

0. Miscellaneous**0.0 Textbooks**

General:

- Physics for Scientists & Engineers (P. A. Tipler, W. H. Freeman & co.)
- University Physics (Young and Freeman, Addison – Wesley)

Specific:

- Properties of Matter (B.H. Flowers, John Wiley & Sons – out of print)
- Gases, Liquids & Solids (M. Tabor, Cambridge University Press)
- Understanding the properties of matter (M. de Podesta, Taylor & Francis)

0.1 Units

The magnitude of physical quantity is given by a number and unit. Numbers without units are meaningless.

The system of units is called Systéme Internationale (S.I). It consists of 7 basic units;

- Time (s, Seconds)
- Mass (kg, kilograms)
- Length (m, metres)
- Electric current (A, Amperes)
- Temperature (K, Kelvin)
- Luminous intensity (cd, Candela)
- Amount of substance (mol, Mole)

All other units can be coherently derived from the basic units i.e. without a numerical factor.

Eg:

- Force (Newton) $1\text{N} = 1\text{kgms}^{-2}$
- Energy, work (Joule) $1\text{J} = 1\text{N.m}$
- Charge (Coulomb) $1\text{C} = 1\text{As}^{-1}$
- Pressure (Force/Area) $\text{Nm}^{-2} = \text{Pascal}$
- Density (Mass/volume) kgm^{-3}

Some units can be incoherently derived:

- Mass: 1 tonne = 1,000 kg
- Time: 1 minute = 60 seconds

0.2 S.I. Decimals

Physical quantities can be very small or large → prefix:

- | | | |
|----------|-------|------------|
| • Femtes | f | 10^{-15} |
| • Piko | p | 10^{-12} |
| • Nano | n | 10^{-9} |
| • Micro | μ | 10^{-6} |
| • Milli | m | 10^{-3} |
| • Centi | c | 10^{-2} |
| • Demi | d | 10^{-1} |
| • Kilo | K | 10^3 |
| • Mega | M | 10^6 |
| • Giga | G | 10^9 |
| • Terra | T | 10^{12} |
| • Peta | P | 10^{15} |

A unit suitable to describe one quantity of a system may not be suitable for another system. E.g. Energy: Latent heat in J, KJ. Single atoms in 10^{-20}J

0.3 Some common non-SI units

For lengths related to atoms / molecules: Ångström - $1\text{Å} = 10^{-10}\text{m} = 1\text{nm}$

For energies related to atoms: Electron-Volts (eV) – $1\text{eV} = 1.602 \times 10^{-19}\text{J}$

An older unit of energy: Calorie – $1\text{cal} = 4.184\text{J}$

Older units of pressure:

1 atmosphere = 101,325 KPa

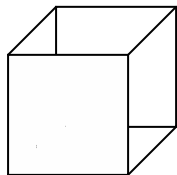
1 bar = 100KPa

1 torr = 133.32 Pa

0.4 Order of Magnitude Estimates

It is often useful to estimate a certain quantity by an easy and crude model.
e.g. estimate the skin area of a human.

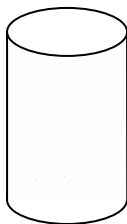
Model (1):



Height: 180 cm
Width: 50 cm
Depth: 25 cm

$$\text{Area: } 2 \times 180 \text{ cm} \times 50 \text{ cm} + 2 \times 180 \text{ cm} \times 25 \text{ cm} + 2 \times 50 \text{ cm} \times 25 \text{ cm} \approx 29,000 \text{ cm}^2 = 2.9 \text{ m}^2$$

Model (2):



Height: 180 cm
Radius: 25 cm

$$\begin{aligned} \text{Circumference of a circle: } & 2 \pi r \\ \text{Area of cylinder} &= 2 \pi r \cdot h + 2 \pi r^2 \\ &= 2 \pi \times 0.25 (1.8 \times 0.25) = 3.2 \text{ m}^2 \end{aligned}$$

Conclusion: skin area of a human is a couple of square metres.

Such calculations are called Order of Magnitude Estimations (or back-of-the-envelope-calculations')

Give answers only to significant figures.

1. Atoms and Molecules

1.1 Matter

Matter is made up of atoms. These in turn are made up of elementary particles:

- Electrons e^- , mass= $m_e=9.1 \times 10^{-31}$ kg, charge= $e=-1.6 \times 10^{-19}$ C
- Protons p , mass= $m_p=1.673 \times 10^{-27}$ kg, charge= $p=1.6 \times 10^{-19}$
- Neutrons n , mass= $m_n=1.675 \times 10^{-27}$ kg, charge=0

Atoms of different elements differ in the number of their elementary particles.

- Number of protons z (atomic number) = no. of electrons (To balance charge – atoms are electronically neutral)
- If an atom loses or gains an electron they are called ions. These carry a charge

Protons and neutrons make up the nucleus (positively charged). Around the nucleus is a 'cloud' of electrons.

Atoms with equal numbers of Z but different numbers of neutrons are called isotopes. The diameter of the nucleus is about 10^5 times smaller than that of the atom, but contains most of its' mass.

$$m_p \approx m_n \approx 200m_e$$

$$r_{\text{nucleus}} \approx 1 \rightarrow 10 \text{ fm}$$

$$r_{\text{atom}} \approx \text{Å} (10^{-10})$$

e.g. for He $\rightarrow z=2, 2p, 2n, 2e^-$

Mass of 1 atom:

$$p: 2 \times 1.673 \times 10^{-27} \text{ kg}$$

$$n: 2 \times 1.675 \times 10^{-27} \text{ kg}$$

$$e: 2 \times 9.1 \times 10^{-31} \text{ kg}$$

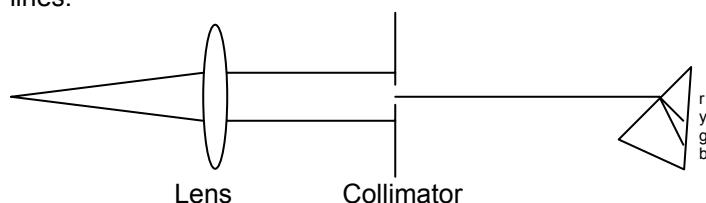
$$\text{Total mass } m = 6.7 \times 10^{-24} \text{ g}$$

Molar mass = mass of 1 atom \times number of atoms in a mole

$$M = m \cdot N_A = 6.7 \times 10^{-24} \text{ g} \cdot 6.02 \times 10^{23} \text{ mol}^{-1} = 4.03 \text{ g} \cdot \text{mol}^{-1}$$

1.2 Atomic Spectra

Early in the 19th century it was discovered that spectra from luminous bodies contained lines.



Presumably Balfour Stewart from Manchester discovered what is today known as Kirchhoff's law:

"Bodies emitting at a certain wavelength also absorb at that wavelength".

The best studied element was Hydrogen by Ångstrom. Swiss teacher Johan Balmer found in 1884 that visible hydrogen lines can be described by

$$\lambda = \frac{(364.6 \text{ nm}) \cdot m^2}{m^2 - 4} \text{ with } m=3,4,5$$

Rydberg showed a more general expression

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right) \text{ with } n_1 \text{ and } n_2 \text{ as integers. } n_1 > n_2$$

$R_H = 1.097 \times 10^7 \text{ m}^{-1}$ – Rydberg constant for Hydrogen.

$n = \dots, 5, 4, 3, 2 \rightarrow n_2 = 1$ Lyman series (UV $90 \rightarrow 120 \text{ nm}$)

$n = \dots, 6, 5, 4, 3 \rightarrow n_2 = 2$ Balmer series (Visible $400 \rightarrow 750 \text{ nm}$)

$n = \dots, 7, 6, 5, 4 \rightarrow n_2 = 3$ Paschen series (IR $1000 \rightarrow 1900 \text{ nm}$)

$n = \dots, 7, 6, 5 \rightarrow n_2 = 4$ Brackett Series (IR $2200 \rightarrow 4000 \text{ nm}$)

$n=7,6 \rightarrow n_2=5$ Pfund series (IR 4500→7500nm)

From the law of energy conservation it is apparent that the different energy when changing between 2 levels is emitted / absorbed as a photon.

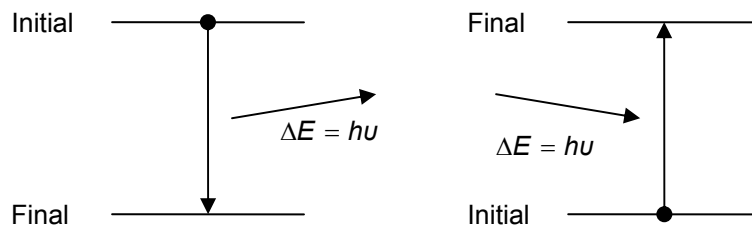
Planck proposed that this energy is quantised.

A wave of frequency ν behaves like a packet of energy.

$$E = h\nu$$

Planck constant $h=6.626 \times 10^{-34}$ Js.

With $\nu = \frac{c}{\lambda}$ where c is the speed of light, $3 \times 10^8 \text{ms}^{-1}$, we see that the emitted / absorbed lines correspond to the transitions between different energy levels



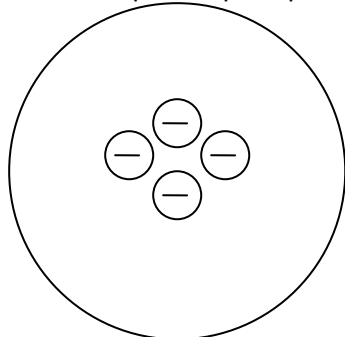
$$h\nu = Rhc \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) = E_i - E_f = \Delta E$$

The sequence of energy levels is given by

$$E_n = \frac{-Rhc}{n^2} \quad n: \text{integer}$$

1.3 Early models of the Atom

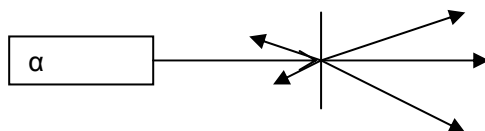
J. J. Thompson's 'plum pudding' model



Electrons are embedded in a fluid that contains most of the mass and enough positive charge to compensate for that of the electrons.

Model was ruled out in 1911 by experiments of Geiger, Masden & Rutherford in Manchester.

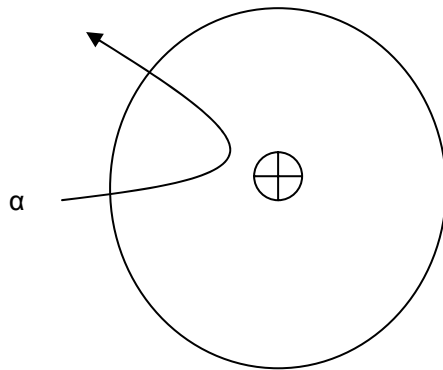
Scattering of α particles in a gold foil



α have a high velocity $\sim 3-6 \text{MeV}$ ($E_{\text{atom}} \sim \text{eV}$)

Few particles that were backscattered (1 out of 10^4).

From scattering theory:

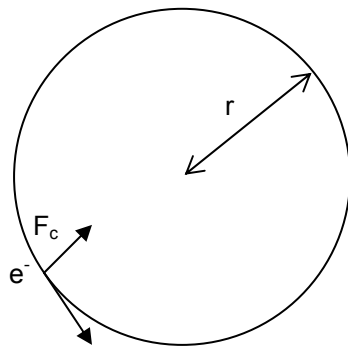


"Atoms are almost empty"

1.4 Bohr's model of the Hydrogen atom

In 1913, Niels Bohr, at that time in Rutherford's lab in Manchester, proposed a model of the hydrogen atom which successfully predicted the observed spectra.

The electron moves under the influence of Coulomb attraction around the nucleus according to classic mechanics.



For simplicity we restrict our calculations to circular orbits. (Allowed are also elliptical orbits with the nucleus in the focus of the ellipse)

Total energy of electron is related to radius.

Potential energy $E_{pot} = \frac{Kq_1q_2}{r} = \frac{ke^2}{r}$ where k is the Coulomb constant =

$$8.988 \times 10^9 \text{ Nm}^2 \text{ c}^{-2} = \frac{1}{4\pi\epsilon_0}$$

$\epsilon_0 = 8.859 \times 10^{-12} \text{ Fm}^{-1}$ electric field constant.

Kinetic energy:

From Newton's law $\sum F = ma$

Coulomb force = centripetal force

$$\frac{Ke^2}{r^2} = \frac{mv^2}{r}$$

$$E_{kinetic} = \frac{1}{2}mv^2 = \frac{1}{2} \frac{ke^2}{r}$$

Note that $E_{pot} = -2E_{kin}$ true for all $\frac{1}{r^2}$ force fields

$$\text{Total energy: } E_{kin} + E_{pot} = -\frac{1}{2} \frac{ke^2}{r}$$

But: electromagnetic theory says that accelerated electrons moving in a circle have to emit radiation. This means that e^- loses energy and spirals into the nucleus.

1. Bohr Postulate

"Electrons can only stay in specific orbits, where they don't radiate. Making transitions between different orbits, they do radiate"

2. Bohr Postulate

"The frequency of the radiation is related to the energy of the different levels"

$$u = \frac{E_i - E_f}{h} \quad (\text{Same as conservation of energy})$$

$$\text{Follows that } u = \frac{1}{2} \frac{ke^2}{h} \left(\frac{1}{r_2} - \frac{1}{r_1} \right)$$

Where r_1 =radius of initial state, r_2 =final state.

Compared to Rydberg: $r \sim n^2$ (n =integer)

3. Bohr Postulate

After trial and error to find a condition that yields $r \sim n^2$:

"Angular momentum of electron is equal to an integer times \hbar "

$$\hbar = \frac{h}{2\pi}$$

$$mvr = n\hbar = \frac{nh}{2\pi}$$

$$v^2 = \frac{n^2 \hbar^2}{m^2 r^2}$$

$$\text{From above: } \frac{ke^2}{r^2} = \frac{mv^2}{r}$$

$$\rightarrow v^2 = \frac{ke^2}{mr}$$

$$r = \frac{n^2 \hbar^2}{mke^2} = n^2 \cdot a_0$$

$$a_0: \text{ first Bohr radius} = \frac{\hbar^2}{mke^2} = 0.0529 \text{ nm}$$

Substituting into equation for v gives

$$v = \frac{mk^2 e^4}{4\pi \hbar^3} \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$

Compare to Rydberg's formula:

$$R_H = \frac{mk^2 e^4}{c4\pi \hbar^2}$$

Energy levels:

$$\text{Total energy was } E = -\frac{1}{2} \frac{ke^2}{mr}$$

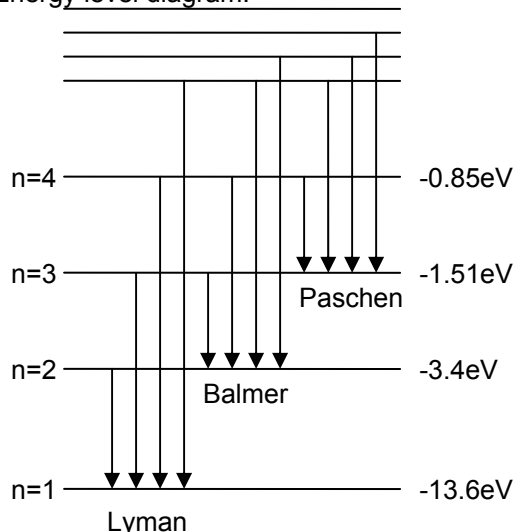
Insert expression for radius:

$$E_n = -\frac{1}{2} \frac{ke^2}{n^2 a_0} = -\frac{1}{2} \frac{mk^2 e^4}{\hbar^2} \frac{1}{n^2}$$

$$\text{or } E_n = -E_0 \frac{1}{n^2} \text{ with } E_0 = \frac{mk^2 e^4}{2\hbar^2} = 13.6 \text{ eV}$$

Note that energy is quantised. Energy of the ground level of hydrogen is $E_n = -13.6 \text{ eV}$

Energy level diagram:



Transitions are performed by emission / absorption of a photon with energy $E = E_i - E_f$.

$$\rightarrow \nu = \frac{E_i - E_f}{h} \rightarrow h = \frac{c}{\nu} = \frac{hc}{E_i - E_f} \lambda$$

Note: same theory holds for hydrogen-like atoms, for example He^+ , Li^{2+} if you take Z along in the calculation.

Example: find the energy and wavelength of the line with the longest wavelength in the Lyman series

Lyman: $n_f=1$, $n_i=2$ – longest wavelength, smallest energy.

$$E = E_i - E_f = \frac{-13.6\text{eV}}{2^2} - \frac{-13.6\text{eV}}{1^2} = -3.4\text{eV} + 13.6\text{eV} = 10.2\text{eV}$$

$$\lambda = \frac{hc}{E_2 - E_1} = \frac{1240\text{eV}\cdot\text{nm}}{10.2\text{eV}} = 121.6\text{nm}$$

UV light.

