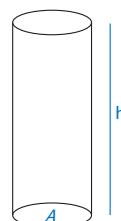
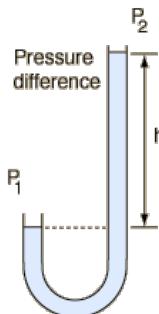
### An Example: $\Delta p = \rho g \Delta h$ Derivation

Consider the pressure exerted on the bottom of a column of fluid of height  $h$  and cross-sectional area  $A$ . The pressure  $p$  on this area is simply  $F/A$ . The force is  $-mg$  (if 'up' is the positive direction of displacement, the force acts in the opposite direction). Given the mass density of the fluid is  $\rho$ ,  $m=\rho V$ . So

$$p = -\frac{mg}{A} = -\frac{\rho V g}{A} = -\rho g h$$

### An Example: Barometric Pressure

We can also use this formula to estimate how the pressure varies with height in the atmosphere. Assuming the atmosphere can be described by the perfect gas equation  $pV=nRT$  (we will explore this equation in detail shortly) and that the mass density of the gas  $\rho = M/V$ , where  $M$  is the mass of volume  $V$ . We can show



$$p = p_0 e^{-\frac{mgh}{k_B T}}$$

where  $m$  is the mass of a gas particle.

We can write an expression for the density of gas in term of the ideal gas equation

$$\rho = \frac{M}{V} = \frac{Mp}{nRT}$$

We know that  $\Delta p = -\rho g \Delta h$  or alternatively,  $dp = -\rho g dh$ , so inserting our expression for the density

$$dp = -\rho g dh = -\frac{Mpg}{nRT} dh$$

If we assume  $M$ ,  $n$ ,  $\rho$ ,  $g$  and  $T$  are all independent of  $h$ , we can solve this by separating variables and integrating

$$\int \frac{1}{p} dp = -\frac{Mg}{nRT} \int dh$$

giving

$$\ln \frac{p}{p_0} = -\frac{Mg}{nRT} h \quad \text{or} \quad p = p_0 e^{-\frac{Mg}{nRT} h} \quad \text{or} \quad p = p_0 e^{-\frac{M_{\text{ref}} g}{RT} h}$$

Note that we have assumed that temperature doesn't change with height, which is clearly a radical approximation of the actual atmosphere!

### Temperature

The temperature of a gas is a measure of the **kinetic energy** possessed by the particles in the gas. The temperature therefore reflects their velocity distribution. The velocity of any single particle within a gas changes rapidly due to collisions with other particles and with the walls of the container. However, since energy is conserved, these collisions only lead to exchange of energy between the particles. This velocity distribution will be covered in detail later.

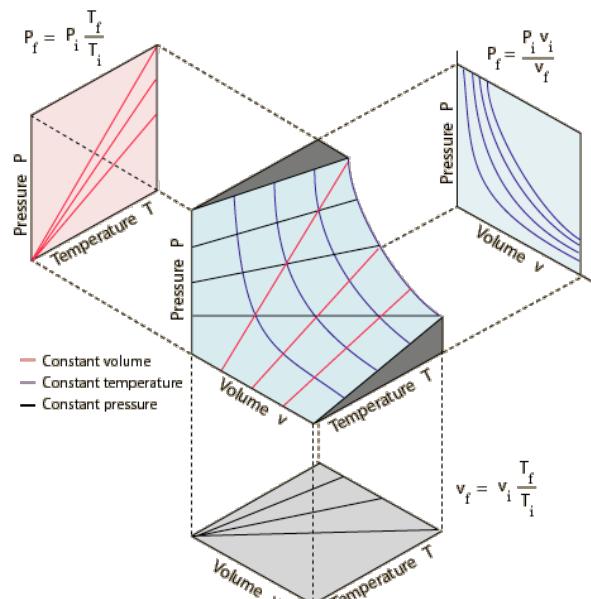
## The Gas Laws

The perfect gas equation is an equation of state that can be used to describe the behaviour of a gas at low pressure.

$$pV = nRT$$

In this equation  $R$  is the molar gas constant,  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ . Note that  $R$  is related to Boltzmann's constant,  $k_B$ , by  $R = N_A k_B$ , where  $N_A$  is Avogadro's number.

This empirical equation was established by combining a series of experimental results obtained from the seventeenth century onwards. All the possible states of an ideal gas can be represented on a three-dimensional  $pVT$  plot.<sup>4</sup> The behaviour when any one of the three state variables is held constant is also shown.



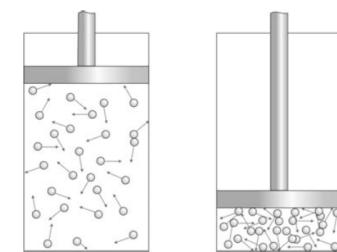
We can rewrite the perfect gas equation as

$$\frac{p_i V_i}{T_i} = \frac{p_f V_f}{T_f}$$

### Boyle's law

If the temperature is fixed, this equation becomes Boyle's law.

$p_i V_i = p_f V_f$  Consider the figure; when the plunger is depressed, the gas occupies a much smaller volume, and there are many more collisions with the inside surface of the plunger, increasing the pressure.



### Charles' Law

If the pressure is constant, then the ideal gas law takes the form of Charles' Law

$$\frac{V_i}{T_i} = \frac{V_f}{T_f}$$

### Pressure-temperature law

We can complete the set of law's by including the relation between pressure and temperature: For a fixed volume, the pressure of a gas is proportional to the absolute temperature of the gas.

$$\frac{P_i}{T_i} = \frac{P_f}{T_f}$$

The primary effect of increasing the temperature of the gas is to increase the speeds of the particles. As a result, there will be more collisions with the walls of the container. For a fixed volume of gas, these factors combine to give an increase in pressure, and for fixed pressure, we must increase the volume.

<sup>4</sup> Plot reproduced from <http://hyperphysics.phy-astr.gsu.edu/hbase/kinetic/idegas.html#c1>

## Ideal Gases

An ideal gas is an approximate model that can be used to simplify calculations on real gases. An ideal gas has the following properties:

1. **The gas consists of particles in constant random motion.**
2. **There are no intermolecular forces between the gas particles.**
3. **The separation of particles is large compared to particle diameter.** (i.e. the volume occupied by the particles is negligible compared to the volume of the container they occupy).
4. **The only interactions between the particles and with the container walls are perfectly elastic collisions.** Recall that an elastic collision is one in which the total kinetic energy is conserved (i.e. no energy is transferred from translation into rotation or vibration, and no chemical reaction occurs).

