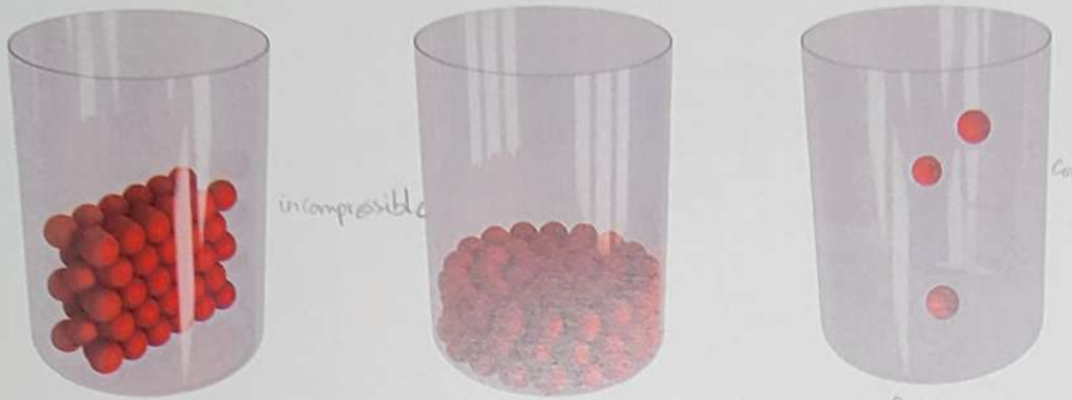
Intermolecular Forces

The fundamental difference between states of matter is the distance between particles.



incompressible

compressible

solid	liquid	gas
ordered, particles do not change position, particles close together, no diffusion	disordered, particles move, particles close, slow diffusion	total disorder, much empty space, rapid diffusion

The state of a substance at a particular temperature and pressure depends on two antagonistic entities:

1- the kinetic energy of the particles, T dependent, keep particles separated.

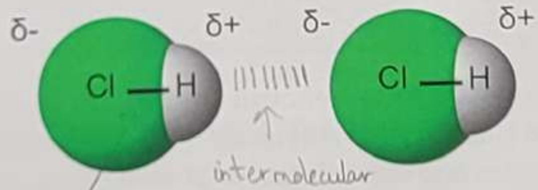
2- the strength of the attractions between particles, draw particles together

between ↓ within the molecule ↓

Inter- vs. Intramolecular Forces

The attractions between molecules are not nearly as strong as the chemical bonds that hold compounds together.

but control physical properties such as boiling and melting point, vapour pressure and viscosity (thickness)



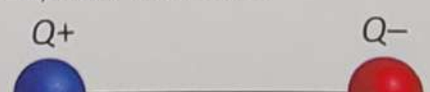
intermolecular attraction (weak)

covalent bond (strong)

Intermolecular (or van der Waals) forces

The strength of an intermolecular force depends on whether or not the species are polar molecules, nonpolar molecules, atoms, or ions. The more polar the molecule or highly charged the ion, the stronger the attraction from one species to another.

intermolecular force is inversely proportional to the distance squared

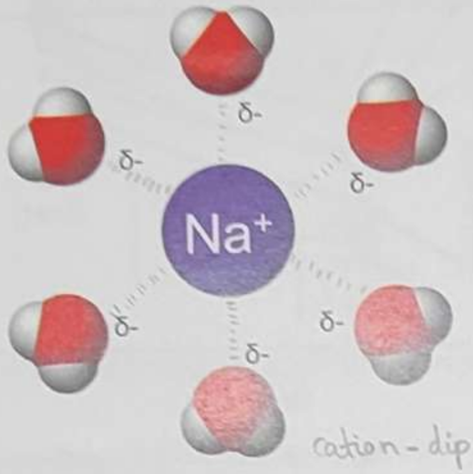


Same concept as in **ionic compounds**, which have strong electrostatic attractions (and repulsions!) between cations and anions that extend through the entire lattice.

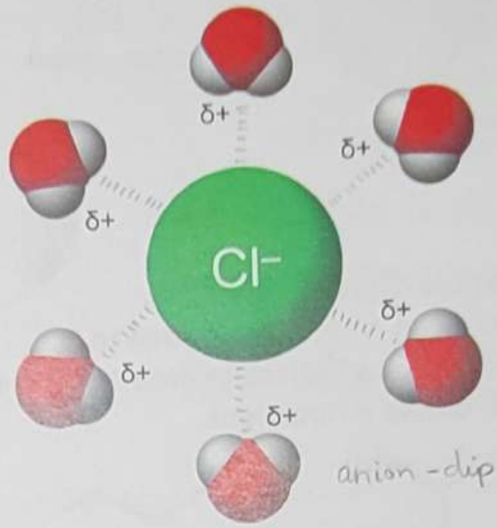
Ion-dipole forces

Ion-dipole interactions are an important force in solutions of ions and in **supramolecular** chemistry. One of the strongest of the intermolecular forces because it is the attraction of a full charge for a partial charge.

These forces are responsible for ionic substances dissolving in polar solvents.



notice the difference in orientation of the water molecule



cation-dipole

anion-dipole

For a soluble solid, together the anion-dipole and cation-dipole forces can overcome the lattice energy

Dipole-dipole forces

Polar molecules have permanent dipole moments. Partially negative ends of polar molecules are attracted to partially positive ends of nearby polar molecules.

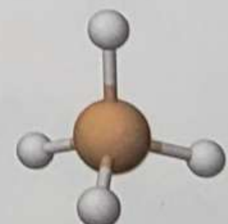
.... = dipole-dipole forces

δ^+ δ^- $\quad$ δ^+ δ^- $\quad$ δ^+ δ^- $\quad$ δ^+ δ^-

H—I .... H—I .... H—I .... H—I

δ^+ and δ^- are partial positive and negative charges

The molar masses of SiH_4, PH_3 and H_2S are similar, but they have very different physical properties:



SiH_4

Substance	Molar mass (g/mol)	Dipole moment (D)	Melting point (°C)	Boiling Point (°C)
SiH_4	32.12	0	-185	-112
PH_3	33.99	0.574	-135	-87.8
H_2S	34.09	0.978	-85.5	-59.6

PH_3

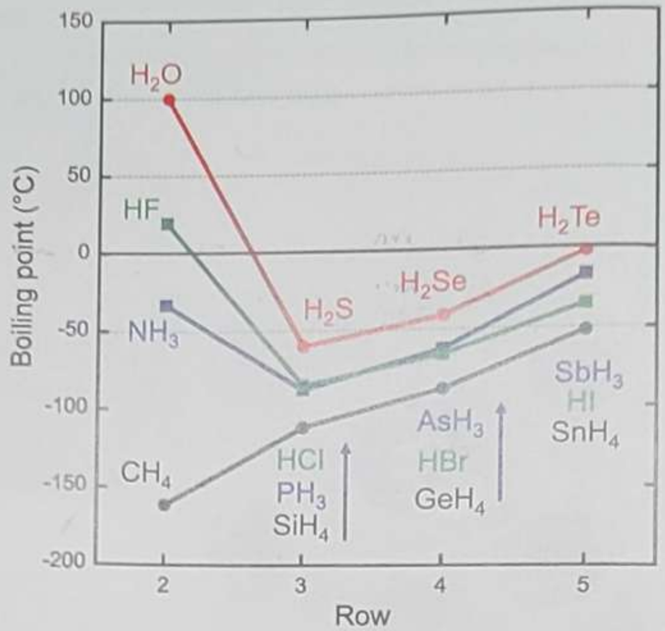
H_2S

dipole moment, dipole-dipole interactions, m.p and b.p, are all greater for the more electronegative element bound to hydrogen