1.4 The Periodic Table of Elements

Bohr's model of the hydrogen atom was good at its' time, but now we use quantum mechanics (In the 2nd or 3rd year...)

Basic results:

The state of each electron is characterised by 4 quantum numbers:

n : principle quantum number.

Gives the energy of the electron.

l : Orbital quantum number.

Related to the angular momentum of the electron $L = \sqrt{l(l+1)}\hbar$

m : Magnetic quantum number

Related to the Z-component of angular momentum. $L_z = m\hbar$

s : Spin. Rotation around itself – generally disregarded.

Possible quantum numbers are:

$$n=1,2,3$$

$$l=0,1,2,\dots,n-1$$

$$m=-l,\dots,-1,0,1,\dots,+l$$

$$s=\pm\frac{1}{2}$$

$n=1,2,3$ etc... are called K,L,M,... shells

$l=0,1,2$, etc... are called s,p,d,f,... orbitals.

The allowed energy levels for hydrogen are the same as those obtained by Bohr. For atoms with more than 1 electron, interactions lead to a dependence on l . For atoms in magnetic fields, the energy levels also depend on m .

Pauli-principle (1925)

“Electronic states are filled such that no two (or more) electrons have the same quantum numbers.”

Orbits:

s: orbital contains $2e^-$

p: orbital contains $6e^-$

d: orbital contains $10e^-$

f: orbital contains $14e^-$

So:

K shell has a total of $2e^-$

L shell has a total of $8e^-$

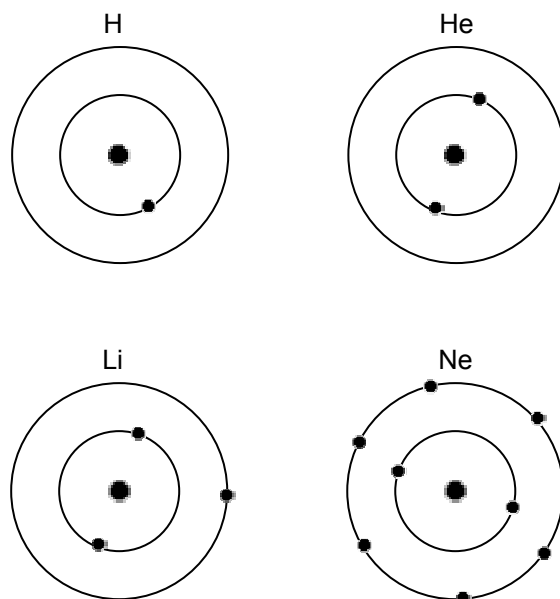
M shell has a total of $18e^-$

Orbitals are filled up as:

$1s^2 2s^2 2p^6 3s^2 3p^6 \dots$

This is called the electron configuration.

For larger atoms we observe deviations from the regularity. The regular fitting of shells reflects the periodicity of the periodic table of elements.



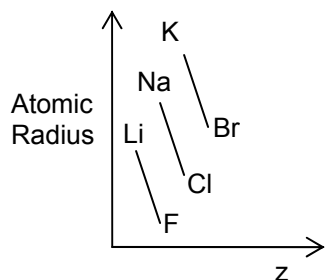
The most stable elements are those with filled shells, i.e. He, Ne, Ar, Kr (Noble / inert gases)

Elements in the same groups of the periodic table have similar chemical properties.

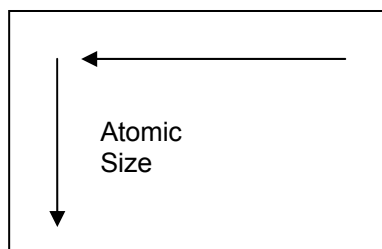
e.g. Li, Na, K, Rb, Cs, Fr – Alkaline metals

or F, Cl, Br, I, At – Halogens

Atomic sizes:



General trend



Periodic Table

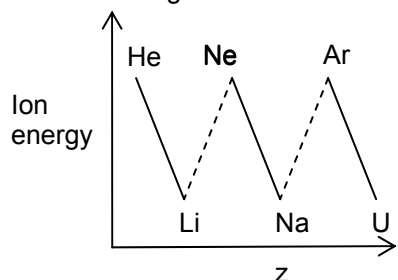
Changes in the atomic radius are due to the increasing charge of the nucleus.

What about ions?

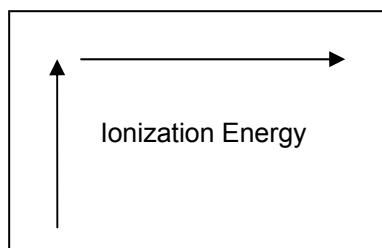
The radii of cations (Positively charged) follows the same trend as those of atoms. e.g. $H^+ \ll H$ (H^+ is the nucleus), $Mg^{2+} < Mg$

The radii of anions (Negatively charged) are always larger than those of the neutral atoms, eg. $s < s^{2-}$.

Ionisation energies:



General trend

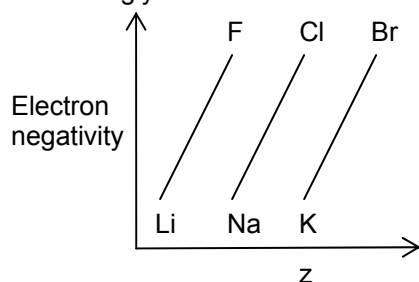


Periodic Table

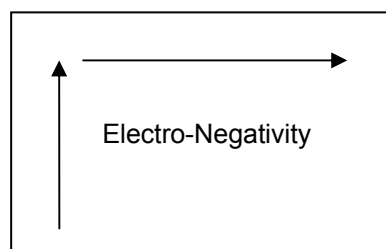
Ionisation energies of the noble gases are very high; those of alkaline atoms are small.

Electronegativity

“How strongly does an atom want an additional electron”



General trend



Periodic Table

Alkaline metals have little tendency to attract e^-
Halogens are strongly electronegative

Elements in the same columns of the periodic table exhibit similar chemical properties.

1.5 Molecular bonding and interactions

Ionic bonds:

Result from electron transfer.

e.g. NaF

Na has 11e⁻, 2 k-shell, 8 l-shell, 1 M-shell

(1s²2s²2p⁶3s¹)

F has 9e⁻, 2 k-shell, 7 l-shell

(1s²2s²2p⁵)

When both atoms approach each other, there will be a transfer of the outermost electron of Na to F, at a certain separation. Sodium now carries a +e charge, F a -e charge → they are both ions.

→ Attraction by Coulomb interaction $\sim \frac{1}{r^2}$

- Ionic bonds are directed
- Not saturated (One positive ion can attract several negative ions)
- Bonds are strong, energies $\sim 10^{-18}$ J

Example: NaCl

- Energy released by an atom acquiring an electron is called electron affinity, for Cl it is 3.62eV

- Ionisation energy of S

Formation of Na⁺ and Cl⁻ ions takes little energy (5.14eV-3.62eV=1.52eV). This is at infinite separation!

As atoms approach each other, the electrostatic potential energy varies as

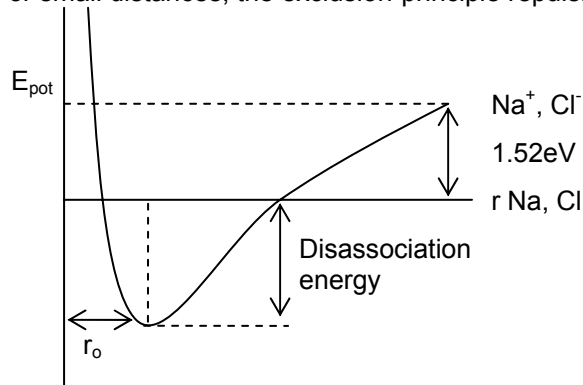
$$E_{pot} = \frac{-ke^2}{r}$$

$$k: \text{Coulomb constant} = \frac{1}{4\pi\epsilon_0}$$

For separation smaller than $r=0.95\text{nm}$, the E_{pot} of attraction is larger than 1.52eV

→ Na⁺ and Cl⁻ ions are formed.

For small distances, the exclusion-principle repulsion assures an equilibrium separation

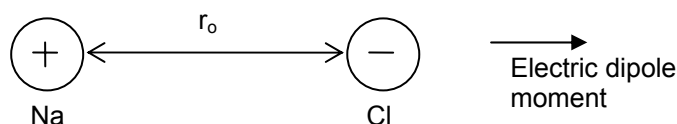


Disassociation energy is energy required to separate ions and form neutral atoms.

Covalent Bonds

- Bonding involves the sharing of electrons
- Is generally found for similar or identical atoms N₂, H₂, CO
- Bonding cannot be described in classical terms, they result from "Exchange interaction"
- Bonds are directed and saturated
- Bonds are relatively strong, energies $\sim 10^{-19}$, 10^{-18}
- Bonds are only purely covalent for identical atoms H₂, N₂, O₂.

- For dissimilar atoms we have a mixture of ionic and covalent bonding, even for NaCl



$$\mu_{ionic} = e_0 r_0 = 3.78 \times 10^{-29} \text{ Cm}$$

$$\text{Measurement of dipole: } \mu_{measure} = 3 \times 10^{-29}$$

Ratio $\frac{\mu_{measured}}{\mu_{ion}} = 0.79 \rightarrow$ NaCl has about 79% ionic bonding, therefore 21% covalent bonding

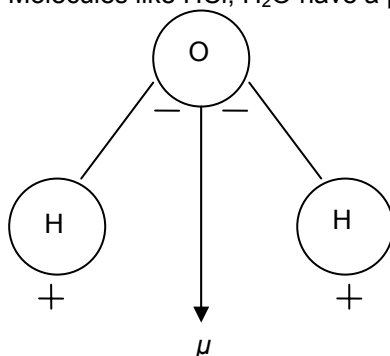
Van der Waal's forces

- Exist between all atoms and molecules
- Bonds are electrostatic in nature, but much weaker than ionic or covalent bonding
- Energies $\sim 10^{-22}$ J
- Van der Waal's forces are responsible for the condensation of virtually all substances into liquids and solids

Three groups of van der Waal's forces are distinguished:

1. Dipole-Dipole forces (Keeson forces)

Molecules like HCl, H₂O have a permanent dipole moment.



Dipole moment interacts with those of neighbours, to produce a net attractive force $\sim 1/r^2$.

2. Dipole-induced dipole forces

- For molecules with a permanent dipole moment and non-polar ones, HCl and Ne
- HCl dipole induces a charge separation in the Ne, i.e. a dipole, leading to an attractive force $\sim 1/r^2$.

3. Dispersion forces

- Observed between two non-polar molecules, i.e. without μ .
- Fluctuations of charge distributions induce dipole moments.

At a given time the first atom has a dipole moment μ (Due to fluctuations)

$$\text{This produces an electric field } E = \frac{2\mu}{r^3} \frac{1}{4\pi\epsilon_0}$$

This induces dipole μ' in second atom. $\mu' = \alpha E$ (α : atomic polarisability)

Dipole in electric field has a potential energy

$$E_{pot} = -\mu' E = -\alpha E^2 = -\frac{4\alpha\mu^2}{r^6} \left(\frac{1}{4\pi\epsilon_0} \right)^2$$

Force is a derivative of potential

$$F = \frac{2E_{pot}}{2r} \sim \frac{const.}{r^7}$$

These forces are always attractive.

Hydrogen Bonding

The nucleus of a hydrogen atom is shared between two atoms (Often observed in biological molecules, e.g. DNA)

Metallic Bonding

These involve the sharing of a "sea" of free electrons by many atoms.

2. States of Matter – Solids, Liquids and Gases

2.1 Phases, Components and Variables of State

After discussing the microscope / atomic world we will now look at many atoms / molecules ($\sim 10^{23}$ atoms)

Now, to take a very extreme viewpoint: start with the universe.

The universe consists of 2 parts:

1. “The system”, the part we are interested in, for example a container with gas, a beaker with liquid, an engine etc...
2. “The surrounding”, the rest of the universe, the place where we make our observations.

- A system can exchange matter or energy or work / heat with the surrounding
- If an exchange of matter and energy is possible, the system is open
- When only energy but not matter transfer is possible, the system is closed
- No exchange of matter or energy, the system is isolated.

Examples:

The heart → open system

A motor → open system

An unplugged refrigerator with a closed door → Isolated

A refrigerator with an open door → closed?

A (Living) elephant → open

Liquid nitrogen in a Dewar → isolated system

The fundamental concepts of thermodynamics are based on “work”, “energy”, and “heat”.
→ think / read about subtle differences.

“Work” is done if a process can be used to displace a weight somewhere in the surrounding.

Work is done by the system if the weight is raised.

Work is done on the system if the weight is lowered.

e.g. a gas: if it expands, weight is lifted, and work is done by the system. And vice versa.

“Energy” is the capacity to do work.

When we do work on a system, its energy is increased. If the system does work, its energy is reduced.

Heat

When energy changes as a result of temperature difference between the system and the surrounding, there is a flow of heat.

Phase

Every day experience: gas, liquid, solid

Formal definition (Gibbs): “A phase is a state of matter that is uniform throughout, not only in chemical composition but also in physical state.”

This makes sense

- A gas or a mixture of gases are a single phase
- Ice in water is a two phase system
- At small scales the definition of a phase can be tricky.

We can talk about a one-phase system when different components are uniform on a molecular scale, and small samples represent the whole system.

Components

The number of components is the minimum number of independent species necessary to define the composition of all the phases present in the system.

Water → 1 component

Water in ethanol → 2 components

This is more complicated when species react.

Example: $\text{CaCO}_3 \leftrightarrow \text{CaO} + \text{CO}_2$

This is a two-component system! We have to specify CO_2 for the gas phase and CaCO_3 for the solid phase. The concentration of CaO is no longer independent.

Degrees of Freedom

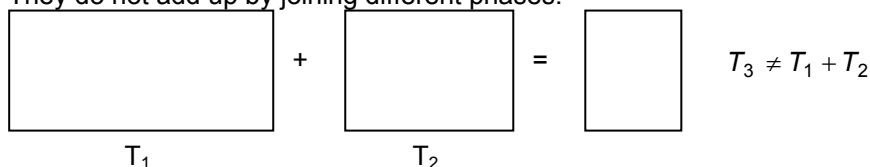
Number of variables we can change independently. Common variables of state are temperature, pressure, volume, but can also use energy, concentration etc...

To describe a system we do not need to give numbers for all variables of space, as they are connected.

Example: p , V , T in an ideal gas $pV=nRT$

1. Intensive variables of state

- Describe qualitative properties
- Independent on mass and special extension, e.g. temperature
- They do not add up by joining different phases.



2. Extensive variables of state

- Describe quantitative properties
- Depend on the mass of the system
- They do add up

e.g. volume: $100\text{ml} + 100\text{ml} = 200\text{ml}$.

Note: all quantities that are the ratio between two extensive variables of state are intensive. e.g. density = m/v .

Thermodynamic systems are described by Gibb's phase rule

$$F = C - P + 2$$

F: Degrees of freedom

C: No. of components

P: Number of phases

e.g. ice in whisky.

$C=2$, $P=2$, $F=2-2+2=2$.

2.2 Properties of states of matter

From everyday life we know three states of matter: Liquids, Gases, and Solids.

This is not a complete list of classifications; there are also:

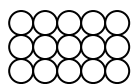
- Liquid Crystal
- Plasma
- Glasses
- Emulsions

There are several cases where it is hard to unambiguously state the state of matter!

But, classical example (of course): water

- Undergoes sharp, easily identifiable and reproducible transitions between states of matter.

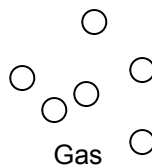
About 150 years ago, Joule.



Ice



Water



Gas

Properties of a gas:

- Fills every volume
- High compressibility
- Low density
- No rigidity (Capability to oppose forces that try to change shape, elasticity)

- Low viscosity
- Atoms / molecules randomly distributed
- Atoms / molecules move quite fast – 10^4cms^{-1}

Properties of a Liquid

- Take the shape of a container
- Low compressibility
- Much higher density than gases, $\sim 10^3$
- No rigidity (No elastic behaviour)
- Atoms / molecules are randomly distributed, but with certain “average” number of neighbours.
- Motion at comparable velocity has gases, but not only translational, also fast vibration motion.
- Viscosity $\sim 10^2$ larger than gases.

Properties of Solids

- Does not take the shape of container
- Low compressibility
- Density similar to liquids
- Rigidity exhibit elasticity
- Atoms are arranged in a 3D lattice
- Very large viscosity
- Motion still fast, but restricted to vibrations about equilibrium point.