If a gas is ideal, its behaviour is described by

$$pV = nRT$$

## Real Gases

In a real gas, the atoms or particles obviously do have a finite size, and at close range they do interact with each other through a variety of intermolecular forces. The ideal gas model breaks down under conditions of high pressure, when the particles are forced close together and therefore interact strongly, and at low temperatures, when the particles are moving slowly and intermolecular forces have a long time to act during a collision.

### The Compression Factor, $Z$

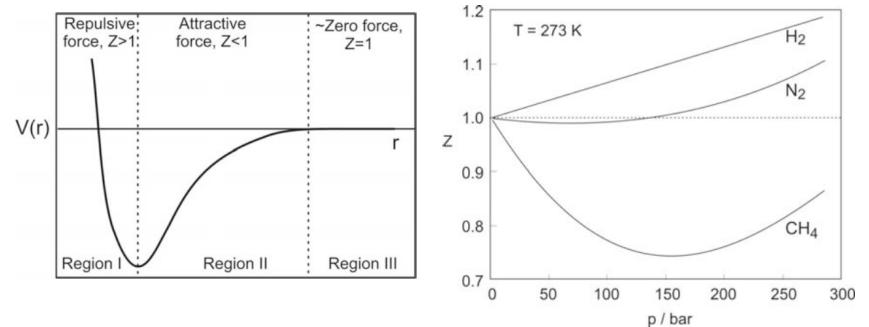
The deviations of a real gas from ideal gas behaviour may be quantified by the compression factor,  $Z$ . At a given pressure and temperature, attractive and repulsive intermolecular forces between gas particles mean that the molar volume is likely to be smaller or larger than for an ideal gas under the same conditions. The compression factor is simply the ratio of the molar volume  $V_m$  of the gas to the molar volume  $V_m^o$  of an ideal gas at the same pressure and temperature.

$$Z = \frac{V_m}{V_m^o} = \frac{pV_m}{RT}$$

The value of  $Z$  tells us about the dominant types of intermolecular forces acting in a gas.

- $Z = 1$  No intermolecular forces.  
Ideal gas behaviour.
- $Z < 1$  Attractive forces dominate.  
Gas occupies a smaller volume than an ideal gas.
- $Z > 1$  Repulsive forces dominate.  
Gas occupies a larger volume than an ideal gas.

To understand the behaviour at higher pressures we can consider a typical intermolecular potential,  $V(r)$ . The value for  $Z$  depends on how this potential is sampled at a given pressure and temperature.

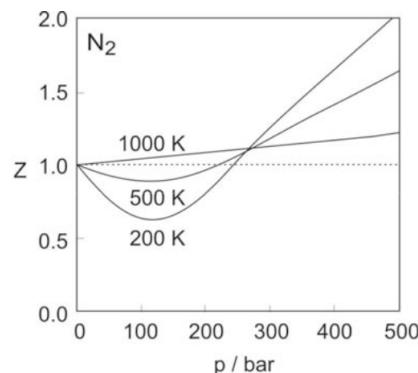


**Region I.** At very small separations electron cloud overlap gives rise to strong repulsive interactions. The particles take up a larger volume than they would in an ideal gas, and  $Z > 1$ .

**Region II.** As the particles approach each other, they experience an attractive interaction. This reduces the molar volume such that  $Z < 1$ , in comparison to an ideal gas.

**Region III.** At large separations the interaction potential is effectively zero and  $Z = 1$ . When the particles are widely separated we therefore expect the gas to behave ideally, thus all gases approach  $Z = 1$  at very low pressures.

The compression factor depends on temperature: (1) At higher speeds there is less time during a collision for the attractive part of the potential to act. (2) Higher energy collisions means that the particles penetrate further into the repulsive part of the potential during each collision, so the repulsive interactions become more dominant. The temperature of the gas therefore changes the balance between the contributions of attractive and repulsive interactions to the compression factor.



The pressure-dependent compression factor for  $N_2$  at three different temperatures is shown above.

## Equations of State for Real Gases

There are a number of ways in which the ideal gas equation may be modified to take account of the intermolecular forces present in a real gas.

### Virial Expansion

One way is to treat the ideal gas law as the first term in an expansion of the form:

$$pV_m = RT \left( 1 + B'p + C'p^2 + \dots \right)$$

This is known as a virial expansion, and the coefficients  $B'$ ,  $C'$  etc are called **virial coefficients**. In many applications, only the first correction term is included.

Often, a more convenient form for the virial expansion is:

$$pV_m = RT \left( 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots \right)$$

### van der Waal's Equation of State

Another widely used equation for treating real gases is the **van der Waal's** equation. The van der Waal's equation of state attempts to account for the size of molecules and the attractive forces between molecules

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$a$  and  $b$  are temperature-independent coefficients;  $a$  accounts for the attractive forces and  $b$  describes the molar volume excluded the particles

# The Kinetic Theory Of Gases

## General Description

The properties of a perfect gas can be understood by considering the random motion of the particles in the gas. The **kinetic theory of gases** provides a quantitative description of this behaviour. The kinetic theory of gases is based on the assumption that the only contribution to the energy of the gas is from kinetic energy.

## Assumptions

Recall the assumptions used in describing a perfect gas

1. **The gas consists of particles in constant random motion.**
2. **There are no intermolecular forces between the gas particles.**
3. **The separation of particles is large compared to particle diameter (i.e. the volume occupied by the particles is negligible compared to the volume of the container they occupy).**
4. **The only interactions between the particles and with the container walls are perfectly elastic collisions.**

## Derivation

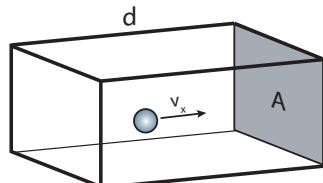
We can construct an expression for the pressure of an ideal gas by applying Newton's laws of motion to the random motion of gas particles in a container of volume,  $V$ .

Our first task is to determine the force on the walls of the container. It is easiest to begin by considering the motion of a single particle in just one dimension.