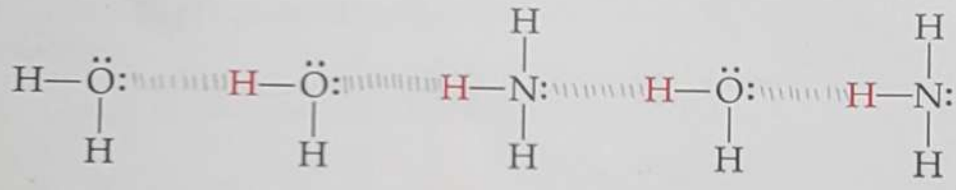
Hydrogen bonding

The series NH_3 to SbH_3, HF to HI and H_2O to H_2Te show a dramatic departure from the overall trend for NH_3, HF and H_2O:

due to an especially strong form of dipole - dipole interaction called hydrogen bonding

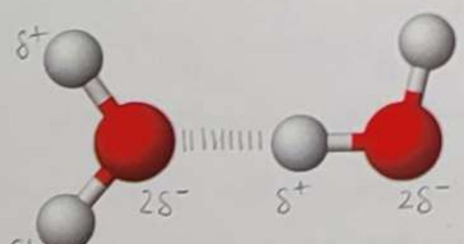


The dipole-dipole interactions experienced when **H is bonded to N, O, or F** are much stronger than other dipole-dipole interactions.

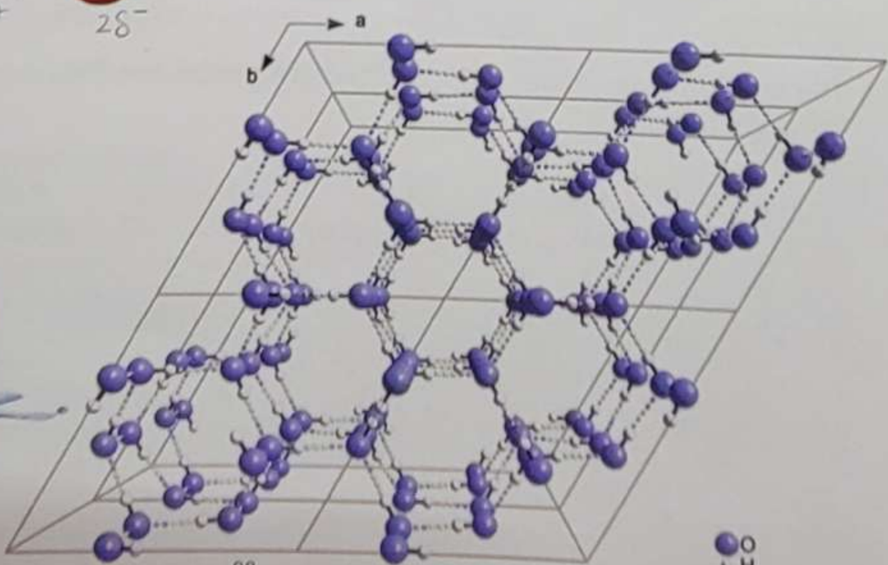


Hydrogen bonding arises in part from the high electronegativity of N, O and F.

When H is bonded to one of those very electronegative elements, the H nucleus is exposed



ice has an open structure due to regular hydrogen bonding



- water is the only non-metal which expands on freezing
- few metals expand on freezing

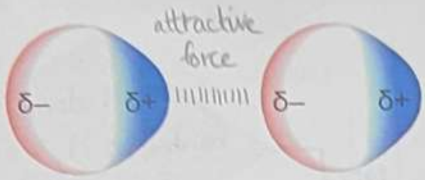
London dispersion forces

All atoms and molecules are weakly attracted to one another through **London dispersion forces**, the attraction of an *instantaneous dipole* for an *induced dipole*. Consider Xe (54 electrons):

(considering particle nature of e⁻s)

For an instant in time, e⁻s can be asymmetrical arranged around the nucleus such that the atom is polarized

instantaneous dipole...



... induces a dipole in a neighbouring atom

London dispersion forces are present in **all molecules**, whether they are polar or nonpolar.

The shape of the molecule affects the strength of dispersion forces:

Long, skinny molecules have stronger dispersion forces than short, broad ones

n-butane

b.p 272K

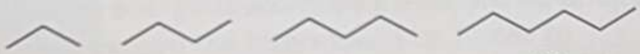
2-methylpropane

b.p 261 K

In any given series, boiling point increases with molecular weight:

more e⁻s, higher surface area, larger dispersion forces

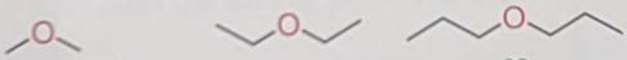
Alkanes
Boiling point °C



-42 0 36 69

(London dispersion forces only)