Amorphous solids can be regarded as liquids with very high viscosity (\rightarrow see old church windows)

Change between phases by changing variables of state, generally pressure p , Volume V , temperature T .

Variables of state are not independent but connected by equations of state
Everyday experience \rightarrow change temperature.

What is temperature?

Concept of temperature is based on sense of touch: “hot”, “cold” – obviously not a good definition.

Temperature is related to the kinetic energy of atoms / molecules, but also inherently macroscopic concept.

Need a definition independent of any molecular model. Construct temp. scales based on measurements of variables of state.

- Volume of a liquid in a capillary (Mercury, Ethanol \rightarrow normal thermometers)
- Pressure of gas in a container of constant volume \rightarrow look up how constant-volume gas thermometers work!
- Electrical resistance of a conducting wire
- Expansion / contraction of a bimetallic strip on heating / cooling.

Celsius temperature scale

- Look at mercury capillary at atmospheric pressure
- Mark position of Hg column in ice water (L_0), and boiling water (L_{100})
- Define ice water as 0°C and boiling water as 100°C
- Divide into 100 intervals

$$T_{(^{\circ}\text{C})} = \frac{L_T - L_0}{L_{100} - L_0} 100^\circ$$

Fahrenheit scale

Similar to Celsius scale, ice point at 32°F , steam point at 212°F .

$$\text{Conversion: } T_{(^{\circ}\text{C})} = \frac{5}{9} (T_{(^{\circ}\text{F})} - 32^\circ)$$

Note these scales depend on pressure.

Kelvin scale

- Uses triple point of water as reference
p=0.006atm, T=0.01°C
- Define the temperature of triple point as 273.16k
- Other temperatures are proportional to pressure. In a constant volume thermometer

$$T = \frac{273.16K}{P^*} P$$

P*: pressure of thermometer at triple point (Depends on amount of substance!)

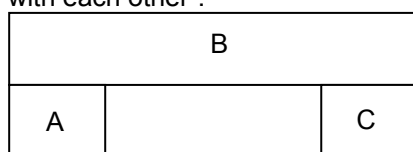
Conversion: $T_{(K)} = T_{(°C)} + 273.15k$

Thermodynamics

In order to correctly measure temperature, the object and the thermometer have to be in thermal equilibrium. This takes time.

0th Law of Thermodynamics

“If two objects are in thermal equilibrium with a third, they are in thermal equilibrium with each other”.



A&C, B&C are in thermal equilibrium. Therefore, A&B is too.

This might sound trivial, but there is no logical way to deduce this fact.

2.3 Phase Transitions

From school you know that when heat flows into a system its temperature (generally) rises. The heat you need to produce a certain temperature difference is proportional to the mass and the heat capacity C.

$$Q = C\Delta T = mc\Delta T$$

C = heat capacity, c=specific heat capacity (KJ.kg⁻¹K⁻¹)

$$c = \frac{C}{M}$$

We can also use the molar specific heat capacity c'.

$$c' = \frac{C}{n} = \frac{mc}{n} = Mc \quad (M=\text{molar mass})$$

c' [J.mol⁻¹k⁻¹]

Note:

- The heat capacity of nearly all metals are about the same c' ~ 25J.mol⁻¹k⁻¹
- Water has a large heat capacity c'~75 J.mol⁻¹k⁻¹, and is good for storing thermal heat.

Leaving school, things become more complicated. Why?

- The heat capacity can be temperature dependant
- The system can change volume, and work is done.

First law of Thermodynamics

“When heat flows into an isolated system, its internal energy increases and work is being done.”

$$\boxed{dQ = dU + dW} \quad (1)$$

Q=heat, U=internal energy, W=work

If Q is related to the change of volume:

$$\boxed{dQ = dU + pdV}$$

Now: introduce thermodynamic quantity, enthalpy H

$$H = U + pV$$

In differentiated form:

$$dH = dU + pdV + Vdp = dQ + Vdp \quad (2)$$

We can now distinguish between heat flow into systems at constant volume and at constant pressure

From (1) we see that

$$\left(\frac{2Q}{2T}\right)_V = \left(\frac{2U}{2T}\right)_V = C_V \leftarrow \text{heat capacity at constant volume}$$

From (2) we get:

$$\left(\frac{2Q}{2T}\right)_P = \left(\frac{2H}{2P}\right)_P = C_P \leftarrow \text{Heat capacity at constant pressure.}$$

Note: C_V and C_P are different quantities! Their difference is relatively small for solids and liquids, but appreciable for gases.

In calorimetry we generally do experiments at constant pressure so we can measure enthalpy.

Recall that heat capacity can be slightly temperature dependant. The enthalpy is given by Kirchhoff's law.

$$H(T) = H(T_0) + \int_{T_0}^T C_p dT \quad C_p = C_p(T)$$

$$\Delta H = H(T) - H(T_0) + \int_{T_0}^T C_p dT \quad \text{Enthalpy change}$$

Latent heat (Phase transition enthalpy)

What happens when we encounter a phase transition?

Common phenomena:

- Solid \rightarrow Liquid (Melting)
- Liquid \rightarrow Solid (Fusion)
- Liquid \rightarrow Gas (Vaporisation)
- Gas \rightarrow Liquid (Condensation)
- Solid \rightarrow Gas (Sublimation)
- Gas \rightarrow Solid (?)

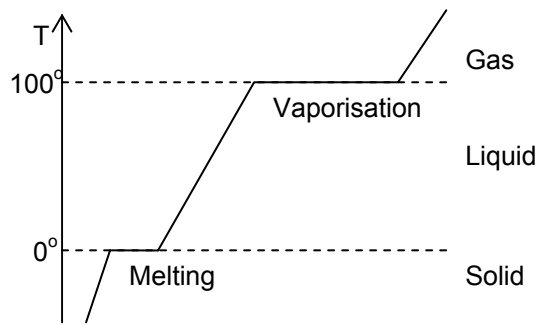
But there are many other phase transitions

- Between different crystal modifications (Carbon \rightarrow diamond under high pressure)
- Between paramagnetic and ferromagnetic phases (Fe)
- Between different liquid crystal phases (~20 phases)

At a phase transition heat flows into a system without causing a temperature change; often called "latent heat".

(At constant pressure ΔH_{melt} , ΔH_{vap} , etc...)

$\Delta H_{\text{transition}}$ has to be added to Kirchhoff if there is a phase transition between T_0 and T .

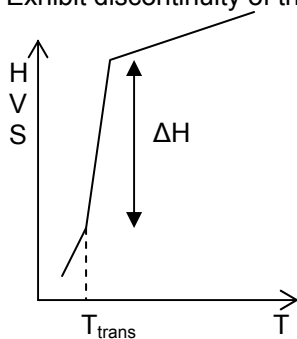


Qualitative understanding: Liquid \rightarrow Gas

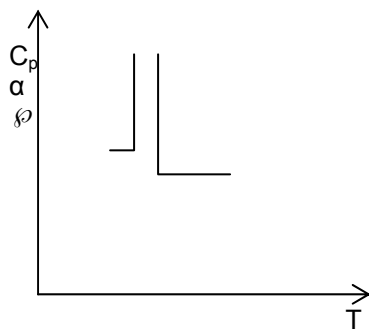
- Energy is needed to overcome attractive forces between atoms / molecules to change from liquid \rightarrow gas.
- Energy put into the liquid increases the potential energy not the kinetic energy.

We distinguish between first and second order phase transitions.

- Exhibit discontinuity of the first order derivative of the chemical potential.



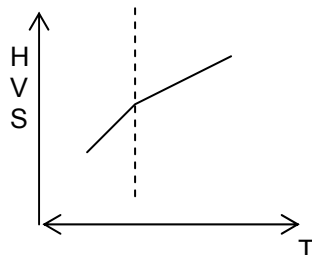
Second order derivatives (Quantities like α thermal expansion coefficient, β compressibility, C_p heat capacity) diverge.



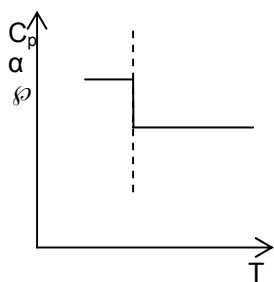
- Vaporisation of Water
- Melting of metals

2nd order transitions

- Exhibit continuous behaviour of H, V, S

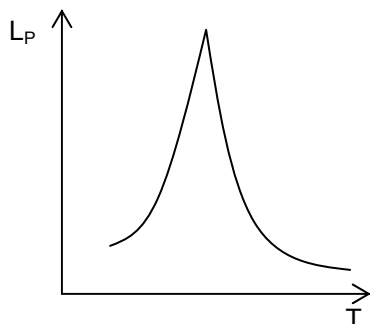


- Discontinuity in α , C_p , β but not divergence!



- Liquid crystals (SmA-SmC)
- Conductor to superconductor

There is also so-called λ -transitions, very similar to 2nd order transitions.



- Order-disorder transition in alloys
- Fluid \rightarrow super fluid He
- Para to ferromagnetic

2.4 Phase Diagrams

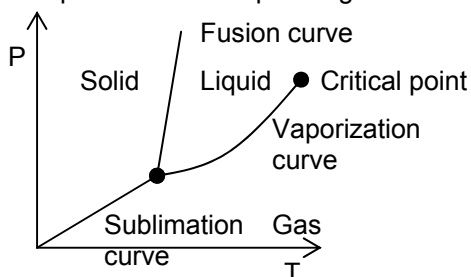
The equation of state of any material can be represented graphically as a surface in the three-dimensional space with coordinates p , V , T .

\rightarrow phase diagram.

- Phase diagrams can be quite complicated
- Often not very useful to represent quantitative information
- But add to our qualitative understanding.
- Easier to understand are projections on to the pT or pV planes.

We learned earlier:

- Each phase is only stable in certain ranges of p , T .
- Phase transitions take place under phase equilibrium. For a given pressure this occurs at a specific temperature.
- We represent this in a p - T diagram



- Each coordinate represents a pair of pT values.
- Only a single phase can exist at each point, except for points on the lines where two phases coexist in phase equilibrium.
- The sublimation, vaporization and fusion curves meet at one point, the triple point
- At the triple point (and only there), all three phases coexist in equilibrium.
- This is a characteristic point for each single component system.

- Triple point of water: $T=273.16\text{K}$, $P=0.0061\times 10^5\text{Pa}$
- A liquid to gas transition can only occur for T and P smaller than the critical point, the end of the vaporization curve (P_c, T_c)
- A gas at the pressure above P_c does not change to a liquid when cooled at constant pressure. Its properties change continuously from those of a gas (low density, large compressibility) to those of a liquid (High density, small compressibility). This happens without a phase transition!
- As we go up the vaporization curve the differences in physical properties become smaller and smaller and vanish at the critical point.
- This is generally not observed in everyday life, because for most materials P_c is very high.
Water: $T_c=649.4\text{K}$, $P_c=221.2\times 10^5\text{Pa}$
(But high-pressure steam boilers in electrical power plants are run at p and T above the critical point)

The lines in the pT diagram are described by the Clapeyron Equation

$$\frac{dp}{dT} = \frac{\Delta H_m}{T\Delta V_m} \quad (\text{m refers to molar quantities})$$

1. Solid-Liquid Boundary

- Melting is associated with $\Delta H_m^{melt} > 0$
- Volume change is often positive
 $\rightarrow \frac{dp}{dT}$ is in most cases (not water) large and positive
- Assuming ΔH_m^{melt} and ΔV_m^{melt} to be independent of p and T , we integrate to

$$p = p^* + \left(\frac{\Delta H_m^{melt}}{\Delta V_m^{melt}} \right) \ln \left(\frac{T}{T^*} \right)$$

p^*, T^* are values on the same point of the fusion curve.

2. Liquid to Gas boundary

- Vaporization is associated with $\Delta H_m^{vap} > 0$
- Value change ΔV_m^{vap} is always large and always positive.
 $\rightarrow \frac{dp}{dT}$ is always positive, but is much smaller than in (1).
- It is $V_m(g) \gg V_m(l)$ and we replace ΔV_m^{vap} by $V_m(g)$
If we assume the gas to be ideal ($pV_m=kT$), we can replace $V_m(g)$ by RT/p and obtain the Clausius-Uapeyron equation

$$\frac{d \ln p}{dT} = \frac{\Delta H_m^{vap}}{RT}$$

- Assuming ΔH_m^{vap} to be independent of temperature we can integrate

$$\ln p = \text{const.} \frac{-\Delta H_m^{vap}}{RT}$$

$$p = p^* \exp \left(\frac{-\Delta H_m^{vap}}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right) \right)$$

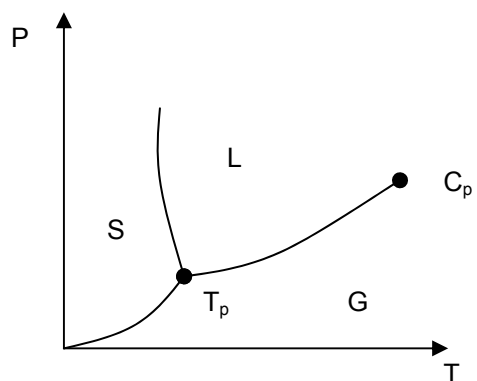
p^* is the vapour pressure at temp T^*

3. Solid-Gas Boundary

- As in (2), replace ΔH_m^{vap} by ΔH_m^{sub}

Phase diagram of water:

(Disregard the 8 different modifications of ice)



- Note the negative slope $\left(\frac{dp}{dt}\right)$ of the fusion curve!!
- Decreasing melting temp, with increasing pressure.
- Why? Because ice contracts on melting
- Water has its largest density at around 4^{10}C
This is why water freezes from the top to the bottom.

3. Gases

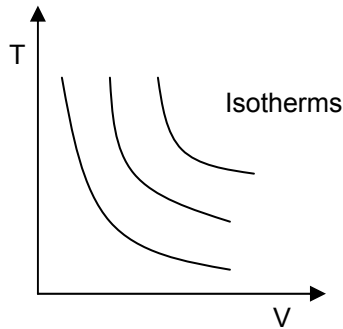
3.1 Ideal Gas

Historical experiments:

Robert Boyle 1661

"The volume of a gas is inversely proportional to pressure"

$$V \sim \frac{1}{p} \text{ or } pV = \text{constant (T, n const.)}$$



Jacques Charles 1787

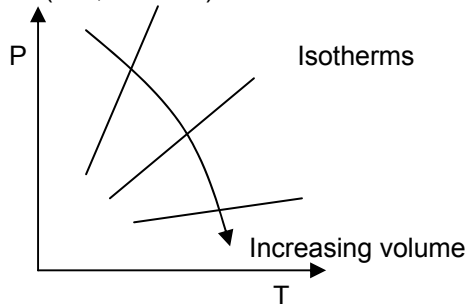
Joseph Gay-Lussac 1802

"Volume is directly proportional to temperature"

$V \sim T$ (at p, n constant)

"Pressure is directly proportional to temperature"

$p \sim T$ (at v, n=const)



Combine both experiments

$$\frac{pV}{T} = \text{const.}$$

$$\text{This implicitly means that } \frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

So we can easily calculate variables of state after changing conditions.

The state of gas is described by p, T, V, n. V, n are extensive variables of state, p, T are intensive.

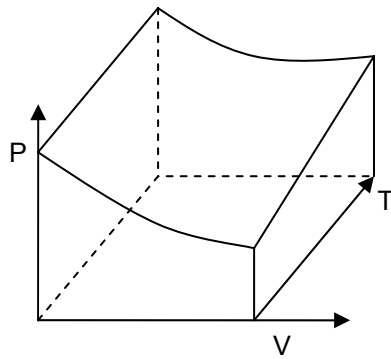
These are not independent but related by the equation of state, the ideal gas law

$$pV = nRT$$

with $R = 8.3143 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ the universal gas constant.

Note that $R = N_A \cdot k$ (N_A = Avogadro's number, k = Boltzmann constant)

The ideal gas law describes a surface in the pVT-diagram.



which gives all possible states of an ideal gas.

At constant amount of substance n :

T =constant, isotherms, hyperboles in the pV -diagram

P =constant, isobars, straight lines in the VT -diagram

V =constant, isochors, straight lines in the pT -diagram

The slope of the tangents are described by partial differential quotients (Some of which have practical importance)

$$\left(\frac{dV}{dT}\right)_P \frac{1}{V} \equiv \alpha \text{ Thermal (Volume) expansion coefficient [K}^{-1}\text{]}$$

$$-\left(\frac{dV}{dP}\right)_T \frac{1}{V} \equiv \chi \text{ Compressibility [Pa}^{-1}\text{, bar}^{-1}\text{]}$$

$$\left(\frac{dP}{dT}\right)_V \frac{1}{P} \equiv \beta \text{ Tension coefficient [K}^{-1}\text{]}$$

Note: if different ideal gases are compared, they all exhibit the same values for α , β , χ .