The momentum change along the  $x$  co-ordinate during one elastic collision of a particle of mass,  $m$  is

$$\Delta p = p_{\text{after}} - p_{\text{before}} = -mv_x - (mv_x) = -2mv_x$$

Since momentum must be conserved, the total momentum imparted to the wall must be  $+2mv_x$ .



The time between collisions for this particle with the wall is simply

$$\Delta t = \frac{2d}{v_x}$$

As pressure is force per unit area, we can work out the force on the wall. From Newton's second law

$$F = ma = \frac{d(p)}{dt} \approx \frac{\Delta p}{\Delta t} = \frac{2mv_x}{2d/v_x} = \frac{mv_x^2}{d}$$

So the pressure exerted by one particle is simply

$$p = \frac{F}{A} = \frac{mv_x^2}{Ad} = \frac{mv_x^2}{V}$$

Pressure obviously doesn't result just from the collisions of one particle in one dimension, but many particles moving in all 3 dimensions.

We can extend our result to cope with the average behaviour of  $N$  particles by multiplying our result by  $N$ .

In addition, particles clearly do not all travel with the same speed, rather there is a distribution of speeds. We must therefore replace  $v_x^2$  with  $\langle v_x^2 \rangle$ , the average squared velocity in the  $x$  direction.

$$p = \frac{Nm \langle v_x^2 \rangle}{V}$$

As there are three dimensions in total, we can simplify things further by realising that the average squared velocity in the  $x$  direction must be the same as that in the  $y$  and  $z$  directions.

$$\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = 3 \langle v_x^2 \rangle$$

Our final expression for the pressure becomes

$$p = \frac{Nm \langle v^2 \rangle}{3V} \quad \text{or} \quad pV = \frac{1}{3} Nm \langle v^2 \rangle$$

As  $\langle v^2 \rangle$  is a constant for any given temperature, the right hand side of this equation is constant. You should recognise this as a form of **Boyle's law** ( $pV = \text{constant}$ ).

To go further we can use the **equipartition theorem** to derive the ideal gas law, relating the above result to temperature. We will state the result here, before examining classical equipartition in more detail:

#### For each degree of freedom there is a $\frac{1}{2}k_B T$ contribution to the internal energy

In our model, there are only three translational degrees of freedom that contribute to the internal energy. As all collisions are perfectly elastic in our model, the total internal energy must be equal to the kinetic energy of the particles. The average kinetic energy is just  $\frac{1}{2}m\langle v^2 \rangle$ , therefore

$$\frac{3}{2}k_B T = \frac{1}{2}m\langle v^2 \rangle$$

Substituting this into our original expression for the pressure

$$pV = \frac{1}{3}Nm\langle v^2 \rangle$$

yields

$$pV = Nk_B T$$

where  $k_B$  is the Boltzmann constant. As  $R = N_A k_B$  we can also write this as

$$pV = nRT$$

which is the perfect, or ideal, gas equation.

## Classical Equipartition

We needed to use the theory of classical equipartition in our derivation the ideal gas equation. The equipartition theorem enables us to estimate the average energy of a system based upon the number of degrees of freedom of the system.

The mean energy of each quadratic contribution to the total energy of a particle is equal to  $\frac{1}{2}k_B T$

or

For each degree of freedom there is a  $\frac{1}{2}k_B T$  contribution to the internal energy

A quadratic contribution to the energy is one that is proportional to the square of a particle's velocity or position.

#### Degrees of Freedom

For any given molecule, the total number of degrees of freedom is given by  $3N$ , where  $N$  is the number of atoms.

#### The Classical Hamiltonian

To continue we need to calculate the total energy of a system; The total energy of a system can be described by its Hamiltonian. Classically, the Hamiltonian is simply the sum of all the contributions to the kinetic and potential energy of the system.

### Translation

For purely translational motion, we have three degrees of freedom corresponding to  $x$ ,  $y$ , and  $z$  directions of translational motion.

$$H = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2)$$

So we predict a  $3/2 k_B T$  contribution to the average energy of the system.

### Rotation

For purely rotational motion of a particle, we would again predict three degrees of freedom corresponding to rotation about the  $x$ ,  $y$ , and  $z$  axes.

$$H = \frac{1}{2}(I_x\omega_x^2 + I_y\omega_y^2 + I_z\omega_z^2)$$

However for linear particles such as diatomics, the moment of inertia about one of these axes, the molecular axis, is vanishingly small. Hence we predict a  $(2 \times \frac{1}{2}) k_B T$  contribution to the average energy of the system for linear particles and a  $3/2 k_B T$  contribution for non-linear particles.

### Vibration

Vibrational motion of bonds have two contributions to the total energy; one from kinetic energy, and one from the potential energy. For example, for a one-dimensional harmonic oscillator

$$H = \frac{1}{2}mv^2 + \frac{1}{2}kx^2$$

So for each vibration, we have two quadratic terms contributing to the total energy. We therefore predict a contribution of  $k_B T$  to the total internal energy for each vibrational degree of freedom.

### Summary

If there are  $3N$  degrees of freedom in total, subtracting the known number of translational and rotational degrees of freedom gives us  $3N-5$  vibrational degrees of freedom for a linear particle and  $3N-6$  vibrational degrees of freedom for a non-linear particle.

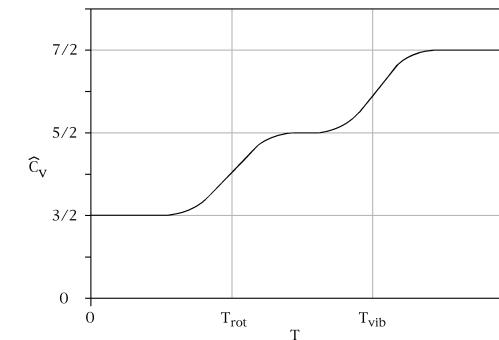
### Heat Capacities and Equipartition

We know from thermodynamics that the heat capacity is related to the internal energy of a system

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V$$

We can use the equipartition theorem to predict the average internal energy of a system, and hence predict the heat capacity.

Contribution to $C_V$			
	trans.	rot.	vib.
monatomic	$3/2 R$	-	-
diatomic	$3/2 R$	$2/2 R$	$R$
linear	$3/2 R$	$2/2 R$	$(3N-5)R$
non-linear	$3/2 R$	$3/2 R$	$(3N-6)R$



This works surprisingly well for many gases (e.g.  $C_V$  for Argon is  $12.47 \text{ JK}^{-1}\text{mol}^{-1}$ ). However, for many others it only functions reliably at high temperature. At low temperatures experimental heat capacities are much lower than those predicted by equipartition. Different degrees of freedom appear to be 'switched on' at different temperatures.