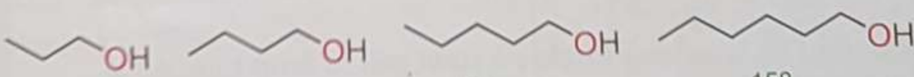
Ethers
Boiling point °C



-24 35 89

(Dipole - dipole + london)
no H - bonding

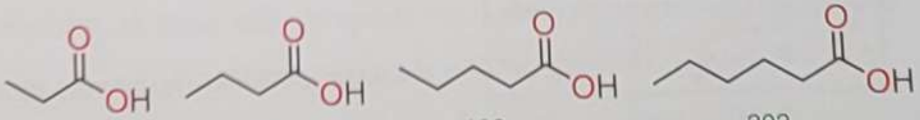
Alcohols
Boiling point °C



97 117 138 158

london + H-bond

Carboxylic acids
Boiling point °C

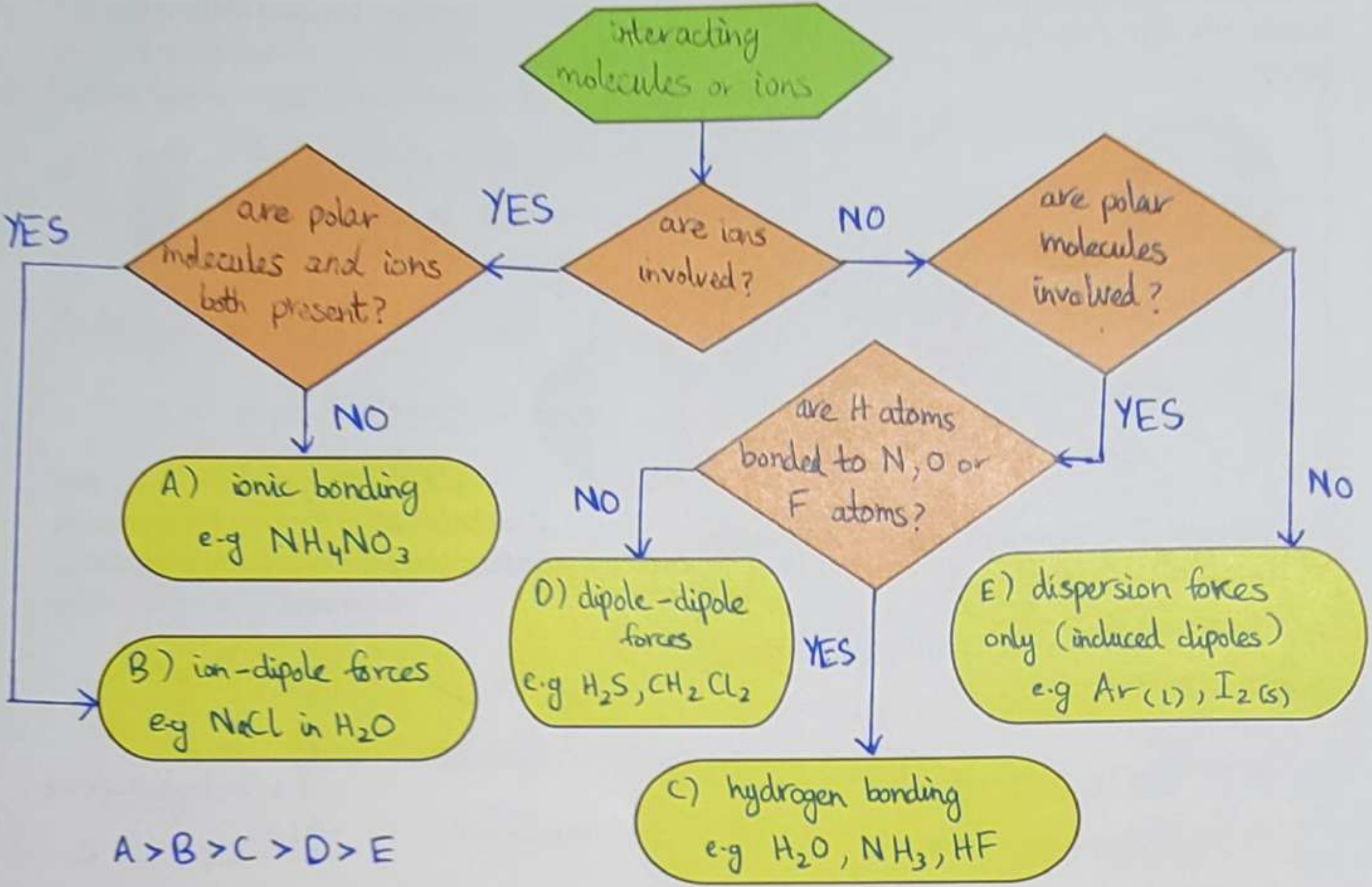


141 164 186 202

The high surface area and flexibility of gecko toe-pads allow them to adhere to most surfaces via a combination of van der Waals forces and contact electrification

two surfaces having opposite charges

Intermolecular forces: a summary



A > B > C > D > E

Properties of Liquids

The properties of a liquid depend on the balance between:

- kinetic energy of particles
- intermolecular attractive forces between particles

Viscosity

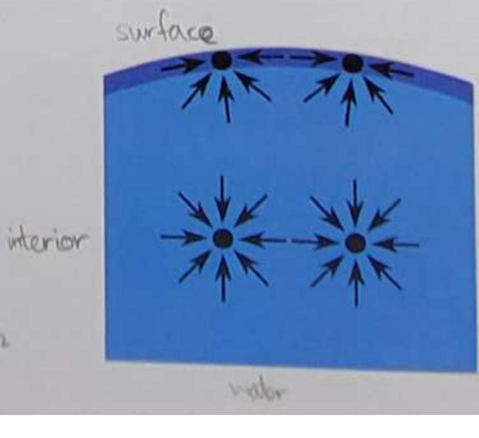
resistance to flow units = Pa s = $kg\,m^{-1}s^{-1}$

Measured by how long it takes a steel ball to drop through a liquid over a specified distance. Liquids are more viscous when their constituent molecules:

- have stronger intermolecular forces
- are easily entangled
- have higher molecular weights

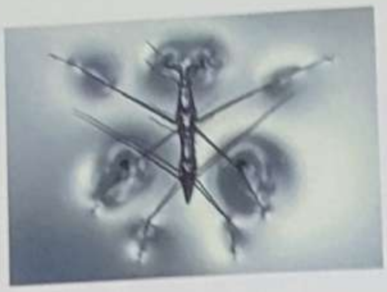
Surface tension

Created by imbalance of forces at the top of a liquid



Surface tension is related to the work required to increase surface area by a unit amount.

Units: $J\,m^{-2}$

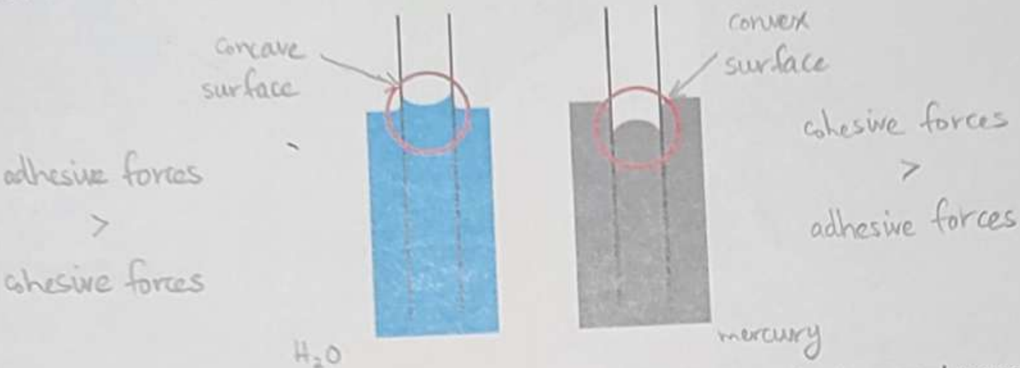


Bugs can float on water because the molecules on the surface assemble more tightly as they form fewer but stronger hydrogen bonds with the water molecules in the bulk.