Mixtures of ideal gases

e.g. N_A mole of gas A in volume V , N_B mole of gas B in volume V

$$P_A = \frac{n_A RT}{V} \text{ and } P_B = \frac{n_B RT}{V}$$

John Dalton "The pressure of a mixture of ideal gases is the sum of the pressures of the individual gases in the respective volume"

$$P = \sum_i P_i = \frac{RT}{V} \sum_i n_i$$

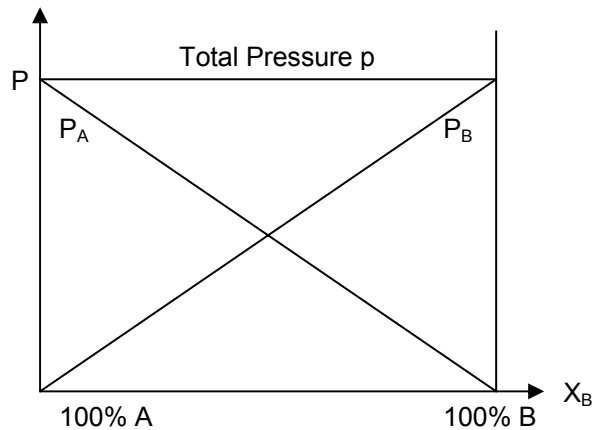
P_i : partial pressures

$$\text{In our example } P = P_A + P_B = (n_A + n_B) \frac{RT}{V}$$

$$\text{Mole fraction } X_i = \frac{n_i}{\sum_i n_i} \text{ between 0 and 1}$$

$$\text{or in our case, } X_A = \frac{n_A}{n_A + n_B}; X_B = \frac{n_B}{n_A + n_B}$$

$$P_i = X_i P$$



Problem with the ideal gas law is that it is only valid for small pressures and large volumes.

This is due to the general assumptions that we make for an ideal gas.

- Atoms / Molecules have no own volume
- No interactions between particles
- The total energy is equal to the kinetic energy (no potential interaction energy)

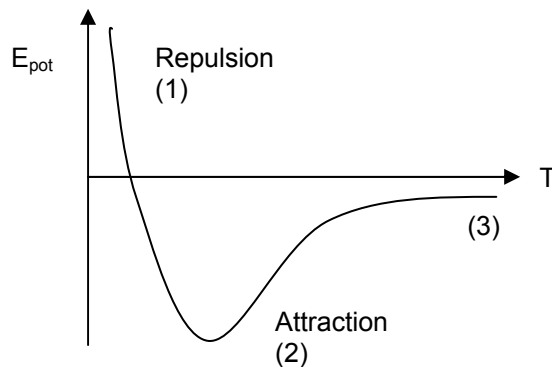
But we had seen before that there are intermolecular interactions:

Repulsive forces (at short distances)

- Particles do have a volume of their own
- Coulomb repulsion from electron clouds

Attractive forces (Over larger distances)

- Van der Waals' interactions



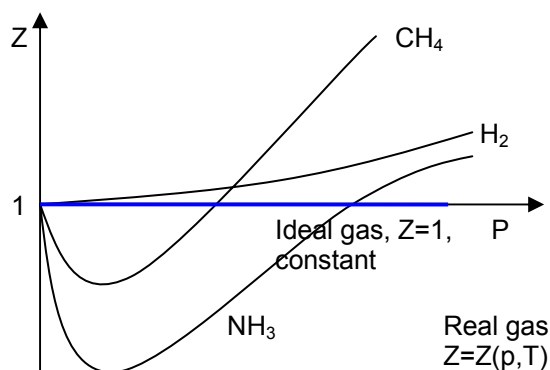
- 1) large pressure, large density
 - Particles are close together. Repulsive forces dominate
 - Gas is harder to compress than ideal gas
- 2) Medium Pressure
 - Particles are close, attractive forces dominate.
 - Gas is easier to compress than ideal.
- 3) Low pressure, low density
 - Particles are far apart, interactions vanish and the gas behaves ideally.

Take $pV=nRT \rightarrow pV_m=RT$ (Ideal gas law in molar form. V_m =molar volume)

Introduce "real-gas-factor"

$$Z = \frac{pV_m}{RT}$$

If the gas is ideal, $Z=1$



3.2 The Van der Waals Equation

Let us modify the equation of state for the ideal gas to include

1) The volume of the atoms / molecules

- Correction term is proportional to number and value of atoms

$$P = \frac{nRT}{V - nb} \text{ "gas with repulsive interaction"}$$

Note: for small pressures it is $V \gg nb \rightarrow$ ideal gas.

2) Attractive interactions

- Reduce pressure of the gas

- Attractive forces proportional to concentration $\frac{n}{V}$

- Reduce the number of collisions as well as momentum transfer. Change in pressure $\Delta P \sim (\# \text{ collisions}) \cdot (\text{Force of collisions}) \sim (n/V)^2$

Correction term $- a \left(\frac{n}{V} \right)^2$

- Leads to van der Waal's equation

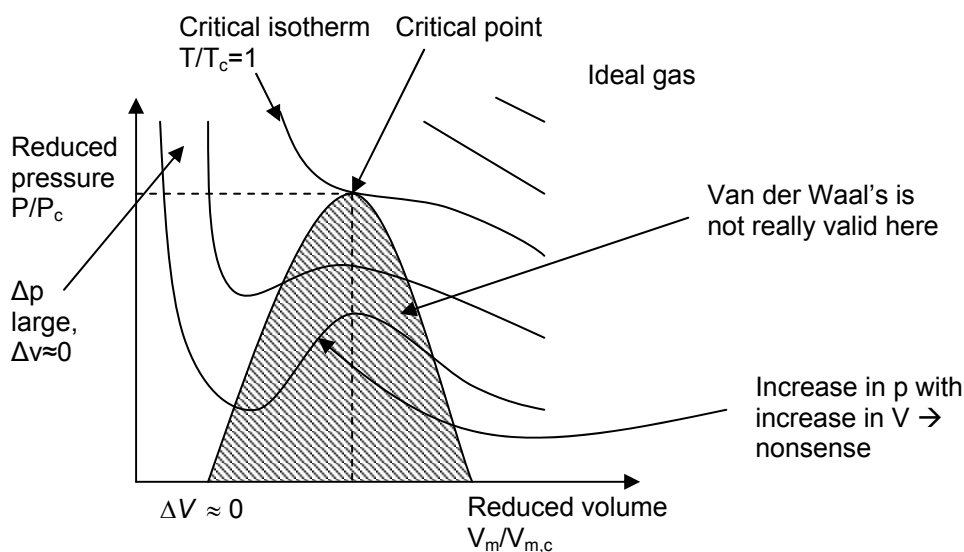
$$P = \frac{nRT}{V - nb} - a \left(\frac{n}{V} \right)^2$$

a, b van der Waal's constants (Different for every gas)

Or in molar form:

$$P = \frac{RT}{V_{mol} - b} - \frac{a}{V_{mol}^2}$$

- Van der Waal's isotherms:



"Liquid can only slightly be compressed."

Remark: above T_c gases can not be liquefied, no matter how large the pressure is.

Example $T_c \ll \text{room temperature}$

O_2 ($T_c=154K$), N_2 ($T_c=126K$)

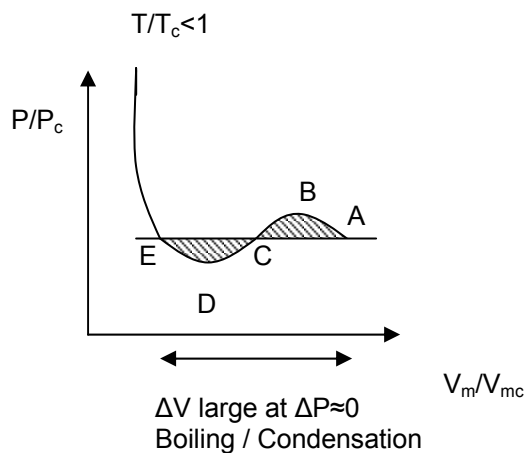
→ liquid air cannot be obtained without cooling.

$T_c > \text{room temperature}$

Propane, Butane.

→ Liquefy by increasing pressure.

Problem: Van der Waal's equation is not valid for very large pressures and close to condensation.



Curves above and below the horizontal line can in special cases be reached.

(E,D) corresponds to an overheated liquid (This can be dangerous)

(A,B) Oversaturated vapour, lack of condensation nuclei. (Used in early day particle physics → cloud chambers)

Remarks:

- At large temperatures and small densities the Van der Waal's equation yields ideal gas behaviour.
- When attractive and repulsive forces are of equal magnitude, gas and liquid coexist.

The critical point can be determined experimentally → determination of the Van der Waal's constant.

The critical isotherm has a point of inflection at T_c .

$$\text{Mathematical condition: } \left(\frac{dp}{dV} \right)_T = 0, \left(\frac{d^2p}{dV^2} \right)_T = 0$$

This gives us three equations (at critical point)

$$P_c = \frac{RT_c}{V_{mc} - b} - \frac{a}{V_{mc}^2}$$

$$\left(\frac{dP}{dV} \right)_T = \frac{-RT_c}{(V_{mc} - b)^2} + \frac{2a}{V_{mc}^3} = 0$$

$$\left(\frac{d^2P}{dV^2} \right)_T = \frac{2RT_c}{(V_{mc} - b)^3} - \frac{6a}{V_{mc}^4} = 0$$

Three equations and three unknowns: a, b, R.

Solving the equation gives:

$$P_c = \frac{a}{27b^2}$$

$$V_{mc} = 3b$$

$$T_c = \frac{8a}{27Rb}$$

Remark: at this point R is still formally a parameter which can be determined from the critical parameter.

V_{mc} is quite hard to determine experimentally.

Choose $V_c = \frac{3RT_c}{8P_c}$ which will lead to $b = \frac{RT_c}{8P_c}$ and $a = \frac{27(RT_c)^2}{64P_c}$

with $R=8.314 \text{ J.mol}^{-1}\text{K}^{-1}$ the universal gas constant. We can thus determine the Van der Waal's constants, a and b from measurements of T_c and P_c . Some examples:

Gas	$a/\text{l}^2.\text{bar}.\text{mol}^{-2}$	$b/\text{l}.\text{m}.\text{l}^{-1}$
NH ₃	4.210	0.037
He	0.034	0.024
N ₂	1.404	0.039
O ₂	1.374	0.032
Air	1.410	0.039

a is related to attractive interaction.

b is related to the volume of atoms / molecules.

Let us check if van der Waals gives some reasonable estimations for real gases.

Example - Nitrogen:

From measurements of the isotherms above the critical temperature T_c we can obtain the van der Waals constants

$$a=0.12 \text{ Pa.m}^6.\text{mol}^{-2}$$

$$b=39.1 \text{ cm}^3.\text{mol}^{-1}$$

Note that b is only 0.2% of the molar volume of the gas $V_m=22.4\text{L}=22400\text{cm}^3$ (under standard conditions)

Calculate the density of 1 mole of N₂, packed into the volume $b=39.1\text{cm}^3.\text{mol}^{-1}$

$$\rho = \frac{M}{b} = \frac{28\text{g}.\text{mol}^{-1}}{39.1\text{cm}^3.\text{mol}^{-1}} = 0.72\text{g}.\text{cm}^{-3}$$

Compares well with the measurement of the density of liquid N₂ which is $0.8\text{g}.\text{cm}^{-3}$.

Estimate the size of a nitrogen molecule:

$$V = \frac{b}{N_A} = \frac{39.1\text{cm}^3.\text{mol}^{-1}}{6.02 \times 10^{23} \text{ molecules}.\text{mol}^{-1}} = 6.5 \times 10^{-23} \text{ cm}^3.\text{molecule}^{-1}$$

Assume that the molecules occupy a cubic volume of side length d $\rightarrow d=4 \times 10^{-10} \text{ m}=4\text{\AA}$.

This is reasonable.

3.3 Theorem of corresponding states

Knowing a, b, and R or T_c , P_c and V_c , we can rewrite the van der Waals equation (in molar form) as:

$$P = \frac{8P_c V_{m,c} T}{3T_c \left(V_m - \frac{V_{m,c}}{3} \right)} - \frac{3P_c V_{m,c}^2}{V_m^2}$$

$$\frac{p}{P_c} = \frac{8 \frac{T}{T_c}}{3 \frac{V_m}{V_{m,c}} - 1} - \frac{3}{\left(\frac{V_m}{V_{m,c}} \right)^2}$$

If we now introduce reduced variables of state
 $P/P_c = \pi$, $T/T_c = \tau$ and $V_m/V_{m,c} = \psi$

we get $\Pi = \frac{8\tau}{3\psi - 1} - \frac{3}{\psi^2}$ – valid for all gases

“Two gases of the same reduced temperature and same reduced pressure have the same reduced volume; they correspond in their states” – Theorem of corresponding states.

3.4 Virial Expansion

The van der Waal's equation describes the deviations from ideal gas behaviour, but not at large pressures and close to condensation.

→ we need more than two adjustable parameters

Let us revisit the real-gas-factor $Z = \frac{pV_m}{RT}$

This can be used to write down empirical equations of state: series expansion

$$Z(p, T) = Z = \frac{pV}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots \text{ - Virial Equation}$$

B, C... are called Virial Coefficients and are different for different gases.

Note: for $V_m \rightarrow \infty$, it is $Z = \frac{pV_m}{RT} = 1 \rightarrow$ ideal gas

What is the relation to van der Waal's equation?

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \text{ and look at}$$

$$Z = \frac{pV_m}{RT} = \frac{V_m}{V_m - b} - \frac{a}{RTV_m} = \frac{1}{1 - \frac{b}{V_m}} - \frac{a}{RTV_m}$$

For small pressures $b/V_m \ll 1$, we can expand Z with respect to $1/V_m$ (in analogy to $(1-x)^{-1} = 1+x+x^2+\dots$)

$$\text{Which gives } Z = 1 + \left(b - \frac{a}{RT}\right) \frac{1}{V_m} + \left(\frac{b}{V_m}\right)^2 + \dots$$

Comparison with Virial expansion gives:

$$B = \left(b - \frac{a}{RT}\right) \text{ and } C = b^2$$

Note: $B=B(T)$

Alternatively, we can expand $Z(T, p)$ with respect to p :

$$Z = 1 + B'p + C'p^2 + \dots$$

Note, $B'=B'(T)$ and $C'=C'(T)$

One finds the following relationships between the virial coefficients of both expansions:

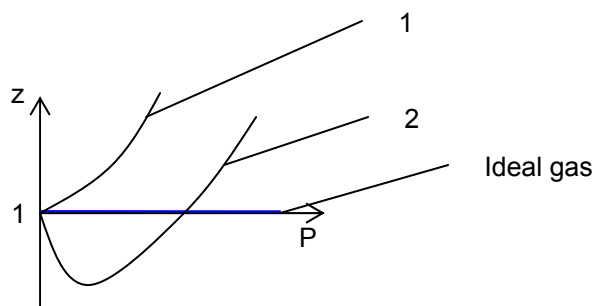
$$B = B'.RT$$

$$C = R^2T^2(C' + B'^2)$$

The virial coefficient B' is important in statistical thermodynamics.

It can be obtained from the slopes of

$$\left(\frac{\partial Z}{\partial p}\right)_T \text{ for } p \rightarrow 0$$



This gives $B' = \frac{B}{RT} = \frac{1}{RT} \left(b - \frac{a}{RT} \right)$

If:

- 1) $B' > 0$, it is $b > \frac{a}{RT}$. Volume of molecules dominates the gas behaviour.
- 2) $B' < 0$ it is $b < \frac{a}{RT}$. Attractive forces dominate gas behaviour.

Remark:

- Up to now, more than 100 equations of state have been proposed for description of real gases
- If they contain only three (or less) adjustable parameters (Like van der Waals), these can be determined by measuring P_c , T_c , V_c
- If they have more adjustable parameters, we need more experiments. These parameters have no simple physical meaning.

3.5 Kinetic theory of Gases

The description of the behaviour of a gas in terms of macroscopic variables p , V , T can be related to microscopic quantities, such as the mass or speed of a molecule.

“Statistical interpretation of the ideal gas equation”

Assumptions:

1. Large number of molecules making elastic collisions with each other and with walls of container.
2. Molecules are point-like, and have a mass m .
3. Molecules are far apart \gg diameter.
4. Molecules move on random paths and do not interact except for the elastic collisions.
(\rightarrow ideal gas)
5. Absence of external forces (neglect gravity)

Remark: Momentum is conserved, so collisions between molecules have no effect on the total momentum in any direction \rightarrow neglect molecular collisions.