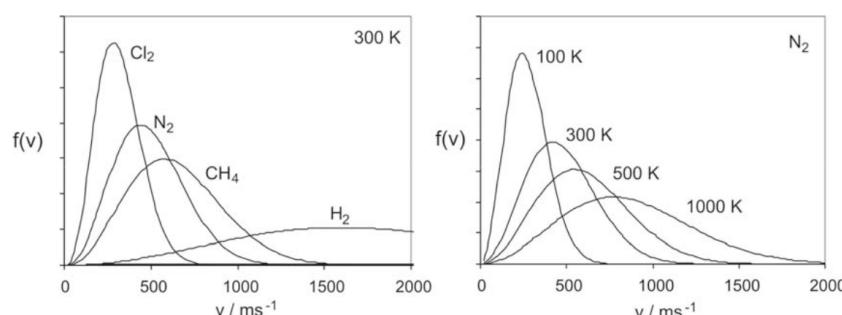
This can only be explained by associating each type of motion with a specific energy, and this requires quantum mechanics.

## The Distribution Of Molecular Speeds

In the previous section on the **kinetic theory of gases** we used the average velocity of the particles in a gas to derive the ideal gas equation. However, in a gas the particles do not all have the same velocity, rather they exhibit a distribution of molecular speeds. The distribution of molecular speeds  $f(v)$  in an ideal gas at thermal equilibrium is given by the Maxwell-Boltzmann distribution.

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

The distribution depends on the ratio  $m/T$ , where  $m$  is the mass of a gas particle and  $T$  is the temperature. The plots below show the Maxwell-Boltzmann speed distributions for a number of different gases at two different temperatures. As we can see, average molecular speeds for common gases at room temperature (300 K) are generally a few hundred metres per second.



We can make two observations:<sup>5</sup>

1. Increasing the temperature broadens the distribution and shifts the peak to higher velocities.
2. Decreasing the mass of the gas particles has the same effect as increasing the temperature (i.e. heavier particles have a slower, narrower distribution of speeds than lighter particles).

<sup>5</sup> A good java applet demonstrating these ideas can be found at:  
<http://intro.chem.okstate.edu/1314F00/Laboratory/GLP.htm>

## The Maxwell-Boltzmann Distribution

To understand why the distribution of molecular speeds has this form, we must understand how this distribution is constructed. In the following version of the derivation much of the hard work is done by means of symmetry arguments.

### Maxwell's Symmetry Argument

First, we need a function that describes the likelihood of a particular particle in a gas having a particular speed.

A **probability distribution function** is an equation that links an outcome of an experiment with its probability of occurring. In our case, the probability that a gas particle has a velocity component  $v_x$  in the range  $v_x$  to  $v_x + dv_x$  is  $P(v_x)dv_x$ , where  $P(v_x)$  is an appropriate (and currently unknown) probability distribution function. If we can determine the functional form of  $P(v)$  in all three dimensions, we can work out the form of the distribution of molecular speeds.

As each velocity component may be treated independently, the total probability of finding a particle with components  $v_x, v_y, v_z$  in the range  $dv_x, dv_y, dv_z$  is the product of the probabilities for each component.

$$P(v_x, v_y, v_z)dv_xdv_ydv_z = P(v_x)dv_x P(v_y)dv_y P(v_z)dv_z$$

Since all directions within the gas are equivalent, we can argue that an alternative to the above distribution function is one in which the distribution function depends only on the total speed of the particle (i.e.  $P(v)$ ) not on each independent velocity component (i.e.  $P(v_x, v_y, v_z)$ ).

So, we need to figure out how to convert the above distribution function into one in terms of  $P(v)$ . An expression for the overall velocity is  $v^2 = v_x^2 + v_y^2 + v_z^2$  so we might construct a probability distribution function as  $P(v_x^2 + v_y^2 + v_z^2)$ , rather than  $P(v_x, v_y, v_z)$ .

Now, for any given speed these two functions must return the same probability, so we can conclude that

$$P(v_x^2 + v_y^2 + v_z^2) = P(v_x)P(v_y)P(v_z)$$

Notice that the sum of the variables on the left is related to the product of the functions on the right.

So what type of function would satisfy this equation? A **Gaussian** function satisfies this relationship (using the fact that  $e^{x+y+z} = e^x e^y e^z$ ). Thus, a suitable solution is:

$$P(v_x) = Ae^{-Bv_x^2}$$

The argument in the exponential is negative because in our model, the probability of finding a particle must decrease as we go to higher particle speeds.

Since  $P(v_x)$  is a probability distribution function, it must be normalised (i.e. the total probability must add up to one).

$$1 = \int_{-\infty}^{\infty} P(v_x) dv_x$$

and so

$$1 = \int_{-\infty}^{\infty} P(v_x) dv_x = \int_{-\infty}^{\infty} Ae^{-Bv_x^2} dv_x$$

This definite integral is of a standard form

$$\int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi}$$

it is therefore straightforward to show

$$1 = \int_{-\infty}^{\infty} P(v_x) dv_x = \int_{-\infty}^{\infty} Ae^{-Bv_x^2} dv_x = A\sqrt{\frac{\pi}{B}}$$

and hence,

$$A = \sqrt{\frac{B}{\pi}}$$

We obviously need another relation between  $A$  and  $B$  to complete our expression for  $P(v_x)$ .

We can also use our probability distribution function to calculate the mean squared speed in the  $x$  direction,  $\langle v_x^2 \rangle$

$$\langle v_x^2 \rangle = \int_{-\infty}^{\infty} v_x^2 P(v_x) dv_x = \sqrt{\frac{B}{\pi}} \int_{-\infty}^{\infty} v_x^2 e^{-Bv_x^2} dv_x$$

This integral also has a standard form

$$\int_{-\infty}^{\infty} x^2 e^{-x^2} dx = \frac{\sqrt{\pi}}{2}$$

so we can solve, giving

$$\langle v_x^2 \rangle = \frac{1}{2B}$$

We can then use our result from the kinetic theory of gases to write an alternative expression for  $\langle v_x^2 \rangle$  and hence determine  $B$ .