Interfacial behavior

Cohesive force: binds like molecules to one another

Adhesive force: binds molecules to the surface



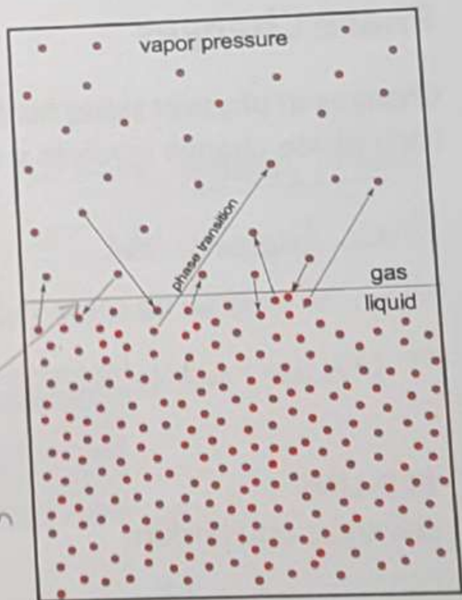
Capillary action: strong adhesive forces draw liquid along sides of tubes and pores, cohesive forces pull along the rest of the liquid

Vapour Pressure and Boiling Point

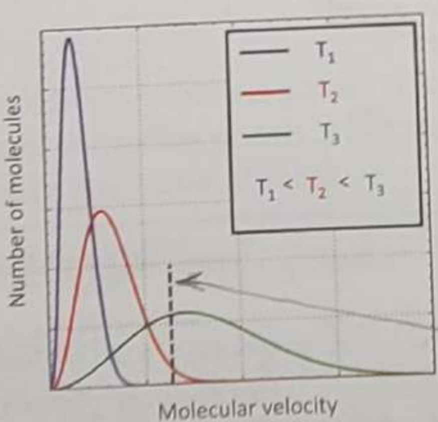
Evaporation occurs when energetic molecules or atoms near the surface of the liquid exceed the intermolecular forces to transition from the liquid to the gas phase. The ease with which this happens dictates both the **boiling point** and the **vapour pressure** of the liquid.

open system: molecules evaporate and are removed

closed system: molecules are evaporating and condensing at same rate: in equilibrium



Vapour pressure increases with temperature.



minimum KE to escape liquid

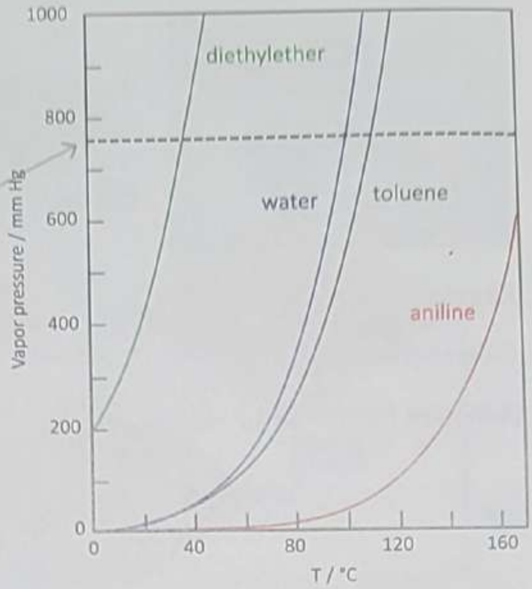
Vaporization: molecules escape the surface of the liquid into the gas phase.

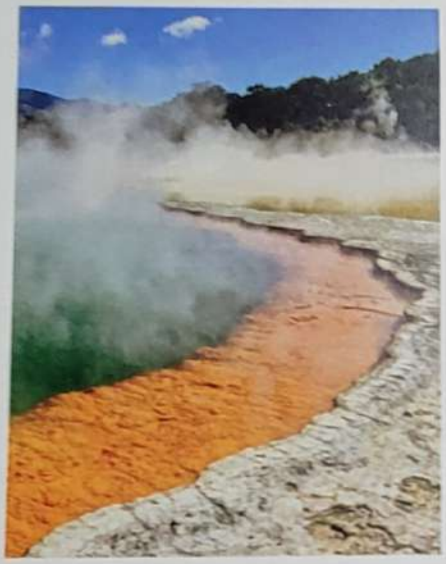
Vaporization is greater when the temperature is higher, the surface area is greater or when the intermolecular forces are weaker.

Boiling occurs when vapour pressure = external pressure.

Normal boiling point:

temperature at which the liquid's vapour pressure is 1 atm (= 760 mm Hg)





Champagne Pool (72-75°C) at Waiotapu geothermal springs, NZ

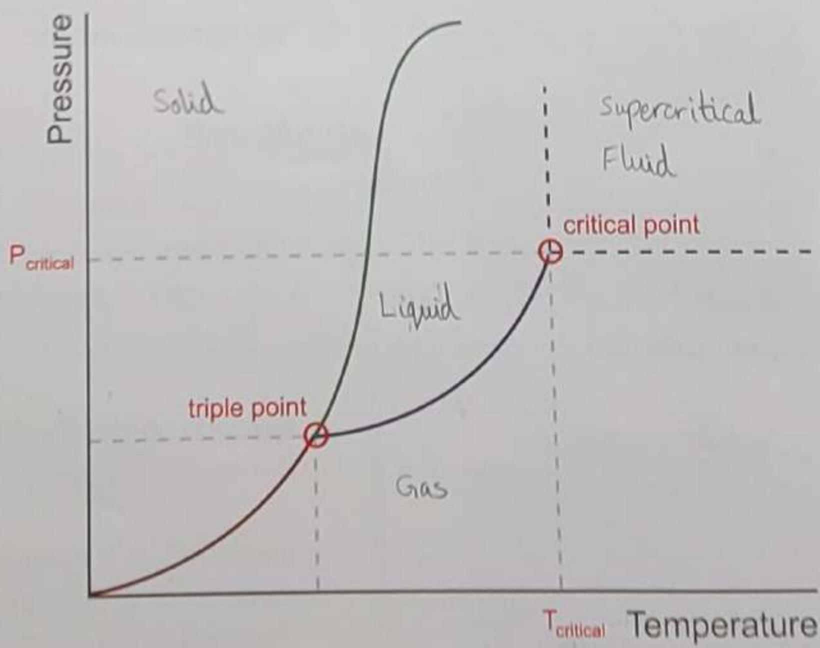
Volatile liquids

- evaporate easily
- have a high vapour pressure at room temperature

Phase Changes

Changes in physical state, with no change in composition.
Each phase change involves a change in the energy of the system.