Pressure exerted by gas

General idea:

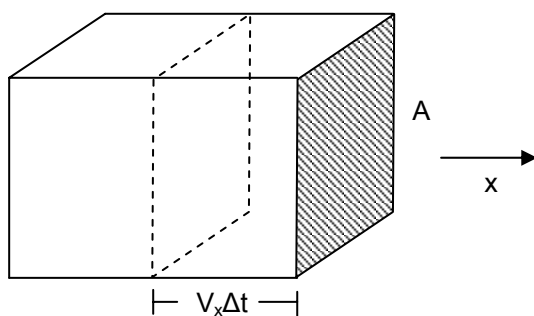
Molecules hit the container walls

\rightarrow Transfer of momentum

\rightarrow Force = change of momentum per time

\rightarrow Pressure = Force / Area.

Consider a rectangular container of volume V containing N molecules each of mass m , moving at a speed v .



Number of molecules hitting the wall A in time interval Δt is those within a distance $v_x \Delta t$ moving to the right.

This is the number of molecules per unit volume $\frac{N}{V}$ times the volume $v_x \Delta t A$ times $\frac{1}{2}$, because an average half of the molecules move to the right.

$$\# \text{ of molecules hitting the wall} = \frac{1}{2} \frac{N}{V} v_x \Delta t A$$

Change of momentum:

before collision $P = mv_x$, after $P = -mv_x$.

$$\Delta P = |2mv_x| \text{ (per molecule)}$$

Total change of momentum in Δt is $2mv_x$ times the number of molecules hitting the wall.

$$\Delta P = 2mv_x \frac{1}{2} \frac{N}{V} v_x \Delta t A$$

$$\text{Force is } F = \frac{\Delta P}{\Delta t} = \frac{N}{V} v_x^2 A$$

$$\text{Pressure: } p = \frac{F}{A} = \frac{N}{V} m v_x^2$$

$$\text{or } pV = Nm v_x^2$$

On left hand side, only macroscopic properties. On right hand side, only microscopic properties

$$pV = 2N \frac{1}{2} m v_x^2$$

This shows the kinetic energy for the motion in the x-direction for a single molecule.

So far we have assumed that all molecules have the same speed but in reality there is actually a speed distribution.

→ Replace v_x^2 by its' average $\langle v_x^2 \rangle$

NB: $\langle \rangle$ = average.

$$pV = 2N \left\langle \frac{1}{2} m v_x^2 \right\rangle \quad (1)$$

(Average kinetic energy for motion in x-direction).

Molecular interpretation of temperature

Compare eq. (1) to the ideal gas equation

$$pV = nRT = Nk_B T$$

k_B = Boltzmann constant.

$$\left\langle \frac{1}{2} m v_x^2 \right\rangle = \frac{1}{2} k_B T \quad (2)$$

Temperature is related to the average kinetic energy of the molecules.

So far we have only looked at the motion along x, but there is nothing special about the x-direction, we also have motion along y and z.

On average it is:

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$$

$$\text{Thus } \langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = 3 \langle v_x^2 \rangle$$

$$\text{And therefore } \langle v_x^2 \rangle = \frac{1}{3} \langle v^2 \rangle$$

Insert into equation (2) to obtain average kinetic energy of a molecule:

$$\langle E_{kin} \rangle = \langle \frac{1}{2}mv^2 \rangle = \frac{3}{2}k_B T \quad (3')$$

Total translational kinetic energy of n moles containing N molecules is thus

$$E_{kin} = N \langle \frac{1}{2}mv^2 \rangle = \frac{3}{2}Nk_B T = \frac{3}{2}nRT \quad (3)$$

The absolute temperature is a measure of the translational kinetic energy!

Equation (3') can be used to estimate the order of magnitude of the speeds of molecules in a gas.

$$\langle v^2 \rangle = \frac{3k_B T}{m} = \frac{3N_A k_B T}{N_A m} = \frac{3RT}{M}$$

M: molar mass.

The square root of $\langle v^2 \rangle$ is called the root mean square (rms) speed.

$$v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{M}}$$

Note that the rms speed is NOT equal to the mean (average) speed of the molecules.

$$\sqrt{\langle v^2 \rangle} \neq \langle v \rangle$$

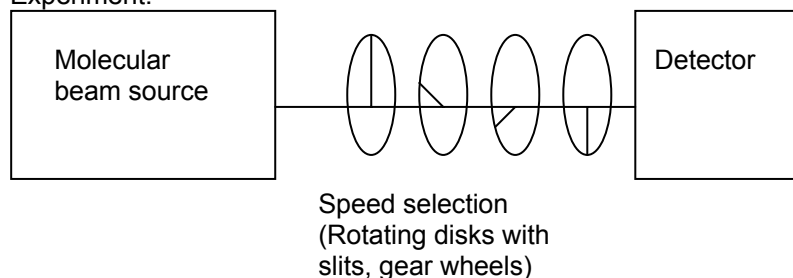
Some examples:

	H ₂	N ₂	O ₂
M/g.mol ⁻¹	2	28	32
v _{rms} /ms ⁻¹	1850	490	460

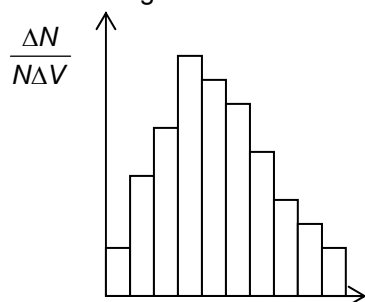
3.6 The Maxwell-Boltzmann Distribution

We had mentioned that molecules do not all have the same speed, but that there is a distribution of the speeds.

Experiment:



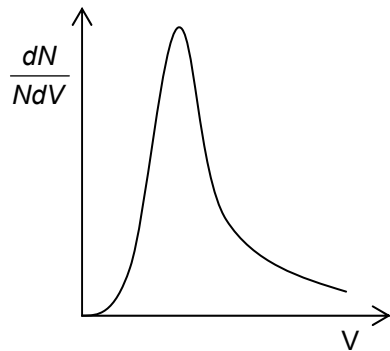
Gives a histogram of molecular speeds.



ΔN: Number of molecules with a speed between V and V+ΔV

N: Total number of molecules.

Now: $\Delta V \rightarrow 0$ leads to a continuous distribution.



In a gas of N molecules, the number that have speeds between v and v+Δv is dN, which is $dN = N.f(v).dv$

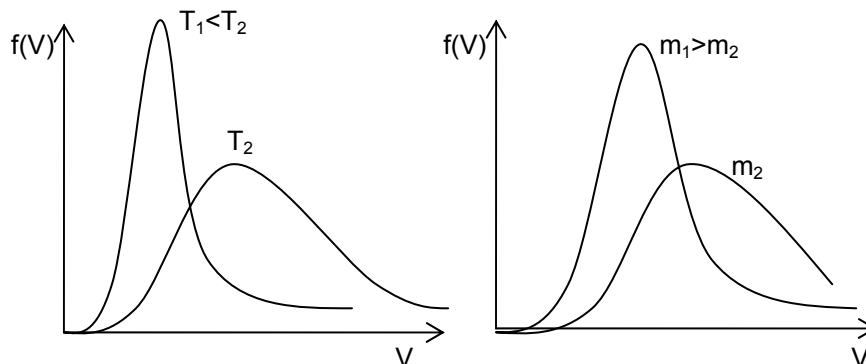
f(v) is the speed distribution function, for gases this is called the Maxwell-Boltzmann Distribution. This can be derived from statistical mechanics (→ See follow-up course).

$$\text{Given by } f(v) = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2K_B T} \right)^{3/2} \cdot v^2 \cdot e^{-\frac{mv^2}{2K_B T}}$$

Or with molar quantities:

$$f(v) = \frac{4}{\sqrt{\pi}} \left(\frac{M}{2RT} \right)^{3/2} \cdot v^2 \cdot e^{-\frac{Mv^2}{2RT}}$$

- The term “ v^2 ” causes the parabolic increase for low molecular speeds
- The exponential function causes the exponential decrease for large speeds.



- Molecules at low temperatures exhibit small molecular speed and have a narrow distribution.
- Light molecules have high speeds and a broad speed distribution.

Consequences:

- Light molecules can easier escape the gravitational field of the Earth
- H_2 and He are quite rare to find in the Earth's atmosphere.

Example:

The rms speed of Hydrogen is 1.93Kms^{-2} . This is about 1/6 the escape velocity at surface of the earth, which is 11.2Kms^{-2} .

Due to the distribution, there is a considerable amount of H_2 atoms with a higher speed than the escape velocity, meaning they will escape into space.

When $v_{\text{rms}} \sim 15\text{-}20\%$ of the escape speed, the particular gas cannot make up the atmosphere.

O_2 has about 4% of molecules with $v_{\text{rms}} > v_{\text{escape}} \rightarrow O_2$ in our atmosphere.

– From determination of the composition of the atmosphere of a distant planet (by the spectral lines) we can estimate the mass of the planet.

From Maxwell-Boltzmann we can define different speeds:

1. Most probable speed (Given by the position of the peak of the distribution function).

$$\text{Condition: } \frac{df(v)}{dv} = 0$$

$$\text{We get } \hat{V} = \sqrt{\frac{2K_B T}{m}} = \sqrt{\frac{2RT}{M}}$$

2. Average speed $\langle v \rangle$ is given by $\langle v \rangle = \sqrt{\frac{8K_B T}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}$

Note that this is the speed we need for calculation of the momentum of the gas.

3. RMS speed

$$v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3K_B T}{m}} = \sqrt{\frac{3RT}{M}}$$

At equal temperatures and molar mass the ratios are:

$\sqrt{\langle v^2 \rangle}$	$\langle v \rangle$	\hat{V}
$\sqrt{3}$	$\sqrt{\frac{8}{\pi}}$	$\sqrt{2}$
1	0.92	0.82

A short excursion on averages

1. Series of values:

Add up all the values and divide by the total number of values

2. From histograms:

$$\sum \text{value} \cdot \text{frequency} / \text{total number of values}$$

3. From distribution curves:

Average of a quantity Q is given by:

Integral over the product of Q and its' distribution function. (Divide by the integral over the distribution function – to normalise.)

$$\langle Q \rangle = \frac{\int_{-\infty}^{\infty} Q \cdot f(Q) dQ}{\int_{-\infty}^{\infty} f(Q) dQ}$$

Example: RMS speed $\langle v^2 \rangle$, disregard normalisation as $\int f(v) dQ = 1$

$$\begin{aligned} \langle v^2 \rangle &= \int_0^{\infty} v^2 f(v) dv \\ &= \int_0^{\infty} v^2 \frac{4}{\sqrt{\pi}} \left(\frac{m}{2K_B T} \right)^{3/2} \cdot v^2 \cdot e^{-\frac{mv^2}{2K_B T}} dv \\ &= \frac{4}{\sqrt{\pi}} \left(\frac{m}{2K_B T} \right)^{3/2} \cdot \int_0^{\infty} v^4 \cdot e^{-\frac{mv^2}{2K_B T}} \end{aligned}$$

Look up integral:

$$\int_0^{\infty} v^4 \cdot e^{-\frac{mv^2}{2K_B T}} = \frac{3}{8} \sqrt{\pi} \left(\frac{2K_B T}{m} \right)^{5/2}$$

This gives

$$\langle v^2 \rangle = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2K_B T} \right)^{3/2} \cdot \frac{3}{8} \sqrt{\pi} \left(\frac{2K_B T}{m} \right)^{5/2} = \frac{3K_B T}{m}$$

$$\rightarrow v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3K_B T}{m}}$$

This is the same result as obtained from the kinetic theory of gases! (Thank god!!!)

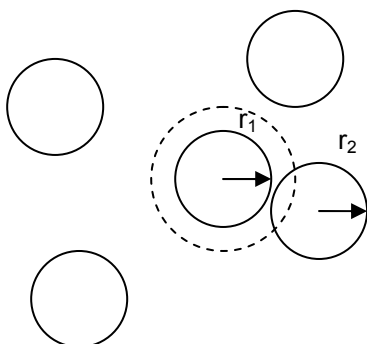
3.7 Molecular collisions and the mean free path

An important quantity for the dynamics of processes is the number of collisions (for example in chemical reactions)

If the molecules would really be point-like they would not collide. In reality, molecules do have a certain diameter in the order of $d \approx 0.3nm$. This is much smaller than the separation between molecules, which is in the order of $3nm$. So the fraction of space

occupied by atoms in a gas (at standard conditions) is only about $\left(\frac{0.3nm}{3nm} \right)^3 \approx 10^{-3}$

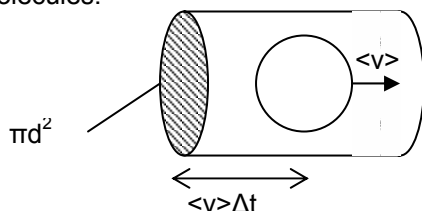
(Note: this is the reason for the factor "b" in the van der Waal's equation).



Molecules collide when they come within a distance $d = r_1 + r_2$.

If all the molecules are identical, $d = 2r_1 = \text{diameter}$ of the molecule.

Consider a molecule moving at an average speed $\langle v \rangle$ through a region of stationary molecules.



It will collide with any molecule whose centre is in circle with radius d .

In the time Δt , the molecule moves a distance $\langle v \rangle \Delta t$, so it collides with every molecule in the volume

$$\pi d^2 \langle v \rangle \Delta t = \sigma \langle v \rangle \Delta t$$

where σ is called collision cross-section.

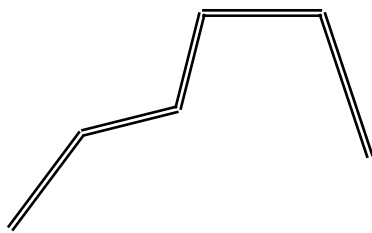
Examples:

$$\text{He: } \sigma = 0.21nm^2$$

$$\text{N}_2: \sigma = 0.43nm^2$$

$$\text{CO}_2: \sigma = 0.52nm^2$$

Note that after each collision the direction of the "cylinder" will change, path of the molecule is a random walk.



Collisions at every position where the path changes direction.

There are N molecules in volume V , so the number of collisions (of one molecule) per unit time is:

$$Z = \sigma \langle v \rangle \frac{N}{V} \text{ With } \langle v \rangle^2 = \frac{8k_B T}{\pi m} \text{ the average speed.}$$

But: the other molecules are not stationary, but move
 \rightarrow look at the relative speed.

$$\langle v \rangle = \sqrt{\frac{8k_B T}{\pi \mu}} \text{ With } \mu = \frac{M_A M_B}{M_A + M_B}.$$

For identical molecules it is $\mu = \frac{M}{2}$ and therefore $\langle v_{relative} \rangle = \sqrt{2} \langle v \rangle$

The number of collisions of a single molecule per unit time is then

$$z = \sqrt{2} \sigma \langle v \rangle \frac{N}{V}$$

Or in terms of pressure and temperature (with $N = n \cdot N_A$, and $R = K_B \cdot N_A$)

$$z = \sqrt{2} \sigma \langle v \rangle \frac{P}{K_B T}$$

To obtain the number of collisions of all molecules, we have to multiply by the number density $\frac{N}{V}$ time $\frac{1}{2}$ [not to double-count collisions (1) with (2) and (2) with (1)].

For identical molecules we get:

$$z_{AA} = \frac{1}{2} z \frac{N}{V} = \frac{\sigma}{\sqrt{2}} \langle v \rangle \left(\frac{N}{V} \right)^2 = \frac{\sigma}{\sqrt{2}} \sqrt{\frac{4K_B T}{\pi m}} \left(\frac{N}{V} \right)^2$$

“the number of collisions of all molecules per unit time and unit volume”.

This is generally a very large number, for example N_2 (at room temperature and normal pressure), $Z_{AA} = 5 \times 10^{34} \text{ s}^{-1} \text{ m}^{-3}$.

For collisions between two different molecules, it was $d = \frac{1}{2}(d_A + d_B) = r_A + r_B$ and we

get:

$$z_{AB} = \sigma \sqrt{\frac{8K_B T}{\pi \mu}} \frac{N_A N_B}{V^2}$$

μ =reduced mass

From the number of collisions we calculate the average distance travelled by a molecule between collisions: mean free path, λ .

$$\lambda = \frac{\langle v \rangle}{Z} = \frac{1}{\sqrt{2} \sigma} \frac{K_B T}{P}$$

given in terms of temperature and pressure because these are the most accessible quantities.

Note: the mean free path is about 2000 times the diameter of a molecule. $\lambda \approx 10^{-7} \text{ m}$.