Using classical equipartition again, for the single degree of freedom we are considering in  $x$ , we have

$$\frac{1}{2}k_B T = \frac{1}{2}m \langle v_x^2 \rangle$$

Therefore

$$B = \frac{m}{2k_B T}$$

Finally (!), we can write out our probability distribution function as

$$P(v_x) dv_x = \left( \frac{m}{2\pi k_B T} \right)^{1/2} \exp - \frac{mv_x^2}{2k_B T} dv_x$$

This is the distribution only for one dimension, as we saw at the beginning of this section for three dimensions, we must multiply three identical distributions.

$$\begin{aligned} P(v_x, v_y, v_z) dv_x dv_y dv_z &= P(v_x)^3 dv_x dv_y dv_z \\ &= \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp -\frac{m(v_x^2 + v_y^2 + v_z^2)}{2k_B T} dv_x dv_y dv_z \\ &= \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp -\frac{mv^2}{2k_B T} dv_x dv_y dv_z \end{aligned}$$

The above expression gives the probability of the speed distribution having components  $v_x, v_y, v_z$ , whereas what we would really like to know is the probability  $P(v)dv$  that the molecular speed lies in the range  $v$  to  $v+dv$ .

This is simply the sum of the probabilities that a particle's velocity lies in range in the range  $v$  to  $v+dv$ . Imagine a 3D plot of  $v_x, v_y, v_z$  components. The range  $v$  to  $v+dv$  is a spherical shell in this plot of volume  $dv_x dv_y dv_z$ . This shell has a radius  $v$  and thickness  $dv$ .

The appropriate volume element for the distribution is therefore the volume of this shell, which is  $4\pi v^2 dv$ . We substitute this for the volume element  $dv_x dv_y dv_z$  in the above expression to give the final form for the Maxwell-Boltzmann distribution of molecular speeds.

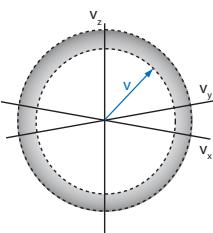
$$P(v)dv = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp -\frac{mv^2}{2k_B T} dv$$

#### An Alternative Derivation of the Maxwell-Boltzmann Distribution

You will not cover **Statistical Thermodynamics** until your second year, when you will learn how the Boltzmann distribution describes how energy is distributed between identical but distinguishable particles.

$$f(E) = A e^{-E/k_B T}$$

This expression can be used as the starting point to derive the Maxwell-Boltzmann distribution of molecular speeds without resorting to lengthy symmetry arguments. Although **not formally a part of this course**, the derivation is included here for reference next year.



Considering the motion of gas particles as purely elastic collisions. For one-dimensional motion, the Boltzmann distribution is

$$f(v_x) = A e^{-mv_x^2/2k_B T}$$

We must again normalise this distribution as the total probability of finding a particle must be equal to unity. We can make use of the definite integral

$$\int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi}$$

where we can substitute

$$x = \sqrt{\frac{m}{2k_B T}} v_x$$

to give

$$A \sqrt{\frac{2k_B T}{m}} \int_{-\infty}^{\infty} e^{-mv_x^2/k_B T} \sqrt{\frac{m}{2k_B T}} dv_x = 1$$

so

$$A = \sqrt{\frac{m}{2\pi k_B T}}$$

The one-dimensional distribution is thus

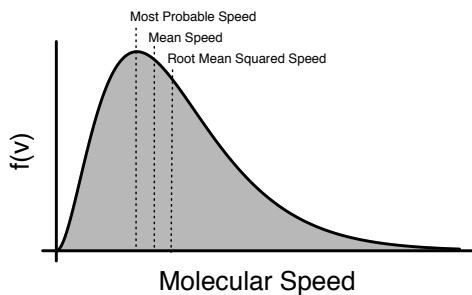
$$f(v_x) = \sqrt{\frac{m}{2\pi k_B T}} \exp -\frac{mv_x^2}{2k_B T}$$

Again, we must multiply three identical probability distribution functions and account for the density of velocity states available to particles (by multiplying by  $4\pi v^2$ ) to give the Maxwell-Boltzmann distribution of molecular speeds.

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

### Mean Speed, Most Probable Speed and Root-Mean-Square Speed

We can use the Maxwell Boltzmann distribution to determine the mean speed and the most probable speed of the particles in the gas.



Since the probability distribution is normalised, the mean speed is determined from the following integral:

$$\langle v \rangle = \int_0^\infty v f(v) dv \\ = \left( \frac{8k_B T}{\pi m} \right)^{1/2}$$

We can find the most probable speed by maximising the distribution with respect to  $v$

$$\langle v_{\text{mode}} \rangle = \left( \frac{2k_B T}{m} \right)^{1/2}$$

For completeness, we can also quote again the root-mean-square speed we found in the previous section when we derived the kinetic theory of gases.

$$\langle v_{\text{rms}} \rangle = \left( \frac{3k_B T}{m} \right)^{1/2}$$

### Collision frequency

Collisions are one of the most fundamental processes in chemistry, and provide the mechanism by which both chemical reactions and energy transfer occur in a gas. The rate at which collisions occur determines the time scale of these events. The rate of collisions is usually expressed as a **collision frequency**, defined as the number of collisions a particle undergoes per unit time. We will use kinetic theory to calculate collision frequencies for two cases: collisions with the container walls; and intermolecular collisions.