Phase diagrams plot states of matter as a function of pressure and temperature



RED LINE
solid/gas equilibrium

deposition ↔ sublimation

GREEN LINE
solid/liquid equilibrium

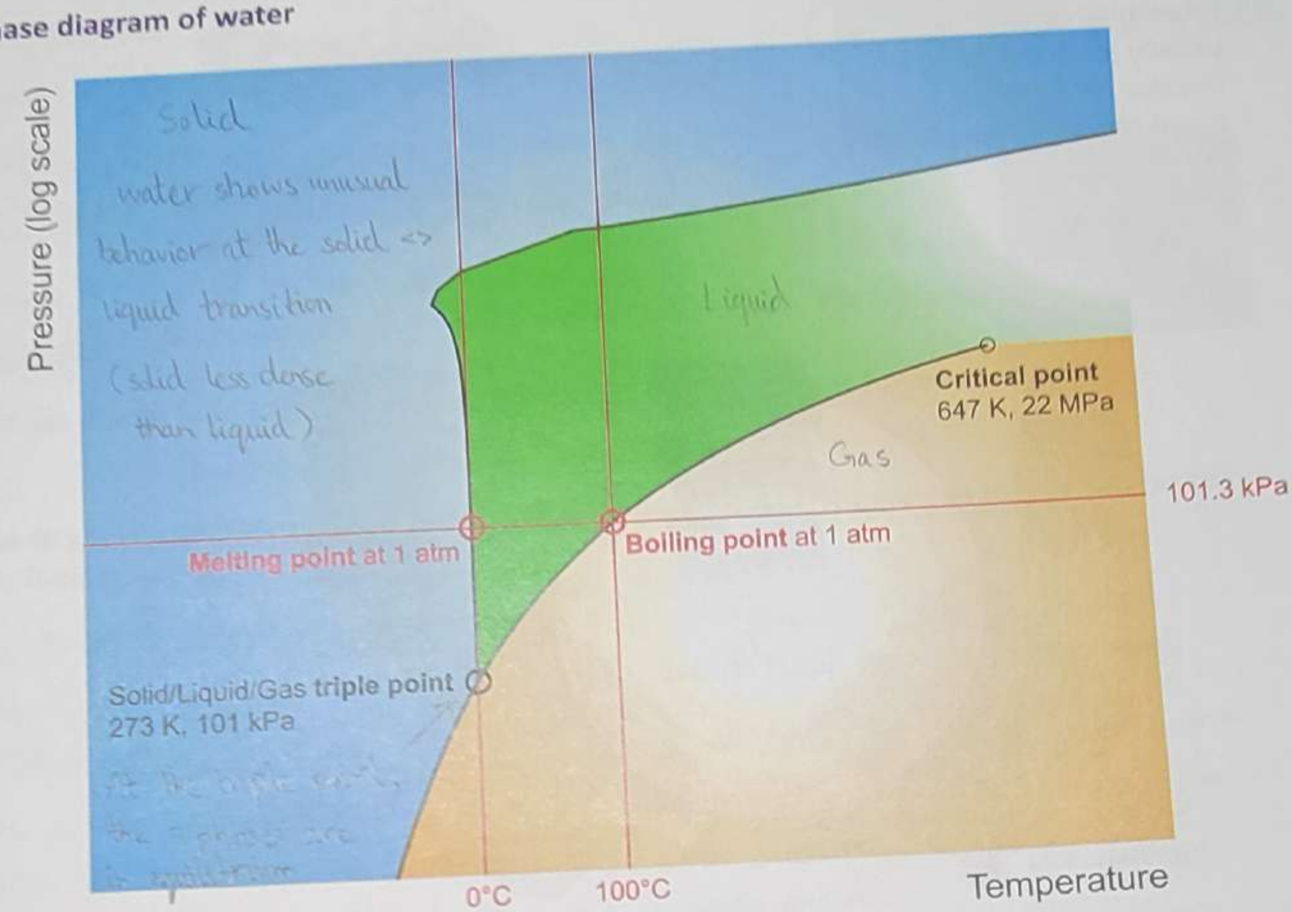
freezing ↔ melting

BLUE LINE
liquid/gas equilibrium

condensing ↔ boiling

A superficial fluid has properties intermediate between a liquid and a gas. $scCO_2$ is used to extract caffeine from coffee

Phase diagram of water



Liquid Crystals

Solids are characterized by their order, and **liquids** by their *lack* of order

Liquid crystals are substances that exhibit one or more ordered phases at a temperature above the melting point

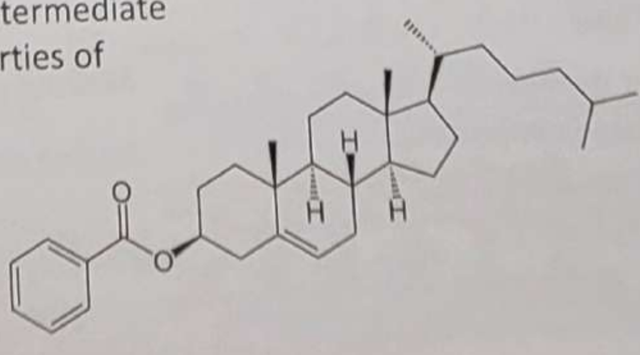
The first systematic report of a **liquid crystal** was cholesteryl benzoate (in 1888).

< 145°C = solid

145°C - 179°C
opaque liquid

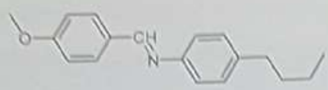
> 179°C
clear liquid

Cholesteryl benzoate passes through an intermediate liquid crystalline phase. It has some properties of liquids and some of solids.

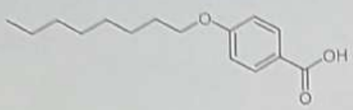


The liquid flows (liquid properties) but has some order (crystal properties)

Liquid crystal molecules are usually long and rod-like. In normal liquid phases they are randomly oriented.



21 – 47 °C



108 – 147 °C

molecules in liquid crystals have some order, but not as much as solids.

nematic
liquid crystal

ordered along the long axis of the molecule only

smectic
liquid crystal

ordered along the long axis of the molecule and in one other dimension

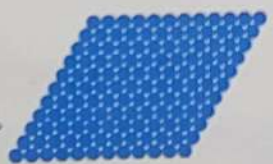
cholesteric
liquid crystal

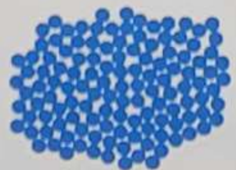
ordered along the long axis of the molecule and in twisted layers

Solids

In solids, the intermolecular forces are strong enough to lock particles into fixed positions. **Crystalline** solids have the particles arranged in a regular repeating pattern. **Amorphous** solids have those particles randomly arranged.

crystalline solid
e.g metals, minerals

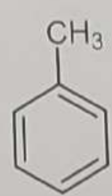


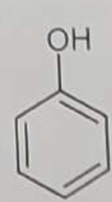


amorphous solid
e.g glass, wax

Molecular solids are atoms or molecules held together by intermolecular forces.

molecular solids are usually soft and have low melting points and low thermal and electrical conductivity





	benzene	toluene	phenol
Melting point (°C)	5	-95	41
Boiling point (°C)	80	111	182

Efficient packing of molecules is important (since they are not regular spheres).

high mp due to efficient packing

high bp due to larger intermolecular forces

high mp & bp due to hydrogen bonding

Metallic Solids

Consist entirely of metal atoms; **metallic** bonding.