Example: O_2 : $\lambda = 70 \text{ nm}$

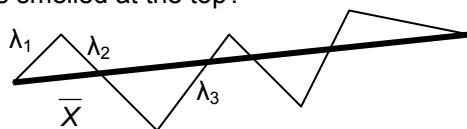
Finally we can calculate the collision time, T , the average time between collisions.

$$T = \frac{\lambda}{\langle v \rangle} \approx 10^{-10} \text{ s}$$

The number of collisions Z , the mean free path λ and the collision time T are important quantities for transport phenomena.

Let's make a (thought) experiment.

If a cigarette is lit at the bottom of a lecture theatre, how long does it take until the smoke is smelled at the top?



Random walk with n steps.

$$\bar{X} = \bar{\lambda}_1 + \bar{\lambda}_2 + \dots + \bar{\lambda}_n$$

$$X^2 = \overline{X^2} = (\bar{\lambda}_1 + \bar{\lambda}_2 + \dots)(\bar{\lambda}_1 + \bar{\lambda}_2 + \dots) = \sum_{i=1} \bar{\lambda}_i^2 + \sum_{i \neq j} \bar{\lambda}_i \bar{\lambda}_j$$

$$x^2 = \sum_{i=1}^n x_i^2 + \sum_{i \neq j} \bar{x}_i \cdot \bar{x}_j$$

$\sum_{i \neq j} \bar{x}_i \cdot \bar{x}_j$ is 0 for a random walk.

$$x^2 = \sum_{i=1}^n x_i^2 = n\lambda^2 \rightarrow x \sim \sqrt{n}\lambda$$

Time taken for the molecule to travel is

$$t = \text{total distance} / \text{average speed} = \frac{n\lambda}{\langle v \rangle} = \frac{x}{\lambda \langle v \rangle}$$

$$x \approx 100m, \lambda = 10^{-7}m, \langle v \rangle = 400ms^{-1}$$

$$t = \frac{100m^2}{10^{-7}m \cdot 400ms^{-1}} = 2.5 \times 10^6 s = 700h$$

If we do the experiment, $t \approx 1 - 2 \text{ min}$

→ macroscopic material displacement, convection, air currents due to ventilation are the major factors to account for the spread of odours.

3.8 Internal energy, work and heat capacity

“Applications of the kinetic theory of gases”

1st law of thermodynamics

$$Q = \Delta U + W$$

$$dQ = dU + dW$$

Q: Heat, U: Internal energy, W: work

Sign conventions:

$W > 0$, work done by system

$W < 0$, work done on system

$Q > 0$, heat put into system

$Q < 0$, heat taken out of system

Recall: $E_{kin} = \frac{3}{2}nRT$ (for n moles of an ideal gas)

In deriving this we assumed that it is equally likely that particles move along x , y and z .

This is a special case of the equipartition theorem.

“When a substance is in equilibrium, there is an average energy of $\frac{1}{2}k_B T$ (per molecule)

or $\frac{1}{2}RT$ (per mole) associated with each degree of freedom.”

“Degree of freedom” here has nothing to do with Gibb's phase rule but is related to translation, rotation and vibration.

Example: mono-atomic ideal gas

$$E_{kin} = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 \rightarrow 3 \text{ degrees of freedom}$$

$$= \frac{3}{2}k_B T \text{ (for 1 atom)}$$

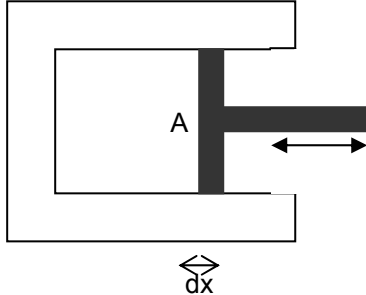
No interaction \rightarrow internal energy of the ideal gas is equal to E_{kin} .

$$U = \frac{3}{2}nRT$$

Internal energy only depends on temperature, not on pressure or volume!!

Work and the pV-diagram

Many types of engines rely on work done by expanding gas against a moveable piston.
(Steam engine, car engine)



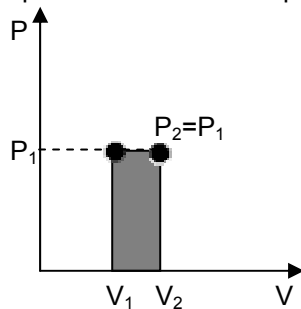
Close to equilibrium (called quasi-static process) the work done by the gas is:

$$dW = Fdx = pAdx = pdV$$

where dV is the increase in volume.

(1) Isobaric Expansion

Expansion at a constant pressure



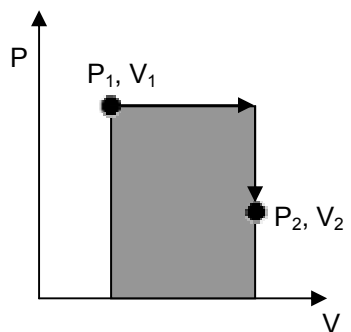
$$W = \int_{V_1}^{V_2} p dV = p \int_{V_1}^{V_2} dV$$

$$W = p\Delta V$$

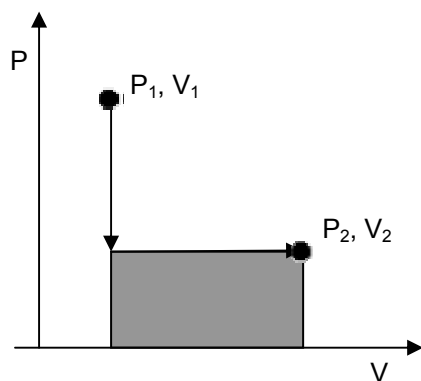
(2) p and V changes

Initial state p_1, V_1 to find final state p_2, V_2 chose temperature of initial and final state to be the same.

Two possibilities:



Heat at constant pressure to V_2 then cool at constant volume to p_2
 $-W = p_1(V_2 - V_1)$

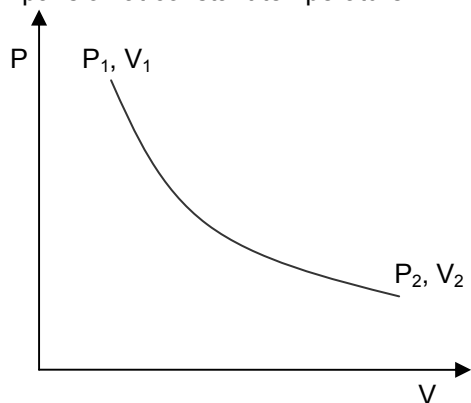


Cooling at constant volume to p_2 then heat at constant pressure to v_2
 $-W = P_2(v_2 - v_1)$

→ Work depends on the path from one state to the other. So does Q.
 Only the internal energy U is independent on path, as the initial and final states have the same temperature.

(3) *Isothermal expansion*

Expansion at constant temperature



Area beneath line is the internal energy U.

$$p = \frac{nRT}{V}$$

$$dW = pdV = \frac{nRT}{V} dV$$

$$W = \int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT \ln \frac{V_2}{V_1}$$

(4) Adiabatic Expansion ($dQ=0$)

→ Tutorials

Heat Capacities

We had noted that there are two heat capacities: C_p and C_v .

$$C_p \neq C_v$$

When heat is added at constant pressure, the gas expands and work is done → $C_p > C_v$.
(Only for liquids and solids it is $C_p \approx C_v$ as $\Delta V \approx 0$)

a) Look at constant volume

$$Q_v = C_v \Delta T$$

from the first law of thermodynamics:

$$Q_v = \Delta U + W = \Delta U \text{ as no work is done.}$$

$$\text{So } \Delta U = C_v \Delta T \text{ or } \boxed{dU = C_v dT} \quad (1)$$

b) Look at heat added at constant pressure

$$Q_p = C_p \Delta T$$

From 1st law of thermodynamics:

$$Q_p = \Delta U + W = \Delta U + pdV$$

$$\text{So } C_p \Delta T = \Delta U + p \Delta V$$

$$\text{or } C_p dT = dU + pdV$$

Insert $dU = C_v dT$ and get:

$$C_p dT = C_v dT + pdV \quad (2)$$

Compare to differential of ideal gas equation $pV=nRT$ with $dp=0$ for constant pressure:

$$pdV + Vdp = [dV = nRdT$$

Insert into (2):

$$C_p dT = C_v dT + nRdT$$

$$\boxed{C_p = C_v + nR} \text{ (for } n \text{ moles of ideal gas)}$$

This holds very well for all gases!

Relation to kinetic theory of gases:

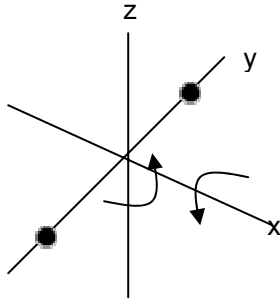
$$\text{We had } U = \frac{3}{2} nRT \rightarrow \boxed{\frac{dU}{dT} = C_v = \frac{3}{2} nR}$$

$$\text{From } C_p = C_v + nR \rightarrow \boxed{C_p = \frac{5}{2} nR}$$

This is true for all mono-atomic gas, He, Ne, Ar, ...

What about diatomic gases like N_2 , O_2 , CO ?

Use equipartition theorem to calculate the internal energy.



Three translational and two rotational degrees of freedom

$$\rightarrow U = \frac{5}{2}nRT$$

$$\rightarrow C_V = \frac{5}{2}nR \text{ and } C_P = \frac{7}{2}nR$$

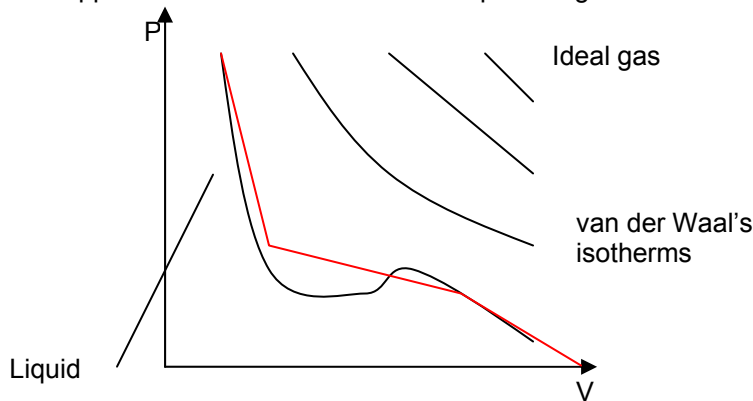
What about rotation around the y-axis?

The nucleus is very small \rightarrow main contribution to the moment of inertia comes from electrons \rightarrow this is very small \rightarrow Neglect it.

This is also the reason why rotation does not contribute to mono-atomic gases.

4. Liquids

What happens when we cool down or compress a gas?



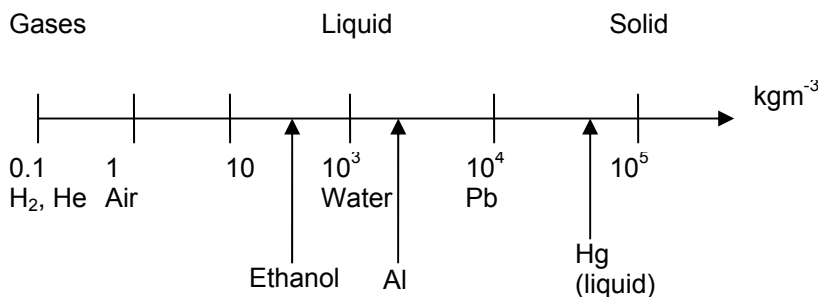
As the molecules become closer and closer the attractive interactions (van der Waal's forces) become increasingly important. Eventually the gas condenses to a liquid.

Properties of liquids:

- Much higher density than gases
- Low compressibility
- No elastic properties
- Much larger viscosities than gases
- Exhibit short range order

An important property of any substance is the density.

$$\text{density} = \frac{m}{V}$$



4.1 Properties of a static, stationary liquid

Pressure of a liquid

When a body is submerged in a liquid, the liquid exerts a force perpendicular to the surface of the body at each point of the surface. This is called the pressure of a liquid.

$$P = \frac{F}{A}$$

F: Force, A: Area

The body will then be compressed. The bulk modulus

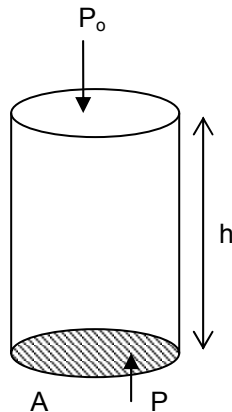
$$B = -\frac{\Delta P}{\Delta V/V} = \frac{1}{k}$$

k: Compressibility

describes how easily a body can be compressed.

- B is large for solids and liquids (1-10GNm⁻²) and is relatively independent on pressure and temperature.
- In contrast, B is small for gases and is pressure and temperature dependant.

Let's look at a column of water of height h.



The density is approximately constant, so the pressure linearly increases with depth (note this is different for gases!)

The weight of the column is

$$mg = \ell v \cdot g = \ell Ahg$$

(ℓ is density)

The net upward force exerted by the pressure difference is $pA - p_o A$, so

$$pA - p_o A = \ell Ahg$$

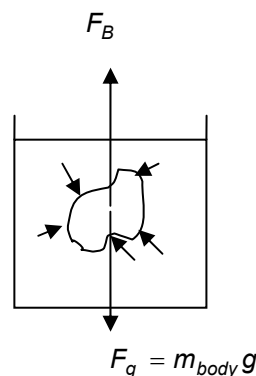
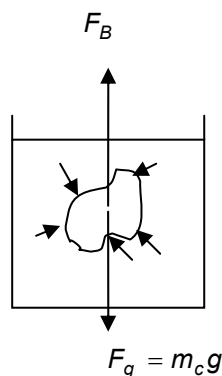
$$p = p_o + \ell gh$$

- This holds for a liquid in any container, independent of the shape of the container.
- If we increase the pressure p_o , the increase of the pressure is the same throughout the whole liquid (Pascal's principle)

Buoyancy

Archimedes' principle:

"A body submerged in a liquid experiences an upward force equal to the weight of the displaced liquid"



The buoyant force F_B partially balances the gravitational force.

So the measured weight F_s of an object that is submerged in a liquid is:

$$F_s = mg - F_B$$

$$F_s = \ell g V - \ell_L g V = \ell g V \left(1 - \frac{\ell_L}{\ell} \right)$$

ℓ_L : Density of liquid

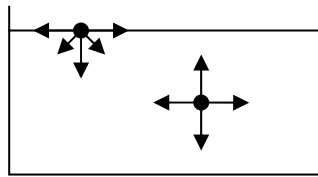
ℓ : Density of object

This can be used to determine the density of (irregularly shaped) objects.

Surface tension

- Molecules of a liquid exert attractive forces on each other.
- There is a zero net force on a molecule inside the volume of the liquid.

- Surface molecules are "drawn into the volume"



→ most liquids tend to minimise their surface area.

(Freely falling raindrops are spherical, NOT teardrop-shaped!)

→ to increase the surface area of a liquid, we have to do work against the attractive forces.

$$dW = \gamma dA$$

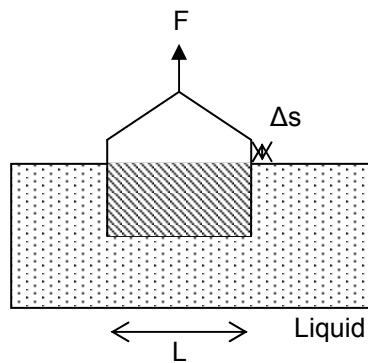
$$\gamma(H_2O) = 0.072 Nm^{-1}$$

$$\text{Organic solvents: } \gamma = 0.025 Nm^{-1}$$

$$\text{Hg: } \gamma = 0.47 Nm^{-1}$$

Surface temperature decreases with increasing temperature.

How can we measure γ ?



$$\Delta W = F\Delta s$$

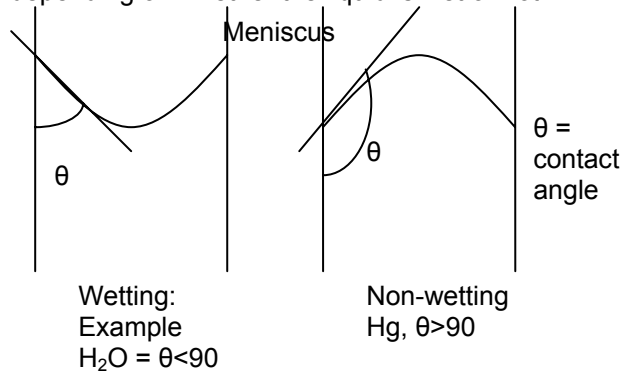
$$\Delta A = 2\Delta s l$$

(Factor of 2 because of front and back surface)

$$\gamma = \frac{\Delta W}{\Delta A} = \frac{F\Delta s}{2\Delta s l} = \frac{F}{2l}$$

Capillarity

When a gas-liquid interface meets a solid surface, the interface curves up or down, depending on whether the liquid is wet or not.

