The Physical Basis Of Chemistry
Properties Of Gases & Classical Mechanics

mark.wallace@chem.ox.ac.uk

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**

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^{-1}	$v(t) = \dfrac{dr}{dt} \equiv \dot{r}$
Acceleration /ms^{-2}	$a(t) = \dfrac{dv}{dt} = \dfrac{d^2r}{dt^2} \equiv \ddot{r}$

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:

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

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

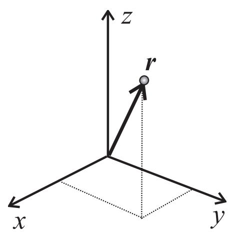
For constant acceleration ($a(t)=a$) we can integrate as we did above to show that the particle's position is described by

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

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

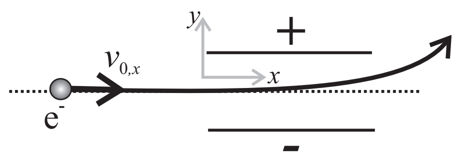


Motion in each **orthogonal direction** can be decomposed into a separate set of equations. This is often a useful tool for breaking down a problem into more manageable parts. We can also combine these equations by describing the motion as a **vector**.

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

An Example: The Cathode Ray Tube

Electrons, initially travelling at 2.4 × 10^6 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 × 10^{14} 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,

$$\begin{aligned} a_x &= 0 \\ v_x &= v_{0x} = 2.4 \times 10^6 \text{ m s}^{-1} \\ r_x &= r_{0x} + v_{0x} t \qquad (r_{0x} = 0) \\ r_x &= 2.4 \times 10^6 t = 0.02 \text{ m} \\ \therefore \quad t &= 8.33 \times 10^{-9} \text{ s} \end{aligned}$$

For motion along the y co-ordinate,

$$\begin{aligned} a_y &= 4 \times 10^{14} \text{ m s}^{-2} \\ v_y &= v_{0y} + a_y t \qquad (v_{0y} = 0) \\ r_y &= r_{0y} + \tfrac{1}{2} a_y t^2 \qquad (r_{0y} = 0) \end{aligned}$$

Substitute for the time the electron spends between the plates,

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

For the angle at which the electrons depart,

$$\tan\theta = \frac{v_y}{v_x} = \frac{a_y t}{v_{0x}} \qquad \theta = 54.2^{\text{o}}$$

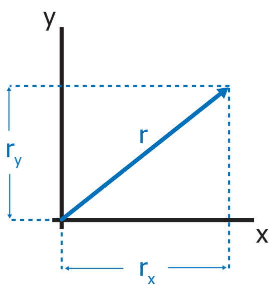
Vectors

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 r with magnitude r and direction θ with respect to the x axis. We can decompose this vector into two orthogonal components r_x and r_y.



Components

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

Magnitude

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

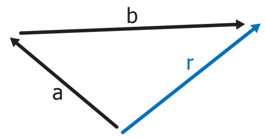
Direction

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

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

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

Vector Addition



Vector Sum

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

Components

$$r_x \;=\; a_x + b_x \qquad r_y \;=\; a_y + b_y$$

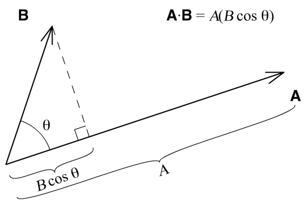
Vector Multiplication

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 $\boldsymbol{A}$ and $\boldsymbol{B}$.

Scalar (Dot) Product

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

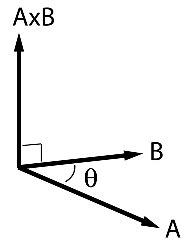
The dot product is a **scalar**. It is the product of the magnitude of one vector (A), and the magnitude of the projection of a second vector (B) along the first.



Vector (Cross) Product

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

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



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}**	**∞**	**Chemistry!**
Weak	10^{-6}	10^{-17} m	Associated with radioactivity
Gravitational	10^{-38}	∞	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

$$F = -\frac{Gm_1 m_2}{r^2} \qquad G = 6.67 \times 10^{-11}\ \mathrm{N\,m^2\,kg^{-2}}$$

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

$$F = mg \qquad g = \frac{Gm_\mathrm{E}}{R_\mathrm{e}^2} \simeq 9.8\ \mathrm{m\,s^{-2}}$$

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

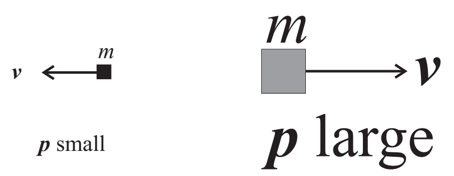
$$F = \frac{q_1 q_2}{4\pi\epsilon_0 r^2} \qquad \frac{1}{4\pi\epsilon_0} = 9.0 \times 10^9\ \mathrm{N\,m^2\,C^{-2}}$$

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

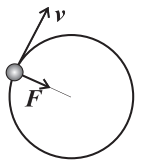
$$\vec{p} = m\vec{v}$$



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**:

$$\vec{F} = \frac{\mathrm{d}\vec{p}}{\mathrm{d}t}$$

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

$$\vec{F} = \frac{\mathrm{d}\vec{p}}{\mathrm{d}t} = \frac{\mathrm{d}(m\vec{v})}{\mathrm{d}t} = m\frac{\mathrm{d}\vec{v}}{\mathrm{d}t} = m\vec{a} \qquad \boxed{\vec{F} = m\vec{a}}$$

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

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

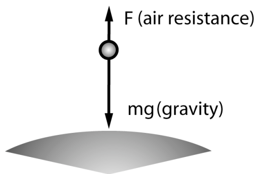
An Example: The Hydrogen Atom

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

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 $F_{\mathrm{air}}=kv$, 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 be 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 $t \rightarrow \infty$, $v \rightarrow v_{\mathrm{T}}$ so $v_{\mathrm{T}} = mg/k$.