Os
m.p. 3306K

valence electrons delocalized throughout the solid
metals vary greatly in the strength of their bonding
band theory is the best description

Au
m.p. 1337K

Ionic Solids

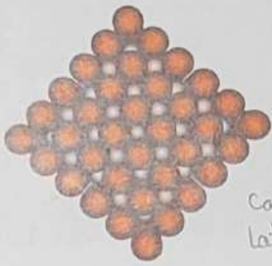
Consist of ions held together by ionic bonds (*i.e.* by electrostatic forces of attraction).

hard, brittle and have high melting points

The larger the charges (Q_1, Q_2) and the smaller the distance (r) between ions, the stronger the ionic bonding.

the structure of the ionic solid depends on the charges on the ions and on the relative sizes of the ions

Calcium fluorite crystal



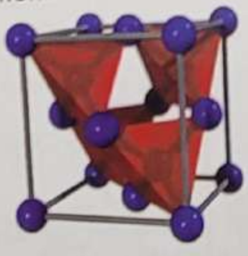
CaF_2 lattice

Covalent-network solids

Consist of atoms held together, in large networks or chains, with covalent bonds.

have much higher melting points and are much harder than molecular solids

diamond



Strong covalent bonds connect the atoms, e.g. quartz (SiO_2) or diamond (C):

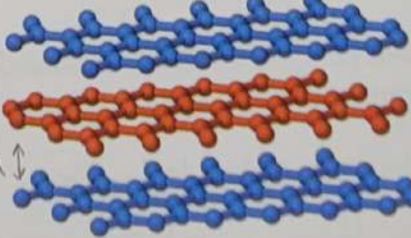
each C atom is tetrahedral
3D array of atoms
diamond is hard and has a high melting point (3550°C)

Strong covalent bonds connect the atoms within the layers of graphite.

each C atom is arranged in a planar hexagonal ring C–C 1.42 Å

Å = 10^{-10} m
So 1.42 Å = 142 pm

the layers are held together by weak dispersion forces



3.35 Å

graphite is a good lubricant

Solids – a summary

This scheme omits amorphous solids, including polymers and glass

Crystalline solids

Atomic solids units are atoms

Molecular solids

units are molecules

low m.p.

iodine (I_2)

Ionic solids

units are cations and anions

high m.p.

calcite ($CaCO_3$)

Nonbonding

held together by dispersion forces

low mp

xenon

Metallic

held together by metallic bonds

variable m.p.

gold (Au)

Network covalent

held together by covalent bonds

high m.p.

quartz (SiO_2)

Band theory of solids

Insulators

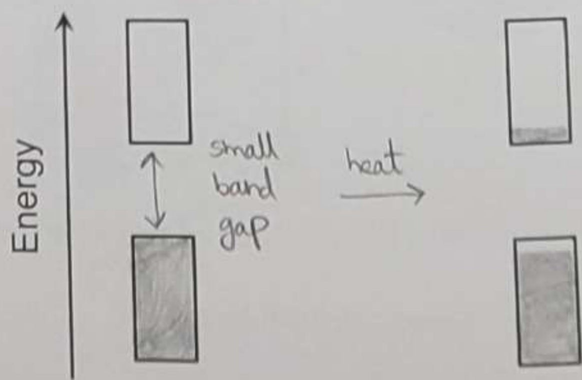
Many non-metals are **insulators**, i.e. electrons can't flow freely through them. Insulators are characterized by having a large **band gap** (energy difference between a filled band and an empty band). Examples include glass, air, rubber, wood, most plastics.

ceramics are usually insulators, but some copper oxides are superconductors!

Semiconductors

Silicon has the same structure as diamond, but a much smaller band gap:

Small enough that infrared energy can be enough to promote electrons from one band to another



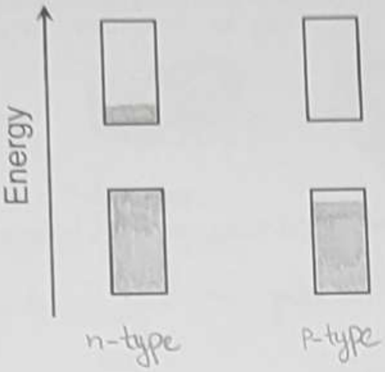
Inorganic compounds that are **semiconductors** tend to have an average of 4 valence electrons, and their conductivity may be increased by **doping**.

e.g Si, GaAs, InP, CdSe

doping = addition of controlled amounts of an impurity to the semiconductors

Doping yields different kinds of semiconductors:

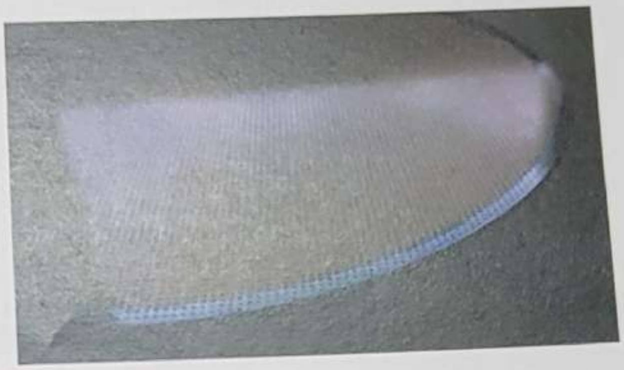
- dopant atom has more valence electrons than the host atom
- adds electrons to the conduction band
- e.g P into Si



- dopant atom has fewer valence electrons than the host atom
- leads to holes in the valence band
- e.g B into Si

Materials for electronics

Many modern devices rely on **silicon** wafers or "chips" containing complex patterns of semiconductors, insulators, and metal wires.

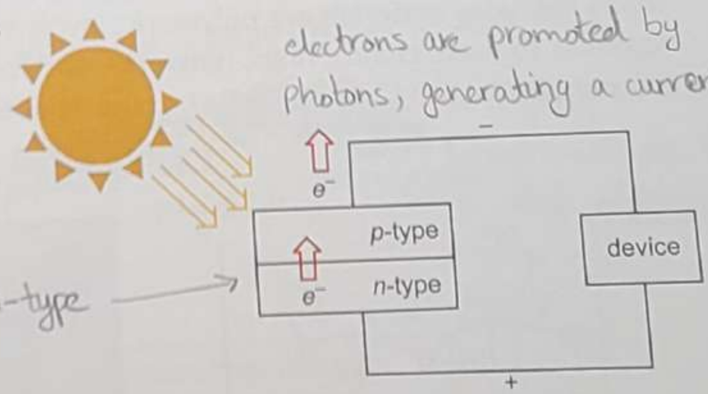


- Si is abundant, cheap, can grow enormous perfect crystals
- nontoxic, can be chemically protected with SiO_2

Semiconductors are also used in the production of **solar energy cells**. If you shine light with an appropriate wavelength on a semiconductor, electrons are promoted to the conduction band, making the material more conductive.

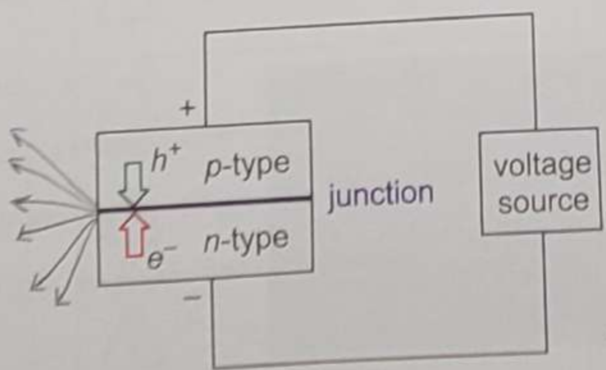
this property is known as photoconductivity

electrons are promoted by photons, generating a current



solar cells are formed by joining n-type and p-type silicon

Light-emitting diodes (LEDs) are used in many types of displays. The mechanism of action is the opposite of that involved in solar cells.