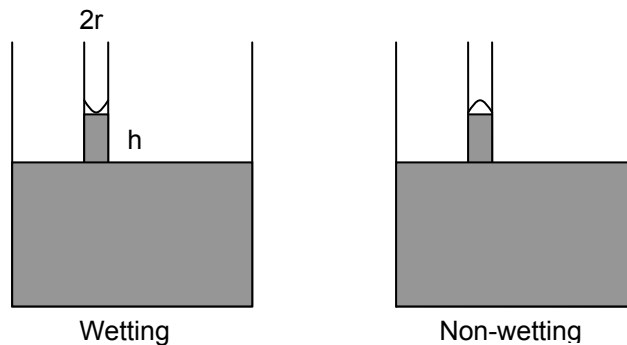


Below the line: liquid. Gas above.

"Wetting" means that the liquid molecules are attracted less strongly to each other than to the solid.

"Non-wetting" → opposite.

Surface tension causes an elevation (for wetting) or a depression (for non-wetting) of the meniscus in a narrow tube. → capillarity.



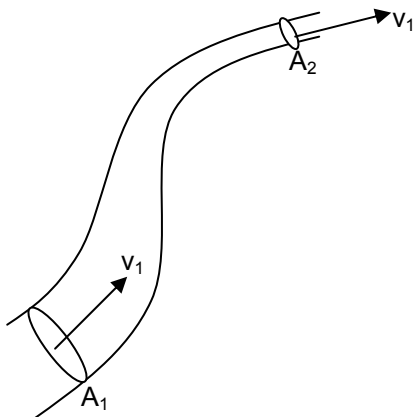
$$h = \frac{2\gamma}{r\rho g}$$

4.2 Flowing liquids

An ideal liquid is:

- Incompressible (i.e. its density cannot change)
- Has no internal friction (i.e. no viscosity)
- The path of an individual particle in a moving liquid is called a flow line.
- If the overall flow pattern does not change with time, we speak of steady flow.
- A streamline is a curve whose tangent at any point is in the direction of the fluid velocity.

The Continuity Equation



At a time interval dt the fluid at A_1 moves a distance $v_1 dt$, so a cylinder of volume $dV_1 = A_1 v_1 dt$ flows into the tube.

At the same time $dV_2 = A_2 v_2 dt$ flows out of the tube.

Incompressible fluid → density = const.

→ A mass $dm_1 = \rho A_1 v_1 dt$ flows across A_1 and a mass $dm_2 = \rho A_2 v_2 dt$ flows across A_2 .

Conservation of mass → $dm_1 = dm_2$

$$\rho A_1 v_1 dt = \rho A_2 v_2 dt$$

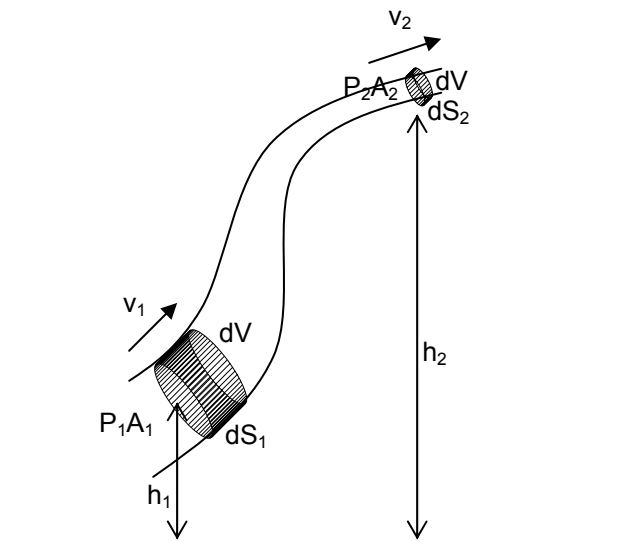
$$\boxed{A_1 v_1 = A_2 v_2} \text{ Continuity equation.}$$

The product Av is called the volume flow rate.

$$\frac{dV}{dt} = Av$$

This can be generalised for compressible fluids by putting in the density. We get:

$$\boxed{\rho_1 A_1 v_1 = \rho_2 A_2 v_2}$$

Bernoulli's Equation:

- Speed of the fluid can vary along the flow path
- The pressure can also vary.

When an incompressible fluid flows along a tube of varying cross-section, then its speed must vary \rightarrow acceleration (provided by surrounding fluid)

\rightarrow pressure must be different in regions of varying cross-section.

Continuity equation \rightarrow volume dV must be equal. $\rightarrow dV = A_1 dS_1 = A_2 dS_2$

The net work done on a fluid element during time dt is

$$dW = p_1 A_1 ds_1 - p_2 A_2 ds_2 = (p_1 - p_2) dV$$

dW is equal to the change in mechanical energy.

$$\text{Net change in kinetic energy } dE_k = \frac{1}{2} \rho dV (v_2^2 - v_1^2)$$

$$\text{Net change in potential energy } dE_p = \rho dV g (h_2 - h_1)$$

Look at $dW = dE_k + dE_p$ gives:

$$(p_1 - p_2) dV = \frac{1}{2} \rho dV (v_2^2 - v_1^2) + \rho dV g (h_2 - h_1)$$

$$p_1 - p_2 = \frac{1}{2} \rho (v_2^2 - v_1^2) + \rho g (h_2 - h_1)$$

$$\boxed{p_1 + \rho g h_1 + \frac{1}{2} \rho v_1^2 = p_2 + \rho g h_2 + \frac{1}{2} \rho v_2^2} \text{ Bernoulli's Equation.}$$

The indices 1 and 2 refer to an arbitrary point in or along the tube, thus:

$$p + \rho g h + \frac{1}{2} \rho v^2 = \text{const.}$$

We note that if the fluid is not moving ($v_1 = v_2 = 0$), the Bernoulli equation reduces to the pressure relation derived for a stationary fluid.

For flow through a horizontal pipe, Bernoulli's equation reduces to $p + \frac{1}{2} \rho v^2 = \text{const.}$

Note: these equations would also hold for an incompressible, frictionless gas.

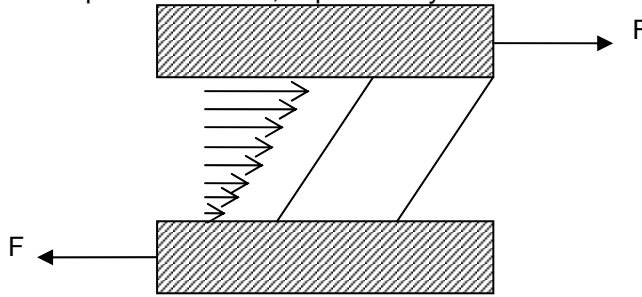
Viscosity

- Viscosity is the internal friction in a fluid.
- Viscous forces oppose the motion of the fluid element with respect to another fluid element.
- A thin boundary layer of the fluid which is in contact with the surface is inverted \rightarrow velocity profile into the bulk of the fluid.

Experience → flow through a pipe, rowing a boat, flow of blood through veins.

Simplest geometry

Parallel plates of area A, separated by a distance L.



Top plate moves with constant velocity v, bottom plate is at rest.

Laminar flow → no turbulence etc.

The fluid experiences a continuous increasing shear strain.

$\frac{F}{A}$ is called the shear stress exerted on the fluid.

In a fluid the shear strain increases continuously as long as a stress is applied. Stress does not depend on the shear strain but its rate of change.

$$\text{Strain rate} = \frac{v}{l}$$

Viscosity is defined as:

$$\eta = \frac{\text{shear stress}}{\text{strain rate}} = \frac{F/A}{v/l} \rightarrow F = \eta A \frac{v}{l}$$

Force is proportional to the speed unit (η): $\text{Pa}\cdot\text{s} = \frac{\text{NS}}{\text{m}^2}$

Viscosities are strongly temperature dependant (most times exponentially) for fluid, decreasing with increasing temperature.

Examples

H₂O T=0°C $\eta = 1.8\text{mPa}\cdot\text{s}$

T=20°C $\eta = 1.0\text{mPa}\cdot\text{s}$

T=60°C $\eta = 0.65\text{mPa}\cdot\text{s}$

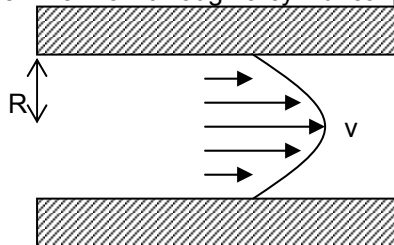
Glycerine T=20°C $\eta = 1410\text{mPa}\cdot\text{s}$

Air T=20°C $\eta = 0.018\text{mPa}\cdot\text{s}$

A fluid whose viscosity is independent of velocity is called Newtonian fluid.

An example for a non-Newtonian fluid is blood (Viscosity decreases for increasing velocity)

Laminar flow through a cylindrical pipe of length L



Without derivation: we note that the velocity at a distance r from the axis of the pipe is given by

$$v = \frac{P_1 - P_2}{4\eta L} (R^2 - r^2)$$

P₁, P₂: pressures at both ends of the pipe.

Flow is always in the direction of lowest pressure.

The volume flow rate $\frac{dV}{dt}$ is given by integration over rings of inner radius r and outer radius $r+dr$, over the cross-section $dA = 2\pi r dr$

$$\frac{dV}{dt} = \frac{\pi}{8} \left(\frac{R^4}{\eta} \right) \left(\frac{P_a - P_b}{L} \right)$$

This is called Poiseuille's equation. Note $\sim R^4$.

Examples:

- Plumbing systems
- Blood pressure

Another often used relation is the force exerted on a sphere of radius r moving through a liquid of viscosity η at a velocity v .

Without derivation:

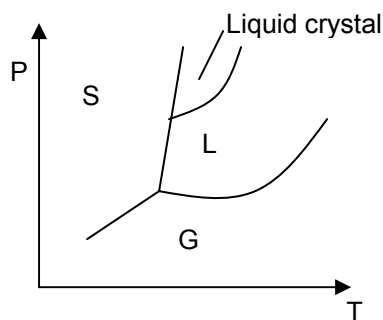
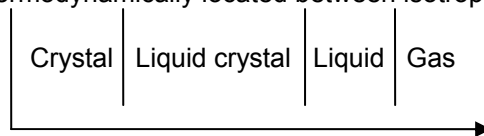
$$F = 6\pi\eta r v$$

Holds for laminar flow.

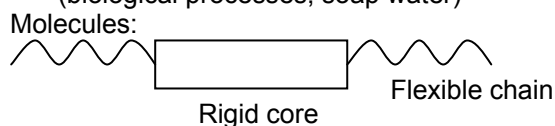
Turbulent flow is too complicated (4th year course on fluid dynamics).

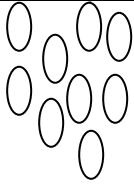
4.3 Liquid Crystals

- Liquid crystals are partially ordered fluids.
- They are liquids showing properties of both liquids (fluidity) and crystals (anisotropy of physical properties – birefringence, electrical conductivity)
- Thermodynamically located between isotropic liquid and the crystal.

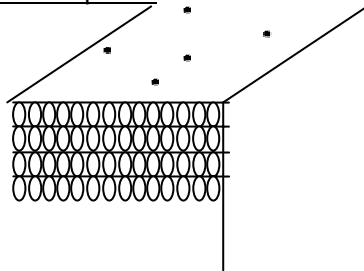


- Thermotropic liquid crystals created by temperature change (LCDs → liquid crystal displays)
- Lyotropic liquid crystals created by change of solvent concentration. (biological processes, soap water)



Nematic phase

- Orientational order of long molecular axis
- No positional order of centres of mass
- Used in LCD displays

Smectic phase

- Orientational order of long axis
- One-dimensional positional order
- Like a 2D liquid.

5. Solids

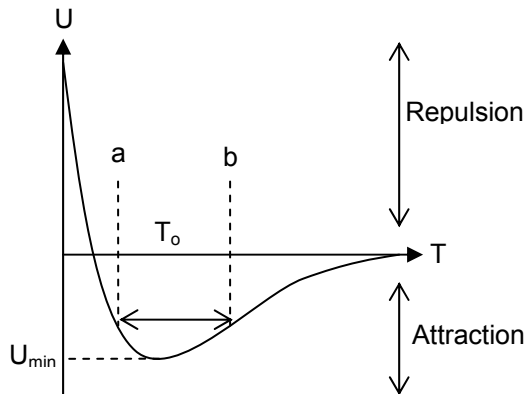
5.1 Potential Energy

We had seen earlier:

- The behaviour of gases is dominated by the kinetic energy
- A combination of kinetic and potential energy leads to the liquid state. (Potential energy arises from van der Waal's forces)
- For solids, the potential energy is most important. (But there is a bit of kinetic energy left)

Atoms are on average in fixed locations:

- No free movement, no place swapping
- No translational kinetic energy
- Translational invariance



In a crystal at equilibrium, all the atoms occupy a position of minimum potential energy, i.e.

$\frac{dU}{dr} = 0$. So at the equilibrium position r_0 , there is no net force.

1) Van der Waal's Solids

For example noble gases at low temperature.

- Filled electron shells
- High ionisation energies
- Inability to form bonds

The potential is generally described by the Lennard-Jones Potential

$$U(r) = 4\varepsilon \left[\left(\frac{a}{r} \right)^{12} - \left(\frac{a}{r} \right)^6 \right]$$

With a: radius of the outer electron shell

- Term $\sim \frac{1}{r^{12}}$ is repulsive
- Term $\sim \frac{1}{r^6}$ is attractive.

$-\varepsilon$ is the minimum potential energy, the energy you need to separate two atoms of the solid to infinity.

ε is related to the latent heat of sublimation (Solid \rightarrow gas), also called the cohesive energy, or lattice energy.

Each atom has N nearest neighbours, with N_A atoms in a mole \rightarrow (Molar) cohesive

energy is $\frac{1}{2} N_A N \varepsilon$ (the $\frac{1}{2}$ to avoid counting interactions twice)

2) *Ionic crystals*

For example NaCl etc.

The long-range attractive contributions to the potential are not only $\sim \frac{1}{r^6}$ term, but also

the Coulomb potential $\sim \frac{1}{r}$

For two atoms, the potential would look like $U(r) = \frac{A}{r^{12}} - \frac{B}{r^6} - \frac{C}{r}$

For many atoms we have to sum up over long range interactions, i.e. more than just nearest neighbours.

The term $\sim \frac{1}{r^6}$ is small as compared to $\sim \frac{1}{r}$. As a result we can neglect the $\frac{1}{r^6}$ term,

giving:

$$U(r) = -\alpha \frac{e^2}{4\pi\epsilon_0 r_0} \left[\frac{r_0}{r} - \frac{1}{12} \left(\frac{r_0}{r} \right)^{12} \right]$$

α : Madelung constant, accounts for the summation over long-range interactions between many atoms. It depends on the crystal structure.

Examples:

$\alpha = 1.7476$ for face-centred cubic (fcc) structures.

$\alpha = 1.7637$ for body-centred cubic (bcc) structures.

$\alpha = 1.6381$ for hexagonal closed packed (hcp) structures.

Comparison of lattice energies for different crystal binding mechanisms:

Ionic:

NaCl 750 KJmol⁻¹

LiF. 100 KJmol⁻¹

Covalent:

Diamond 720 KJmol⁻¹

Ge, Si

Dipole Binding

H₂O (Ice) 50 KJmol⁻¹

HF 29 KJmol⁻¹

Van der Waal's (Molecular crystals)

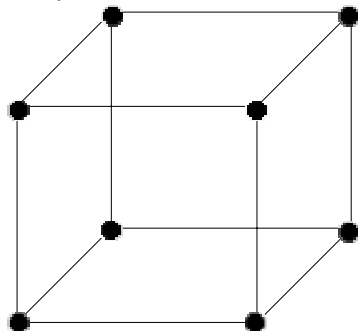
Ar 8 KJmol⁻¹

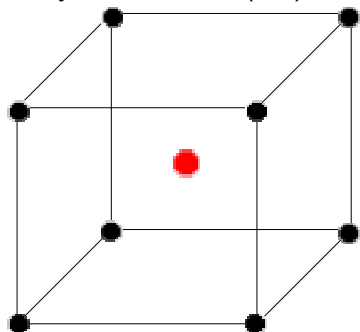
CH₄ 10 KJmol⁻¹

Metallic

Na 109 KJmol⁻¹

Fe 394 KJmol⁻¹

5.2 *Crystal Structures*1) *Simple Cubic unit cell*

2) *Body centred cubic (bcc)*

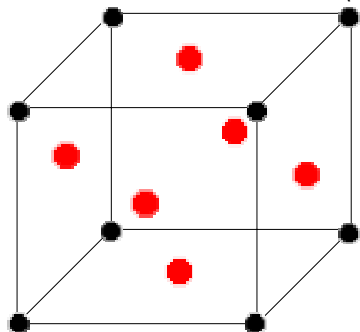
An atom in each corner, and one in the centre of the cube.
This is the same as two interdigitated simple cubic cells.