#### Collisions With The Container Walls

We have already done much of the work required to calculate the frequency of collisions with the container walls. For a wall of area  $A$ , all particles in a volume  $A v_x \Delta t$  with positive velocities will collide with the wall in the time interval  $\Delta t$ . We can use our probability distribution  $P(v_x)$  to determine the average value  $\langle V \rangle$  of this volume

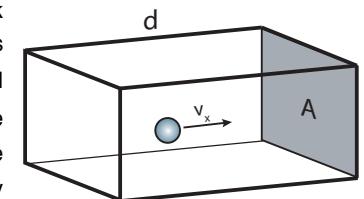
$$\langle V \rangle = \int_0^\infty V P(v_x) dv_x \\ = A \Delta t \int_0^\infty v_x \sqrt{\frac{m}{2\pi k_B T}} \exp\left(\frac{-mv_x^2}{2k_B T}\right) dv_x$$

We can solve this using the standard integral

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

yielding

$$\langle V \rangle = A \Delta t \left( \frac{k_B T}{2\pi m} \right)^{1/2}$$



Multiplying the result by the number density of particles,  $N/V = p/k_B T$ , yields the number of collisions occurring in the time interval  $\Delta t$ . For unit time and unit area ( $A = 1 \text{ m}^2$ ,  $\Delta t = 1 \text{ s}$ ), this yields a collision frequency,  $z_{\text{wall}}$

$$z_{\text{wall}} = \frac{p}{k_B T} \left( \frac{k_B T}{2\pi m} \right)^{1/2} = \frac{p}{(2\pi m k_B T)^{1/2}}$$

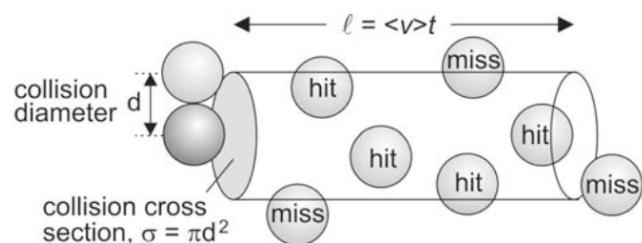
### An Example, Your Desk

Calculate the number of collisions for air (i.e.  $\text{N}_2$  molecules) at 1 bar pressure and 298 K on a  $1 \text{ m}^2$  area (like your desk). [about  $2.9 \times 10^{27}$  collisions every second!]

### Collisions Between Particles

To determine the number of collisions a particle undergoes with other particles per unit time, we need to introduce the concept of the **collision cross section**,  $\sigma$ . This is defined as the cross sectional area that the centres of two particles must lie within if they are to collide.

In our kinetic model, the particles act like hard spheres (there are no intermolecular forces) and a collision only occurs when the centres of two particles are separated by a distance equal to the particle diameter,  $d$ .



Imagine that we have ‘frozen’ the motion of all of the particles except one. We can see that this particle will only collide with particles whose centres are within the cross sectional area  $\sigma = \pi d^2$ . In a time interval  $\Delta t$ , this particle will move a distance  $<\nu>\Delta t$ , represented by the length of the cylinder.

The number of collisions the particle undergoes in the time interval  $\Delta t$  will therefore be equal to the number density of particles in the gas,  $N/V = p/k_B T$ , multiplied by the volume  $\sigma <\nu>\Delta t$  of the ‘collision cylinder’ the particle has sampled.

We want to know the number of collisions per unit time, so set  $\Delta t = 1 \text{ s}$ . Since the particles are not really stationary, we need to replace  $<\nu>$ , the average speed of one particle in the gas, by  $<\nu_{\text{rel}}>$ , the mean relative velocity of the gas particles.

The collision frequency is therefore:

$$z = \sigma <\nu_{\text{rel}}> \frac{N}{V} = \sigma <\nu_{\text{rel}}> \frac{p}{k_B T}$$

This collision frequency,  $z$ , is the number of collisions made by a single particle per second. Usually what we would like to know is the total collision frequency, or collision density,  $Z$ ; the total number of collisions occurring in the gas per unit volume, so we must multiply by  $N/V$

$$z = \sigma <\nu_{\text{rel}}> \frac{N}{V} = \sigma <\nu_{\text{rel}}> \frac{p}{k_B T}$$

To progress we substitute the expression for the mean relative speed,  $<\nu_{\text{rel}}> = \sqrt{2} <\nu>$  that we derived earlier when considering the mean relative speed.

$$\begin{aligned} <\nu> &= \int_0^\infty v f(v) dv \\ &= \left( \frac{8k_B T}{\pi m} \right)^{1/2} \end{aligned}$$

so the collision frequency is

$$Z = \frac{1}{2} \sigma \sqrt{2} \sqrt{\frac{8k_B T}{\pi m}} \left( \frac{N}{V} \right)^2$$

The additional factor of  $1/2$  in this expression ensures that we avoid double counting of each collision, so the collision of particle X with particle X’ is counted as the same collision as that of X’ with X.

Using the fact that we can relate concentrations  $[X]$  and number densities using  $[X]N_A = N/V$ , we can write this equation as

$$Z_{XX} = \sigma \left( \frac{4k_B T}{\pi m} \right)^{1/2} N_A^2 [X]^2$$

Collision densities can be enormous. As an example, for N<sub>2</sub> gas under standard conditions, with a collision diameter of 0.28 nm,  $Z_{XX} = 5 \times 10^{34} \text{ s}^{-1} \text{ m}^{-3}$ .

We can easily extend this equation to cover collisions between different types of molecule obtaining

$$Z_{XY} = \sigma \left( \frac{8k_B T}{\pi \mu} \right)^{1/2} N_A^2 [X][Y]$$

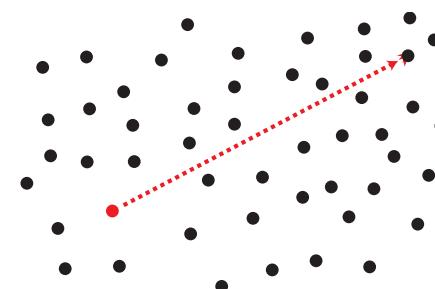
## Mean Free Path

The average distance a particle travels between collisions is called the mean free path,  $\lambda$ .

The time between collisions is just the inverse of the collision frequency ( $1/z$ ). If the particle is travelling at a mean speed  $\langle v \rangle$ , then (since distance = velocity x time) the mean free path is

$$\lambda = \frac{\langle v \rangle}{z}$$

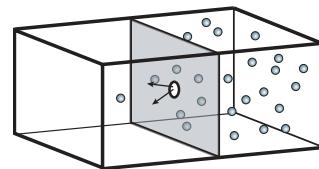
At standard pressure and temperature, the mean free path is generally of the order of a few tens of nanometres. This is an order of magnitude larger than the average molecular separation, you can check this. Since  $z$  is proportional to pressure,  $\lambda$  is inversely proportional to pressure, e.g. doubling the pressure will halve the mean free path.