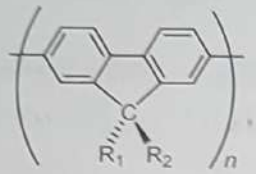
a voltage is applied and electrons in the conduction band from the n-side combine at the junction with the holes from the p-side

light is emitted when photons have energy equal to the band gap

Organic LEDs (**OLEDs**) have some advantages over traditional LEDs.

lighter, more flexible, and may be brighter and more energy efficient

made from conducting organic polymers



some problems with lifetime of devices, especially for blue (higher E)

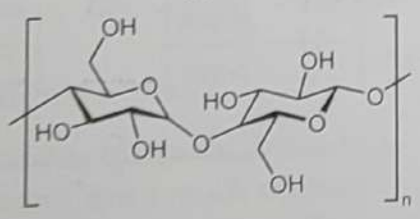
Enable the creation of curved and flexible displays

Polymers

= monomers

Many everyday materials are polymeric, involving simple organic molecules linked together to make chains, rings, networks, and folded constructs. For example, **cellulose** is a polysaccharide ("polysugar") chain of repeating glucose molecules.

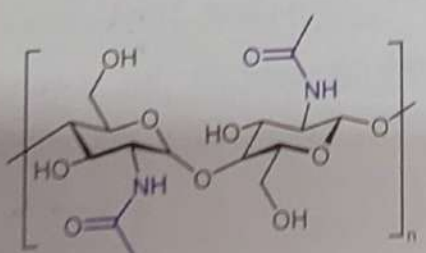
poly glucose



paper

cotton

If the repeat glucose unit has an amide group attached to it, the resulting polymer is called **chiti**



Insect and crustacean exoskeletons are composite materials made of chitin and calcium carbonate

Humans have also used polysaccharides in imaginative ways. The air freshener ***Febreze*** contains a cyclic sugar called a **cyclodextrin**, a ring-shaped molecule that captures odor molecules:

β-cyclodextrin

putrescine

$H_2N(CH_2)_4NH_2$

rotting meat

cadaverine

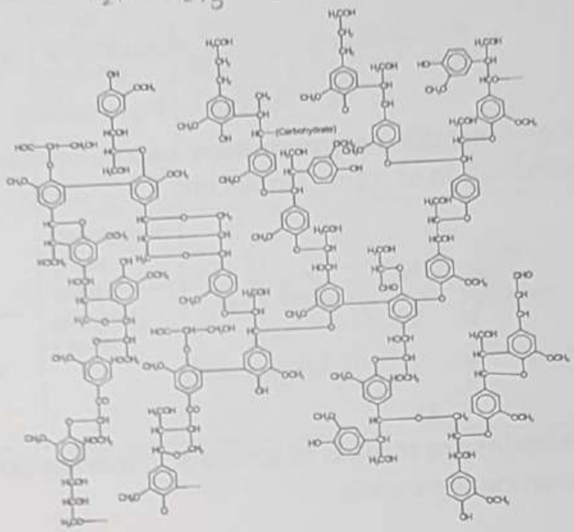
$H_2N(CH_2)_5NH_2$

ethanethiol

CH_3CH_2SH

gas leaks

Lignin is a polyphenolic crosslinked polymer found in wood. Small lignin molecules are called **tannins**.



Lignin is rigid and resistant to rot

Complex cross-linked structure

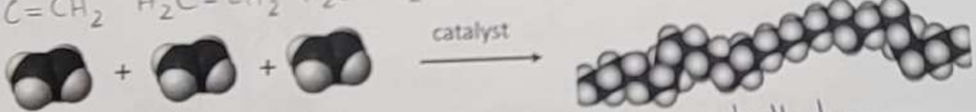
Bakelite, the first commercial plastic, is a phenolic resin

Making polymers

Many synthetic polymers have a backbone of C–C bonds.

$-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$

$H_2C=CH_2$ $H_2C=CH_2$ $H_2C=CH_2$



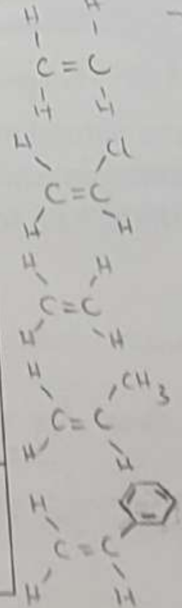
ethylene ethylene ethylene polyethylene

the coupling of monomers through multiple bonds is called addition polymerization

ethene = ethylene

addition polymers

2 HDPE	High-density polyethylene (HDPE)	Bottles, grocery bags, milk jugs, recycling bins, playground equipment
3 V	Polyvinyl chloride (PVC)	Pipe, window profile, siding, fencing, lawn chairs, non-food bottles
4 LDPE	Low-density polyethylene (LDPE)	Plastic bags, various containers, dispensing bottles, tubing
5 PP	Polypropylene (PP)	Auto parts, industrial fibres, food containers, dishware
6 PS	Polystyrene (PS)	Cafeteria trays, plastic utensils, coffee cup lids, toys, clamshell containers, packaging



monomers

Addition polymers are formed by breaking the C=C π bond and forming a new C-C σ bond between the monomer and the polymer chain.

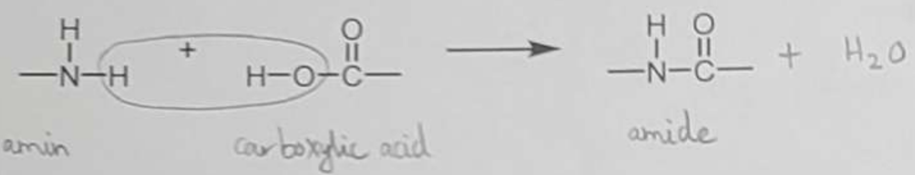
because σ bonds are stronger than π bonds, addition polymers are hard to depolymerize

Plastics are polymeric materials that can be formed into various shapes, usually with heat and pressure.

thermoplastic materials can be reshaped (e.g polyethylene)

thermosetting plastic materials are shaped by an irreversible process (cannot be reshaped by melting and resolidifying)

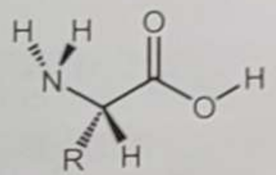
Condensation polymerization: two molecules are joined to form a larger molecule by the elimination of a small molecule. e.g water, methanol, acetic acid



polymers formed from two different monomers are called copolymers

Proteins are formed of amino acid monomers (which contain both amine and carboxylic functional groups).
$-NH_2$ $-COOH$

Structure of a generic neutral amino acid:

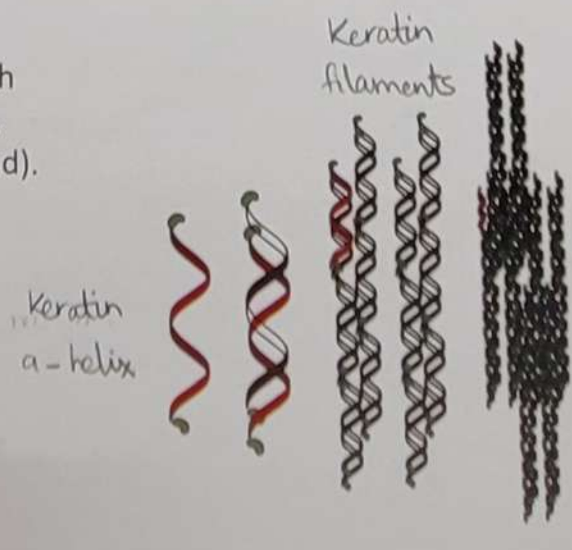


There are hundreds of amino acids known though only 22 appear in the genetic code