Example: CsCl.

Outside atoms would be Cs^+ , the middle one would be Cl^- .

(Each ion has 8 nearest neighbours of the opposite charge)

Some mono-atomic examples: Ba, Cs, Fe, K, Li, Na (8 nearest neighbours)

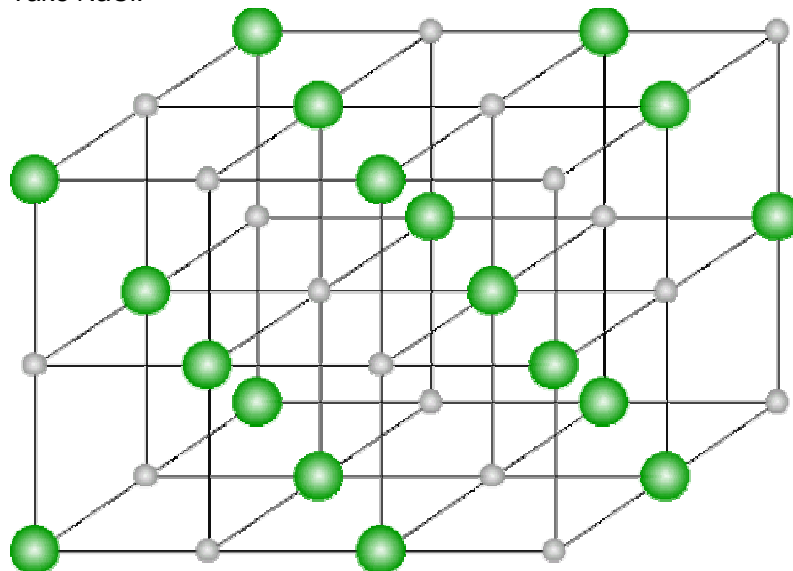
3) *Face-centred cubic unit cell (fcc)*

An atom on each corner of the cube, and atoms on each face of the cube.

Example: NaCl, LiF, KF, KCl, AgCl.

The minimum potential energy is observed when each ion has 6 nearest neighbours of the opposite kind.

Take NaCl.



Some examples of monoatomic fcc structures:

Most of the noble gases: Ar, Ne, Kr, Xe
 Many metals: Ag, Al, Au, Ca, Cu, Pb, Pt and others
 (12 nearest neighbours)

Look up:
Diamond Structure
Hexagonal close packed structure

5.3 X-Ray diffraction and Bragg's law

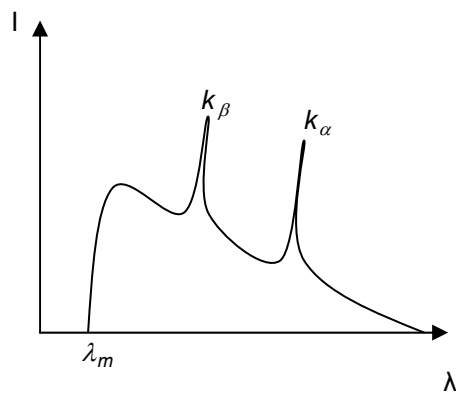
Every periodic structure diffracts electromagnetic radiation. Diffraction pattern is visible, depending on wavelength and periodicity. We use a wavelength comparable to the periodicity of the structure.

→ Atomic distances in a crystal are $\sim 10^{-10}\text{m}$

→ Visible light is not good for structure determination

→ But X-Rays are, $\lambda \sim 10^{-10}\text{m}$, $f \sim 10^{19}\text{s}^{-1}$

X-Rays are generally produced by bombarding a target element (often Cu) with a high-energy electron beam. This gives out an x-ray spectrum:



Continuous background, due to the slowing down of the electrons (Bremsstrahlung)

The low-frequency cutoff λ_m is related to acceleration by voltage V , and it is independent of target element.

$$\lambda_m = \frac{hc}{eV}$$

Superimposed on the continuous background is the characteristic spectrum, due to electron transitions. It is similar to Bohr's model, only it has to be for a many-electron system.

For diffraction experiments we filter out one line (Often $k_{\alpha 1}$) by using a monochromator.

The incident X-Rays induce oscillating dipoles (electric dipoles) in each scattering atom.

These emit scattered waves of the same frequency.

The scattered waves are NOT in phase, because each of the scattering centres has a different distance from the source.

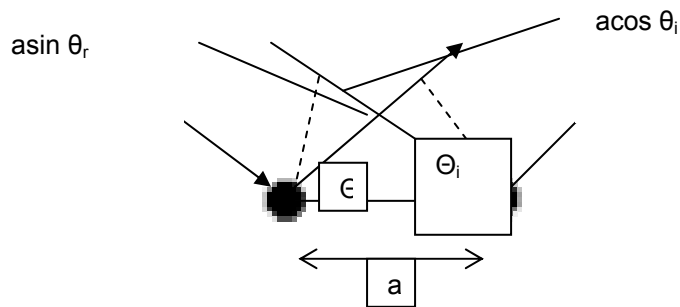
Note that this is different from a diffraction grating!!

The "X-Ray diffraction pattern" is more an interference pattern than a diffraction pattern. It results from the superposition of all the scattered waves.

→ Diffraction spots wherever there is constructive interference.

There are two conditions for this:

1.

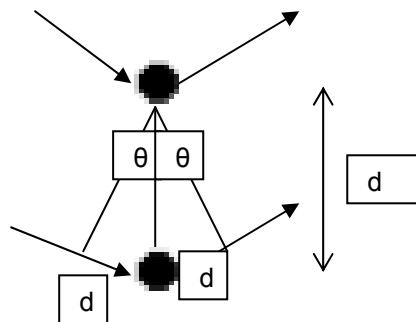


Constructive interference when:

$$a \cos \theta_i = a \cos \theta_r$$

$$\theta_i = \theta_r = \theta$$

2.



Constructive interference for adjacent rows when path difference is an integer multiple of the wavelength.

This is Bragg's equation.

$$2d \sin \theta = n\lambda \quad (n=\text{integer})$$

- $n=1$ (First order reflections) gives a series of diffraction spots, corresponding to each set of lattice planes (Each set will have a different d)

- $n=2$ (Second order reflections) gives another set of spots, etc.

→ The whole scattering pattern is unique for certain crystals → can determine its' structure.

In crystals $\sim 10^{20}$ atoms scatter coherently

→ Long-range order

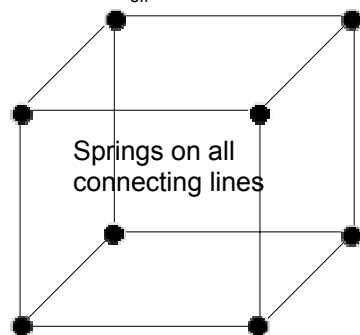
In liquids $\sim 20^3$ atoms scatter coherently

→ Short-range (fuzzy) order.

In gas there is no coherent scattering → no diffraction pattern.

5.4 Heat capacity of solids

In a first approximation we consider a mono-atomic crystal made up of atoms at fixed positions, which can vibrate, similar to being connected by springs with an effective spring constant k_{eff}



→ Each atom can vibrate in the x, y or z direction.

Total energy of an atom is

$$E = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \frac{1}{2}k_{\text{eff}}x^2 + \frac{1}{2}k_{\text{eff}}y^2 + \frac{1}{2}k_{\text{eff}}z^2$$

→ Each of those atoms has six degrees of freedom.

Using the equipartition theorem, the molar internal energy of a solid is

$$U_m = 6 \frac{1}{2}RT = 3RT$$

Thus:

$$c_{p,m} \approx c_{v,m} = 3R = 25 \text{ J mol}^{-1} \text{ K}^{-1}$$

Known as Dulong-Petit-Law.

Even though we are employing a rather crude model, the value compares quite well to measurements.

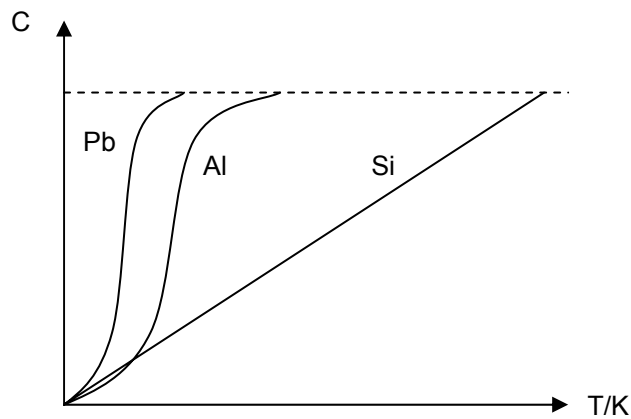
Examples: at 20°C

Al: $C = 24.2 \text{ J mol}^{-1} \text{ K}^{-1}$.

Fe: $C = 25.1 \text{ J mol}^{-1} \text{ K}^{-1}$.

Pb: $C = 26.5 \text{ J mol}^{-1} \text{ K}^{-1}$.

At lower temperatures the Dulong-Petit law breaks down, because vibrations are frozen in.



Quantitative understanding → quantum mechanics.

5.5 Simple Elasticity

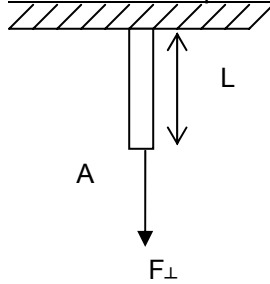
- Solid can be deformed by applying forces, this can be stretching, squeezing or twisting.
- We introduce a quantity stress, a force per unit area. Strain describes the resulting deformation.
- For small deformations, stress and strain are proportional. The proportionality constant is called the elastic modulus,

$$\frac{\text{stress}}{\text{strain}} = \text{elastic modulus}$$

Hooke's law.

Note: in general elastic properties depend on direction (they are anisotropic) → description by tensors. (→ Solid State Physics)

1. Tensile and compressive stress and strain



Define: tensile stress as

$$\frac{F_{\perp}}{A} \text{ unit Pa} = \frac{N}{m^2}$$

The fractional change of length of a body under tensile stress is called

$$\text{tensile strain} = \frac{l - l_0}{l_0} = \frac{\Delta l}{l_0}$$

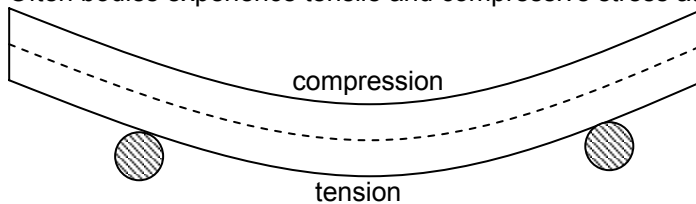
(Dimensionless number)

The tensile elastic modulus is called Young's Modulus.

$$Y = \frac{F_{\perp}/A}{\Delta l/l_0} = \frac{F_{\perp} l_0}{A \Delta l}$$

Note: compression is just the same, only that Δl has an opposite direction.

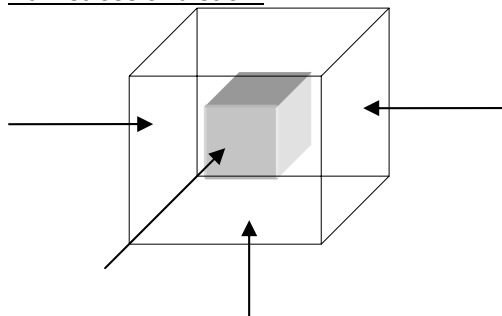
Often bodies experience tensile and compressive stress at the same time:



The centre line does not experience either tension or compression.

Examples: Suspension bridges, arches in cathedrals, traffic lights.

2. Bulk stress and strain



In volume deformations pressure takes the role of stress. (Remember pressure in a fluid)

Increase the pressure from p_0 to $p_0 + \Delta p$ causes a fractional change of volume (strain):

$$\text{Bulk strain} = \frac{\Delta V}{V}$$

We thus have a bulk Modulus:

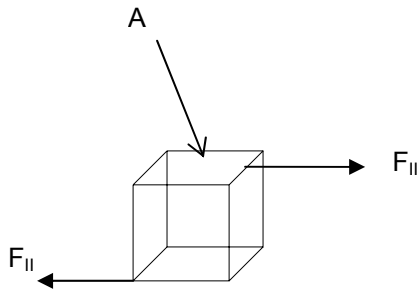
$$B = - \frac{\Delta p}{\Delta V/V_0} \text{ units: Pa} = \frac{N}{m^2}$$

The reciprocal bulk modulus is the compressibility.

$$K = \frac{1}{B} = - \frac{1}{V_0} \frac{\Delta V}{\Delta p}$$

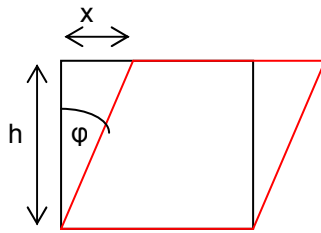
Note: for small pressure changes in a solid or a liquid, B can be constant. This is not the case for gases, where B depends on p_0 .

3. Shear Stress and Strain



Shear stress is a force tangential to the surface divided by the area.

$$\text{Shear stress} = \frac{F_{||}}{A}$$



$$\text{Shear strain} = \frac{x}{h} = \tan \phi$$

For small forces the shear modulus is

$$S = \frac{F_{||}/A}{x/h} = \frac{F_{||}h}{Ax} \approx \frac{F_{||}}{A\phi} \quad (\text{For small } \phi) \text{ Units: } Pa = \frac{N}{m^2}$$

Note: Gases and liquids do not exhibit a shear modulus.

Example: Scissors and knives work by applying a shear stress until the strain is so large that it breaks the molecular (or chemical) bonds.

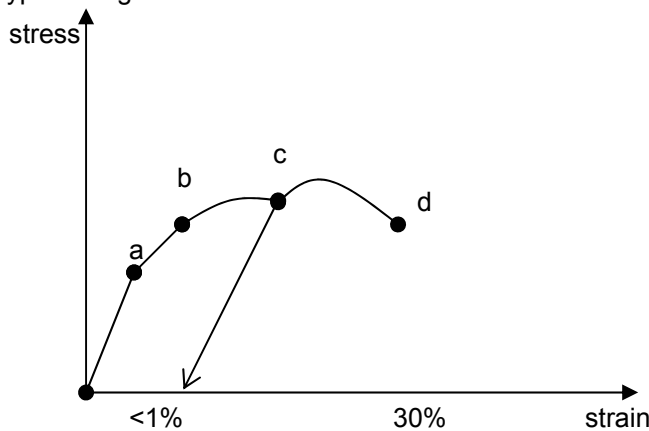
Some examples:

	$Y/Pa \cdot 10^{10}$	$B/Pa \cdot 10^{10}$	$S/Pa \cdot 10^{10}$
Al	7	7.5	2.5
Fe	21	16	7.7
Cu	11	14	4.4
Pb	1.6	4.1	0.6

Elasticity and Plasticity

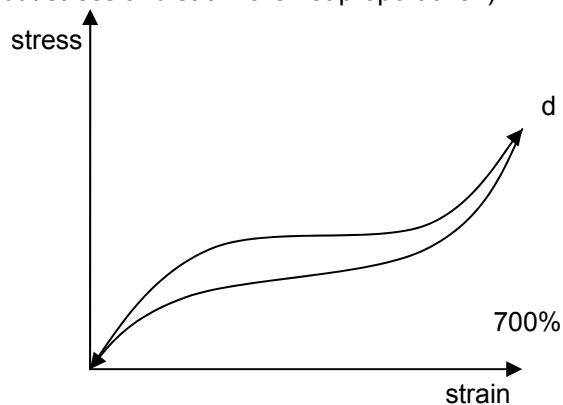
Plot stress against strain.

Typical diagram for metal:



- Up to (a) we have the proportionality limit, described by Hooke's law.
- Up to (b) we have the elastic limit and reversible deformations.
- For larger stress we have plastic deformation (plastic flow) → irreversible deformations, hysteresis.

- At (d) we eventually observe fracture. Rubber is a material for which elastic behaviour is observed over a large strain region (but stress and strain are not proportional!)



Some thoughts on the January exam:

Exam questions will be similar to those discussed during the tutorials. They will not be harder, but also not easier.

Questions will be calculations, but also conceptual.

Values of constants will not need to be memorised (Although some trivial knowledge will be taken for granted, e.g. density of water, molar mass of H₂O or C, etc...)

Need to memorise some important formulae, concepts and diagrams – marked on notes.

Keep track of units!