## Applications Of Kinetic Theory

### Effusion

Effusion occurs when a gas escapes into a vacuum through a small hole, of area  $a$ . The diameter of the hole is smaller than the mean free path in the gas, so that no collisions occur as the particles pass through the hole. The rate of escape of the particles is then just the rate at which they strike the hole.



$$\text{Rate} = \frac{dN}{dt} = z_{\text{wall}}a = \frac{pa}{(2\pi mk_B T)^{1/2}}$$

Note that the rate of effusion is inversely proportional to the square root of the molecular mass. As the gas leaks out of the container, the pressure decreases, so the rate of effusion will be time dependent. The rate of change of pressure with time is

$$\frac{dp}{dt} = \frac{d}{dt} \left( \frac{Nk_B T}{V} \right) = \frac{k_B T}{V} \frac{dN}{dt}$$

Substituting for  $dN/dt$  and integrating gives

$$p = p_0 \exp -t/\tau \quad \text{where} \quad \tau = \left( \frac{2\pi m}{k_B T} \right)^{1/2} \frac{V}{a}$$

If we plot  $\ln(p)$  inside our chamber against  $t$ , we can determine  $p_0$  and  $\tau$ . For constant temperature and volume, measurement of  $\tau$  provides a simple way of determining the molecular mass,  $m$ .

### Transport Properties Of An Ideal Gas

A transport property of a substance describes its ability to transport matter or energy from one location to another. Examples include thermal conductivity (the transport of energy down a temperature gradient), electrical conductivity (transport of charge down a potential gradient), and diffusion (transport of matter down a concentration gradient).

When dealing with transport properties, we are generally interested in the rate at a property is transported. The **flux** describes the amount of matter, energy, charge etc. passing through a unit area per unit time.

Transport of some property generally occurs in response to a gradient in a related property, and the flux is generally proportional to the gradient. Note that both the flux and the gradient are vector properties. For example, if there is a concentration gradient in some direction  $z$ , there will be a component of mass flux,  $J_z$ , in the same direction.

$$J_z \propto \frac{d\rho_N}{dz}$$

Here,  $\rho_N = N/V$ , the number density.

Fortunately for us, many transport properties can be dealt with using essentially the same mathematical treatment.

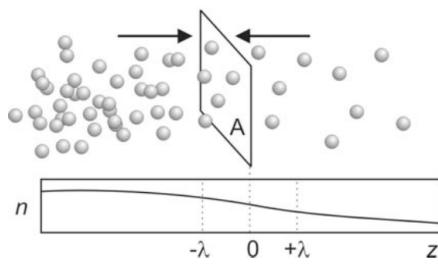
## Diffusion

The relation between matter flux and the concentration gradient is often referred to as **Fick's first law of diffusion**. The constant of proportionality is called the diffusion coefficient, and is usually given the symbol  $D$ .

$$J_z = -D \frac{d\rho_N}{dz}$$

Note the negative sign; matter diffuses down a concentration gradient from higher to lower concentration. We can use kinetic theory to show the molecular origins of Fick's first law of diffusion, and to determine a value for the diffusion coefficient,  $D$ .

Consider the flux of particles arriving from the left and from the right at an imaginary 'window' within a gas along the  $z$  axis. There is a decreasing concentration gradient from left to right.



Since the motion of the gas particles is randomised on each collision, the furthest a given particle is able to travel in a particular direction is on average equal to a distance of one mean free path,  $\lambda$ .

To a first approximation, we can assume that all of the particles arriving at the imaginary window over a time interval  $\Delta t$  have arrived there from a distance  $\lambda$  to the left or right, and the number densities of particles arriving from the left and right will therefore reflect the number densities at  $z = -\lambda$  and  $z = +\lambda$ , respectively.

If we approximate our concentration gradient to be linear between these two points with a gradient equal to that at the location of our imaginary window ( $z=0$ ). We can then write these two number densities as

$$\rho_N(-\lambda) = \rho_N(0) - \lambda \left( \frac{d\rho_N}{dz} \right)_0 \quad \text{and} \quad \rho_N(+\lambda) = \rho_N(0) + \lambda \left( \frac{d\rho_N}{dz} \right)_0$$

from the left and right respectively.

We have calculated the number of collisions with a wall before, and for unit area and unit time:

$$z_{\text{wall}} = \frac{N}{V} \left( \frac{k_B T}{2\pi m} \right)^{1/2} = \frac{N \langle v \rangle}{V 4}$$

so the fluxes from the left and right are therefore

$$J_{\text{left}} = \frac{\langle v \rangle \rho_N(-\lambda)}{4} = \frac{\langle v \rangle}{4} \left( \rho_N(0) - \lambda \left( \frac{d\rho_N}{dz} \right)_0 \right)$$

and

$$J_{\text{right}} = \frac{\langle v \rangle \rho_N(+\lambda)}{4} = \frac{\langle v \rangle}{4} \left( \rho_N(0) + \lambda \left( \frac{d\rho_N}{dz} \right)_0 \right)$$

The net flux in the  $z$  direction is therefore

$$J_z = J_{\text{left}} - J_{\text{right}} = -\frac{1}{2} \left( \frac{d\rho_N}{dz} \right)_0 \lambda \langle v \rangle$$

This shows that the flux is proportional to the concentration gradient, and hence proves Fick's first law. It would appear that the diffusion coefficient is given by

$$D = \frac{1}{2} \lambda \langle v \rangle$$

Although this is almost right, the approximations we have made are not exact. For example, within a distance  $\lambda$  from our window, some particles are lost through collisions before they can contribute to our matter flux, and this effect must be corrected for.

A more rigorous treatment yields

$$D = \frac{1}{3} \lambda \langle v \rangle$$

We can use this result to predict the way in which the rate of diffusion will respond to changes in temperature and pressure. Increasing the temperature will increase  $\langle v \rangle$ , and therefore increase the diffusion rate, while increasing the pressure will reduce  $\lambda$ , leading to a reduction in the diffusion rate.

### An Example: Noble Gas Diffusion

By what factor would you expect the diffusion coefficients of Helium and Neon to vary if the atomic radii are 31 and 38 pm and atomic masses 4.002 and 20.17 amu, respectively?

From the above equation, and the previous expressions for  $\lambda$  and  $\langle v \rangle$ , we can deduce that the diffusion coefficient is proportional to  $r^{-2}$  and  $m^{-1/2}$ . Therefore upon going from He to Ne we can expect an increase in diffusion coefficient of 3.37 times.