A chain of condensed amino acids forms a polypeptide.
That sequence will fold to form a protein:

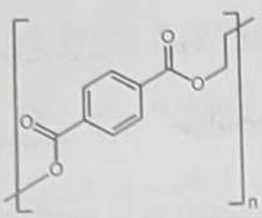
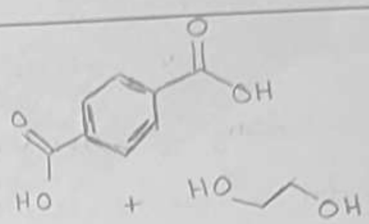
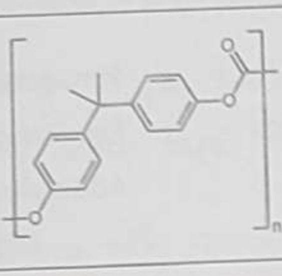
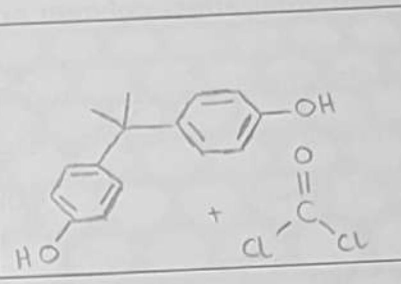
The folded protein shown to the right is a lysozyme, an enzyme that catalyzes the hydrolysis of components of cell walls.

Some natural materials are polymeric proteins, such as **collagen** (cartilage, tendons, skin), **keratin** (nails, feathers, hair, scales), and **fibroin** (silk, spider thread).



Polymer molecules are attracted to each other by a variety of covalent and intermolecular forces

Chemists also make polymers using amide linkages. Nylon was the first synthetic condensation polymer discovered, and others soon followed based on ester linkages:

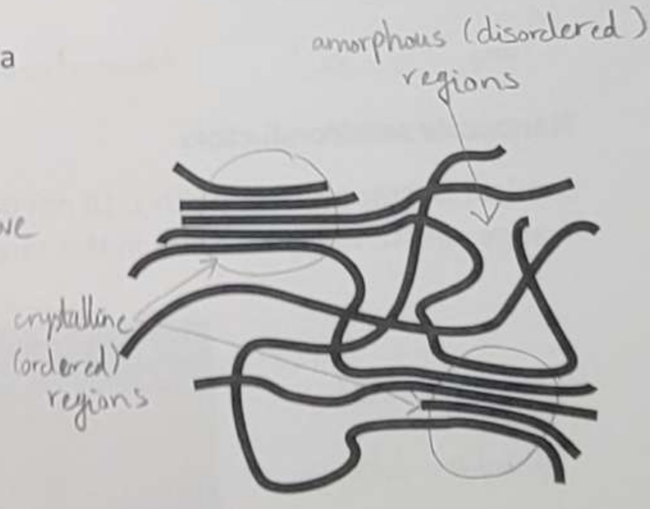
Name	Structure	Common name	Uses	Monomer(s)
Polycapro-lactam		Nylon 6	Clothing, string	
Polyethylene terephthalate		Polyester, Dacron PET	Soda bottles, clothing	
Polycarbonate (bisphenol A)		Lexan	bulletproof glass, safety glasses, DVDs	

Structure and physical properties of polymers

Synthetic and natural polymers commonly consist of a collection of *macromolecules* of different molecular weights.

Intermolecular forces between chains give order to polymers

Crystallinity is order



Factors that affect polymer properties include molecular properties, additives, and fabrication. Stretching or extruding a polymer can increase crystallinity.

Crystallinity is also strongly influenced by average molecular mass.

e.g LDPE (plastic wrap) ~10^4 amu, HDPE (milk carton) ~10^6 amu

Polymeric properties may be modified by additives with lower molecular mass.

Plasticizers decrease interactions between chains and make polymers pliable.

Cross-linked polymers are more rigid than straight-chain polymers:

e.g vulcanization of natural rubber involves crosslinking of an unsaturated polymer with sulfur (S_8)

vulcanized rubber is more elastic and less reactive than natural rubber

Cross-linking of natural polymers makes them harder. For example, the keratin in hair has less cross-links (disulfide bridges) than in fingernails.

Factors that affect polymer properties

Chain length	Cross-linking	Stereochemistry
Branching	Double bonds, aromatic rings	Fabrication
Polar groups	Substituents	Additives

Nanomaterials

"nano" = 10^{-9} nanomaterials have dimensions of 1 – 100 nm

Nanoscale semiconductors

Semiconductor particles with 1-10 nm diameters are called ***quantum dots***. Band gaps change substantially with size in this range.

increasing particle size (decreasing band gap)

fluorescent CdSe quantum dots

increasing band gap

Nanoscale metals

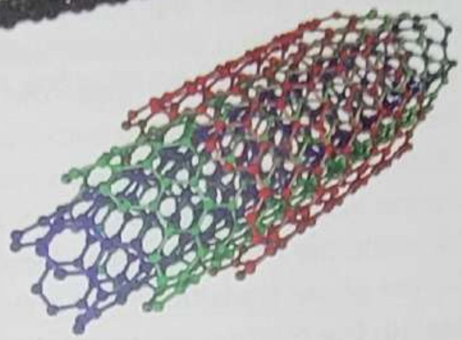
Metals in the 1-100 nm size range are interesting nanomaterials.

- known for centuries that finely divided metals have strange properties
- medieval craftsmen dispersed precious metals in molten glass to make deep red and yellow colours

Carbon nanotubes

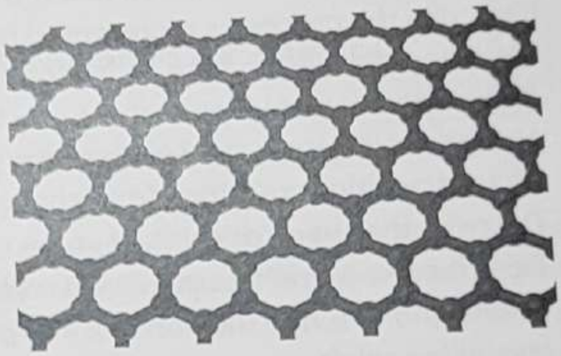
Sheets of graphite rolled up and capped at one or both ends.

- 1000's of nm long but only 1nm wide
- single-walled and multi-walled tubes
- interesting electronic and structural (mechanically very strong) properties
- promising for use as "nanowires"



Graphene

A single **unrolled** sheet of graphite.



- made by peeling single sheets from graphite using scotch tape
- A "semi-metal", with record thermal conductivity
- can sustain current densities 6 times that of copper