### Thermal Conductivity

Similarly to mass transport, if there is a temperature gradient along  $z$ , there will be a component of **energy flux** along  $z$ , which will determine the rate of thermal diffusion (or thermal conductivity). Again, since energy flows down a temperature gradient, the constant of proportionality,  $\kappa$  (kappa) takes a negative sign.  $\kappa$  is known as the coefficient of thermal conductivity.

$$J_z = -\kappa \frac{dT}{dz}$$

We can derive this equation and obtain a value for the coefficient of thermal conductivity,  $\kappa$ , using almost an identical approach to that used above for diffusion:

Again consider the flux of particles upon an imaginary window from the left and right, but this time we will assume that the gas has a uniform number density (i.e. there is no concentration gradient). Instead let us assume there is a temperature gradient, with the temperature decreasing from left to right. We will assume that the average energy of a particle is  $\varepsilon = \alpha k_B T$ , where  $\alpha$  is the appropriate fraction given by the equipartition theorem (for example, a monatomic gas has  $\varepsilon = 3/2 k_B T$ ).

Using almost identical arguments to those above for diffusion, namely that particles are on average reaching the window from a distance of one mean free path away, from regions in which their energies are  $\varepsilon(-\lambda)$  and  $\varepsilon(+\lambda)$ , we obtain expressions for the energy fluxes from left and right, and again calculate the net flux.

$$J_z = J_{\text{left}} - J_{\text{right}} = -\frac{1}{2} \left( \frac{dT}{dz} \right)_0 \alpha k_B \rho_N \lambda \langle v \rangle$$

Again, this is an approximation, and the true flux is

$$J_z = -\frac{1}{3} \left( \frac{dT}{dz} \right)_0 \alpha k_B \rho_N \lambda \langle v \rangle$$

This shows that the energy flux is proportional to the temperature gradient, and that the coefficient of thermal conductivity,  $\kappa$ , is given by

$$\kappa = \frac{1}{3} \alpha k_B \rho_N \lambda \langle v \rangle$$

We can simplify this by recognising that for an ideal gas, the heat capacity at constant volume is given by  $C_V = \alpha k_B N_A$ . Substituting this into the above yields

$$\kappa = \frac{1}{3} \lambda \langle v \rangle C_V [X]$$

where  $[X] = \rho_N / N_A = N / (N_A V)$  is the molar concentration. Note that because  $\lambda \propto 1/p$  and  $[X] \propto p$ , the thermal conductivity is essentially independent of pressure.<sup>6</sup>

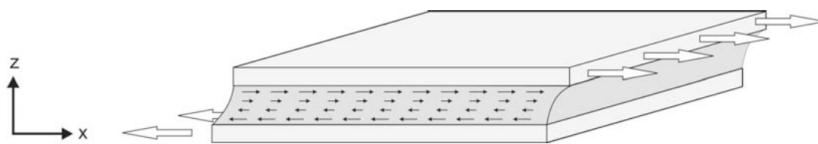
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<sup>6</sup> This is true at all but very low pressures. At extremely low pressures, the mean free path becomes larger than the dimensions of the container, and the container itself starts to influence the distance over which energy may be transferred.

## Viscosity

Viscosity describes a fluid's resistance to deformation when subjected to a shear stress.

When a force is applied to an object or material, the material exerts an opposing force (by Newton's third law). A shear stress is present when the force is applied parallel to a face of the material. An example of shear stress would be the stress induced in a liquid trapped between two glass plates when the plates are moved across each other.



We can also think of viscosity as a measure of the internal friction within a fluid, and hence its internal resistance to flow, as when a fluid flows, a shear stress is induced as 'layers' of fluid try to move over each other.

Shear stress results in different velocity components of the fluid (in the  $x$  direction) as we move through the depth of the fluid (in the  $z$  direction). We therefore have a gradient in  $v_x$  along the  $z$  direction, and in analogy to diffusion and thermal conductivity, this gives rise to a flux in  $v_x$  (or equivalently momentum  $p_x$ ) along  $z$ .

$$J_z = -\eta \frac{dv_x}{dz}$$

here  $\eta$  is the coefficient of viscosity (or more usually just 'the viscosity') of the fluid.

We can carry out a similar treatment to those above for diffusion and thermal conductivity: We assume that (in the  $z$  direction) particles incident on our imaginary window (in the  $xy$  plane) from the left carry momentum  $p_x(-\lambda) = mv_x(-\lambda)$  and those from the right carry momentum  $p_x(+\lambda) = mv_x(+\lambda)$ .

Our fluxes are now

$$J_{\text{left}} = \frac{1}{4} \langle v \rangle \rho_N m v_x(-\lambda) = \frac{1}{4} \langle v \rangle \rho_N \left[ mv_x(0) - m\lambda \left( \frac{dv_x}{dz} \right)_0 \right]$$

and

$$J_{\text{right}} = \frac{1}{4} \langle v \rangle \rho_N m v_x(+\lambda) = \frac{1}{4} \langle v \rangle \rho_N \left[ mv_x(0) + m\lambda \left( \frac{dv_x}{dz} \right)_0 \right]$$

The net flux of momentum  $p_x$  in the  $z$  direction is therefore

$$J_z = J_{\text{left}} - J_{\text{right}} = -\frac{1}{2} \rho_N m \lambda \langle v \rangle \left( \frac{dv_x}{dz} \right)_0$$

Again we need to correct this expression to give

$$J_z = -\frac{1}{3} \rho_N m \lambda \langle v \rangle \left( \frac{dv_x}{dz} \right)_0$$

The flux is proportional to the velocity gradient, as required, and we see that the coefficient of viscosity for an ideal gas is given by

$$\eta = \frac{1}{3} \rho_N m \lambda \langle v \rangle = \frac{1}{3} m \lambda \langle v \rangle N_A [X]$$

As with thermal conductivity, the viscosity is independent of the pressure. However, the viscosity does have a  $T^{1/2}$  dependence on temperature, as the mean velocity  $\langle v \rangle \propto T^{1/2}$ . Note that this means that, unlike a liquid, the viscosity of a gas increases with temperature, since the increased velocity of the gas particles increases the momentum flux.

In general, for a liquid the viscosity decreases with increasing temperature, as in a liquid most of the energy goes into overcoming intermolecular forces, thereby making it easier for the particles to move past each other. In the gas phase we are able to neglect intermolecular forces to a good approximation, but in a liquid these forces have a major effect.